Energy Storage Research in Switzerland –
The SCCER Heat & Electricity Storage
Novartis Celebrates Frontiers of Chemistry

Novartis Chemistry Lecture Day
Thursday, February 4, 2016

Horburg Auditorium, WKL-430.3.20
Müllheimerstrasse 195
4057 Basel

Program

Morning Session: Total Synthesis of Natural Products
Chair: Dr. Peter von Matt, NIBR GDC ATI

08:30h – 08:45 h Opening Remarks
08:45h – 09:45 h Prof. Mohammad Movassaghi
Massachusetts Institute of Technology, Cambridge, MA, USA
09:45h – 10:15 h Coffee Break
10:15h – 11:15 h Prof. Tohru Fukuyama
Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan
11:15h – 12:15 h Prof. Brian M. Stoltz
California Institute of Technology, Pasadena, California, USA

Afternoon Session: Late Stage Functionalization
Chair: Dr. Fabrice Gallou, TRD CHAD

14:00h – 15:00 h Prof. Varinder K. Aggarwal
University of Bristol, Cantock's Close, Bristol, UK
15:00h – 16:00 h Prof. Cristina Nevado
University of Zürich, Zürich, Switzerland
16:00h – 16:30 h Coffee Break
16:30h – 17:30 h Prof. Eric N. Jacobsen
Harvard University, Cambridge, MA, USA
17:30h Apéro

Symposium organized by NIBR GDC and TRD CHAD
Energy Storage Research in Switzerland – The SCCER Heat & Electricity Storage

The declared aim of the Swiss Energy Strategy 2050 is the transition from nuclear power to a highly efficient energy system with power supply based on renewable sources, to meet the CO2 emission targets. For a smooth transition, an important factor is to expand and strengthen the knowledge in the energy field through the increase of personnel resources, e.g. scientists, engineers, technicians alongside with the development of new technologies. Besides other actions taken by the Swiss Government, in 2014 eight Swiss Competence Centers for Energy Research (SCCER) have been established, receiving their funding through the Commission for Technology and Innovation Switzerland (CTI). The Centers cover different action fields in energy research, viz. Mobility,[1] Efficiency,[2] Supply of Electricity,[3] Grids,[4] Biomass,[5] Economy & Environment,[6] as well as Heat and Electricity Storage.[7]

The Centers are organized as virtual consortia of industrial and academic institutions (Cantonal Universities, Universities of Applied Sciences, Federal Institutes of Technology and Research Institutions, respectively) with the intention to maximize the technological outcome by combining the strongest competencies in each area of expertise.

Energy Storage is a key element within the Federal Energy Strategy since energy, sourced from renewables like wind and solar energy, is only available on an intermittent, stochastic basis. Storing excess energy during times of low energy demand and releasing it in times of high energy demand is not only useful from an energetic perspective, it also may create an economic value within the energy market. With an increasing contribution of the aforementioned renewable energy sources to the electricity mix, the significance of energy storage increases. This is clearly demonstrated by countries having installed large capacities of wind and photovoltaic power, e.g. Germany and Denmark. Large intermittent discrepancies between electricity production and demand are being observed with the consequence of a strongly fluctuating electricity price causing also challenges to the stability of the power supply system. In order to stabilize the grid, an increase in short-term electricity storage capacity (hrs) with high response time is needed within the next years. In the long run, seasonal storage becomes important to ensure constant electricity supply without conventional fossil based power generation.

Heat, aside from electricity, is one of the most required types of energy today. About 50% of the primary energy carriers are transformed to heat by modern industrialized societies required for space heating, hot water and process heat. Thus, it becomes obvious that a sensible use of energy must not neglect the questions related to heat storage.

The research and development within the SCCER Heat and Electricity Storage concentrates on five different topics with the involvement of more than 20 research groups from eleven public institutions as well as from the private sector. In detail, R&D is performed on direct electricity storage in batteries, electricity storage in hydrogen and synthetic fuels, short-term and seasonal heat storage as well as the interaction and integration of different storage technologies.

Within this special issue of CHIMIA entitled Energy Storage Research in Switzerland we have the opportunity to present 15 papers from the participating groups of the SCCER Heat & Electricity Storage highlighting their research in this exciting, interdisciplinary field of Energy Storage forming a perfect place to find an overview of the Swiss activities.

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The Editorial Board of CHIMIA is very grateful to the guest editors Prof. Dr. Thomas J. Schmidt and Dr. Jörg Roth for the successful realization of this special issue on Energy Storage Research in Switzerland - The SCCER Heat & Electricity Storage; providing readers with an excellent overview of an interdisciplinary project with great significance for the future.
Energy Storage Research in Switzerland – The SCCER Heat & Electricity Storage

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Markt, Apparate, Chemikalien und Dienstleistungen
Evaluation of Metal Phosphide Nanocrystals as Anode Materials for Na-ion Batteries

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Abstract: Sodium-ion batteries (SIBs) are potential low-cost alternatives to lithium-ion batteries (LIBs) because of the much greater natural abundance of sodium salts. However, developing high-performance electrode materials for SIBs is a challenging task, especially due to the ~50% larger ionic radius of the Na\textsuperscript{+} ion compared to Li\textsuperscript{+}, leading to vastly different electrochemical behavior. Metal phosphides such as FeP, CoP, NiP\textsubscript{2}, and CuP\textsubscript{2} remain unexplored as electrode materials for SIBs, despite their high theoretical charge storage capacities of 900–1300 mAh g\textsuperscript{-1}. Here we report on the synthesis of metal phosphate nanocrystals (NCs) and discuss their electrochemical properties as anode materials for SIBs, as well as for LIBs. We also compare the electrochemical characteristics of phosphides with their corresponding sulfides, using environmentally benign iron compounds, FeP and FeS\textsubscript{2}, as a case study. We show that despite the appealing initial charge storage capacities of up to 1200 mAh g\textsuperscript{-1}, enabled by effective nanosizing of the active electrode materials, further work toward optimization of the electrode/electrolyte pair is needed to improve the electrochemical performance upon cycling.

Keywords: Anode materials · Li-ion batteries · Na-ion batteries · Nanocrystals · Synthesis

1. Introduction

Lithium-ion batteries (LIBs) have become the battery technology of choice for applications demanding high energy and power densities, such as portable electronics and electric vehicles, and also show great promise for the large-scale grid storage of electricity. Yet, the irregular geographic distribution and relatively low natural abundance of lithium salts raise doubts as to the future security and cost of supply. In this regard, conceptually identical sodium-ion batteries (SIBs) are a favorable alternative due to the much greater abundance (by a factor of \(10^3\)) and therefore lower price of sodium salts.\textsuperscript{[1]} However, the seemingly simple replacement of the Li\textsuperscript{+} ion with its 50% larger group I neighbor has drastic consequences for the resulting electrochemistry. For instance, both silicon and graphite, which are well-known anode materials with outstanding lithium ion storage properties, show negligible capacities for sodium ions.\textsuperscript{[2]} Extensive research toward new electrode materials is needed to advance the development of high-performance SIBs.

Of all possible anode materials for SIBs, red phosphorus (P) is probably the most appealing candidate due to its low cost, nontoxicity and, most importantly, extremely high sodium capacity (2596 mAh g\textsuperscript{-1} for P↔Na,P, the highest Na\textsuperscript{+} capacity known) at a low desodiation potential (~0.6 V vs. Na/Na\textsuperscript{+}). However, similarly to other alloying/conversion type materials, P suffers from massive volume changes during sodiation/desodiation (\(\Delta V = 291\%\), by molar volume) leading to the mechanical disintegration of the electrodes and therefore rapid capacity fading due to loss of electrical contact. The other main disadvantage of P is its relatively low electronic conductivity, causing slow reaction kinetics. Although noticeable progress has been demonstrated for P-based SIB anodes,\textsuperscript{[3]} typically very large amounts of conductive carbons are used to provide sufficient conductivity as well as mechanical stability of the electrodes, and often high capacities with good cycling stability can only be achieved at low charge/discharge currents of ~100 mA g\textsuperscript{-1} (~0.05 C).

In this study, we were intrigued by the possibility of addressing the aforementioned issues facing P-based SIB anodes by using metal phosphate nanocrystals (NCs) as the active material. Generally, nanostructured materials often show improved electrochemical performance over their bulk counterparts due to mitigation of the effects caused by volumetric changes and improved ionic and electronic conductivities upon homogeneous mixing with conductive carbon additives.\textsuperscript{[4]} Moreover, metallic inclusions, which form \textit{in situ} upon electrochemical conversion of the transition metal phosphate to alkali metal phosphate, are also expected to improve the electronic connectivity within the electrode. Despite the additional mass of the transition metal, theoretical specific charge-storage capacities of metal phosphides are still extremely high (900–1300 mAh g\textsuperscript{-1}), surpassing all of the main alternatives to P such as Sn (847 mAh g\textsuperscript{-1}) and Sb (660 mAh g\textsuperscript{-1}). Herein, we present the sodium and also lithium storage properties of highly uniform FeP, CoP, NiP\textsubscript{2} and CuP\textsubscript{2} NCs prepared \textit{via} colloidal synthesis methods. It should be noted that, with the exception of a recent study on FeP\textsubscript{2},\textsuperscript{[5]} this is the first report on the electrochemical performance of such metal phosphides in SIBs. All of the phosphate NCs investigated in this work show high charge-storage capacities, close to the theoretically expected values. In comparison to the corresponding metal sulphide NCs, the phosphides...
exhibit lower desodiation potentials and are hence better suited as SIB anode materials, but suffer from very fast capacity loss upon cycling. Further work on the optimized formulation of the electrodes and the selection of suitable electrolytes and electrolyte additives is needed to improve long-term cycling stability.

2. Experimental

2.1 Synthesis of Metal Phosphide Nanocrystals

2.1.1 FeP Nanowires (NWs)

In a typical experiment, 2.5 g tri-n-octylphosphine oxide (TOPO, 99%, Strem) and 3 mL tri-n-octylphosphine (TOP, ≥97%, Strem), previously dried at 100 °C under vacuum for 1 h, were heated to 300 °C under Ar. At 300 °C, 0.5 mL of Fe stock solution, prepared by mixing 1 mL TOP and 0.25 mL Fe(CO)₅ (99.99%, Strem), was injected into the TOP/TOPO mixture. After 30 min, a second injection of 0.5 mL of stock solution was carried out. The reaction was stopped after an additional 30 min. FeP NWs were precipitated by adding hexane and ethanol, separated by centrifugation, and re-dispersed in chloroform containing 1 wt% oleic acid. The second precipitation was induced by adding ethanol. After centrifugation, the FeP nanowires were re-dispersed in chloroform and stored under ambient conditions.

2.1.2 NiP₂ NCs

In a typical experiment, 4.5 mL octadecene (ODE, 90%, Sigma-Aldrich), 6.4 mL oleylamine (OLA, 95%, Strem) and 0.25 g (1 mmol) nickel(II) acetylacetonate (≥98%, Merck) were dried at 110 °C under vacuum for 1 h to remove water and low-boiling point impurities. Then, 2 mL of TOP were added to the flask under Ar atmosphere and the reaction mixture was heated to 320 °C for 75 min. The flask was cooled to 200 °C by flowing air and then 200 mg (6.4 mmol) of red phosphorous were added. The reaction mixture was then heated again to 330 ºC and it was held at this temperature for 22 h. CuP₂ NCs were isolated and purified identically to the NiP₂ NCs above.

2.1.4 CuP₂ NCs

In a typical experiment, 4.5 mL ODE, 6.4 mL OLA and 0.262 g (1 mmol) copper(II) acetylacetonate (≥97%, Sigma-Aldrich) were dried at 110 °C under vacuum for 1 h to remove water and low-boiling point impurities. Then, 2 mL of TOP were added to the flask under Ar and the reaction mixture was heated to 320 °C for 65 min. The flask was cooled to 200 ºC by flowing air and then 105 mg (3.4 mmol) of red phosphorous were added. Then the reaction mixture was heated again to 330 °C and it was held at this temperature for 22 h. CoP NCs were isolated and purified identically to the NiP₂ NCs above.

2.2 Characterization of Metal Phosphide Nanocrystals

Transmission electron microscopy (TEM) was performed using a JEOL JEM-2200FS instrument operated at 200 kV, using carbon-coated Cu grids as substrates (Ted-Pella). Powder X-ray diffraction (XRD) was measured using a STOE STADI P diffractometer (with Cu-Kα, λ = 1.540598 Å).

2.3 Electrode Preparation, Cell Assembly and Electrochemical Measurements

In order to evaluate the electrochemical properties of FeP, CoP, NiP, and CuP, NCs, Na-ion and Li-ion half-cells were assembled. Prior to electrode preparation, organic ligands were removed from the surface of the NCs by stirring them in a 1 M solution of hydrazine in acetonitrile for 2 h at room temperature, as is commonly performed for colloidal quantum dots. Electrodes were prepared by mixing the respective metal phosphide NCs (63.75 wt%) with carbon black (21.25 wt%, TIMCAL), carboxymethylcellulose (CMC, 15 wt%) and water as a solvent using a planetary ball-mill at 500 rpm for 1 h. The aqueous slurries were coated onto Cu current collectors, which were dried at 80 °C under vacuum overnight prior to cell assembly. For electrochemical testing, coin cells with an elemental Na or Li were assembled in a Ar-filled glovebox (O < 0.1 ppm, H₂O < 0.1 ppm) using either 1 M NaClO₄ in propylene carbonate (PC) with 10% fluoroethylene carbonate (FEC) or 1 M LiPF₆ in a 1:1 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with 3% FEC. FEC was added to the electrolyte in both the Li and Na coin cells to improve capacity retention. All electrochemical tests were carried out at room temperature and the capacities were reported relative to the mass of the metal phosphide NCs.

3. Results and Discussion

3.1 Synthesis and Characterization of Metal Phosphide Nanocrystals

FeP NWs were synthesized according to the procedure reported by Qian et al. In order to obtain NiP₂ NCs, a two-step procedure was developed. First, NiP NCs were synthesized according to a known protocol reported by Popczun et al. We then added a second step: conversion of the as-prepared NiP NCs into NiP₂ NCs by adding red P to the reaction mixture, followed by heating at 330 °C for 22 h. Analogously, this two-step approach was also applied in the synthesis of CuP₂ and CoP NCs, simply by replacing nickel(II) acetylacetonate with the respective copper or cobalt salt (for details, see the Experimental section). Fig. 1 summarizes the characterization of the metal phosphide NCs obtained by these methods. FeP NCs were on average ~300 nm in length and ~7 nm in width. CoP, NiP, and CuP NCs exhibited diameters of 25, 10 and 60 nm, respectively. All materials showed phase-pure XRD patterns, indexed according to the standard ICSD files for these compounds.

3.2 Electrochemical Performance of Metal Phosphide Nanocrystals

Fig. 2 shows the electrochemical performance of the metal phosphide NCs in Na-ion and Li-ion half-cells. Na-ion cells were cycled at a current rate of 100 mA g⁻¹ in the potential range of 0.02–2.5 V. For Li-ion cells, current rates of 300 mA g⁻¹ and a potential range of 0.02–2.0 V were used. Assuming the formation of Na₂P or Li₂P via the general conversion reaction

\[ \text{MP} \times 3\text{xe}^- + 3\text{xA}^+ \leftrightarrow \text{xA}_3 \text{P} + \text{M} \]

(M = Fe, Co, Ni, Cu; A = Li, Na),

the metal phosphides FeP, CoP, NiP, and CuP, have theoretical capacities of 926, 894, 1333 and 1282 mA h g⁻¹, respectively. In close agreement, CuP₂ indeed showed the highest capacity in the first cycle. However, the capacities of all studied materials rapidly faded during cycling. The compounds with higher P content, NiP, and CuP₂, showed higher initial capacities but poorer capacity retention. Namely, for CuP NCs the charge capacity decreased from 1140 mA h g⁻¹ to 570 mA h g⁻¹ within the first 16 cycles. For the FeP, CoP and
NCs in Li-ion half-cells (Fig. 2b). Due to the irreversible decomposition of the electrolyte forming the solid electrolyte interface (SEI) (see Figs 2c and 2d). Notably, rather poor coulombic efficiencies of 92–95% for Na-ion and 96–98% for Li-ion cells were obtained during subsequent cycles, indicating continuous deterioration and reformation of the SEI caused by pulverization of the electrode material.

Figs 2c and 2f show the galvanostatic discharge and charge voltage profiles for the first cycle for all tested metal phosphate NCs. For sodium ion storage, a desodiation potential of ~0.6 V vs. Na/Na⁺, which is at the same potential as reported for the electrochemical reaction of red P with Na.[15] This implies that metal phosphides rather convert into elemental P and that cycling proceeds mainly by the reaction $P + 3e^- + 3Na^+ \rightarrow Na_3P$, as has been suggested for FeP.[9] In Li-ion half-cells, the majority of delithiation occurs at a potential of more than 1.0 V showing that metal phosphides are generally better suited as SIB anode materials due to lower voltages of desodiation.

3.3 Comparison of FeP and FeS₂ NCs as Anode Materials for Na-ion Batteries

Clearly, from the prospects of low cost and low toxicity, iron-based sodium storage electrode materials are the most interesting candidates, in particular when the other chemical constituents of the compound comprise equally abundant elements such as phosphorus and sulfur. Hence, iron sulfides can be seen as a main alternative to phosphides. Similar difficulties with capacity fading might occur for FeS₂ (pyrite) due to its large (~280%) volume expansion upon Na₂S formation.[10] In order to compare the electrochemical performance of Fe phosphides and sulfides, we synthesized pyrite FeS₂ NCs with sizes from 50–100 nm and tested them under the same conditions as the FeP NCs. The synthesis, characterization and electrochemical properties of FeS₂ NCs have been detailed in our recent report.[11] Assuming the formation of Na₂S, FeS₂ NCs possess a theoretical maximum capacity of 894 mAh g⁻¹, similar to the value for FeP (926 mAh g⁻¹). However, as can be seen in Fig. 3, the electrochemical performance of FeS₂ and FeP NCs is in fact very different. Whereas FeP NCs exhibit stable capacities with capacity fading might occur for FeS₂ (pyrite) NCs. The only relevant previous investigation of FeP as a SIB anode material is the recent report by Li et al.[5] in that work, anodes prepared by ball-milling FeP showed much faster capacity fading, from 460 mAh g⁻¹ to ~200 mAh g⁻¹ within 40 cycles at a current of 50 mA g⁻¹. Compared to FeP NCs, the only obvious drawback of FeS₂ NCs is the higher desodiation potential (Figs 3b and 3c), that is, however, well compensated by good capacity retention.

4. Conclusion

In conclusion, we have prepared NCs of FeP, CoP, NiP₂ and CuP₂ using colloidal...
Fig. 2. Electrochemical performance of metal phosphide nanocrystals. Galvanostatic cycling of metal phosphide NCs in Na-ion (a) and Li-ion half-cells (b) with the respective coulombic efficiency plots (c, d). Galvanostatic charge and discharge curves for the first cycle for Na-ion (e) and Li-ion (f) half-cells. Electrodes were composed of 63.75% metal phosphide NCs, 21.25% CB and 15% CMC. 1 M NaNO₃ in PC with 10% FEC served as the electrolyte for Na-ion and 1 M LiPF₆ in EC:DMC (1:1) for Li-ion half-cells. Galvanostatic cycling tests were carried out with a current of 0.02–2.0 V for Li-ion half-cells.

that metal phosphides are inherently less stable than their corresponding sulfides and this instability is a combined effect of large volumetric changes and phosphorus-specific processes, such as the reactivity of NaP towards the electrolyte.[11] Further progress towards high performance phosphate-based electrodes is expected to result from smart electrode engineering by designing secondary structures in which the metal phosphate NPs are encapsulated into conductive carbons,[12] thereby eliminating the direct large-area contact with the electrolyte. Furthermore, a sensible choice of the electrolyte and electrolyte additives might enable the higher stability of the SEI layer in future studies.

Acknowledgements

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Fig. 3. Comparison of the electrochemical performance of FeP and FeS$_2$ NCs. Galvanostatic cycling of FeS$_2$ and FeP in Na-ion half-cells (a) and the respective charge/discharge curves (b, c). Galvanostatic cycling tests were carried out with a current of 100 mA g$^{-1}$ in the potential range of 0.02–2.5 V.

Electrode Engineering of Conversion-based Negative Electrodes for Na-ion Batteries

Leonie O. Vogt, Cyril Marino, and Claire Villevieille*

Abstract: Due to lower costs and higher abundance of sodium, Na-ion battery technology can offer a good alternative to Li-ion batteries. Much research is focusing on developing new cathode and anode materials but the importance of the electrode engineering on the electrochemical performance is often neglected. The electrode composition is especially crucial for conversion reaction-based materials where the composite electrode (active material, conducting additive and binder) has to buffer the huge volume change occurring upon cycling. This work highlights the differences observed on Sn-CMC electrode performance by using different Sn particle sizes (micro- and nanoparticles) and evaluating the role of the conductive additive in the electrode. Carbon fibers (VGCF) demonstrate a good ability to surround micrometer particles but not especially nanometer particles leading to an improvement in the performance of microparticles but not of nanoparticles. For a high loading electrode suitable for full cell applications (>3.5 mg/cm² of active material), nanometer particles show limited performance for long-term cycling. The combination of VGCF with micrometer particles seems to be the most promising composition to obtain good performances for conversion reaction based-materials.

Keywords: Electrode engineering · Na-ion batteries · Negative electrode · Sn particle · VGCF

Li-ion batteries are starting to reach their limits in terms of energy density, cost, and abundance, and progress is slower than expected. Thus, researchers are currently re-investigating other alkali metals as Li substitutes, mainly focusing on Na. This system has been considered to be purely academic, and no real applications or prototypes have been developed to investigate its viability or possible commercialization, the only exception being the high temperature Na-S system, which was commercialized in the 1960s. Recently however, the amount of research and number of papers devoted to the development of active materials for Na-ion batteries has increased exponentially, leading the community to consider the commercialization of Na-ion batteries in the near future.[2–6] Electrochemically, specifically voltage and theoretical specific charge, there is no advantage to replacing Li with Na. However, when considering additional parameters such as abundance and cost, Na-ion batteries may be competitive with the currently available Li-ion batteries. Another significant advantage in terms of both cost and weight is that no alloy exists between sodium and aluminum. This means that Al can be used as a cheaper current collector for both the positive and negative electrodes, lowering the total weight and cost of the cell pack. Furthermore, the electrolyte in Na-ion batteries has a higher conductivity compared to that of Li-ion batteries. The larger ionic radius of Na compared with Li results in a low de-solvation energy, which strongly influences the kinetics and allows high power Na-ion batteries to be envisaged. To achieve commercialization, suitable anodes[2,4,7–11] and cathodes[12–21] must be developed and studied in depth as the Na-system is often not analogous to the Li-system. A couple of years ago, the observation that pure commercial elements, such as Sn or Sb can electrochemically react with Na, leading to sustainable reversible capacities as high as 500 mAh/g over more than 100 cycles (twice as much as hard carbon), surprised the scientific community.[7,22] These results were especially interesting considering the immense volume change upon cycling, which exceeds 400%. However, while the search for new materials is progressing rapidly, the engineering of the electrodes is quite often neglected. Many groups in the literature reported as an example that polyvinylidene fluoride binder (PVDF) works poorly in Na-ion batteries and that other type of binders should be used instead.[23–25] We were one of the first groups to demonstrate that the know-how acquired over the past few decades on Li-ion battery technology cannot be transferred one-to-one to the emerging Na-ion batteries.[26] In fact, we demonstrated that the most commonly used binder in Li-ion batteries (PVDF) is not suitable for Na-ion batteries as it decomposes to create NaF during cycling and thus the electrode loses its integrity and cannot accommodate the volume change of the conversion-based electrode materials anymore.[26] Besides the binder, carbon-conductive agents (carbon fibers, super P, acetylene black, carbon nanotubes, etc.) are another source of variation from group to group, where many different types are used but it is difficult to establish which of them leads to the best cycling performance with conversion-based electrode materials for Na-ion batteries.[27–29]

The influence of the particle size (of the active material) is another often neglected factor in literature, since articles either focus on nanoparticles or they focus on solid-state bulk particles (tens of μm range). The comparison between both particle sizes (nano and micro range) is not often reported and it is difficult to assess the advantages and drawbacks of each since the loading of the electrodes (using either nano or micro range) can differ by a factor of 5 to 10.[9,30–33] Based on the common approach of using very low loading for nanoparticle active materials (unsuitable
for battery application) it is not surprising that nanoparticles are often presented to be better in terms of cycling stability, long-term cycling and power performance, as for example reported recently by Nam et al.\cite{34–39} and others.

In this article, we establish an engineering guideline for conversion-based negative electrodes used in Na-ion batteries. Sn was selected as a model conversion-based material that undergoes high volume changes during cycling. Due to the instability of the PVDF binder in Na-ion batteries, shown previously, it was decided to use the promising binder Na-CMC. Here we compare the impact of different particle sizes on the electrochemical performance in electrodes of comparable loading. Additionally, we investigate the impact of the carbon conductive agent in both the micro-particle and the nanoparticle systems, looking specifically at the use and impact of carbon Super C and carbon fiber. The best combination of binder/conductive additive/particle size for improved cycling performance of conversion-based negative electrodes in Na-ion batteries is then elucidated.

**Experimental Section**

**Electrode Preparation**

For the electrode preparation we used two different tin powders: Sn-micro (ABCR, 325 mesh) (hereafter called m-Sn) and Sn-nano (ABCR, ca. 100 nm, hereafter called n-Sn). For the conductive agent, two different types were used: carbon black SuperC65 (CB, Imerys) and vapor-grown carbon fibers (VGF, Showa Denko). Electrodes without VGF were prepared by casting a suspension of 70 wt% Sn-micro (or Sn-nano), 18 wt% CB and 12 wt% carboxymethyl cellulose sodium salt (CMC, Alfa Aesar) in deionized water onto aluminum foil, used as current collector (described in the article as composition 1). For electrodes containing VGF, the ratio between the elements was modified to 70 wt% Sn-micro (or Sn-nano), 9 wt% CB, 9 wt% VGF and 12 wt% CMC (described in the article as composition 2). Once dried in air, 13 mm diameter electrodes were punched out and were dried under vacuum at 120 °C for a few hours. The loading of active material on the electrodes was between 2.8 mg/cm² and 3.5 mg/cm².

**Electrochemistry**

Electrochemical cells were assembled in an Ar-filled glove box using the electrode, a glass-fiber sheet as the separator and metallic sodium (Sigma-Aldrich, 75 μm) as counter electrode. A mixture of 1 M NaClO₄ dissolved in propylene carbonate (PC) was used as electrolyte. The cell performance was measured in galvanostatic mode at 25 °C between 5 mV and 1.0 V at a C/30 rate and monitored by an ASTROL cycling device. An additional potentiostatic step of 2h was added at the end of each discharge and charge to ensure proper sodiation and desodiation. All the potentials mentioned in the manuscript are given versus Na+/Na.

**Scanning Electron Microscopy (SEM)**

SEM measurements were performed in a Carl Zeiss Ultra55 scanning electron microscope using the secondary electron mode.

**Results and Discussion**

**Influence of Particle Size**

The SEM pictures of m-Sn and n-Sn electrodes are displayed in Fig. 1 and show the impact of the particle size on the electrode engineering. The m-Sn electrode reveals a broad range of particle sizes from ca. 1 μm to 15 μm. Some Sn particles are close to each other and in other areas there are big gaps, indicating a certain inhomogeneity at the micrometer range in the dispersion of the particles in the electrode. The images also show some Sn particles that are only partially covered by the carbon Super C and the CMC binder and some cracks around the particles. Those fractures occurring in the electrode can be problematic considering the huge volume change occurring during the sodiation of Sn particles (especially for the m-Sn electrode). Particles that are only partially connected to the carbon/binder/current collector are likely to be totally disconnected during the cycling due to the strong strain caused by the volume change upon sodiation. This phenomenon would lead to a decrease of the cell performance. The n-Sn electrode shows a narrow particle size distribution since the Sn particles are below 500 nm, with most of them around 100 nm diameter. At low magnification (micrometer range SEM picture, Fig. 1, bottom), the Sn nanoparticles seem to be well dispersed and embedded in the carbon/binder matrix unlike the m-Sn electrode. Thus, upon cycling versus Na the nanoparticle system is expected to accommodate the volume expansion better than the microparticle system. However, the picture taken at higher magnification (Fig. 1, bottom) reveals some n-Sn agglomerates, indicating that the electrode engineering could be optimized further. This agglomeration of nanoparticles may be a result of the high nanoparticle loading used here, as compared to the low loading generally reported in literature. In both cases, the images also indicate a good porosity such that the wettability of the electrode should not be a cause of fading.

![Fig. 1. SEM images of m-Sn-micro (top) and n-Sn electrodes (bottom) in electrode composition 1.](image-url)
Coulombic efficiency in the case of n-Sn is relatively low compared to the m-Sn.

The difference observed between the two electrodes m-Sn and n-Sn can be explained by the difference in particle size. The nanoparticles have such high surface area that when cycling in a potential window where the electrolyte is reduced, more electrolyte decomposition occurs and consequently more solid electrolyte interphase (SEI) forms, leading to a low Coulombic efficiency. With every cycle the SEI layer is thickened, its isolating character leads to an increased resistance which finally hinders cyclability. For the m-Sn the fading is mainly caused by the particle fracture which occurs during sodiation. In fact when fully sodiated the particles expand 420%, leading to cracking which can cause loss of electrical contact of some particles. Those parts become dead materials that cannot cycle anymore, leading to a gradual fading of specific charge. These results are in accordance with the SEM observations and predictions, in that m-Sn was seen to integrate less well in the carbon/binder matrix than n-Sn (Fig. 1) and consequently it is more likely to suffer from pulverization and electrical disconnection of particles, leading to gradual specific charge fading as seen in Fig. 2. However compared to the n-Sn electrode, the m-Sn electrode has a better specific charge after 20 cycles, coming from the fact that during cycling most probably after each fracture of the particle, a core-shell process is occurring and thus ‘new-fresh’ Sn can be revealed and can be cycled, which helps to maintain the specific charge higher than the isolating n-Sn.

The galvanostatic curves presented in Fig. 3 validate our hypothesis about the SEI formation in the n-Sn system. At ca. 0.4 V during the first sodiation a long potential plateau ascribable to the SEI formation is visible in the n-Sn sample whereas almost nothing appears in the same voltage range for the m-Sn electrode.

For the rest of the first sodiation, we can see the three characteristic potential plateaus of Na-Sn alloys at 0.2 V, 0.07 V and 0.01 V. For the n-Sn electrode, those potential plateaus are slightly lower in potential, indicating a higher polarization. This higher polarization probably arises from the larger SEI formation which hinders the lowest sodiation plateau to be accessed since with the additional overpotential it lies below the 5 mV cut-off voltage. On desodiation, a first potential plateau appears in the m-Sn electrode at 0.16 V but no such potential plateau is seen for the n-Sn electrode. Thereafter the desodiation plateaus of the n-Sn electrode (0.27 V and 0.54 V) are analogous to those of the m-Sn electrode (0.26 V and 0.53 V), with the slight shift in potential being attributable to the higher polarization in the n-Sn system (thicker SEI).

At the 10th cycle (Fig. 3, right), the polarization has grown in both electrodes such that the lowest potential plateau is no longer accessible for both systems. In general the different potential plateaus on sodiation are no longer distinguishable for m-Sn electrode and for the n-Sn electrode only two vague potential plateaus are visible at ca. 0.3 V and ca. 40 mV. In contrast, on desodiation potential plateaus are still distinguishable for both m-Sn and n-Sn allowing some comparison to the first cycle.

For m-Sn the two potential plateaus at 0.27 V and 0.54 V are the most prominent features but have shortened in comparison to the 1st cycle. For n-Sn a new, small potential plateau is seen at 0.22 V followed by one at 0.28 V. Then the potential increases rapidly with a small bend at 0.55 V and another at 0.81 V.

So far we demonstrated that when the loading of the electrodes is the same, nanoparticles do not outperform microparticles after a few cycles. Instead, n-Sn shows a poor Coulombic efficiency and a dramatic specific charge fading. Nanoparticles can only compete with microparticles if the loading is low. However, due to the limited storage capacity such low loading is not commercially viable. A similar comparative approach was used to investigate the most suitable conductive agent and optimal electrode engineering conditions for the best electrochemical performances.

**Influence of Conductive Additive**

SEM pictures of the electrode designed with VGCF are shown in Fig. 4 and can be compared with the one having only Super C as a conductive additive (Fig. 1). The VGCF, a long rod shape of around 100 nm diameter, can easily be distinguished in composition 2. For both particle sizes, the observations made previously about the dispersion of Sn particles in Super C-based electrodes are also valid for VGCF-based electrodes: the micrometer particles are not homogeneously distributed in the electrode and the nanometer particles agglomerate slightly. The new electrode constituent, VGCF, shows a homogeneous dispersion throughout the electrode.

For m-Sn VGCF electrodes, the Sn particles are covered by the VGCF (Fig. 4), such that electrode fractures around the micro Sn particles are bridged by the fibers. This is expected to lead to better electrical contact in the electrode during cycling.

For the n-Sn, the situation is slightly different since the diameter of the VGCF is roughly the same as the one of the primary particles. For the m-Sn VGCF electrodes, the Sn particles are covered by the VGCF (Fig. 4), such that electrode fractures around the micro Sn particles are bridged by the fibers. This is expected to lead to better electrical contact in the electrode during cycling.
particles. The interaction between the n-Sn particles and the VGCF is therefore limited and VGCF mainly serves to connect aggregates.

Looking now at composition 2 (with VGCF, Fig. 5), we can see that the trend between m-Sn and n-Sn is roughly the same as the one observed for composition 1. While the composition 2 does not seem to affect cycling for n-Sn, for m-Sn it increases and helps to maintain the specific charge. As already stated before for m-Sn, when particle fracture occurs upon sodiation, this can lead to some particles becoming disconnected leading to uncyclable material. Due to their length and high conductivity carbon fibers can combat this problem, allowing more Sn particles to stay connected to the carbon/binder matrix and current collector, which leads to a higher specific charge retention (ca. 400 mAh/g after 20 cycles). In n-Sn electrodes where the particles are well integrated and disconnection is not a problem but instead a thick SEI layer causes trouble, the addition of VGCF does not improve cycling performance.

This demonstrates that it is crucial to understand the cause of capacity fading and use the appropriate electrode engineering to combat the drawbacks of the active material. The VGCF improves the long-term cycling performance of the m-Sn electrode due to better electrical contact. However, there is a small cost in Coulombic efficiency due to SEI formation on the surface of the carbon fibers. For n-Sn, where thick SEI formation leads to dramatic specific charge fading, VGCF cannot help but instead, a coating of the Sn particles may help to reduce electrolyte decomposition to improve long-term performance. The galvanostatic curves of m-Sn for the 1st and 10th cycle in composition 1 and composition 2 are shown in Fig. 6. In the first cycle, a new feature at ca. 0.42V for the composition 2 electrode can be seen. This extra ‘bump’ is most probably due to the SEI formation at the surface of the VGCF leading to a slightly reduced Coulombic efficiency as previously mentioned. We notice a similar plateau in the n-Sn galvanostatic curve for the composition 1. The addition of VGCF to the electrode composition reduces the overpotential compared to the standard Super C electrode, which is seen by the different Na-Sn sodiation potential plateaus all lying at slightly higher potential.

This means that the lowest of the three characteristic tin sodiation potential plateaus at 0.01 V is fully accessible which leads to a higher specific charge for composition 2. On desodiation the curves obtained with composition 2 are analogous to the ones of composition 1 except that the potential plateau at ca. 0.16 V, which corresponds to the lowest potential plateau in sodiation, is longer.

At the 10th cycle, features observed on sodiation have merged into sloping curves for electrode composition 1 and electrode composition 2. As already observed with composition 1, on desodiation the different potential plateaus are still distinguishable. With composition 1, the lowest potential plateau at 0.16 V is no longer visible, however, with composition 2 an activity is still present at this potential. At ca. 0.28 V both compositions show a potential plateau, however with composition 2,
it is much longer. At higher potentials, the last potential plateau at 0.55 V matches for both compositions. These differences in ‘length’ (i.e., specific charge) indicate that VGCF is of great help to maintain the cohesion of m-Sn electrodes during the high volume changes occurring while cycling.

The same analysis was conducted for the n-Sn electrodes, and the galvanostatic curves are plotted and presented in Fig. 7. For the first sodiation the curves match almost perfectly between the two compositions. Only a tiny difference at $ca$. 0.45 V and at 10 mV where the last potential plateau is slightly shorter can be seen. On desodiation we notice that the capacity retention is better for composition 1 than for composition 2 (though only 20–30 mAh/g). After 10 cycles, the specific charge fades dramatically compared to the first cycles. The curves turn smoother compared to the first cycle which makes it difficult to see the different potential plateaux characteristic of the Na-Sn reaction. In both sodiation and desodiation we can see an increase of the polarization for the electrode with composition 2, which can be attributed to a thicker SEI resulting in higher resistance. A thicker SEI can be attributed to the nanoparticles themselves, since their specific area is high and leads to more electrolyte decomposition and when VGCF is present additional SEI formation occurs on its surface. On sodiation, we can notice a small feature at around 0.4 V attributed most probably to the SEI, and then a potential plateau at around 50 mV attributed to the nanoparticles themselves, 12% carboxymethyl cellulose binder, 9% Super C65 and 9% VGCF shows the best electrochemical performance. We thus stress the need for careful electrode engineering already at the stage of fundamental research, to be able to make conclusive statements about how materials and their performances compare.

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Fig. 7. Galvanostatic curves for the 1st (left) and 10th (right) cycle for n-Sn electrodes using either the composition 1 or the composition 2.

Nanomaterials Meet Li-ion Batteries

Nam Hee Kwon*, Jean-Pierre Brog, Sivarajakumar Maharajan, Aurélien Crochet, and Katharina M. Fromm*

Abstract: Li-ion batteries are used in many applications in everyday life: cell phones, laser pointers, laptops, cordless drills or saws, bikes and even cars. Yet, there is room for improvement in order to make the batteries smaller and last longer. The Fromm group contributes to this research focusing mainly on nanoscale lithium ion cathode materials. This contribution gives an overview over our current activities in the field of batteries. After an introduction on the nano-materials of LiCoO$_2$ and LiMnPO$_4$, the studies of our cathode composition and preparation will be presented.

Keywords: Cathode · Composite structure · Li-ion batteries · Nano-LiCoO$_2$ · Nano-LiMnPO$_4$_

Nano-LiCoO$_2$

Today’s commercial Li-ion batteries are typically based on the layered structure of the high-temperature (HT) phase of LiCoO$_2$ as active material in the form of a micron-sized powder, using a carbon additive as well as a binder to increase the electronic conductivity and to process the so-obtained paste into a cathode.\[1\] Commercial HT-LiCoO$_2$ is produced via a solid-state synthesis operating under oxygen at very high temperature (600 – 900 °C) and over long times (2 – 3 days).\[2,3\] Using the precursor method, the Fromm group was able to simplify the reaction conditions and to reduce i) the production time, ii) the reaction temperature as well as iii) the grain size. Indeed, by reacting dry CoCl$_2$ with different ratios of LiOR in dry THF (R = Ph, tBu, Et, Me), we were able to obtain Li-Co alkoxides and aryloxides which combined the two metal ions. Compounds such as [(thf)$_2$Li($\mu$-OR)$_2$Co($\mu$-OR)$_2$Li(thf)]$_2$ (for R = Ph) and [(thf)$_2$Li($\mu$-OR)$_2$Co($\mu$-OR)$_2$Co($\mu$-OR)$_2$Li(thf)]$_2$ (R = Ph, R’ = tBu) could be identified.\[4\] While the second compound has the correct stoichiometric ratio between the metal ions and solely yields HT-LiCoO$_2$ as combustion product, the first compound yields also Li$_2$CO$_3$ upon heating in air. This byproduct can be eliminated by a short washing step with water.\[4\] Optimizing the alkoxide and aryloxide ligands, it was possible to generate the desired high-temperature phase of LiCoO$_2$ at as low as 350 °C and within two hours. The so-obtained nano-powders of different sizes, depending on the precursor and the temperature gradients used during combustion, are now being studied by us for their electrochemical performance in Swagelok and coin cells. In comparison with the commercial micron-scale material, the nano-sized LiCoO$_2$ is expected to possess a higher Li-ion diffusivity as the grains are smaller and the Li-ions should be able to migrate in and out of the grains much easier. Therefore, the reversible capacities of nano-sized LiCoO$_2$ are higher at high C-rates (>1 C) compared to the micron-sized LiCoO$_2$.\[5,6\] We will soon report on these results.

Nano-LiMnPO$_4$

In parallel to this research on LiCoO$_2$, we are also developing the technology around nano-scale LiMnPO$_4$, an olivine-type material with high structural stability.\[7\] Compared to the commercially used LiFePO$_4$, the Mn-analogue has a 20% higher energy density based on its higher potential versus Li$^+$/Li. On the other hand, it has a lower ionic and electronic conductivity resulting in a poor capacity and rate capability.\[8\] One way to overcome these drawbacks is to generate nano-scale LiMnPO$_4$ and to add conductive carbon additives.\[9–13\] Indeed, smaller particles reduce the Li-ion diffusion pathway and improve the ionic conductivity, while carbonaceous material such as graphite or carbon black improves the electronic conductivity (Scheme 1).\[12\]

We therefore studied different syntheses to obtain nanoscale LiMnPO$_4$ in order to gain control over grain size and shape, ii) the influence of the particle size, and iii) the amount of carbon additive necessary to obtain full capacity.

In a previous publication,\[12\] it was shown that for sample sizes ranging from 410 nm to 140 nm, the smaller the particle size, the better the reversible capacity (Fig. 1).

We therefore fine-tuned and improved the synthesis pathway using the polyol direct precipitation method (Scheme 2) in order to obtain yet smaller particles with different shapes.

In particular, we added a ligand exchange step to eliminate remaining surfactant from the surface of the particles, reducing thus the amount of remaining carbon residue after the final heating step.\[15\]
Indeed, we succeeded in controlling the reaction conditions such that we could reduce the particle sizes below 30 nm obtaining different shapes, from spherical to rod-like (Fig. 2), and, more importantly, in very high yield.\textsuperscript{[15]}

The nanoscale LiMnPO$_4$ shown in Fig. 2 (c) was used to study the best composition of a cathode in terms of carbon additive content. The higher percentage of active material versus carbon additive required to improve the electronic conductivity, the better is the capacity per weight of an electrode. While in the literature, amounts of 20–40\% of carbon are reported, we could show that as little as 10\% of carbon black could give rise to the full theoretical capacity of 170 mAh/g at a charging rate of C/40 (Fig. 3).\textsuperscript{[15]} This brings LiMnPO$_4$ into the game as potential commercial product for cathode materials of future Li-ion batteries.

Fig. 1. The reversible capacities of LiMnPO$_4$ consisting of different particle sizes. The smallest particle size showed the highest reversible capacity.\textsuperscript{[13,14]}

Carbon Additives and Cathode Preparation Methods

Since many different carbon additives are available on the market, and since the generation of homogeneous nanocomposites is non-trivial, we decided to study both aspects. In a first test, four different commercial carbon additives, two graphitic and two carbon black materials, were tested under similar conditions with commercial micron-scale LiCoO$_2$.\textsuperscript{[16]} The platelet-shaped graphite material has a lower specific surface area compared to the nanosized carbon black with spherical particles. We expected that carbon black would thus perform better than graphite, as it would mix better with the LiCoO$_2$-particles. In parallel, we also investigated the influence of the ball-milling on the formation of the composites.\textsuperscript{[17]} For this study, we expected a longer ball-milling to lead to a more ho-
mogenuous composite and hence to better electrochemical properties.

For the generation of the composite, SEM and TEM analyses surprisingly showed that the platelet-shaped graphite assembles homogeneously with micron-sized LiCoO₂ using the ball-milling method. Furthermore, a 5-min ball-milling process provided better results and smaller particles than a 30-min or 60-min ball milling or no ball-milling at all. Graphite thus turned out to provide a superior quality of the composite cathode material with a still high specific surface area. It also gives better quality cyclic voltammograms (Fig. 4, top) and leads to higher specific surface area. It also gives better quality cyclic voltammograms and leads to higher specific capacities (Fig. 4, bottom) of the LiCoO₂ electrodes compared to nano-sized spherical carbon black.

The nano-sized carbon black on the other hand aggregates during the ball-milling process and forms isolated clusters for which the specific surface area is dramatically reduced. Furthermore, the thick coating of nano-carbon black on the LiCoO₂ particles renders the contact with the liquid electrolyte difficult. We further assume that a long ball-milling process turned out to provide a superior quality of nanoparticles into porous inorganic shells[16–21]. We have thus started to investigate the use of encapsulated nanoparticles as anode material for Li-ion batteries. Within the framework of the NRP-70 of the Swiss National Science Foundation, research on the next generation batteries, such as Li-air and Li-water are ongoing in order to provide new membranes in collaboration with the group of H.G. Park at ETHZ, as well as electrolytes, which can also serve in classical Li-ion batteries.

Within the framework of the SCCER ‘Heat and Electricity Storage’, we contribute to the work package WP1 by providing our nanoscale cathode materials, assembling half cells against Li-metal and full cells against anode material provided by e.g. the group of M. Kovalenko from ETHZ. In situ and operando studies of our composite materials are ongoing in collaboration with the group of P. Novak and C. Villevieille at the PSI. The Fromm group also collaborates with the Peter Broekmann group of WP4 of the SCCER, and we have worked here on the synthesis and electrochemical analysis of pseudocapacitor multilayer thin films.[22]

Conclusions, Ongoing Work, and Outlook

We are now able to provide nano-scale LiCoO₂ and LiMnP₅O₁₀ in a multi-gram scale to partners who wish to test battery packs. Furthermore, the Fromm group has considerable expertise in the encapsulation of nanoparticles into porous inorganic shells,[16–21] We have thus started to investigate the use of encapsulated nanoparticles as anode material for Li-ion batteries. Within the framework of the NRP-70 of the Swiss National Science Foundation, research on the next generation batteries, such as Li-air and Li-water are ongoing in order to provide new membranes in collaboration with the group of H.G. Park at ETHZ, as well as electrolytes, which can also serve in classical Li-ion batteries.

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Stress-induced Ageing of Lithium-Ion Batteries

Marcel Held* and Urs Sennhauser

Abstract: Lithium-ion batteries are well established for use in portable consumer products and are increasingly used in high power electro-mobility and photovoltaic storage applications. In hybrid and plug-in electric vehicles degradation and useful lifetime at standard operation conditions are critical parameters in addition to performance and safety. Here stress-induced ageing of commercially available high power battery cells of the type A123 AHR32113M1 Ultra-B, consisting of a LiFePO₄ cathode and a graphite anode have been investigated. A usually accepted capacity loss for electric vehicles of 20% was reached after 8560 stress profiles corresponding to a driving distance of almost 200'000 km. Cycling with a stress profile applying constant power corresponding to the average power and energy of a full stress profile and starting at 60% state of charge showed a much faster capacity loss. Electric impedance measurements show the dependence of the capacity loss and constant phase element at low frequency, indicating Li-ion diffusion blocking in the cathode. Microscopic analysis of anode, separator, and cathode, shows defect formation in bulk material and at interfaces.

Keywords: Electrochemical impedance spectroscopy · Li-ion batteries · Microscopy · Stress cycles

1. Introduction

Lithium-ion rechargeable batteries provide high volumetric and gravimetric energy and power density, have no memory effect and show very little self-discharge when not in use. Despite some early safety and lifetime concerns they are now well established for use in portable consumer electronic products and they are increasingly used in electro-mobility, energy storage, aerospace, and medical implants. Li-ion batteries, including cells and management electronics, are optimized for the various applications concerning performance, environmental conditions, load profile, useful lifetime, biocompatibility, and system reliability and costs. Despite extensive investigations in industrial and academic work[1–4] to identify degradation mechanisms of connectors, electrodes, electrolytes, separators, and various interfaces, standardized procedures for different applications have yet to be established.

In this study the focus lies on capacity loss for different stress cycles, state of charge (SOC) ranges, and storage periods. Electrochemical impedance spectroscopy and microscopy studies have been performed to investigate capacity loss and degradation processes. Adapting the battery power cycling to the worldwide harmonized light vehicles test procedure (WLTC) to electric vehicles allows an estimation of their total cruising range until 20% of the nominal capacity is lost.

2. Test and Electrical Measurement Procedures

In this work commercial high power battery cells of the type A123 AHR32113M1 Ultra-B, consisting of a LiFePO₄ cathode and a graphite anode were investigated. New battery cells exhibit a nominal voltage of 3.3 V, a capacity of 4.4 Ah, and a maximum discharge power of 550 W. This type of battery has been designed for hybrid power trains of light vehicles.[5] The full battery consists of 70 single cells in series to provide a total capacity of 1.04 kWh and a maximum power of 20 kW.

In order to study the capacity loss, rechargeable Li-ion cells are usually cycled by a complete charge and discharge process. For automotive applications, so-called worldwide harmonized light vehicles test procedures (WLTP) were developed to measure the real power consumption during drive cycles (WLTC).[6] In this work the WLTC driving cycle class 3 – comprising low, medium, high, and extra high speed parts – was used to derive the power stress profile of a single cell of the battery pack (Fig. 1). The maximum power is 284.5 W for charging and 356.8 W for discharging and the average power 80.56 W for charging and 55.52 W for discharging. The total time of the stress profile is 1800 seconds whereas 996 seconds are charging and 804 seconds discharging. In order to optimize the overall energy consumption of the hybrid power train and to keep the battery in a defined state the state of charge (SOC) of the cell is 60% (2.64 Ah) at beginning and end of the power stress cycle.

Cell 1 was aged with WLTC power stress cycles. During each cycle the cell fluctuates between 42% and 100% SOC. Intermediate characterization measurements were performed every 51 cycles.

For cell 2 the average power values of the WLTC procedure were used to first discharge the cell for 804 s and then charge it for 996 s. With this procedure the cell was completely discharged and charged, i.e. SOC fluctuated between 0 and 100%. The average power values of the power stress profile were also taken for cell 3 and cell 4, but with modified time and SOC spans. Cell 3 was discharged and charged with 0.88 Ah between 40% and 60% SOC, whereas cell 4 was discharged and charged with 1.76 Ah between 20% and 60% SOC. Cells 3 and 4 had been stored for 10 months at 25 °C ambient temperature and were (over-)discharged. However they were revitalized by slow charging showing
a lower discharge capacity of 3.79 Ah (cell 3) and 3.87 Ah (cell 4).

Cell 5 served as unstressed reference for microscopic analysis. Capacity measurements were performed between power stress cycles in order to determine the discharge capacity of the cells. The characterization procedure started with a complete discharge of the cell to the discharge end voltage of 1.6 V. Then the cell was charged using the constant current–constant voltage procedure (1 C: voltage limit of 3.8 V, termination current of 0.22 A equivalent to 0.05 C) to determine the charge capacity. In order to obtain the discharge capacity the cell was discharged with a current of 0.88 A (0.2 C) to the end voltage of 1.6 V. Impedance spectroscopy (IS) was conducted on cell 1 in a frequency range from 1 mHz to 10 kHz. During the cycling experiments, the IS at 183 different aging stages was measured, one every 51 stress profiles. At each stage four spectra were recorded: at 20, 40, 60, and 80% SOC. All stress tests and characterization measurements were performed in a temperature-controlled safety chamber at 23 °C using the Maccor Series 4000 with a FRA 0355 setup. The IS at 183 different aging stages was measured, one every 51 stress profiles. At each stage four spectra were recorded: at 20, 40, 60, and 80% SOC. All stress tests and characterization measurements were performed in a temperature-controlled safety chamber at 23 °C using the Maccor Series 4000 with a FRA 0355 setup.

3. Results and Discussion

3.1 Discharge Capacity

For standard applications end-of-life of batteries is usually defined to be reached when the capacity is reduced to 80% of their nominal discharge capacity.[7] With cycling according to the WLTC procedure cell 1 was fluctuating on each cycle between 42% and 100% SOC. It reached 80% of the nominal capacity after 8560 WLTC stress profiles (Fig. 2), corresponding to a vehicle-driven distance of 195,779 km. Cell 2 was cycled between 0% and 100% SOC with the average power of the WLTC procedure. End-of-life capacity of 80% was reached after 1175 cycles (Fig. 2).

The total energy throughput to reach the 80% nominal capacity was 284.2 kWh for cell 1 and 38.1 kWh for cell 2, respectively. This demonstrates that the total capacity throughput until end-of-life is reached strongly depends on stress profiles and is application specific. During the storage period at room temperature before stress cycling cells 3 and 4 lost about 15% of their nominal capacity. The comparably inferior performance of cells 3 and 4 can be explained by their storage time in a discharged state. This shows that the absolute cell capacity is not always a conclusive indicator for its state of health and over-discharged periods have to be considered when evaluating stress induced ageing and estimating residual lifetime. In conclusion, the WLTC profile was gentler compared to pure charge–discharge cycles with comparable power stresses, as performed with cells 2 to 4 (Table 1).

3.2 Impedance Spectra

Impedance spectra of cells 1 to 4 taken at 60% SOC are presented in Fig. 3. Spectra of cell 1 have been already published by Cuervo Reyes et al.[8] At medium frequencies an increase of the resistance Re(Z) with ageing is observed. At the initial state cells 1 and 2 show a typical RC-semicircle, which is attributed to the charge transfer resistance at the cathode-electrolyte interface and the current collector interfaces. Their shift to the right and up at the end of life is an indication of increased impedance of electrode contacts and electrolyte.

Cells 3 and 4 show a different impedance characteristic already at the initial state because they were stored for long periods in a discharged state, which leads to decomposition of electrolyte and probably to dissolution of copper from the anode contact. The low frequency end of the impedance is dominated by the concentration-driven Li-ion mass transport in the cathode, which for ideal diffusion should appear as a straight line with slope one.[9,10] A change of this slope with ageing has been reported and discussed within the constant phase element model[9] in which the increase of the slope of impedance is explained by sub-diffusive ion transport. The constant phase behavior has the form $Z = (i\omega)^{-\alpha}$ for concentration-driven transport, and $Z = (i\omega)^{-\alpha} - 1$ for voltage-driven electronic transport with $\alpha = 0$ for perfect insulators and $\alpha = 1$ for perfect diffusive transport.
Table 1. Summary of stress cycle parameters until cells reached 3.52 Ah discharge capacity

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</tbody>
</table>

Considering that Li-ion cells are complex systems composed of inhomogeneous materials with local deviations of ionic and electronic conductivity one cannot exclude from impedance spectra alone that electronic transport in the cathode can become the limiting factor at low frequencies, too.

### 3.3 Microscopic Analysis

To perform microscopic analysis cells 4 and 5 were opened, unrolled (Fig. 4), and samples of about 1.5 × 2.5 cm at selected positions have been extracted. The end faces of the samples were properly cut with a picosecond laser and afterwards polished with the Ga-beam of about 20 nA and 30 keV of a FEI Helios NanoLab 660 G3 UC DualBeam Ga-FIB/SEM microscope. For imaging and material analysis, an electron beam with secondary electron detection (SE) and EDX were used. High resolution ion beam imaging was done with a Zeiss Orion He-FIB with a specified spatial resolution of 0.35 nm. An overview of the polished cross section showing a stack with anode, separator, cathode, and again separator is given in Fig. 5. To reduce material re-deposition during the FIB polishing process on the approximately 160 μm thick cross section, separate regions were polished from two opposite faces and combined in the split image of Fig. 5 for better visualization of layers and interfaces. Starting from the top of the polished cross section the carbon anode with interlaced copper, a separator with three layers (high-low-high density), the LiFePO₄ anode with interlaced aluminum, and again a separator with three layers at the bottom starting the next stack of the rolled topology of the cell can be identified. The copper and aluminum sheets of anode and cathode, respectively, are connected to the outside of the battery cell. In Fig. 6 an expanded view of the three-layered separator is given.

The carbon anode is irregularly structured with surface corrugated grains and voids with size of order 1 – 10 μm. At the interface of carbon and copper conductor (Fig. 7) strings of residual binder are shown. In He-ion images (expanded insert in upper-right corner of Fig. 7) particles with a size of about 10 nm at the surface of the carbon grains and the copper interface can be observed. They are also observed on cathode and separator surfaces. They may be explained by salt precipitation from the electrolyte and may have grown during the drying process.

In the LiFePO₄ cathode of cell 4 regions of enhanced density with a size of several microns are observed (Fig. 8). EDX analysis (Fig. 9) reveals that they contain an order of magnitude more carbon than on average, presumably added by the cell manufacturer to increase the conductivity of otherwise poorly conductive LiFePO₄.
material. To estimate the influence of this inhomogeneous carbon distribution on cathode efficiency, further investigations are required.

At the interface in the cathode of LiFePO₄ and Al (Fig. 10) the formation of cavities at the few micrometer scale can be observed. In the expanded insert in the upper-right corner it is observed that for a large part of the cross section the cracking did not occur at the interface itself, but a few tens of nanometers into the LiFePO₄ cathode layer.

In conclusion the strong dependence of useful lifetime of LiFePO₄ batteries from the stress profile, state of charge, and environmental conditions require quantitative estimations of the influence of the different material degradation processes of the complex battery system for efficient optimization. Microscopic analysis of stressed and unstressed cells combined with electronic and ionic transport modeling and finite element calculations may contribute to resolve some ambiguous interpretations of impedance spectroscopy data.

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Storing Renewable Energy in the Hydrogen Cycle

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Abstract: An energy economy based on renewable energy requires massive energy storage, approx. half of the annual energy consumption. Therefore, the production of a synthetic energy carrier, e.g. hydrogen, is necessary. The hydrogen cycle, i.e. production of hydrogen from water by renewable energy, storage and use of hydrogen in fuel cells, combustion engines or turbines is a closed cycle. Electrolysis splits water into hydrogen and oxygen and represents a mature technology in the power range up to 100 kW. However, the major technological challenge is to build electrolysers in the power range of several MW producing high purity hydrogen with a high efficiency. After the production of hydrogen, large scale and safe hydrogen storage is required. Hydrogen is stored either as a molecule or as an atom in the case of hydrides. The maximum volumetric hydrogen density of a molecular hydrogen storage is limited to the density of liquid hydrogen. In a complex hydride the hydrogen density is limited to 20 mass% and 150 kg/m³ which corresponds to twice the density of liquid hydrogen. Current research focuses on the investigation of new storage materials based on combinations of complex hydrides with amides and the understanding of the hydrogen sorption mechanism in order to better control the reaction for the hydrogen storage applications.

Keywords: Electrolysis · Energy storage · Hydrides · Hydrogen · Synthetic hydrocarbons

Introduction

The energy turnaround requires the storage of large amounts of renewable energy, including seasonal storage. In central Europe for the complete coverage of our energy demands a storage capacity that corresponds to 2000 kg of oil per capita would be required. The transition from an energy economy based on mining resources, i.e. materials and fossil fuels, to a society based on renewable energy and closed materials cycles is essential for the global development towards a sustainable and prosperous economy. The growth of the world population depends on wealth distribution, and according to the analysis of Hans Rosling the world population is going to increase to approx. 11 billion people in 2100. The extrapolation is based on the assumption that global wealth will continue to grow and the birth rate will accordingly decrease worldwide. The global energy demand is expected to increase from today to 2050 by a factor of 3. This will only be possible if the materials cycles are closed, especially the materials used as energy carriers. Despite the plans to reduce energy consumption in the western industrialized countries in the future the political strategies are to grow economically, which is only possible with growing consumption. Physically, wealth is the availability of materials and energy, therefore, increasing wealth requires an increase in energy and material consumption. More than 80% of the energy demand today is covered by fossil fuels, i.e. hydrocarbons that release CO₂ and H₂O upon combustion with air. Unlike water CO₂ does not precipitate out of the atmosphere. Due to the limited resources of fossil fuels and materials, and the effect of the increasing CO₂ concentration in the atmosphere on the climate, a large part of the increasing energy demand must be covered by renewable energy sources. Therefore, the hydrogen cycle, i.e. the production of hydrogen from renewable energy and water, the storage of hydrogen and the combustion of hydrogen in a fuel cell, internal combustion engine or a turbine offers a technical feasible solution to produce an energy carrier directly from renewable energy in a naturally closed cycle.

In this article we describe the basis and current level of technological development of water electrolysis and hydrogen storage in hydrides and describe the recent developments and achievements connected to the Swiss Competence Center in Energy Research (SCCER).

Hydrogen Production by Electrolysis

The Swiss company Lonza SA was founded in Gampel (VS) in 1897 and used electricity to produce calcium carbide and acetylene. In the beginning of the 20th century the products expanded to synthetic fertilizers from nitrogen and ammonia and, therefore, the need for hydrogen grew. Around 1940 Lonza decided to produce the hydrogen on site. Ewald A. Zdansky was mandated to develop a gas generator able to deliver the hydrogen requirements for the chemical production. Due to the hydroelectric power available in the region Zdansky worked on the construction of an industrial electrolyzer in collaboration with the Giovanola Frères SA (GFSA), located in Monthey, that had the large manufacturing tools to produce the first prototype electrolyzer.[1] In 1950 the development led to a patent of the high-pressure industrial electrolyzer (Zdansky-system) manufactured at GFSA and commissioned at Lonza.[2] The market demand for electrolyzers was growing and Lonza sold the intellectual property of the high pressure electrolyzer to LURGI (‘Metallurgische Gesellschaft’) in Butzbach, Germany. LURGI commercialized the electrolyzers and further improved the design of the electrodes and the mechanical assembly in collaboration with GFSA in Monthey, where Jürgen Borchardt (a LURGI engineer) managed the research and development. More than 100 alkaline high-pressure electrolyzers with a power...
of up to 4 MW were installed worldwide. In 1996, the intellectual property as well as the customer database were acquired by GFSA and LURGI discontinued the electrolyzer development and manufacture and closed the electrolyzer section. However, GFSA faced financial shortages in 2001 and the daughter company, GTeC SA, created in 2002 based on the electrolysis activities, also went out of business soon after. Finally, the technology of the high-pressure electrolysis was transferred to a new company, IHT Industrie Haute Technologie SA (IHT) in 2003 with the goal to further develop the large-scale electrolyzer units and replace the asbestos membranes with new materials keeping the particular properties of very long lifetime (>30 years) and high energy efficiency (>80%).

Electrolysis is based on the splitting of water by means of an electrical potential. Hydrogen is evolved on the cathode (–) and oxygen on the anode (+). Between the electrodes is an electrolyte, which acts as an electrical insulator and ionic conductor. The ions transferred between the electrodes are H⁺, OH⁻ or O²⁻ and the corresponding electrolyzers are called acidic (PEM), alkaline or solid oxide. Between the electrodes a membrane separates the evolved gases H₂ and O₂.

The membrane has to fulfill several requirements, e.g. stability under operating conditions, separation of the gases, mechanical separation of the electrodes, ion conduction and mechanical support for pressure differences between the two sides in the cell. Electrolysis requires catalytic electrode materials for a low overpotential of the electron transfer and an electrolyte, but high resistance for electrons and separates the two gases hydrogen and oxygen. A technical electrolyzer is a compromise between the ion conductivity of the electrolyte and the mechanical stability and gas separation of the membrane.

The polymer electrolyte membrane (PEM) electrolyzer transports H⁺ ions in a solid polymer (Nafion®) at around 60 °C (Fig. 1a). The ion conductivity of the PEM is in the order of 6 S/m and water is provided on the oxygen side (anode). Therefore, high purity hydrogen is produced on the cathode. The challenges in the further technical development of PEM electrolyzers are the increase of the conductivity of the polymer membrane, the chemical and mechanical stability of the polymer and the dissipation of the heat produced during the electrolysis process.

The alkaline electrolyzer consists of a microporous membrane (ZrO₂, in poly-phenylene sulphide, Zirfon PERL®) filled with electrolyte that provides the OH⁻ ion conductivity in the order of 120 S/m at 80 °C (Fig. 1b). The 25 wt% KOH in water electrolyte is pumped on the anode and cathode side, while the water is consumed on the cathode (H₂) electrode and half of it appears on the anode (O₂) electrode. Therefore, the electrolyte concentrates at the cathode and dilutes on the anode, the electrolyte from the two sides has to be mixed in order to compensate for the concentration difference. The evolved gases hydrogen and oxygen are extracted from the circulation electrolyte in gas separation units. A heat exchanger allows to maintain the electrolyte at the operation temperature.

The solid oxide electrolyzer (SOEC) transports O²⁻ ions in a solid oxide (ZrO₂, +8 mol% Y₂O₃, La₀.₅Sr₀.₅Ga₀.₈Mg₀.₂O₃) with a conductivity of 1 S/m at 500–850 °C (Fig. 1c). Water vapor is provided on the cathode and therefore the evolved hydrogen contains water and is dried subsequently, while the oxygen on the anode is pure.[5] The major advantage of high-temperature water electrolysis is the possibility to split water partially by heat provided by the steam in installations where lots of high-temperature heat is available.

The LURGI high-pressure electrolyzers are still the most efficient and world largest electrolyzers today, followed by the ambient pressure alkaline electrolyzers from NEL® (former Norsk Hydro) (Fig. 2). Currently mainly alkaline systems are found at a production rate above 30 Nm³/h hydrogen. These large scale electrolyzers exhibit a significantly higher efficiency compared to PEM electrolyzers of comparable power. There are only a few suppliers of electrolyzers on the western market. Very little is known about the developments in Asia, where certainly companies in China and Japan are working on the development of large-scale electrolyzers. Hydrogencics® delivers alkaline electrolyzers (250 kW) and Proton OnSite (Diamond Lite SA) delivers PEM electrolyzers with a power up to 200 kW. Recent development for large-scale PEM electrolyzers by Proton OnSite® and SIEMENS® will soon make systems >1 MW available.

**Hydrogen Storage**

The critical point of hydrogen is at a temperature of 32 K,[11] therefore, hydrogen does not exist as a liquid at ambient temperature.[12] The volume of the hydrogen is reduced by compression and liquefaction. The volume of 1 kg of liquid hydrogen at 20.217 K and 70.78 kg m⁻³.

Compression of hydrogen allows increasing the density of the gas up to approximately half of the density of liquid hydrogen at ambient conditions (35 kg/m³) and requires an isothermal compression work corresponding to 1 kWh/kg per pressure decade or less than 5% of the heating value. Modern high-pressure composite cylinders[13] allow to store up to 4 mass% of compressed hydrogen at pressures up to 800 bar. The mechanical stability[14] of the composite over many hundred pressure cycles and the hydrogen diffusion across the material are beside the safety concerns the major challenges of the development of high pressure hydrogen storage systems.

Liquid hydrogen storage at 20 K is a non-equilibrium storage method and suf-
fers from continuous loss of hydrogen due to evaporation at ambient temperature. The storage systems are open or semi-open in order to limit the pressure increase in the storage tank. The energy demand for the liquefaction process is theoretically 3.92 kWh/kg, technically around 10 kWh/kg. The hydrogen density in the storage system depends on the size of the storage. Liquid hydrogen storage is the method of choice for air and space applications, where large amounts of hydrogen are consumed in a short time and the energy cost for liquefaction is not an economic concern. The major challenges of the liquid hydrogen storage technology are the thermal insulation of the storage tank and the safe release of the evaporated hydrogen.

Materials with a large specific surface area physisorb hydrogen by the Van der Waals interaction. This rather weak interaction, isosteric heat of adsorption,[17] varies between 4 and 8 kJ/mol H₂, allows to absorb at maximum one molecular monolayer of (liquid) hydrogen on the substrate material. This leads to an adsorption proportional to the surface area of approx. 1.5 mass% of hydrogen on a material with a specific surface area of 1000 m²/g.[18] The adsorption of hydrogen on all kind of nano-structured or porous materials,[19] e.g. graphite, carbon nanotubes, zeolites, metal organic frameworks, is described by the lattice gas model of Brunauer-Emmet and Teller.[20] Due to the rather weak interaction, significant adsorption of hydrogen requires low temperatures around 100 K. The major technical and scientific challenges of hydrogen storage by physisorption is the increase of the interaction energy and the search for materials with large specific surface areas.

Hydrogen dissociates and chemisorbs on many metals, intermetallic compounds and alloys (Fig. 3).[21] The hydrogen atoms diffuse on the subsurface layer and intercalate on interstitial sites. The electron density on the interstitial sites of the metal lattice determines the bonding energy of the hydrogen.[22] Partial substitution of the metal elements allows the electron density to be modified and therefore influences the stability of the hydride formed. The thermodynamics of the hydride formation is described by the lattice gas model[23] and leads to the Van’t Hoff equation[24]

\[ R\ln(p/p_0) = \Delta H/T - \Delta S. \]

At low concentration (up to 0.1 H/M) hydrogen forms a solid solution followed by a phase transition into solid solution into the hydride phase (1 H/M). The entropy change upon hydrogen adsorption ΔS corresponds for many systems to the standard entropy of hydrogen ΔS = 130 J/(mol·K) and an equilibrium pressure of 1 bar at 20 °C is found for a hydride with ΔH = T·ΔS = −38 kJ/mol H₂. Hydrogen occupies sites with a radius greater than 0.037 nm[25] and a distance between intercalated hydrogen atoms greater than 0.21 nm.[26] Intercalated hydrogen can reach more than twice the density of liquid hydrogen, e.g. in metal hydrides and complex hydrides. The highest volumetric density was found in metal hydrides[27] to be 150 kg·m⁻³. Metal hydrides have many applications, e.g. battery electrode materials, catalysts, sensors, stationary marine hydrogen storage and hydrogen purifiers, selective separators and compressors. The gravimetric hydrogen density of metallic hydrides is less than 3 mass%.

The elements Al and B form complex hydrides with hydrogen, e.g. alanates Na-AlH₄ and borohydrides LiBH₄. With the discovery of the Ti-catalyzed hydrogen desorption from NaAlH₄ in 1996[28] a wide research field on a new class of solid storage materials was opened. Few years later the alanates were complemented by the borohydrides.[29,30] The stability of the complex hydrides is determined by the localization of the charge[31] on the central atom (Al, B) and, therefore, is proportional to the electronegativity of the cation-forming element. The enthalpy of formation of a series of borohydrides was computed by a DFT calculation and a linear correlation between the enthalpy of formation and the electronegativity of the cation-forming element was found.[32] ΔH [kJ/mol BH₄⁻] = 247.4·EN – 421.2 where EN is the Pauling electronegativity[33] of M in M(BH₄⁻). A similar equation can be derived for alanates ΔH [kJ/mol AlH₄⁻] = 308·EN – 411. Therefore, by applying the Pauling electronegativity of B (2.04) and Al (1.61), a general equation for the enthalpy of formation is derived ΔH [kJ/mol ZHₓ⁻] = 143·EN(B, Al) – 224·EN(B, Al).[34] The formation of the complex hydrides requires wet chemical synthesis; only a few products have been successfully synthesized from the elements. The formation reaction is often different from the hydrogen desorption reaction. Furthermore, the enthalpy of formation of the complex hydride is much larger than the enthalpy of the hydrogen desorption reaction.[35] Alanates tend to desorb via an intermediate hexahydride.
and finally form the elemental hydride, while borohydrides do not exhibit a hexahydride. The hydrogen desorption reaction from borohydrides is accompanied by the desorption of diborane, a product of a side reaction of the hydrogen desorption. This side reaction depends on the stability and mobility of B\textsubscript{2}H\textsubscript{6} and BH\textsubscript{3}, respectively, therefore, above a temperatures of 200 °C no diborane is observed. The alanates and borohydrides have the potential to store up to 7 mass% and 20 mass% of hydrogen, respectively. The volumetric hydrogen density reaches, similar to metal hydrides, around 150 kg/m\textsuperscript{3}. The scientific and technical challenges are the synthesis of the complex hydrides preferably directly from the elements, the control of the desorption reaction including the development of the catalysts. New complex hydrides, which are liquid at room temperature and desorb hydrogen close to ambient temperature are under investigation. With the complex hydrides, the gravimetric hydrogen storage density in hydrides was increased by an order of magnitude from around 2 mass% to 20 mass% in the last 20 years.

With the complex hydrides the gravimetric and volumetric hydrogen density is even greater than that of the hydrocarbons and has reached the maximum densities possible based on the current knowledge of hydrides (Fig. 4). Comparing the available energy from the combustion of hydrocarbons and hydrides, the hydrides deliver twice as much energy because the hydrogen and the carbon is oxidized, while in case of the complex hydride only the hydrogen is oxidized and the host material remains unreacted. The hydrogen storage density of 20 mass% corresponds to an energy density of 7.8 kWh/kg. Therefore, the gravimetric and volumetric energy density of a hydrogen storage system is limited to less than half of the energy density of hydrocarbon fuels, e.g. diesel (12.8 kWh/kg, 10 kWh/l).

**Outlook**

The potential of complex hydrides for large-scale hydrogen storage is huge, but requires a better understanding and improved control of the hydrogen sorption reaction. The reaction pathway in complex hydrides exhibits various intermediates and transition states depending on the type of the central atom, Al, B, or N, and on the reaction conditions. The knowledge of the reaction pathway and the identification of the transient states is of fundamental importance in order to control the hydrogen absorption and desorption processes. Furthermore, development of new materials requires methods to synthesize the complex hydrides as well as overcome the activation barriers by an appropriate catalyst. In other cases it may be important to develop methods to stabilize a certain hydride or to avoid the formation of undesired intermediates, e.g. diborane or ammonia. Finally, the knowledge of the reaction mechanism represents an added value concerning all safety issues of complex hydrides. Beside the pure hydrides, composites, e.g. borohydrides and amides, represent a wide field of new storage materials with interesting properties. While the complex hydrides are in a very early stage of development to the hydrogen storage application, metal hydrides are on a technology readiness level that allows the construction of large-scale hydrogen storage systems.

Metal hydrides represent surfaces,[360] which offer atomic hydrogen and absorb CO\textsubscript{2}, and, therefore, provide sites for the catalytic reduction of CO\textsubscript{2} to hydrocarbons. The reaction mechanism of the CO\textsubscript{2} reduction will be investigated in detail with the goal to identify the parameters determining the C–H and C–C bonds. The understanding and control of the CO\textsubscript{2} reduction reaction bridges between the pure hydrogen storage and the storage of hydrogen in synthetic hydrocarbons.

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Hydrogen Storage in the Carbon Dioxide – Formic Acid Cycle

Cornel Fink, Mickael Montandon-Clerc, and Gabor Laurenczy

Abstract: This year Mankind will release about 39 Gt carbon dioxide into the earth’s atmosphere, where it acts as a greenhouse gas. The chemical transformation of carbon dioxide into useful products becomes increasingly important, as the CO₂ concentration in the atmosphere has reached 400 ppm. One approach to contribute to the decrease of this hazardous emission is to recycle CO₂ for example reducing it to formic acid. The hydrogenation of CO₂ can be achieved with a series of catalysts under basic and acidic conditions, in wide variety of solvents. To realize a hydrogen-based charge-discharge device (‘hydrogen battery’), one also needs efficient catalysts for the reverse reaction, the dehydrogenation of formic acid. Despite of the fact that the overwhelming majority of these reactions are carried out using precious metals-based catalysts (mainly Ru), we review here developments for catalytic hydrogen evolution from formic acid with iron-based complexes.

Keywords: Aqueous solution · Carbon dioxide · Fe · Formic acid · Homogeneous catalysis · Hydrogen storage · Phosphine ligands · Ru

**CO₂/HCO₃⁻/CO₃²⁻ hydrogenation**

Atmospheric carbon dioxide (CO₂) is an almost infinite source of carbon and if utilized as a C₂ building block, countless feedstock chemicals and compounds could be synthesized.[1] Despite its obviously huge potential for the chemical industry, it is not a widespread exploited resource. Several reasons account for this situation such as difficulties to capture CO₂ with economic efficiency from air (approximately 400 ppm). A currently more promising method seems to be to capture carbon dioxide at the source (e.g. power plants) and process the off-gas for further applications.[2] The high thermodynamic stability of the CO₂ (ΔH° = –393.5 kJ/mol)[3] is another challenge.[4] Nature managed to process carbon dioxide as the sole carbon source for all plant life by mastering sunlight-driven photosynthesis,[5] a brilliant concept which inspires scientists to mimic the procedure for hydrogen production and storage.[6]

An alternative approach for the reduction of carbon dioxide, besides electrochemical or photochemical reduction, is via a catalytic reaction, to hydrogenate CO₂ to form formic acid (HCOOH), methanol (H₂COH) or methane (CH₄). Various metals, ranging from precious rare elements such as ruthenium, rhodium, palladium, iridium or osmium down to abundant bulk metals (iron, cobalt, copper), in combination with countless different ligands have been screened towards their ability to hydrogenate carbon dioxide. Although Ru(II) complexes with phosphine ligands are predominant for this task, the number of other successfully tested metal complexes such as iron-based Fe(II)-tris(2-diphenylphosphino)ethyl-phosphine (PP₃) is steadily increasing.[7] The applied reaction conditions are as diverse as the catalysts. Nonetheless, in all – except one[8] – cases, the reductions were carried out under basic conditions, which rather frames bicarbonate (HCO₃⁻) or carbonate (CO₃²⁻) as the substrate rather than CO₂.[9] High hydrogen- and carbon dioxide pressures shift the equilibria towards formic acid formation, while increased temperatures accelerate the reaction rate, but exhibit an detrimental effect on the absolute yield since the hydrogenation of bicarbonate is an exothermic process (ΔG° = –35.4 kJ/mol; ΔH° = –59.8 kJ/mol; ΔS° = –81 J/mol·K).[10]

The reduction of carbon dioxide with heterogeneous and homogeneous catalysts has been under investigation for many decades. A milestone in CO₂ fixation with heterogeneous catalysts was achieved by the Nobel Prize laureate Sabatier in the 1910s by reducing CO₂ directly to methane (Sabatier process). For practical reasons, the focus in the further course of this review article will be on homogeneous catalysis, bearing the advantage that homogeneous catalytic processes can be studied on a molecular level more straightforwardly, which is relevant for mechanistic studies and the fine tuning of the catalysts allows better selectivity. Successful homogeneous catalytic hydrogenations of bicarbonate with homogenous catalysts have been reported as early as from the beginning of the last century.[11] More recent publications from the 1970s describe already more advanced systems, which produced esters (HCOOEt),[12] and upon hydrolysis HCOOH, whereas others formed formate directly in the presence of triethylamine (basic conditions) and catalytically active transition metal complexes (pH₃)[p(CO₂)] = 1:1, 50 bar, RT).[13] Leitner et al. reported on a homogeneous catalyst, formed in situ from [{Rh(cod)Cl}] and Pb₂P(CH₃)₄PPh₃, which produced up to 1150 moles formate per mole rhodium.[14] In 2010, Nozaki presented an Ir-trihydride-pincer complex, which achieved an astonishing TON (turn over number) up to 3 500 000 (after 48 h reaction time) and TOF (turnover frequency) of 150 000 h⁻¹.[15] The latest developments in the field are neatly summarized in several recent reviews.[16]

Important research on the formation of methanol from CO₂ and the reverse reaction, liberation of hydrogen, was done by the Milstein group and numerous high-impact publications give proof of their excellent work.[17] Another approach, based on a three-step cascade synthesis, was reported by the Sanford group.[18] To produce methanol, three different homogeneous
catalysts transform carbon dioxide successively to methanol via reduction of CO₂ to formic acid, then esterification (formate ester) and finally hydrogenation of the ester to obtain free methanol (Fig. 1). While the first two steps are well present in literature, the final hydrogenation is an innovative feature of their work.

Formic acid has an advantage over methanol and methane in terms of hydrogen storage efficiency since no water as co-product is formed during the reduction process (starting from CO₂), which consumes valuable hydrogen equivalents (Fig. 2). Accordingly, formic acid (or more precisely the formate salts) is a promising candidate for constructing a ‘hydrogen battery’, where the energy is stored as reversibly bound hydrogen.[10]

In 2000, we reported on the water-soluble tertiary phosphine ruthenium(II) complex, [RuCl(PTA)] (PTA = 1,3,5-triaza-7-phosphaadamantane), as a pre-catalyst which is capable of hydrogenating bicarbonate (HCO₃⁻) in aqueous solution and does not depend on amines or other additives.[20] The hydride species, which was observed at 60 bar H₂ in acidic aqueous solution, is [RuH₂(PTA)] (pH = 2.0) while [RuH(PTA)Cl] was detected in basic media (pH = 12). Moreover, the turnover frequency of the catalyst depends strongly on the pH. An initial TOF of 800 h⁻¹ was measured in a 9:1 CO₂/HCO₃⁻ mixture (pH = 5.86), whereas a reduced reaction rate was observed in very basic solutions (substrate Na₂CO₃). More detailed investigations on the active species suggested that HCO₃⁻ is the primary substrate, which was confirmed later.[21] The observed induction period at the beginning of the catalytic cycle could originate from the slow formation of the catalytically active species. Furthermore, studies on water-soluble rhodium(II) complexes with meta-monomesulfonated triphenylphosphine (mTPPMS) ligands confirmed the pH dependency of hydride species. It was shown that the pH change caused by CO₂ treatment in aqueous solution affects the distribution of catalytically relevant hydride species.[22] mTPPMS was further examined in combination with Ru(II), where the dimeric [[RuCl(μ²-Cl)(mTPPMS)]₂] complex was identified as a suitable pre-catalyst for bicarbonate hydrogenation, yielding HCOONa under mild conditions (50 °C, pH(H₂) = 10 bar; Fig. 3).[23] The reaction did not require amine additives, nonetheless the reaction rate was considerably higher after the addition of quinoline. The proposed reaction mechanism involves Ru(II)-hydride species with the generalized formula [RuHₓ(mTPPMS)] and HCO₃⁻ as substrate, where X represents H, HCO₃⁻ or the product HCOO⁻. Under harsher conditions, at 80 °C and 95 bar, previously unreached high TOFs of 9600 h⁻¹ for water-soluble Ru(II) phosphine complexes in aqueous solution were measured.

Another class of catalytically active complexes are the Ru(II) arene compounds with the general formula [(η⁶-arene)Ru(II)Cl(PTA)].[24] These complexes can exchange one or both Cl⁻ for hydrides, forming [(η⁶-arene)Ru(II)H(PTA)Cl] and [(η⁶-arene)Ru(II)H₂(PTA)]. Besides the ability to hydrogenate bicarbonate, an interesting dynamic behavior of the compounds was noticed. During prolonged hydrogenation at elevated temperatures, an excess of PTA leads to the loss of the arene group, and the resultant complexes show catalytic activity for hydrogenation of HCO₃⁻. Identified species were [RuH₂(PTA)Cl], [RuH(PTA)₂], [RuH₂(PTA)₂], [RuH(PTA)Cl] and [RuH(PTA)]₂⁺. At the end of the experiment, the in situ formed catalyst reached almost full conversion of bicarbonate. Interestingly, no initial induction period was observed as described for the direct application of [RuCl₂(PTA)] catalysts.[20] Later, a series of imidazolium-tethered ruthenium(II)-arene complexes was synthesized and their application for catalysis was subsequently assessed,[25] Dimeric Ru(II) salts with the general structure [[RuCl(μ²-Cl)(η⁶-arene)]₂] were treated with phosphine ligands (PPh₃, PCy₃) which lead to catalyst precursors. These complexes were active in aqueous solution on the reduction of bicarbonate and carbonate. High-pressure NMR measurements allowed the identification of a bicarbonate-hydride intermediate.

A similar group of compounds was scrutinized in 2007.[26] There, the water-soluble Ru(II) complexes [Cy₆RuX(PTA)] (X = Cl, Br, I; mPTA = 1-methyl-1,3,5-triaza-7-phosphaadamantane) acted as precatalysts in the hydrogenation of HCO₃⁻ and CO₃⁻ in amine- and additive-free aqueous solution under reasonable conditions (30–80 °C, pH(H₂) = 100 bar).

<table>
<thead>
<tr>
<th>Energy content [MJ/kg]</th>
<th>Storage efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ + CO₂ ⇌ HCOOH</td>
<td>5.22</td>
</tr>
<tr>
<td>3H₂ + CO₂ ⇌ CH₃OH + H₂O</td>
<td>15.2</td>
</tr>
<tr>
<td>4H₂ + CO₂ ⇌ CH₄ + 2H₂O</td>
<td>30.15</td>
</tr>
</tbody>
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Fig. 2. CO₂ hydrogenation in respect to consumed H₂ equivalents.

Fig. 3. Time course of HCO₃⁻ reduction by [[RuCl₂(mTPPMS)]₂] and mTPPMS; final concentration of sodium formate did not exceed the initial bicarbonate concentration; no other products were detected. Reprinted from ref. [23] with permission from Applied Catalysis A: General.
The activities are described as moderate for bicarbonate hydrogenation.

A NMR study confirmed in 2007 the existence of a previously proposed intermediate in the catalytic hydrogenation of carbon dioxide/bicarbonate in aqueous media. \(^\text{[2]}\) The water-soluble Ru(ii) precatalyst with the structure [RuCl\(_2\)(PTA)(9-anSe\(_3\))] (9-anSe\(_3\) = 1,4,7-trithiacyclononane) has low catalytic activity for the hydrogenation of bicarbonate but allowed the identification of an important intermediate by \(^1\)H, \(^13\)C, and \(^31\)P NMR spectroscopy, where a hydride and a bicarbonate are coordinated to the Ru center. Accordingly, the \textit{in situ} observed catalytically active species can be described as [Ru(H)(CO\(_2\))\((\text{PTA})(9\text{-anSe})\)] (Fig. 4). \(^\text{[2]}\) The reduction of carbon dioxide takes place via bicarbonate hydrogenation and the rate-limiting step seems to be the intramolecular transfer of hydrides on the substrate.

Beside ruthenium(ii) complexes, iridium(iii) complexes showed comparable catalytic activity in aqueous phase carbon dioxide (HCO\(_3\)) hydrogenation. \(^\text{[7]}\) We investigated two water-soluble iridium complexes, [Cp*Ir(PTA)\(_2\)] and [Cp*Ir(PTA)\(_2\)Cl\(_2\)] as catalyst precursors. The monophosphine compound performed poorly while the bisphosphine precatalyst demonstrated moderate activity for bicarbonate hydrogenation. Furthermore, the catalysts were fully characterized (solution and solid state, Fig. 5) \(^\text{[27]}\) and the catalytically active species [Cp*IrH(PTA)]\(^+\) was identified by multi-nuclear NMR studies and independent synthesis. Optimal conditions for the hydrogenation were found at higher temperatures and a slightly basic pH of 9.

\[\text{RuCl}_2(\text{PTA})_2,\text{ which afforded 0.2 M FA aqueous solutions at 40 °C and 200 bar (p(H\(_2\));p(CO\(_2\)) = 3:1), however the same compound achieved excellent 1.9 M formic acid in DMSO (p(H\(_2\));p(CO\(_2\)) = 1:1, 100 bar, 50 ºC (Fig. 6), in D\(_2\)O, H-D exchange in formic acid.}\]

The high stability of the catalyst allowed multiple recycling without detectable decreases in activity in both reaction media. Moreover, the catalyst exclusively produces formic acid and the final pH was measured as 2.70, proving the robustness of the catalyst in an acidic environment.

It was only in 2010 when, in collaboration with Beller’s group, a homogeneous iron catalyst for bicarbonate hydrogenation was discovered. \(^\text{[7]}\) Different iron-containing precursors and numerous phosphine- and nitrogen-containing ligands were studied. An excellent catalyst, Fe(BF\(_4\))\(_2/PP_3\) (PP\(_3\) = tris[2(diphenylphosphino)ethyl]phosphine), which forms \textit{in situ}, was identified, hydrogenations proceed smoothly with low catalyst loadings of 0.14 mol% at 80 ºC. NaOOCH was produced in 88% yield with a turnover number of 610, the active species were identified by multi-nuclear NMR spectroscopy and an X-ray crystal structure of the initial [FeH(PP\(_3\))] was obtained. The catalyst was tested on other substrates, verifying that amides and esters are also accessible by hydrogenating CO\(_2\). Methyl formate was produced in good yield (56%) and a maximum TON of 585 was accomplished – two times higher than the best previously reported iron catalysts. In addition, dimethylformamide was formed in high yield (75%) with a TON of 727, which was previously only known from precious metal systems (Ru, Ir, or Rh), and N-formylpiperidine was obtained in 41% yield (TON = 373). Ethyl or propyl formate esters were formed as well, the yields and TONs were lower compared to those of methanol (MeOH) based systems. It was known from earlier publications that the presence of base is crucial for favorable thermodynamics. \(^\text{[59]}\)

Later in 2012, a new generation of iron-based catalysts was presented. \(^\text{[36]}\) The addition of fluorotris-2-(diphenylphosphino)phenylphosphine iron(iii) tetrafluoroborate to a methanolic bicarbonate solution afforded high TONS\(_{\text{MeOH}} > 7500\) and TONs\(_{\text{DCOOH}} > 750\) (100 ºC; p(H\(_2\)) = 60 bar; 0.005 mmol...
The homogeneous catalyst [RuCl₃(phenylphosphine)] was identified by high-pressure NMR studies. Furthermore, a tetradeutate phosphorus ligand, which is easy obtainable in a one-pot reaction, was essential for successful catalysis. The synthesized complexes are stable at high temperatures (>100 °C) and under air.

A novel synthesis route for formate salts, an important industrial precursor, was discovered by Beller’s group in 2014.[32] In their study, a series of ruthenium pincer complexes was examined towards simultaneous methanol oxidation and bicarbonate reduction (hydrogenation), a green process without involving toxic gases (CO) to synthesize formate salts with excellent TOF >1300 h⁻¹, TON up to 18000, and total conversions over 90%. Above all, this is the first report about combined catalytic dehydrogenation of methanol and reduction of HCOO⁻ to a formate salt. The application of a commercially available pincer complex, HPNPb₆/Ru, resulted in a TON over 18000 (36 h) for the formation of KOOCH.

Table 1. Formic acid consumption rates, hydrogen production rates, and turnover frequencies of the continuous system at 150 bar constant pressure.

<table>
<thead>
<tr>
<th>T [°C]</th>
<th>HCOOH input [mL · min⁻¹]</th>
<th>H₂ outflow [mL · min⁻¹]</th>
<th>TOF [h⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.21 ±0.01</td>
<td>140 ±10</td>
<td>230 ±5</td>
</tr>
<tr>
<td>120</td>
<td>0.42 ±0.01</td>
<td>290 ±10</td>
<td>460 ±24</td>
</tr>
</tbody>
</table>

50 mL reactor, 12 mL initial solution of HCOOH/HCOONa (9:1, 4M), [Ru(H₂O)₆]tos₆ (125 mmol), mTPPTS (250 mmol).

Fig. 8. Water-soluble m-triphenylphosphine trisulfonated ligand.
the aqueous homogeneous systems, even after 92 recycling experiments. However, according to the XRF spectra, when these solid catalysts were washed with water, the Ru–mTPPTS complex could be removed gradually, showing that the zeolites here were mainly acting as physical adsorbents. The catalyst immobilization on mesoporous silica was successful and led to a patent application.\cite{36}

In 2010, the effect of the water-soluble sulfonated phosphine ligands on ruthenium-catalyzed generation of hydrogen from HCOOH was investigated. Different phosphines were synthesized by changing substituents, thus varying the bulkiness, basicity, hydrophobicity. It was shown that the best ligands were mTPPTS and mTPPDS (triphenylphosphine, m-disulfonated) that offer a good compromise between steric effects and phosphine basicity, alongside with a good stability and an excellent solubility in water.

So far, viable results in our group were obtained using ruthenium-based catalysts, but the need for precious metal has inherent drawbacks. Due to its scarcity, it is relatively expensive; the large scale and industrial use could have limitations. With the idea of using a non-precious metal-based catalyst, a collaboration between our group and Beller’s resulted in the development of an outstanding system, with TOF up to 92'000, based on [Fe(BF\(_4\))]\(2\)·6H\(_2\)O metal precursor with PP\(_3\) as ligand capable of selective formic acid dehydrogenation in propylene carbonate solution (Table 2).\cite{38}

\[ 2\text{Fe}^2+ + n\text{H}_2 \Rightarrow 2\text{Fe}^3+ + n\text{H}_2\text{O} \] (1)

The reversible hydrogen storage has been achieved using different conditions and catalysts. In order to come closer to the realization of a practical H\(_2\) storage–discharge device, the equilibrium position of formic acid/amine–CO\(_2\) systems has been examined as a function of pressure and temperature under isochoric conditions.\cite{32} It appears that high yields of formic acid dehydrogenation into H\(_2\) and CO\(_2\) are favored by low gas pressures and/or high temperatures and H\(_2\) uptake is possible at elevated H\(_2\)/CO\(_2\) pressures. The development of systems capable of charging/discharging is of great interest, as it could be used for small and portable applications.

Recently we have evaluated and summarized the potential of the formic acid for hydrogen storage and delivery.\cite{43} The review widely explains the trends using both homogeneous and heterogeneous catalysts, explaining the advantages and the disadvantages of each method. Obviously heterogeneous catalysts are easier to recycle, but in general, homogeneous catalysts tend to be more active and selective, although the gap is closing. The alternative hydrogen storage possibilities were also reviewed, focusing on the different approaches, including both chemically or physically bound H\(_2\), comprising the use of formic acid.\cite{41}

For a long period, only neutral and anionic ligands were used as catalyst precursors for the liberation of hydrogen from HCOOH. In 2013 we published the use of cationic phosphine precatalysts for formic acid dehydrogenation.\cite{42} To obtain such phosphines, ammonium methyl substituents were introduced into the triarylphosphines. Several similar ligands were tested, varying in the charge (from 1+ to 6+) and in bulkiness. The best results were achieved with a 2+ ligand, charged twice on the same aryl group. Comparing the dehydrogenation reaction rates with these phosphines to the mTPPTS under similar experimental conditions, the cationic ligands are more efficient. This could be due to the overall positive charges, which renders the environment cationic around the central metal atom and, therefore, leads to a faster coordination/migration of the negatively charged species (HCOO\(^-\), H\(_2\)O, and H\(_2\)). However, it is more difficult to synthesize such cationic ligands, and they are less robust, being sensitive to oxygen.

In the case of pressurized reaction systems it is not easy to determine the concentration of dissolved species such as HCOOH, HCOO\(^-\), CO\(_2\), Na\(_2\)CO\(_3\), and NaHCO\(_3\), as well as the pH, in situ, under H\(_2\) and/or CO\(_2\) pressure.\cite{43} It can be done by multinuclear NMR spectroscopy, as the chemical shift for \(^13\)C and \(^1\)H NMR are dependent on the pH of the solution and then with a calibration curve it is then possible to relate the pH to the chemical shift of the H and C atoms of the formic acid.

For the solute concentration, it was found that the integrals of formic acid, formate, carbonate, bicarbonate and carbon dioxide NMR signals are proportional to their concentrations if appropriate long relaxation delay times (D1) were chosen in the experiments. This tool has been proven valuable to investigate reaction kinetics.

Table 2. Selective iron-catalyzed hydrogen evolution from formic acid using iron precursors.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>(V_{2\text{h}}) [mL]</th>
<th>(V_{3\text{h}}) [mL]</th>
<th>TON(_{2h})</th>
<th>TON(_{3h})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>([\text{Fe(BF4)}_2]\cdot6\text{H}_2\text{O/PP}_3)</td>
<td>146</td>
<td>215</td>
<td>562</td>
<td>825</td>
</tr>
<tr>
<td>2</td>
<td>([\text{Fe(BF4)}_3]\cdot6\text{H}_2\text{O/PP}_3)</td>
<td>333</td>
<td>505</td>
<td>1279</td>
<td>1942</td>
</tr>
<tr>
<td>3</td>
<td>([\text{FeH}\text{(PP}_3\text{)}]\text{BF}_4)</td>
<td>194</td>
<td>295</td>
<td>745</td>
<td>1135</td>
</tr>
<tr>
<td>4</td>
<td>([\text{FeH/PP}_3\text{)}]\text{BF}_4/\text{PP}_3)</td>
<td>319</td>
<td>500</td>
<td>1227</td>
<td>1923</td>
</tr>
<tr>
<td>5</td>
<td>([\text{FeH}\text{H}(\text{PP}_3\text{)}]\text{BF}_4)</td>
<td>189</td>
<td>294</td>
<td>727</td>
<td>1129</td>
</tr>
<tr>
<td>6</td>
<td>([\text{FeH}\text{(H}_2\text{)}]\text{PP}_3\text{)}\text{BPh}_3)</td>
<td>174</td>
<td>264</td>
<td>670</td>
<td>1015</td>
</tr>
<tr>
<td>7</td>
<td>([\text{FeCl}\text{(PP}_3\text{)}]\text{BF}_4)</td>
<td>0.4</td>
<td>0.4</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

![Fig. 9. Tris[2-(diphenylphosphino)ethyl]phosphine ligand.](image-url)
and mechanisms in H\textsubscript{2} storage/delivery with the carbon dioxide–formic acid systems under H\textsubscript{2} and CO\textsubscript{2} pressures (Fig. 10).\textsuperscript{[43]}

In the meantime, research on mTPPTS was still going on and the mechanism of the first ‘fast’ cycle for formic acid dehydrogenation catalyzed by mTPPTS ruthenium complex was elucidated.\textsuperscript{[34,44]}

Using NMR techniques and time-resolved manometry, the dehydrogenation reaction was intensively studied and some key catalytic intermediates were identified. With those data, a rational cycle was proposed, explaining the transition to the slow cycle.

The iron(ii) based catalytic precursors were further investigated (Fig. 11).\textsuperscript{[44]}

Optimization of the conditions (solvent, concentration, temperature) led to highly efficient catalyst systems with comparable activity to most known noble-metal catalysts used for this transformation. Spectroscopic investigations (IR, Raman, UV/Vis, XAS) revealed the presence of different iron formate and hydride complexes. The iron κ\textsuperscript{2}-formate [Fe(κ\textsuperscript{2}-OOCH)(PP\textsubscript{3})] was observed for the first time under in situ reaction conditions and identified as the key active species for the catalysis. The deactivation of the catalyst by chloride could also be monitored easily by in situ IR spectroscopy and correlated with the evolution of H\textsubscript{2} gas. Computational studies were also carried out to support the proposed reaction pathways.

**Acknowledgements**

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**Fig. 10.** Chemical shifts of the HCOO\textsuperscript{-}/HCOOH \textsuperscript{13}C NMR doublet (c\textsubscript{total} = 0.1 M) (blue squares, left axis) and \textsuperscript{1}H NMR singlet (c = 0.1 M) (red triangles, right axis) as a function of pH. Reprinted from ref. [42] with permission from Dalton Transactions.

**Fig. 11.** Summary of the activation and deactivation pathways of the Fe(BF\textsubscript{4})\textsubscript{2}·6H\textsubscript{2}O/PP\textsubscript{3} catalyst system as well as proposed species formed based on the results of spectroscopic analyses. Reprinted from ref. [45] with permission from Chemistry - A European Journal.
Redox Flow Batteries, Hydrogen and Distributed Storage

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Abstract: Social, economic, and political pressures are causing a shift in the global energy mix, with a preference toward renewable energy sources. In order to realize widespread implementation of these resources, large-scale storage of renewable energy is needed. Among the proposed energy storage technologies, redox flow batteries offer many unique advantages. The primary limitation of these systems, however, is their limited energy density which necessitates very large installations. In order to enhance the energy storage capacity of these systems, we have developed a unique dual-circuit architecture which enables two levels of energy storage; first in the conventional electrolyte, and then through the formation of hydrogen. Moreover, we have begun a pilot-scale demonstration project to investigate the scalability and technical readiness of this approach. This combination of conventional energy storage and hydrogen production is well aligned with the current trajectory of modern energy and mobility infrastructure. The combination of these two means of energy storage enables the possibility of an energy economy dominated by renewable resources.

Keywords: Electrical energy storage · Hydrogen · Redox flow batteries

1. Introduction

1.1 Growing Challenges for the Electrical Grid

Around the world, concerns about energy security, sustainability, and the environment have prompted a re-evaluation of the ways in which we produce and consume (or more precisely, convert) energy. As a result, there is a growing effort to transition the global energy mix from conventional sources, such as fossil fuels and nuclear energy, to more sustainable sources such as hydro, wind and solar. Indeed, from 2002 to 2012, the net renewable electricity generation worldwide increased by 62.5%\textsuperscript{[1]}.

As of 2013, 25.4% of European electricity, and 13.6% of overall energy (including transport, electricity, and heating/cooling) was derived from renewable resources.\textsuperscript{[2]} Moreover, these values are set to grow significantly in the coming years. By 2020, the European Union is targeting 20% reliance on renewables for its overall energy mix.\textsuperscript{[3]} These targets are primarily being met through the installation of wind, photovoltaic, and concentrated solar generation facilities. However, the growing penetration of electric vehicles also plays a key role in shifting the energy mix by reducing the need for petroleum.

While these changes to the energy mix represent significant progress toward social, environmental, and political goals, they also represent a growing challenge for the world’s electrical grids. Currently, most electrical grids are designed to produce electricity ‘just in time’ – as additional load is added to the grid, generating stations must simultaneously ramp up to meet the demand and keep the grid voltage and frequency stable. As consumer demand is inherently unpredictable, some ‘reserve’ generation capacity needs to be available at all times to cope with large increases in demand. This reserve capacity has traditionally taken the form of redundant generating stations which are idle, but synchronized with the grid so that they can react immediately (so called ‘spinning reserve’). These resources are both inefficient and costly, as they are spinning (i.e. consuming fuel), but primarily operating at zero-load. Nonetheless, this model for the electrical grid is quite satisfactory for coping with highly variable demand for electricity, provided that the supply of electricity is reliable. However, with the growing implementation of renewable resources such as wind and solar, this assumption is rapidly losing its validity.\textsuperscript{[4]}

For grids with a large penetration of renewable energy, both supply and demand become unpredictable. Solar irradiation can vary significantly from minute to minute depending on cloud formations and other atmospheric conditions. A passing cloud can cause megawatts of solar generation to suddenly disappear from the grid, necessitating other generating stations to rapidly ramp up their output to maintain the stability of the grid. As the cloud passes, the solar generation becomes available again, requiring the other generating stations to suddenly curtail their output to compensate. The availability of wind is equally unpredictable. If these fluctuations are not compensated for, the power quality (i.e. line voltage and frequency) on the grid can deteriorate, eventually causing localized or even cascading power outages. As the energy mix continues to evolve, favouring renewable resources, these fluctuations will become increasingly disruptive, pushing beyond the ramping limitations of conventional power stations. A larger share of ‘spinning reserves’, primarily gas-fired generators, will need to be allocated to stabilize the system. In effect, this means that it becomes increasingly necessary to burn fossil fuels simply to utilize renewable energy sources, and of course this largely undermines the goal of using renewable energy in the first place (e.g. reduced dependence on fossil fuels, reduced atmospheric emissions, etc.).

The growing use of electric vehicles can create similar problems of grid insta-
bility. Owners of these vehicles expect to be able to recharge in a timeframe which is reasonably similar to conventional liquid-fuelled vehicles. These quick charging stations can easily consume over 100 kW each, and charging may take up to an hour or more. Moreover, drivers will expect to be able to charge whenever necessary, creating a large magnitude, unpredictable load on the grid. Finally, each driver who replaces a petroleum-fuelled vehicle with an electric vehicle is essentially shifting load from the petroleum infrastructure to the electrical grid. This will increase the total load on the electrical grid, which will not only require additional generators, but will also tax the electrical transmission and distribution infrastructure. As the infrastructure reaches its limits, blackouts will become increasingly common.\(^4\)

Hydrogen-fuelled vehicles have been considered as an alternative to fossil-fuelled vehicles for years. Unfortunately, however, hydrogen is commonly obtained by reforming fossil fuels, resulting in hydrogen which is not truly ‘clean’ (in the sense of being carbon neutral). Electrolyzers may be used to obtain hydrogen by water splitting. Currently, however, the electricity used to drive the electrolysis comes from fossil fuel and nuclear resources, again undermining the advantages of this approach. Moreover, common alkaline electrolyzers are not very tolerant of highly variable, intermittent operation, making them somewhat incompatible with most renewable resources. Polymer electrolyte membrane (PEM) electrolyzers are more capable of coping with an intermittent power supply, but they require large amounts of precious metal catalysts (e.g. Pt and Ir), making them very costly. Finally, the lack of a hydrogen distribution infrastructure has largely undermined efforts to transition to a ‘clean’ hydrogen energy economy.

The current grid architecture is able to tolerate the existing level of unpredictability on the demand side. However, the present trajectory of energy production and consumption will significantly stress the system in the coming years. Fundamentally, the notion of ‘just-in-time’ electricity production is incompatible with unpredictable energy sources, such as wind and solar, and large, unpredictable loads, such as electric vehicles. In order to achieve the energy goals of this decade, a more flexible grid infrastructure is needed, and the key to achieving this flexibility will be large-scale electrical energy storage.\(^4\)

### 1.2 The Role of Energy Storage in Tomorrow’s Electrical Grid

An electrical grid with a large amount of energy storage capacity moves away from the paradigm of ‘just-in-time’ energy production by essentially decoupling energy production from consumption. Instead, such a grid operates on an ‘as available’ or ‘on demand’ basis – energy is stored whenever it is available from the generation infrastructure, and supplied to consumers according to demand. In effect, the energy storage infrastructure acts as a buffer between generation and consumption.\(^5\) This buffering is critical for the next evolution of the electrical grid for two reasons; it protects consumers from variability in generation (e.g. clouds passing over a solar station), and it protects generators from large variability in demand (e.g. electric vehicle charging). Thus, grid-scale energy storage is necessary to enable the widespread implementation of renewable energy sources and electric vehicles.

However, there are numerous additional benefits to electrical energy storage. Such systems can be used to offset the ‘peaks’ in electrical demand. In such a regime, energy is stored when demand is low, and then time-shifted to periods when demand is high. Large electrical consumers (e.g. steel mills) may engage in this practice to reduce their peak demand (known as ‘peak shaving’), and the accompanying demand charges. Meanwhile, electrical generators may do the same in order to reduce their perceived load (known as ‘load levelling’), thereby avoiding the need to start up costly peak generating units. Additionally, small independent power producers may utilize energy storage assets to capitalize on fluctuations in the price of electricity (a practice known as ‘energy arbitrage’). Grid operators may use electrical energy storage to help regulate voltage and frequency on the grid. Moreover, energy storage installations may be placed downstream of congested transmission lines, and used to alleviate congestion in a manner similar to load levelling. In some cases, this strategy allows grid operators to defer transmission line upgrades which would otherwise be necessary to serve peak demand for only a few hours per day.\(^5\)

All of these applications give rise to a growing market, which promises to be quite large in the coming years. According to Deutsche Bank Research, in the next twenty years approximately 30 billion Euro will be invested in electrical energy storage infrastructure within Germany alone.\(^6\) By 2040, they estimate that 40 TWh of storage will be required to cope with the expected surpluses. At the global scale, Citi Group estimates that the global market for energy storage will reach 240 GW, amounting to a market size of more than 400 billion USD.\(^7\) It is interesting to note the different orders of magnitude between the projected power (GW) and energy (TWh) requirements for future energy storage systems. It is clear that from a market perspective, the value of these systems lies in their energy capacity.

Several technologies are being considered to address the growing technical needs and market opportunities. Indeed, from a technological standpoint large-scale electrical energy storage is not a new concept. Large pumped hydroelectric stations have long been used to store energy by pumping water from a low elevation to a higher elevation. To recover this energy, the water is allowed to flow downhill under the influence of gravity, passing through a turbine along the way. Unfortunately, this approach is highly geographically constrained, as it typically requires existing natural features such as mountain lakes to be practical.\(^5,8\) In a similar approach, air is compressed into a reservoir to store energy, and allowed to expand through a turbine to recover the energy. These systems tend to be quite large, and have a relatively low efficiency due to heat rejection during the compression step.\(^5,8\) Instead, it is desirable to have an efficient, scalable, flexible technology that can be deployed to a variety of locations.

Various other technologies, such as high energy flywheels, semiconducting magnetic energy storage, and electrochemical capacitors have been proposed as well. While these systems are relatively modular and suitable for power conditioning applications, they do not provide the energy capacity needed to time-shift the energy produced by renewable resources.\(^5,8\) Instead, electrochemical systems appear to be the most promising for these applications.

Several battery technologies are currently being considered and demonstrated for grid-scale deployment.\(^5\) High-temperature sodium batteries provide high energy density and relatively long lifetime. However, these systems must operate at high temperatures (250–350 °C) in order to maintain conductivity. Large, containerized arrays of lithium ion batteries have also been proposed and demonstrated. These systems are very sensitive to temperature, and thus require good auxiliary thermal management systems. Moreover, very complex battery management systems are required to keep all of the individual cells balanced and prevent overcharging. Perhaps the largest concerns, however, are safety and cost. Even the recently released Tesla Powerwall costs between 350 and 430 USD/kWh,\(^10\) falling short of the U.S. Department of Energy target of 100 USD/kWh.\(^10\) Moreover, the serious fire hazard presented by these batteries is well known at the small scale.\(^11\) For a grid-scale installation, the results could be catastrophic. For these reasons, one of the most promising candidates for grid-scale energy storage is the redox flow battery.
2. Redox Flow Batteries

A redox flow battery (RFB) is a type of secondary battery system in which charge is stored and released by oxidizing or reducing active species in a flowing solution. The active species remain solubilized in the surrounding electrolyte during operation. During charging, the electrolyte is pumped through an electrochemical cell, consisting of two electrodes separated by an ion-exchange membrane (Fig. 1). Current is supplied to the electrodes via conductive current collectors, polarizing the electrodes. As a result of polarization, redox reactions occur at the surfaces of the electrodes, resulting in the oxidation (positive half-cell) and reduction (negative half-cell) of the active species dissolved in electrolytes. These charged electrolytes then pass out of the electrochemical cell and into storage reservoirs. To discharge the system and recover the stored energy, the electrochemical process is reversed. The unique aspect of RFBs is their system architecture consisting of a central electrochemical cell/stack and external tanks. In conventional batteries, the active material is stored within the cell itself; in effect coupling the power output and energy capacity. By storing the electrolytes externally, the energy capacity can be scaled arbitrarily by increasing the volume of stored electrolytes. Similarly, the power output of RFB systems is determined by the cell area. This decoupling of power and energy makes RFBs highly scalable and flexible, which in turn makes them uniquely suited for grid-scale applications.[13]

The specific redox chemistry is another key aspect of these systems. The redox chemistry determines the maximum energy density (according to the solubility of the active species) and the typical operating voltage. Numerous redox chemistries have been proposed and demonstrated. Among the most common are: Fe/Cr, Zn/Br, and all-vanadium (V/V). Other chemistries involving two-phase processes also exist: all-iron (Fe/Fe), all-copper (Cu/Cu), H/Br, V/air, etc.[13–18]

Among the numerous redox chemistries that can be utilized in an RFB architecture, the all-vanadium chemistry is perhaps the most prototypical. We consider it here, as an illustrative example. In a vanadium redox flow battery (VRFB), V(IV) is oxidized to V(V) in the positive half-cell during charging, while V(III) is reduced to V(II) on the negative half-cell:

\[ V(IV) + e^- \rightarrow V(III) + e^- \]

Protons conduct the current through the membrane; upon charge, a number of protons equal to the number of transferred electrons are transferred from the positive electrolyte into the negative electrolyte. Upon discharge, the opposite reactions occur. The standard cell potential is ca. 1.25 V. The activated vanadium species are typically dissolved in an aqueous supporting electrolyte containing sulfuric acid, although other acids, such as methanesulfonic acid and hydrochloric acid have also been used.[19] Since both half-cells are based on vanadium active species, cross-contamination between the two half-cells is not a major concern. In effect, unintentional mixing of the two electrolyte streams results in a chemical discharge and subsequent loss of stored energy, but does not otherwise degrade the solutions.[13–17]

Regardless of the composition of the electrolyte, the maximum energy density of the system is typically determined by the limits of solubility of the active species. In practice, the concentration of active species is limited from 1 to 2 M, yielding an achievable energy density of approximately 25 to 40 Wh per litre of electrolyte.[13–17] This is the main technical limitation of modern flow battery systems – the energy density is intrinsically limited by the solubility of the active species.

Significant effort has been placed on enhancing the solubility of the various active species in solution. In particular, previous work has focused on improving solubility by changing the composition of the supporting electrolyte[19–22] and introducing various additives.[23–27] Although significant progress has been made, these approaches are unlikely to yield disruptive improvements in energy density. Moreover, they are highly dependent on the specific chemistry, and thus cannot be readily generalized to other redox chemistries.

3. Dual-Circuit Redox Flow Battery

3.1 Two Levels of Energy Storage

The dual-circuit redox flow battery was developed in order to bypass the energy density limitations of conventional RFBs, by adding a second ‘level’ of energy storage.[28,29] Energy may be stored conventionally, in the liquid electrolyte, or converted to hydrogen gas through indirect electrolysis of water. This design allows energy exceeding the conventional capacity of the battery to still be captured and stored in the form of hydrogen. The energy stored within the hydrogen may be returned to the electrical grid using stationary fuel cells, or used to power fuel cell vehicles, to enrich natural gas, or in other industrial processes. In this way, excess energy is never wasted. This approach enables continuous storage of surplus renewable energy, even when the conventional storage capacity of the battery has been reached. Moreover, this approach eliminates the need to oversize the battery.

In order to accomplish this, a secondary flow circuit was added to each half of the redox flow battery architecture (Fig. 2). On the negative half-cell, the secondary flow circuit contains a catalytic reactor where the negative electrolyte is chemically discharged, producing hydrogen gas according to Eqn. (3):

\[ 2H^+ + 2D^- \rightarrow H_2 + 2D \]  

where D− is an electron donor. The production of hydrogen consumes protons in the electrolyte solution. It is critical to maintain a relatively constant concentration of protons in order to ensure good electrolyte conductivity and maintain the solubility of the active species throughout the cycle.
Thus, a source of protons is also needed. These protons are liberated in the positive catalytic reactor via the water oxidation reaction:

\[ 2\text{H}_2\text{O} + 4\text{A}^\cdot \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{A} \]  

(4)

where \( \text{A}^\cdot \) is an electron acceptor. The protons liberated by this reaction pass from the positive half-cell to the negative half-cell, via the membrane, providing additional reactant for the hydrogen evolution reaction. Thus, if water is added stoichiometrically, both of these reactions may proceed indefinitely, assuming a constant supply of electrolytes with appropriate redox potentials to drive water oxidation (Eqn. (4)). For this reason, the \( \text{Ce}(\text{iii})/\text{Ce}(\text{iv}) \) couple was utilized for our proof-of-concept work:

\[ \text{Ce}(\text{iv}) + e^- \rightarrow \text{Ce}(\text{iii}), E^\circ = 1.72 \text{ V} \]  

(5)

Despite sufficient thermodynamic potentials to drive the indirect water electrolysis reactions, catalysts were still needed to enhance the kinetics of the reactions. \( \text{RuO}_2 \) was utilized to drive the water oxidation reaction, due to its suitability in acidic conditions. For the hydrogen evolution reaction, \( \text{Mo}_2\text{C} \) was utilized. These catalysts lower the overpotential sufficiently to allow both reactions to proceed spontaneously in the presence of the charged electrolytes. \([29]\)

Using the V/Ce redox chemistry, and the catalysts mentioned above, we demonstrated the proof-of-concept at the laboratory scale. \([29]\) Specifically, indirect hydrogen evolution and water oxidation were demonstrated at the surface of \( \text{Mo}_2\text{C} \) and \( \text{RuO}_2 \), respectively, using the fully charged V and Ce electrolytes. Moreover, the conversion efficiency and apparent reaction rate for both reactions were determined. The hydrogen evolution reaction, in particular, was found to have nearly 100% conversion efficiency. \([29]\) Based on the success of this preliminary work, it was decided to begin scaling up the process to a more industrially-relevant scale.

3.2 Scale-up and Demonstration

In order to further validate the dual-circuit approach and determine its technical readiness, a demonstration project was undertaken. The basic platform for this development effort was a CellCube 10 kW/40 kWh all-vanadium redox flow battery produced by Gildemeister Energy Solutions (Fig. 3b). The battery was installed at a site in Martigny, Valais, Switzerland (Fig. 3a). After installation and commissioning, we began the process of retrofitting the battery with the necessary secondary circuit and catalytic reactor for hydrogen generation. As the commercial RFB is based on the all-vanadium redox chemistry, the water oxidation reaction is not possible on the positive half. Accordingly, we have focused our efforts on demonstrating the hydrogen evolution reaction.

One of the key steps in this effort was the development of a catalyst which could be practically employed at this scale. A fixed bed of the microparticulate \( \text{Mo}_2\text{C} \) catalyst used in our proof-of-concept work would cause too much pressure drop in the secondary hydraulic circuit. Moreover, such small particles could become entrained in the flow of the electrolyte and travel into the electrolyte storage tank, causing uncontrolled hydrogen evolution inside the tank. For these reasons, we decided to use a supported catalyst. A spray-coating process was developed to synthesize \( \text{Mo}_2\text{C} \) on the surface of inert, spherical supports. The spherical supports provide reasonable surface area while maintaining large interstitial voids for electrolyte and gas to flow through. Initially, porous alumina supports were used, however the mechanical stability of the catalytic coating on these spheres was not satisfactory. After several iterations, 3 mm ceramic beads (Demstone 2000, Saint Gobain, Germany) were found to provide good adhesion and mechanical strength for the catalytic coating.

Having developed a suitable catalyst, the next step was to design the catalytic reactor. Initially, a horizontal fixed bed reactor design was used. Charged electrolyte was injected at one end of the reactor, flowing through the catalytic bed and generating hydrogen. Hydrogen could be collected from the headspace above the catalytic bed. Baffles were installed along the length of the reactor to help promote mixing of the electrolyte throughout the reactor. Unfortunately, this reactor design had problematic mass transport characteristics. The hydrogen evolution reaction caused the electrolyte in the catalytic bed to foam. This foam had sufficient capillarity to block many of the interstitial voids between particles, severely limiting the utilization of the catalyst.

To address this limitation, a new reactor was recently designed and built (Fig. 3c). This reactor is a vertical, multi-stage fixed bed reactor. In each stage, electrolyte is injected at the bottom of the catalytic bed. The liquid then flows up, through the catalytic bed, until reaching the raised outlet and flowing into the next stage (Figs 3d,e). The hydrogen gas is collected from the headspace in each stage. In total, the reactor contains eight stages, each containing ca. 2 g of \( \text{Mo}_2\text{C} \).

This reactor design has several advantages over the previous reactor design. The large number of stages increases the residence time of the reactor, allowing greater conversion of the electrolyte in a single pass. Moreover, the vertical flow of the electrolyte helps to facilitate the shedding of hydrogen bubbles from the catalytic bed. This helps to prevent blocking of the catalyst, and increases the amount of conversion achieved in each stage.

We have recently started characterizing the performance of this new reactor design. Our initial results indicate that the reactor is very well suited for hydrogen production, and is able to provide a higher conversion rate as a result of the various improvements introduced. It appears that full conversion of the electrolyte may be achieved for flow rates up to 1 L/minute. At this flow rate, the
battery can be completely chemically discharged in 16.7 hours, which is equivalent to a conventional discharge at ca. 2.4 kW. If a greater equivalent discharge power is needed, several reactors may be placed in parallel.

4. Looking Forward

The dual-circuit redox flow battery discussed here provides a unique approach for enhancing the energy capacity of redox flow battery systems. Since this approach does not alter the fundamental RFB architecture, existing systems can be easily retrofitted to enable the production of hydrogen. Moreover, besides indirect water electrolysis, other industrial processes can potentially be accomplished using this system architecture, such as the oxidation of H₂S and SO₂ to produce sulfuric acid. More generally, the concept of indirect electrolysis could be extended to other electrosynthetic processes, for example for the on-site production of chlorine (chlorine transport through inner cities such as Lausanne being a hazardous process) or for the production of hydrogen peroxide, which is an environmentally friendly oxidant.

In a broader context, this system is representative of the growing importance of diverse energy storage infrastructure. The interplay between hydrogen and electricity will become increasingly important in the coming years. It is clear that large-scale energy storage is needed to facilitate the widespread implementation of renewable energy sources. Growing reliance on electric vehicles will further reinforce this need. For mobile applications, hydrogen energy storage is particularly beneficial due to its high energy density, and the ability to instantly refuel vehicles. However, widespread hydrogen infrastructure is lacking and remains a significant barrier to the acceptance of hydrogen fuelled vehicles.

Nonetheless, we can imagine a future which capitalizes on the synergies between electricity and hydrogen. Energy storage technologies, such as redox flow batteries, may be installed at renewable energy generation sites to buffer supply and demand. Additional energy storage sites may be installed at nodes throughout the distribution system in order to flatten the load on the network and provide greater reliability. As more storage capacity comes online, this will enable further implementation of renewable resources, starting a cycle of constructive feedback for both technologies. Moreover, the overall energy storage capacity available in the grid will make it more tolerant to the large amplitude perturbations caused by the charging of battery electric vehicles. Some of these distributed energy storage sites may also function as fuelling sites for hydrogen fuelled vehicles. Hydrogen can be produced directly on-site by electrolysis of water, avoiding the need for a hydrogen distribution infrastructure. In some cases, indirect water electrolysis, as seen in the dual-circuit flow battery system presented here, may be utilized. However, conventional RFBs can also be used as a buffer between renewable resources and conventional electrolyzers, allowing the electrolyser to operate at a constant load. In both cases, the electricity used to drive the electrolysis will be derived primarily from renewable resources, rather than fossil fuel or nuclear resources, producing truly ‘clean’ hydrogen.

A future grid powered solely by renewable energy sources is rapidly becoming possible with ongoing advances in technology. The dual-circuit redox flow battery system can play a key role as an energy management platform, directly connecting the producer’s needs to the consumer’s re-
requirements. Its ability to produce hydrogen on demand provides an additional degree of freedom compared to classical batteries, increasing the versatility of large-scale electrochemical energy storage in a renewable energy grid.

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CO₂ Hydrogenation: Supported Nanoparticles vs. Immobilized Catalysts

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Abstract: The conversion of CO₂ to more valuable chemicals has been the focus of intense research over the past decades, and this field has become particularly important in view of the continuous increase of CO₂ levels in our atmosphere and the need to find alternative ways to store excess energy into fuels. In this review we will discuss different strategies for CO₂ conversion with heterogeneous and homogeneous catalysts. In addition, we will introduce some promising research concerning the immobilization of homogeneous catalysts on heterogeneous supports, as a hybrid of hetero- and homogeneous catalysts.

Keywords: CO₂ · Heterogeneous catalysis · Hydrogenation · Immobilization

Introduction

Over the last decades the global CO₂ emission has continuously increased with fossil fuel combustion and industrial processes such as cement and metal production contributing the largest share. In 2013 a new record of 35.3 billion tons of emitted CO₂ has been reached.[1] Due to tougher policies on the emission of greenhouse gases a main focus has been to adapt long-standing processes to reduce CO₂ emission in the first place. However, the simple capture and storage of CO₂ would increase the energy requirements of an industrial plant by 25–40% presenting challenges in the form of gas separation and fixation.[2] Consequently the simple usage of CO₂ as a carbon source and C1-building block for the synthesis of more valuable chemicals or fuels would not only reduce the overall emission but also present a solution in respect to finding alternatives for fossil fuels. Therefore nowadays – at least from the research point of view – CO₂ can be considered as an abundant carbon source (Fig. 1) and a part of the methanol economy.[3]

Nevertheless activation of the CO₂ molecule is challenging and requires high energies in form of high temperatures, high pressures and/or the use of active reactants. Essentially its considerable Gibbs free energy of formation (CO₂ ΔG°298.15K = −394.4 kJ/mol) has to be overcome. One solution to this thermodynamic problem is the usage of co-reactants with higher Gibbs free energy such as H₂, methanol, or even epoxides, the latter being used in the synthesis of (cyclic) carbonates from CO₂. The splitting of the C=O double bond and the formation of a C–H or C–C bond can be achieved if a reducing agent is used in the presence of a catalyst. Since renewable energies have been the focus of current research, the usage of H₂ as the reducing agent – provided it comes from renewable/excess energy – would greatly contribute to a more environmentally friendly conversion of CO₂ and to incorporate CO₂ in the fuel cycle.

The application of various mainly transition metal catalysts lowers this activation energy and allows the conversion of CO₂ to hydrogenation products such as CO, methane, methanol and dimethyl ether (DME), formic acid and dimethylformamide (DMF), but also more complex molecules like (cyclic) carbonates or carboxylic acids.[4]

This review will focus on selected examples of heterogeneous CO₂ hydrogenation catalysts and compare them to immobilized homogeneous hydrogenation catalysts.

Supported Nanoparticles as CO₂ Hydrogenation Catalysts

As shown in Fig. 1, the hydrogenation of CO₂ – depending on the catalytic systems and the reaction conditions – can lead to various products, mainly methane (methanation), hydrocarbons (related to Fischer-Tropsch – FT), CO (reverse water gas shift) and methanol. Below we will illustrate each reaction and the current state of the art.

Reverse Water Gas Shift Reaction

The reverse water gas shift (RWGS) reaction corresponds to the hydrogenation of CO₂ into CO and H₂O (Eqn. (1)) and is considered to be an intermediate step for CH₄ and olefin production in FT-related re-

Fig. 1. CO₂ hydrogenation with heterogeneous and homogeneous catalysts, a general view.
actions. This endothermic RWGS reaction – favored at high temperature – is catalyzed by several metals. Much attention has been given to Ni,5 Pt,6 Cu,6 and Au.8 Three different mechanisms have been proposed for the RWGS reaction: (i) direct dissociation of CO$_2$ into CO and O*, (ii) formation of CO$_2$ species (HCOO)*, or (iii) carboxyl (COOH) intermediates.5,8,9b,22 While the systems are typically very complex, it has been proposed that the active site under reaction conditions (CO/CO$_2$/H/H$_2$O) in CeO$_2$ supported Pt and Au catalysts correspond to partially oxidized Pt and Au species.11 In addition, based on a kinetic approach of the corresponding reverse reaction (RWGS), corner atoms of Au NPs on TiO$_2$ are the most likely active sites.12

$$\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad (1)$$

As discussed above, several reaction pathways are possible. The direct dissociation pathway involves splitting CO$_2$ on the surface of the metal surface into CO* and O*; the surface O* being then reduced by H$_2$ or surface H to H$_2$O*, leading after desorption to CO and H$_2$O. In the formate mechanism, following the initial H transfer to CO$_2$, formate species are formed and decomposed into CO$_2$ and O*. Alternatively, surface H* can react with CO$_2$ to generate COOH* intermediates, which then evolve into CO and surface OH groups. This mechanism has first been proposed by calculations using Cu(111) surfaces.13 While proposed to be favored on Pt, Ag, and Pd, direct CO$_2$ dissociation would be favored on Cu, Rh, and Ni.18 This process has also been proposed to be favored at the interface between CeO$_2$ and Cu in CeO$_2$/Cu(111).10 While under debate, it is clear that the metal the support and the reaction conditions can favor one or the other mechanism, and much work has to be undertaken to understand these systems at a molecular level.

**Methanation**

Methane can be obtained via the hydrogenation of CO$_2$ (Eqn. (2)). While mainly investigated with supported Ni,3 metals such as Ru,8,9b,22 Rh9b and Pd8e,24 are also known to participate in this reaction. Since CO$_2$ methanation is exothermic, lower reaction temperatures favor higher methane yields.

$$\text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O} \quad (2)$$

The performance of CO$_2$ methanation catalysts is affected by the nature of the support materials. For example in the case of CeO$_2$-based catalysts, it was found that CeO$_2$ increases the amount of adsorbed CO$_2$ and promotes the conversion of thus-formed surface carbonate into CO.22 It has been proposed to increase the rates of the first steps associated with the RWGS reaction (Eqn. (1)). In addition, since CeO$_2$-containing catalysts show high activity in the methanation of CO, it is not too surprising that the overall CO methanation is favored on these catalysts as well, leading to high CH$_4$ selectivity (close to 100%).21c,22 ZrO$_2$-containing materials are also interesting support candidates for CO$_2$ methanation.21a In the related system Ni/ CeO$_2$/ZrO$_2$, the incorporation of a part of Ni species in the fluorite-structured Ce$_{67}$Zr$_{26}$O$_{25}$ improved the stability of the catalysts for CO$_2$ methanation at 350 °C (H/CO$_2$/Ni$_x$ = 36/9/10, GHSV = 43,000 h$^{-1}$ and TOF = 0.4 s$^{-1}$, Table 1).16,21b In addition, Ni sintering can be suppressed by the addition of noble metals (such as Ru and Rh) to the Ni catalyst, leading to longer catalyst lifetime.20 Adding Pt to Co catalysts also led to an increased catalyst lifetime.17 The additions of promoters such as Na, K and La to Ru/TiO$_2$ catalysts can also improve the rate in CO$_2$ methanation as well.22

**Methanol and Related Dimethyl Ether Synthesis**

In the 1960s ICI developed an efficient low-pressure process (50–100 bar, 200–300 °C) for methanol synthesis from syngas (Eqn. (3)) using CuZnO/Al$_2$O$_3$ catalysts. More recently, this catalyst and related systems have also been investigated for CO$_2$ hydrogenation to methanol (Eqn. (4)). For Cu catalysts, the nature of the active sites and the elementary steps are still debated, possibly involving Cu$^0$ and/or Cu$^+$: the effect of support and promoter on the Cu catalysts for methanol synthesis has been investigated in depth; for example, reported supports/promoters are ZnO,8b ZrO$_2$,9b,26 MgO,28b TiO$_2$,10 and Ga$_2$O$_3$.29

$$\text{CO} + 2 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$$

$$\text{CO} + 3 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad (4)$$

The interaction of Cu with ZnO greatly enhances the activity and selectivity of the methanol synthesis. Possible explanations involve the stabilization of Cu($t^2$g) centers26c or the better dispersion of Cu species by ZnO. It has also been proposed that the active sites are defective surfaces of nanoparticulate Cu over Cu/ZnO/Al$_2$O$_3$.26a ZrO$_2$ is also known as one of the promising supports and/or promoters for methanol production from CO$_2$. For instance, methanol production turnover frequency is 27 times higher (7.3 × 10$^{-4}$ s$^{-1}$) with Cu/ZrO$_2$/SiO$_2$ than with Cu/SiO$_2$ (2.7 × 10$^{-4}$ s$^{-1}$).56 In addition, selectivity of methanol over Cu/ZrO$_2$/SiO$_2$ was four times higher (43%) than that over Cu/SiO$_2$ (11%).59 This effect of ZrO$_2$ is likely due to a combination of parameters: improvement of Cu dispersion,50 increase in CO adsorption51 and increased number of edges, corners, defects and oxygen vacancies by incorporation of Cu into nanocrystalline ZrO$_2$. It has also been suggested that Cu$^0$ sites at the interface between Cu$^+$ and ZrO$_2$ play a key role in the methanol synthesis.26b

Recently, catalysts based on Cu/CeO$_2$ have been reported as an alternative to traditional Cu/ZnO and Cu/ZrO$_2$ systems, creating a metal-oxide interface that allows a better adsorption and activation of CO$_2$.10 Worthy of note the ternary catalyst Cu/CeO$_2$/TiO$_2$ showed even higher activity for methanol production with TOF of $8.1 \times 10^{-4}$ s$^{-1}$ at 573 K (Table 1) compared to Cu/CeO$_2$(111) and Cu/TiO$_2$(100), NiGa$_2$/SiO$_2$ catalysts are also superior to Cu/ZnO/Al$_2$O$_3$, owing to low CO production via RWGS.33 Very recently, hybrid oxide catalyst based on MnO$_2$ and mesoporous

Table 1. Selected catalysts for CO$_2$, CH$_4$, and MeOH production via CO$_2$ hydrogenation.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Temp./°C</th>
<th>Pressure/bar</th>
<th>Product</th>
<th>TOF/ s$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(110)</td>
<td>237</td>
<td>5.1</td>
<td>CO</td>
<td>0.01</td>
<td>[14]</td>
</tr>
<tr>
<td>Pt/TiO$_2$</td>
<td>300</td>
<td>1</td>
<td>CO</td>
<td>0.10</td>
<td>[15]</td>
</tr>
<tr>
<td>Ni/CeO$_2$/ZrO$_2$</td>
<td>350</td>
<td>1</td>
<td>CH$_4$</td>
<td>0.429</td>
<td>[16]</td>
</tr>
<tr>
<td>Rh/γ-Al$_2$O$_3$</td>
<td>200</td>
<td>1</td>
<td>CH$_4$</td>
<td>0.010</td>
<td>[8c]</td>
</tr>
<tr>
<td>Pt/MCF-17+/Co/MCF-17</td>
<td>250</td>
<td>1</td>
<td>CH$_4$</td>
<td>0.038</td>
<td>[17]</td>
</tr>
<tr>
<td>Ru/Al$_2$O$_3$</td>
<td>350</td>
<td>1</td>
<td>CH$_4$</td>
<td>0.03</td>
<td>[18]</td>
</tr>
<tr>
<td>Ni-Zr alloy</td>
<td>300</td>
<td>1</td>
<td>CH$_4$</td>
<td>0.054</td>
<td>[19]</td>
</tr>
<tr>
<td>Cu-Zn-Al-Zr oxides</td>
<td>270</td>
<td>50</td>
<td>MeOH</td>
<td>0.009</td>
<td>[20]</td>
</tr>
<tr>
<td>Cu/ZrO$_2$/SiO$_2$</td>
<td>250</td>
<td>6.5</td>
<td>MeOH</td>
<td>0.073</td>
<td>[9a]</td>
</tr>
<tr>
<td>Cu/CeO$_2$/TiO$_2$(110)</td>
<td>303</td>
<td>5</td>
<td>MeOH</td>
<td>8.1</td>
<td>[10]</td>
</tr>
</tbody>
</table>
spinel CoO$_2$ catalyzes the CO$_2$ conversion to methanol in higher yields than the individual catalysts MnO$_2$, SiO$_2$, and Co$_3$O$_4$, respectively,[34] implying that the interface of MnO$_2$ and Co$_3$O$_4$ contains specific active sites for the CO$_2$ conversion.

Dimethyl ether (DME) is a useful chemical and an attractive alternative to liquefied petroleum gas (LPG), and can be synthesized by a multi-step process involving methanol production via CO$_2$ hydrogenation to methanol (Eqn. (3)) and subsequent methanol dehydration to DME (Eqn. (5)).

$$2 \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \quad (5)$$

In a one-step DME synthesis approach, methanol consumption via methanol dehydrogenation can abate the catalyst’s surface concentration of the intermediate methanol, and in turn overcome the equilibrium limitation of CO$_2$ conversion at low temperatures. Methanol dehydrogenation takes place on γ-Al$_2$O$_3$[35] and acidic zeolites (HZSM-5)[35] and SAPO[40]. Therefore DME can be synthesized directly over physical mixtures of solid acids and methanol synthesis catalysts. Note that methanol dehydrogenation is an exothermic reaction, leading to higher DME selectivity at lower reaction temperatures. It is reported that the methanol synthesis is the rate-determining step when Cu-based methanol catalysts are employed.[36]

Olefins

The hydrogenation of CO$_2$ to olefins derives from the combination of RWGS reaction (Eqn. (1)) converting CO$_2$ to CO and the Fischer-Tropsch (FT) process (Eqn. (6)), yielding hydrocarbons.

$$\text{CO} + 2 \text{H}_2 \rightarrow (\text{CH}_2)_x + \text{H}_2\text{O} \quad (6)$$

Accordingly, the reaction has been studied mainly on traditional catalysts for FT synthesis such as iron and cobalt catalysts with promoters. The olefins are likely produced on surface carbides, which are formed in situ via decomposition of CO on metal surfaces, following the Boudard reaction (Eqn. (7)).

$$\text{CO} + \text{CO}_2 \rightarrow \text{C} + 2 \text{CO} \quad (7)$$

The role of promoters, such as K,[37] Na,[37b] Li,[37b] Mn,[37a,38] and La[39] species, is considered to enhance the activity of the catalyst in RWGS (due to improvement of Fe/Co adsorption) and the carburation of Fe or Co species. In addition, Mn has been proposed to play the role of structural promoter as well, leading to higher dispersion of Fe species on support materials.[38] The presence of noble metals such as Ru on Co-K catalysts further enhanced the conversion of CO$_2$ and the selectivity of C5+ hydrocarbons.[37b]

Immobilized Homogeneous Catalysts for CO$_2$ Hydrogenation

The most prominent reactions in homogeneous CO$_2$ hydrogenation are the syntheses of formic acid and methanol, however the generation of formic acid and its derivatives yields much higher TONs and TOFs than that of methanol, since the conversion of CO$_2$ to methanol usually requires the combination of several catalysts or concurrent reactions. In general, the conversion of CO$_2$ to formic acid is highly reversible in the presence of the catalyst; hence the employment of a base to remove the formic acid from the equilibrium is necessary.

State of the Art in Homogeneous Catalysis

Pioneering work on the hydrogenation reactions of CO$_2$ started in the 1970s, using various transition-metal complexes of Ru, Os, Rh, Ir and Pr.[40] Greater performances were reached much later using Ru catalysts such as 2-(a) and supercritical CO$_2$ (scCO$_2$) as a solvent, resolving miscibility issues reported previously.[41]

Since 2000 ruthenium[42] and iridium[43] have been used the most frequently for the hydrogenation of CO$_2$ to formic acid derivatives (Figs. 2 and 3). Worthy of note, [RuCl$_2$(PTA)$_3$] (PTA = 1,3,5-triisopropylbenzenesulfonate) has the highest activity of CO$_2$ hydrogenation in homogeneous media.[44] Nozaki et al.[45] reported a catalyst system containing 2-(a) and scCO$_2$ to achieve high performance. The Ru complex 2-(a) is a highly active catalyst for the hydrogenation of CO$_2$ to formic acid (TON = 34000, TOF = 99100 h$^{-1}$).

![Fig. 2. Selected ruthenium catalysts used in CO$_2$ hydrogenation reactions.](image)

![Fig. 3. Iridium catalysts used in CO$_2$ hydrogenation reactions.](image)
aza-7-phosphaadamantane) (7) allows the conversion of CO$_2$ to formic acid without the addition of base at low temperatures in DMSO.$^{[42a]}$ Applying other hydrogen sources than H$_2$, such as isopropanol or methanol, ruthenium and iridium complex with N-heterocyclic carbenes (4, 14)$^{[42b-j]}$ as well as PNP pincer-type$_{[43a,44]}$ ligands (8, 9) were used to convert CO$_2$ to formate. Iridium catalysts have also proven to be very effective to promote CO$_2$ hydrogenation. Ir$_{\text{iii}}$ pincer trihydride complex 13 catalyzes the hydrogenation of CO$_2$ into potassium formate (HCOOK) with a TON of 3.5×10$^3$ and TOF of 150 000 h$^{-1}$ using an aqueous KOH solution at 120 °C and 6 MPa (H$_2$:CO$_2$=1:1),$^{[13a,45]}$ The pincer ligand, which is believed to be non-innocent in the catalytic cycle,$^{[45]}$ seems to be superior to other ligand systems such as N$_2$N-bidentate (15)$^{[43b-a]}$ imine-diphosphine (16)$^{[44]}$ or N-heterocyclic carbenes.$^{[46]}$

Non-precious-metal-based catalysts based on Fe$_{\text{iii}}$,$^{[47]}$ Co$_{\text{ii}}$,$^{[48]}$ and Cu$_{\text{ii}}$ have also been discovered (Fig. 4), but suffer from relatively low TON/TOF compared to the precious-metal-based catalysts.

More recently the direct synthesis of methanol from CO$_2$ with homogenous catalysts was reported using (i) a cascade reaction applying two different ruthenium catalysts together with Sc(OTf)$_3$ as a Bronsted/Lewis acid catalyst (5)$^{[42c-d]}$ (ii) a tandem capture of CO$_2$ with aminoethanols combined with the subsequent hydrogenation with a PNN Ru catalyst (12)$^{[50]}$ and (iii) a specific ruthenium phosphine complex, generated in situ from [Ru(acac)$_3$] and the tridentate ligand Triphos (1.1.1-tris(diphenylphosphinomethyl)ethane) (10) in the presence of HNT$_3$, as an acid catalyst.$^{[42d-f]}

**Immobilization Strategies**

With the associated difficulty to separate reactants/products from the active phase, a large research effort has focused on immobilizing highly active homogenous catalysts on a variety of supports. Different strategies have been applied including encapsulation, intercalation or entrapment of the catalyst as well as anchoring the ligand to a support.$^{[51]}$ However, efficient, immobilized CO$_2$ hydrogenation catalysts are still rare. Organo-silica hybrid materials based on the co-condensation of silylated derivatives of [Ru(dppp)Cl$_2$] (dppp = bis-(diphenylphosphinopheno)propane) (Fig. 5) with tetraethoxysilicate (TEOS) were the first to be reported.$^{[52]}$ While molecular [Ru(dppm)Cl$_2$] and [Ru(dppp)Cl$_2$] display very good activities for the formation of DMF from CO$_2$ and H$_2$, with TOFs of 190 000 h$^{-1}$ and 26 500 h$^{-1}$ respectively,$^{[53]}$ the corresponding immobilized systems display much lower TOFs: materials purely consisting of the silylated precursors 24 or 25 (no TEOS added) reach TOFs of 3030 h$^{-1}$ and 2300 h$^{-1}$ respectively, while dilution with 20 to 200 equiv. TEOS dramatically decreased the TOFs to 500–970 h$^{-1}$.$^{[52c]}

Alternatively, immobilization of [Ru(TPPTS)$_2$]$_2^+$ (TPPTS = tris(3-sulfonic acid)phosphine trisodium salt) was possible on a Dowex ion exchange resin, phosphine functionalized polymers as well as zeolites.$^{[54]}$ While solely applied for the decomposition of formic acid into H$_2$ and CO$_2$, both the ion exchange resin and the polymer support led to stable catalysts that did not leach and maintained their activity over several cycles. Most of the zeolites however could not withstand the acidic reaction conditions.

Furthermore, immobilization was also accomplished by the post-functionalization of a poly(styrene)-block-poly(ethylene glycol) polymer (ArgoGel-NH$_2$) containing free amine moieties.$^{[55]}$ Condensation of the free amine with formaldehyde and a secondary phosphine led to supported bidentate phosphine ligands that could easily substitute the ligands in [RuCl$_2$(PPh$_3$)$_2$] or cis-[RuH$_2$(PPh$_3$)$_2$] yielding the bound compounds 26–29 respectively (Fig. 5). The functionalized beads showed a similar activity compared to the homogeneous equivalent in the synthesis of DMF in supercritical CO$_2$ (scCO$_2$). At 100 °C and could easily be recovered and reused. 26 in contrast to 27–29 showed no decrease in activity over four cycles (TON 1560–1960). Similar anchoring strategies have described for the coordination of IrCl$_3$ or RuCl$_3$ to hybrid organosilica materials containing propylamine or alkylphosphate.

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Fig. 4: Non-precious-metal-based catalysts used in CO$_2$ hydrogenation reactions.

Fig. 5: Immobilization strategies for Ru$_{\text{ii}}$-hydrogenation catalysts.

Fig. 6: Immobilized Ru-NHC complexes on mesoporous silica.
moieties. While reported as active and recyclable, the nature of the catalyst is not clear.\cite{30}

More recently, the immobilization of a ruthenium N-heterocyclic carbene (NHC) complex for the CO\(_2\) hydrogenation to amides was accomplished by a different strategy, where the density of the organic functionalities (ligands) is controlled through a templating approach and the metal is covalently anchored to a N-heterocyclic carbene ligand.\cite{28} The immobilized catalyst is prepared by reacting imidazolium-functionalized mesoporous silica with \([\text{RuCl}_3(p\text{-cymene})]\) yielding the surface bound Ru-NHC compound in 60% yield (30).\cite{28} Substitution of the cymene ligand with PMe\(_3\), resulted in the respective surface bound Ru-phosphine-NHC compound (31) (Fig. 6).

Hydrogenation reactions of CO\(_2\) in the presence of pyrrolidine yielding 1-formylpyrrolidine (50 bar CO\(_2\), 30 bar H\(_2\), 100 °C) showed that 30 had a very low TON of 24.7 with \([\text{RuCl}_3(p\text{-cymene})]\) which is one of the best catalysts under chosen reaction conditions (TON 2900 and 3100 respectively). However metal leaching proved to be a problem concerning the recyclability of the materials.

Conclusion

Heterogeneous catalysts are already used in industrial applications due to their high thermal stability and recyclability leading to low operation costs for chemical processes.\cite{99} Generally in ambient pressure reactions CO\(_2\) is converted into CO over transition metal catalysts and into CH\(_4\) over Ru, Rh and Rht catalysts, whereas CO\(_2\) is hydrogenated to methanol (and dimethyl ether) under high-pressure over Cu-based catalysts and to olefins over Fe- and Co-based catalysts. ZnO, ZrO\(_2\), and CeO\(_2\) are so far the best support materials for most of the CO\(_2\) hydrogenation reactions, probably due to their large CO\(_2\) adsorption capacity and high activity towards the conversion of CO\(_2\) into CO. The addition of alkali or lanthanide metals has been shown to enhance CO\(_2\) conversion and help to furnish olefins under high pressure.

On the other hand, numerous homogeneous catalysts have appeared more recently with tailored properties by tuning of the organic ligands. They have become consequently more active and/or selective, but they still suffer from lower thermal stability, difficulty of regeneration as well as separation from the products, limiting their industrial applications. While immobilization on supports appears to be a promising strategy, immobilized CO\(_2\) hydrogenation catalysts always show lower TON/TOF\(_{\text{cat}}\) compared to the homogeneous analogues.

Here deactivation by interaction with the support, metal leaching and simple regeneration protocols still present great challenges, which need to be surmounted. The right combination and choice of support, linker and homogeneous catalyst will be important for the generation of stable and active immobilized catalysts.

Acknowledgement

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Soft Approaches to CO\textsubscript{2} Activation

Shoubhik Das, Felix D. Bobbink, Aswin Gopakumar, and Paul J. Dyson*

Abstract: The utilization of CO\textsubscript{2} as a C1 synthon is becoming increasingly important as a feedstock derived from carbon capture and storage technologies. Herein, we describe some of our recent research on carbon dioxide valorization, notably, using organocatalysts to convert CO\textsubscript{2} into carboxylic acid, ester, formyl and methyl groups on various organic molecules. We describe these studies within the broader context of CO\textsubscript{2} capture and valorization and suggest approaches for future research.

Keywords: Catalysis · CO\textsubscript{2} activation · Green chemistry · Sustainable chemistry

Valorization of CO\textsubscript{2} is currently receiving increasing attention as it is non-toxic, cheap and is becoming increasingly abundant in the atmosphere,\textsuperscript{[1]} which has a direct impact on climate change.\textsuperscript{[2]} However, the activation of CO\textsubscript{2} is challenging, as CO\textsubscript{2} is highly inert due to the carbon being in the highest oxidized form, which leads to high thermodynamic and kinetic stability.\textsuperscript{[3]} Energy-rich substrates such as epoxides\textsuperscript{[4]} and aziridines\textsuperscript{[5]} can overcome this high activation barrier under harsh reaction conditions (Scheme 1). In addition, strong nucleophiles such as Grignard reagents,\textsuperscript{[6]} organolithium,\textsuperscript{[7]} organoboron\textsuperscript{[8]} and organozinc\textsuperscript{[9]} reagents have been also used to form new C–C bonds encompassing CO\textsubscript{2} (Scheme 1). The reduction of CO\textsubscript{2} to simple compounds such as formic acid and methanol with homogeneous transition metal catalysts has also been a field of intensive research.\textsuperscript{[10]}

It should be noted that these procedures, although employing energetic reagents, often require high pressures of CO\textsubscript{2} and harsh reaction conditions, which tends to hinder the development of these methodologies on an industrial scale. Despite these difficulties some processes are being commercialized, for example, Bayer recently announced that it will produce polyols incorporating 20% CO\textsubscript{2} in an installation with a 5,000 metric ton capacity (Scheme 2).\textsuperscript{[11]} However, to reach more widespread applications, on a scale that would have a sizeable impact on carbon capture and sequestration technologies,\textsuperscript{[12]} reaction conditions preferably need to be mild, \textit{i.e.} at atmospheric pressure, and take place at moderate temperatures. For this purpose finding new catalysts is highly important.

Organocatalysts such as N-heterocyclic carbenes (NHCs) are able to activate CO\textsubscript{2} at atmospheric pressure, potentially allowing the harsh reaction conditions usually required for CO\textsubscript{2} activation to be overcome.\textsuperscript{[13]} In general, organocatalysts are less expensive than metal-based catalysts, are readily accessible and, consequently, represent an interesting avenue for further investigations.\textsuperscript{[14]} Moreover, these small organic molecules are typically non-toxic and environmentally friendly. Based on these above-mentioned properties, combined with our on-going research activities on imidazolium salts,\textsuperscript{[15]} we decided to evaluate the ability of carbene catalysts to fix CO\textsubscript{2} onto organic molecules such as amines and alkynes to provide easy access to a range of valuable molecules, \textit{e.g.} \textit{N}-methylated amines, \textit{N}-formylated amines, alkynyl carboxylic acids or esters, \textit{etc.}

Amine derivatives are important intermediates in the chemical and pharmaceutical industries, the functionality being found in agrochemicals, dyes and flavors, fragrances and medicines.\textsuperscript{[16]} We found that NHCs can methylate different aromatic, heteroaromatic and aliphatic amines using CO\textsubscript{2} as the carbon source with diphenylsilane as the reductant under ambient conditions and in high yield.\textsuperscript{[17]} Aromatic, heteroaromatic and aliphatic amines react smoothly leading to excellent yields (Scheme 3). Cantat and coworkers have also shown that amines can be methylated using hydroboranes and a proazaphosphatrane as organocatalyst.\textsuperscript{[18]}

Both electron-donating and withdrawing substituents on the aromatic ring at the \textit{para} position react well whereas amines

\[ \text{HOOC} \quad \text{FG} \quad \text{R}_1 \quad \text{R}_1 \quad \text{O} = \text{C} \quad \text{O} \quad X \quad \text{X} = \text{O}, \text{NTs} \]

Scheme 1. Examples of reactions using CO\textsubscript{2} as a reagent with highly reactive substrates.

\[ \text{Cat} \quad \text{CO}_2 \quad \text{via:} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{OH} \quad \text{O} \quad \text{O} \quad \text{OH} \]

Scheme 2. An example of the synthesis of polycarbonate polyols using CO\textsubscript{2} as a C1 source.\textsuperscript{[19]}
with electron-withdrawing groups are less reactive and require prolonged reaction times. Steric hindrance on both sides of the amine has minimal effect on the yield of the reaction. Various symmetric and nonsymmetric amines were also reacted under the optimized reaction conditions (5 mol% IMes, 1 atm. CO₂, 3 equiv. Ph₂SiH₂, DMF, 50 °C) and the procedure worked well with these substrates. The carbene catalyst IMes is also tolerant to heteroaromatic amines such as picoline, indoline and 1,2,3,4-tetrahydroquinoline. Additionally, primary amines react in a similar fashion to secondary amines, selectively forming dimethylated products. We also evaluated the use of IMes in the N-methylation of complex molecules such as nortriptyline, cinacalcet, duloxetine and sertraline obtaining pure products in good yields without degradation or separation problems (Fig. 1).

The functional group tolerance of a reaction potentially enhances the overall sustainability of the route in the synthesis of complex structures, since protecting and deprotecting steps are not necessarily required, leading to a high atom economy. The selectivity of the carbene catalyst was evaluated using some particularly challenging substrates with different functional groups attached to different parts of the amine. Remarkably, it was found that nitrile, nitro, double and triple carbon–carbon bonds, ether, and ester substituted amines were well tolerated, providing the corresponding N-methylated amines in good to excellent yield. Moreover, methylation took place chemoselectively even in the presence of a ketone group, which could have been reduced by the silane.[20] To demonstrate the chemoselective potential of the reaction it was used to prepare naftifine, an antifungal drug for the topical treatment of fungal infections in a two-step catalytic procedure (Scheme 4). The NHC catalyst was also used to prepare 13C-labelled naftifine using 13CO₂ in 78% yield.

During the N-methylation reaction, the carbene catalyst IMes is also tolerant to heteroaromatic amines such as furan derivatives. Additionally, primary amines react in a similar fashion to secondary amines, selectively forming dimethylated products. We also evaluated the use of IMes in the N-methylation of complex molecules such as nortriptyline, cinacalcet, duloxetine and sertraline obtaining pure products in good yields without degradation or separation problems (Fig. 1).

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During the N-methylation reaction, the corresponding N-formyl compound was observed as an isolatable intermediate. Therefore, tuning the catalyst and catalytic conditions to recover N-formylated products as a major (only) product is of value as N-formylated compounds are also versatile compounds employed as intermediates in organic synthesis and the formyl group is also present in pharmaceuticals.[21] Formyl groups are often used as protecting groups in organic synthesis and, in particular, N-formylated amino acid esters and peptides have been used widely in peptide synthesis as well as for precursors of isocyanides that find use in multicomponent reactions.[22]

We discovered a thiazolium carbene, closely related to vitamin B1, which is a potent N-formylation catalyst that operates under CO₂ at atmospheric pressure.[23] The catalyst is selective for different primary amines and amino acid esters. Aromatic, heteroaromatic, alicyclic and aliphatic amines afforded yields of up to 90% (Scheme 5).

Different amino acids such as methionine and tryptophan ethyl ester react smoothly under the optimized reaction conditions (7.5 mol% thiazolium carbene catalyst, 1 atm. CO₂, PMHS, DMA, 50 °C). Moreover, para-bromo-substituted amines afford the corresponding products in 80% yield without any signs of reductive dehalogenation taking place. The catalyst is also tolerant to heteroaromatic amines such as furan derivatives. We also performed the reaction on a multigram scale without the N-methylated products being observed.

Interestingly, N-methylated products can be obtained with the thiazolium carbene catalyst at higher temperatures, i.e. 100 °C (Scheme 6). As mentioned above, the potential of the reaction it was used to prepare naftifine, an antifungal drug for the topical treatment of fungal infections in a two-step catalytic procedure (Scheme 4). The NHC catalyst was also used to prepare 13C-labelled naftifine using 13CO₂ in 78% yield.

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catalyst is closely related to vitamin B1, which in nature is used to decarboxylate pyruvate, a metabolite obtained from glycolysis.\[24\]

We have extended the concept of fixing CO\(_2\) via organocatalysts towards terminal alkynes.\[25\] In terminal alkynes the proton is suitably acidic so the addition of a base leads to the formation of the corresponding acetylide anion. Acetylide anions are strong nucleophiles that can spontaneously attack a weak electrophile such as CO\(_2\) to generate alkynyl carboxylic acids. Alkynes functionalized with carboxylic acids are widely found in medicinally relevant compounds and they also find uses as synthons in organic synthesis. While several metal-based catalysts have been reported for this reaction, we found that the thiazolium carbene compound catalyzes the carboxylation reaction to give the corresponding alkynyl carboxylic acids or esters, depending on the conditions, in excellent yield (Scheme 7). This protocol opens up access to a pool of highly functionalized propiolic acids from CO\(_2\).

In addition to our studies on homogeneous organocatalysts we have been studying dispersed transition metals nanoparticles that catalyze selective N-formylation and N-methylation reactions (Fig. 2). In general, homogeneous catalysts usually give better selectivities than their heterogeneous counterparts as they tend to operate under milder conditions.\[26\] Nevertheless, we discovered a viable palladium nanoparticle catalyst (palladium is known to efficiently activate/store hydrogen),\[27\] for these reactions using diphenylsilane as the hydrogen source. A wide variety of palladium nanoparticles were prepared and compared to classical heterogeneous systems such as Pd/Al\(_2\)O\(_3\), CuAlO\(_2\) and Pd/CuZrO\(_2\) and Pt-MoO\(_x\)/TiO\(_2\).\[28\] These reported heterogeneous catalysts employ hydrogen, but operate under harsh reaction conditions and require prolonged reaction times to achieve high yields. In contrast, our hydrosilylation approach functions under ambient pressures at relatively low temperatures (50–80 °C). Such conditions also enable a sinter-free environment to the unsupported palladium nanoparticles, which can be detrimental to recycling experiments.

The selectivity towards N-formylated or N-methylated products depends on the nature of the palladium nanoparticles. From the results obtained so far, there is not an obvious correlation between the particle size and the selectivity, but catalysts such as palladium on activated carbon (commercial grade, Pd content 10 wt%), did not promote either reaction.

In summary, despite the rise in strategies for avoiding CO\(_2\) production, gigatons of CO\(_2\) are produced each year to fulfill the world’s energy and chemical demands. And although there is a considerable mismatch in the amount of CO\(_2\) produced and the amount that would be consumed for chemical applications, the long-term goal to produce fuels such as methane, methanol and hydrocarbons from CO\(_2\) using renewable energy could one day end dependence on fossil fuels. Hence, using CO\(_2\) as a C1 carbon source warrants inten-
sive study and all types of catalysts, i.e. homogeneous, heterogeneous, organo and enzymatic.

In the examples provided herein, a relatively small fraction of the product is derived from CO₂ and, for a greater impact, the majority of the carbon atoms in any organic product should be derived from CO₂. Progress in this direction should be feasible by combining the selective catalysts described here with a process that generates basic chemicals from CO₂. A CO₂ refinery powered by renewable energy could ultimately produce not only fuels, but also sophisticated organic structures that meet the needs of a modern society.

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Electrochemical CO$_2$ Reduction – A Critical View on Fundamentals, Materials and Applications

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Abstract: The electrochemical reduction of CO$_2$ has been extensively studied over the past decades. Nevertheless, this topic has been tackled so far only by using a very fundamental approach and mostly by trying to improve kinetics and selectivities toward specific products in half-cell configurations and liquid-based electrolytes. The main drawback of this approach is that, due to the low solubility of CO$_2$ in water, the maximum CO$_2$ reduction current which could be drawn falls in the range of 0.01–0.02 A cm$^{-2}$. This is at least an order of magnitude lower current density than the requirement to make CO$_2$-electrolysis a technically and economically feasible option for transformation of CO$_2$ into chemical feedstock or fuel thereby closing the CO$_2$ cycle. This work attempts to give a short overview on the status of electrochemical CO$_2$ reduction with respect to challenges at the electrolysis cell as well as at the catalyst level. We will critically discuss possible pathways to increase both operating current density and conversion efficiency in order to close the gap with established energy conversion technologies.

Keywords: CO$_2$ reduction reaction · Electrolyzer · Energy conversion · Gas diffusion electrode · Power-to-gas/liquid

1. Introduction

Reducing the emissions of greenhouse gases by increasing the fraction of renewable energies at the expense of fossil fuels is one of the most important scientific, technological and economic challenges humankind is currently facing.[1] To achieve this aim and to tackle the undesired effects of climate change, considerable efforts are being undertaken worldwide to develop effective CO$_2$ capture and storage technologies.[2–4] Based on these, one can think how to re-cycle CO$_2$ to more valuable products. Its electrochemical conversion into carbon-neutral products might be considered as one promising approach towards reducing atmospheric CO$_2$ and storing a surplus of renewable energies at the same time. In principle, the electrochemical CO$_2$ reduction reaction (CO$_2$RR) could be performed in an electrolysis type of device, called a CO$_2$-electrolyzer or co-electrolyzer. This energy conversion device can be considered as the central part of power-to-gas/power-to-liquid processes that operate using the excess of electricity generated from renewable sources.[5,6] In analogy with a water electrolyzer, a CO$_2$-electrolysis cell is fed with H$_2$O at the anode, where the oxygen evolution reaction (OER) occurs, whereas CO$_2$ is supplied to the cathode where it is electrochemically reduced. The electric energy would be chemically stored either in the form of feedstock chemicals (starting material for further synthesis) or as fuels. Ideally, CO$_2$RR should yield to a single energy-rich compound. However, selective CO$_2$ conversion into specific reaction products remains a challenging task at present due to the multiple proton-coupled electron transfer steps involved in this reaction.[7]

This work attempts to give a short overview on the status of electrochemical CO$_2$ reduction with respect to challenges at the catalysts as well as at the electrolysis cell level. It critically discusses possible pathways to increase both operating current density and conversion efficiency in order to make co-electrolysis a technically and economically feasible option for the transformation of CO$_2$ into a chemical feedstock or fuel thereby closing the CO$_2$ cycle.

2. Identifying Valuable CO$_2$RR Products

Table 1 provides a simple cost analysis for all major CO$_2$ reaction products that can be obtained from a CO$_2$-electrolysis cell. For designing and establishing an economically reasonable CO$_2$ conversion process one needs first to estimate the total costs for the electrochemical production of specific CO$_2$RR products and to compare these in a second step with data from well-established chemical synthesis routes. As a benchmark for our approach, we use data for H$_2$ production from alkaline water electrolysis, an already established and commercially available energy storage technology. In the case of alkaline water electrolysis, large-scale energy storage plants can daily produce $\sim 1000$ kg H$_2$ with an electric energy at $0.05$ kWh$^{-1}$. Under these conditions, the price for H$_2$ production reaches $\sim 4$ kg H$_2^{-1}$ (Table 1). Main contributions to the total production costs originate from electricity (58%) and capital expenses (32%).[8,9] The most severe drawback of the alkaline water electrolysis technology is its low operating current density of $\sim 0.2$ A cm$^{-2}$. Nevertheless, when compared to proton exchange membrane (PEM) electrolyzers, which are operated at current densities that are up to one order of magnitude higher than those of the alkaline electrolyzers, there is no major benefit using PEM-based electrolyzers. The reasons...
are related to higher component costs in case of the PEM electrolyzers. In addition, the PEM electrolyzers typically target only small forecourt applications (daily production of ca. 10–100 kg H₂). Based on these numbers, it is possible to estimate the production costs for specific CO₂RR products under the assumption that the capital costs are similar for both alkaline water and CO₂ electrolyzers. In a first step, we calculate the production volumes per electrolysis unit by assuming similar operating current densities (0.2 A cm⁻²) as applied in alkaline water electrolyzers. Eqn. (1) is used to convert the production volume of H₂ (V₇H₂ in kgₚ₇H₂ h⁻¹) into the respective production volumes of specific CO₂RR products (Vₓₐₙₓox in kg h⁻¹) via the ratio of the molar masses (M in g mol⁻¹) and the number of electrons exchanged to produce 1 mol of product (nₑ, 2 for H₂/CO/CH₃OH; 6 for CH₄, 8 for CH₃H₂ for CₓHₓ). 

\[ Vₓₐₙₓox = V₇H₂ \frac{Mₓₐₙₓox}{M₇H₂} \cdot \frac{nₑ}{nₑₓₐₙₓox} \]

Production volumes per electrolysis unit are listed in Table 1 for various CO₂RR products. Further assuming that a CO₂ electrolysis cell operates at a similar energy efficiency as an alkaline water electrolyzer, the production costs of 1 mol CO₂RR product become a fixed number besides the costs for CH₄ and CH₃H₂ by electrolysis appears therefore to be highly counterproductive, at least from an economic point of view. The same is true for methanol, which can be considered as an energy carrier such as H₂.[12] What seems to be more promising is the generation of CO from CO₂. CO production costs ranging from $0.27 to $0.54 kg⁻¹ are well below the current market price of $0.65 kg⁻¹ (Table 1). In addition, the global market for CO is extremely large as reflected by the annual CO production of 210,000 Mt. CO in combination with H₂ (syngas) serves as an important chemical precursor for a number of industrial processes (e.g. Fischer-Tropsch synthesis). Another interesting product of the CO₂RR is formate (it should be kept in mind that only formic acid, obtained by the protonation of formate, is a valuable product). Estimated production costs are factors of 2–4 lower than the current market price for formate/formic acid ($0.34 vs. $0.8–1.2 kg⁻¹, Table 1). Formic acid is widely used as a preservative and an anti-bacterial agent in livestock feed. The market for formic acid with a yearly production of 0.8 Mt is, however, much smaller compared to the global demand for CO/syngas. An electrochemical conversion of CO₂ into formate/formic acid has a high potential to become an economically competitive process.

### 3. Energy Efficiency of CO₂ Electrolysis

The cost analysis presented above relies on the basic assumption that CO₂-electrolysis cells would reach similar current densities to those featured in alkaline water electrolyzers (0.2 A cm⁻²). However, such large current densities cannot be reached by CO₂ electrolyzers based on liquid aqueous reaction environments. This general limitation originates from the low solubility of CO₂ in aqueous electrolyte solutions (∼30 mM in H₂O at atmospheric pressure) thus resulting in diffusion-limited current densities which typically do not exceed values of 0.03 A cm⁻². These are one order of magnitude below the current densities reported for alkaline water electrolysis.

**Table 1.** Current and estimated costs of production by CO₂-electrolysis for H₂, CH₄, CₓHₓ, HCOO⁻ and CH₃OH.

<table>
<thead>
<tr>
<th>Product</th>
<th>Produced by</th>
<th>Current market price [S kg⁻¹]</th>
<th>Current production volume [Mt y⁻¹]</th>
<th>Production price by electrolysis [S kg⁻¹]</th>
<th>Production volume per electrolysis unit [Mt y⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>steam reforming, partial oxidation of methane or gasification of coal[13]</td>
<td>2-4[14]</td>
<td>65</td>
<td></td>
<td>0.0003</td>
</tr>
<tr>
<td>CH₄</td>
<td>methanogenesis or hydrogenation of CO₂[15]</td>
<td>&lt;0.08[15]</td>
<td>2400[16]</td>
<td>2.4</td>
<td>0.0007</td>
</tr>
<tr>
<td>CₓHₓ</td>
<td>pyrolysis or vapocracking[17]</td>
<td>0.8-1.5[18]</td>
<td>14[17]</td>
<td>1.6–3.2</td>
<td>0.0009</td>
</tr>
<tr>
<td>CO</td>
<td>Boudouard reaction[19]</td>
<td>0.65</td>
<td>210000</td>
<td>0.27–0.54</td>
<td>0.005</td>
</tr>
<tr>
<td>HCOO⁻/HCOOH</td>
<td>hydrolysis from methyl formate and formamide[20] or by-product of acetic acid production</td>
<td>0.8-1.2[20]</td>
<td>0.8[21]</td>
<td>0.17–0.34</td>
<td>0.008</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>From natural gas, coal, biomass, waste[22,23]</td>
<td>0.4-0.6[23,24]</td>
<td>100[23]</td>
<td>0.70–1.4</td>
<td>0.002</td>
</tr>
</tbody>
</table>

*The lowest price is calculated by assuming the cell device efficiency of an alkaline water electrolyzer. The highest price is obtained by considering that a co-electrolysis device is operating at half the efficiency of an alkaline water electrolyzer and so that the production price of individual products will be twice higher.

*Estimated on the basis of a daily production from an alkaline water electrolyzer of ca. 1000 kg H₂.
troyzers. From a technical point of view, there could be an addition a severe contamination issue associated with aqueous reaction environments. A ppm level of metallic contaminants, typically present in aqueous electrolyte solutions, would already be sufficient to irreversibly poison the catalyst surface during CO electrolysis, e.g. with Fe trace contaminants that get electroplated during operation. These metallic contaminations further shift the selectivity of the electrode reaction towards hydrogen formation thus lowering the faradaic efficiency (FE), ratio of CO,RR current to total current, for specific products of the CO,RR. These circumstances require a careful and most likely rather costly purification of the electrolyte solutions for the CO,RR. Contributions to the production costs originating from these extra electrolyte purification steps are not considered in Table 1.

Under the assumption of only kinetic and ohmic losses, the cell potential $E_{\text{cell}}$ for the CO, electrolysis can be derived on the basis of Eqn. (2):

$$E_{\text{cell}} = E_{\text{rev}} + \eta_{\text{kin}} + \eta_{\text{ohmic}} + iR_{\text{ohmic}}.$$ [2]

$E_{\text{cell}}$ corresponds to the reversible potential (listed in Table 3 further down). The $iR_{\text{ohmic}}$ term in Eqn. (2) accounts for voltage losses caused by the finite ionic conductivity of the electrolyte solution (see Table 4 for typical $R_{\text{ohmic}}$ values). The $\eta_{\text{kin}}$ and $\eta_{\text{ohmic}}$ terms in Eqn. (2) refer to the overpotentials of the anodic (OER) and cathodic (CO,RR) half-cell reactions, respectively. Reliable information on the CO,RR and OER reaction kinetics specifically for gas diffusion configurations are, however, rare in literature. For the sake of simplicity we therefore estimate CO,RR and OER overpotentials from experimental data available for polycrystalline catalyst materials in aqueous reaction environments. For such considerations we assume that the particular catalyst performance does not alter when going from an ideal aqueous environment to a gas diffusion configuration. Catalyst materials that perform best toward specific CO,RR product are listed in Table 2. Their kinetic performance can be derived from Fig. 1A which relates current density and applied overpotential in a semi-logarithmic plot ($\eta_{\text{kin}}$ vs $\log(i_{\text{kin}})$). The linear correlations observed between $\eta_{\text{kin}}$ and $\log(i_{\text{kin}})$ in Fig. 1A are clear fingerprints of Tafel behaviors in this specific current density range (with 100–150 mV decade$^{-1}$ Tafel slopes), which confirm that these curves are dominantly charge-transfer controlled and not limited by mass transport. On the basis of this catalytic performance for model electrodes having roughness factors of ca. 1 cm$^{-2}$ cm$^{-2}$, we compute kinetic controlled curves (not shown) for technical electrodes prepared from metal nanoparticles with different diameters and corresponding surface areas,[37–39] again listed in Table 2. For doing this, we assume that the kinetic performance of the catalysts will not be affected by the transition between aqueous and gas-phase reaction media (as it has been demonstrated for fuel cells[40]) nor by particle-size effects.

Based on the CO,RR and OER kinetic overpotentials (Fig. 1A) and the electrolyte resistances (Table 4), the cell voltage $E_{\text{cell}}$ is calculated from Eqn. (2) as function of the applied current and is shown for the various electrolysis cells in Fig. 1B. From these theoretical polarization curves, device efficiencies ($\xi_{\text{Electrolyzer}}$) are estimated using Eqn. (3):

$$\xi_{\text{Electrolyzer}} = \frac{\Delta H^\circ}{\Delta G^\circ} \frac{\eta_{\text{rev}}}{E_{\text{cell}}}.$$ [3]

$\Delta H^\circ$ and $\Delta G^\circ$ in Eqn. (3) relate to enthalpies and respective Gibbs free energies of the overall (co-)electrolyzer cell reactions as listed in Table 3. The validity of our approach can be verified on the basis of the calculated efficiency for a PEM electrolyzer, in good agreement with performance data reported elsewhere.[41] It can be seen in Fig. 1A that CO and HCOO$^-$ are the

![Figure 1](image-url)

**Table 2.** Summary of the half reactions and corresponding catalysts at play in (co-)electrolysis cells, along with the electrode roughness factor values projected on the basis of the catalyst loading and average particle size.

<table>
<thead>
<tr>
<th>Half Cell Reaction</th>
<th>Catalyst</th>
<th>Loading$^a$ [mg$^{-2}$ cm$^{-2}$]</th>
<th>$d_{\text{cat}}$ [nm]</th>
<th>Surface area$^b$ [cm$^{-2}$ cm$^{-2}$]</th>
<th>Roughness Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ + 2H$^+$ + 2e$^-$ ⇌ CH$_4$ + 2H$_2$O</td>
<td>Cu</td>
<td>5</td>
<td>50</td>
<td>13</td>
<td>670</td>
</tr>
<tr>
<td>2CO$_2$ + 12H$^+$ + 12e$^-$ ⇌ CH$_4$ + 4H$_2$O</td>
<td>Ag</td>
<td>5</td>
<td>100</td>
<td>5</td>
<td>270</td>
</tr>
<tr>
<td>CO$_2$ + 2H$^+$ + 2e$^-$ ⇌ CO + H$_2$O</td>
<td>Sn</td>
<td>5</td>
<td>100</td>
<td>7</td>
<td>430</td>
</tr>
<tr>
<td>CO$_2$ + H$^+$ + 2e$^-$ ⇌ HCOO$^-$</td>
<td>Pt</td>
<td>0.5</td>
<td>3</td>
<td>90</td>
<td>450</td>
</tr>
<tr>
<td>H$_2$O + $\frac{1}{2}$O$_2$ + 2H$^+$ + 2e$^-$</td>
<td>IrO$_2$</td>
<td>1.5</td>
<td>10</td>
<td>50</td>
<td>750</td>
</tr>
</tbody>
</table>

$^a$Typical catalyst loading values in alkaline and PEM-electrolyzers. $^b$Average particle size diameters based on values reported in the literature for Cu black particles, carbon-supported Ag-nanoparticles, and battery Sn-anodes. The values for Pt and IrO$_2$ are typical of fuel cells and electrolyzers. Assuming spherical metal particles with all of their area exposed to the reaction medium.
CO$_2$RR products generated with the lowest overpotential (–0.6 and –0.45 V at 0.2 A cm$^{-2}$), as opposed to C$_2$H$_4$ and CH$_4$ (–0.9 and –1.1 V at 0.2 A cm$^{-2}$). This is in line with our previous conclusions that CO and HCCO$^-$ are the most economically interesting products to be considered from the CO$_2$RR (Table 1). Ultimately, when comparing all electrolyzers efficiencies (Fig. 1C), the CO$_2$ to CO or HCCO$^-$ electrolyzers have efficiencies in the range 55–60% at 0.2 A cm$^{-2}$, close to that of an alkaline water electrolyzer (80%). Moreover, the projected efficiency of the CO$_2$-electrolysis cells would certainly benefit from improvements in CO$_2$-reduction electrocatalysis, and from the development of membranes with better ionic conductivities. This optimization is therefore addressed in the following sections.

4. CO$_2$ Electrolysis Cell Design

Our cost estimation for the diverse CO$_2$RR products (Table 1) was based on the assumption that the electrolysis device operates at the same current density as an alkaline water electrolyzer (0.2 A cm$^{-2}$). However, as already discussed above, these current densities cannot be achieved by electrolysis cells that use liquid electrolytes as source for dissolved CO$_2$ reactants. In the following we will review several electrolysis cell designs that would allow achieving high current densities for the CO$_2$RR. These different types of electrolyzers can be classified according to the nature of the electrolyte used in these devices.

4.1 CO$_2$ Electrolysis at Low pH Conditions

PEM electrolysis configurations, based on the use of 50–100 μm thick proton exchange membrane acting as electrolyte and separator between the anode and cathode, allow an order of magnitude larger current densities than alkaline water electrolyzers.$^{[41]}$ The pH in the membrane and at the gas diffusion electrode/electrolyte interfaces is highly acidic with pH ≈ 0 where the HER, considered as a parasitic side reaction for the CO$_2$RR, proceeds at the highest rates compared to other pH conditions.$^{[42]}$ As an example, Delacourt et al. used a PEM electrolysis configuration with a silver-based GDE as cathode that was fed with gaseous CO$_2$ as reactant.$^{[27]}$ In this case no CO$_2$ reduction product was detected (only H$_2$) although silver is considered as the most active catalyst material for the CO$_2$ to CO pathway. Even if most reports claim that the high HER currents are the sole reason why cathode electrodes cannot be polarized below CO$_2$ reduction onset potential, it should be noted that since PEM electrolyzer configurations allow 3 orders of magnitude higher current than electrochemical measurements in liquid electrolyte to be achieved, and assuming a Tafel slope for the HER of ca. 120 mV decade$^{-1}$,$^{[30]}$ an electrode interface in a PEM electrolyzer can be polarized at ca. 360 mV lower potential than in a liquid-based electrochemical device. Nonetheless, this extended potential domain probed in the work of Delacourt et al. did not allow them to detect any CO$_2$ reduction product. As a conclusion, it is more than likely that a CO$_2$-electrolysis configuration adapted from a PEM electrolyzer would not be a suitable solution.

4.2 CO$_2$ Electrolysis in an AEM-type Configuration (High / Neutral pH Conditions)

The counterpart of the PEM technology in terms of pH conditions is an anion exchange membrane (AEM). Here, OH$^-$ species are exchanged through quaternary ammonium moieties that are covalently attached to the polymer backbone of the membrane. The AEM regulates the pH at the electrode/membrane interface to a value close to 14.$^{[43,44]}$ Moreover, the use of an AEM, in a so-called AEM electrolyzer device, would allow similar current densities to PEM electrolyzers with the advantage of using noble-metal free anode electrodes for the oxygen evolution reaction.$^{[17–19]}$ It is in particular the alkaline pH which makes the AEM configuration attractive for the CO$_2$ electrolysis since the FEs of the CO$_2$RR are reported to be significantly higher at elevated pHs. In this context it is interesting to note that the initially high pH of 14 in a pristine AEM cannot be maintained in presence of CO$_2$, where the following equilibrium reaction occurs:$^{[50]}

\[
(OH^-)_{\text{membrane}} + CO_2 \rightleftharpoons (HCO_3^-)_{\text{membrane}}
\]

and the pH is expected to regulate in the range of 7–10.

A CO$_2$ electrolysis test based on an AEM electrolyte has been conducted using a silver-based gas diffusion electrode as cathode material.$^{[27]}$ Here, the HER was still favored over the CO$_2$RR thus resulting in low FEs in the range of only 1%.$^{[27]}$ Further studies utilizing the most recent and stable versions of AEMs$^{[46]}$ would need to be undertaken in order to rationalize these results and to clarify whether a CO$_2$-electrolysis configuration adapted from an AEM electrolyzer can be a suitable solution.

4.3 CO$_2$ Electrolysis at Neutral pH Conditions

Studies performed in liquid electrolyte solutions identified an optimum pH range for the CO$_2$RR from 7 to 10. It has further been reported that not only the pH but also the nature of anionic and cationic species in the aqueous electrolyte solution has a great influence on the particular mechanism of CO$_2$ reduction and the resulting FEs (the interested reader is referred to
ref. [7]). Several electrolysis designs have already been reported in literature for such near-neutral pH conditions and these cell configurations can be grouped into two main kinds: either the electrolyte remains stagnant, e.g. immobilized by a matrix, or the liquid electrolyte is flushed in a flow-cell type of reactor. A prime example of the first kind of cell design is proposed in the work of Delacourt et al. where a Na-fion® membrane in a potassium-form was utilized.[27] Some features of this approach resemble the design of a PEM electrolyzer. However, in this present case the carriers for the ion current are the K+ ions that are transported across the polymer membrane. Moreover, the reactants are dissolved in liquid (aqueous) media and transported by convection to the anode (e.g. KOH solution for OER) and cathode (CO2 saturated 0.5 M KHCO3 for CO2RR), respectively, in order to balance exchanged charges from the cathodic and anodic reactions. From a performance point of view, the small currents (~0.02 A cm-2) can be attributed to limitations caused by the solubility of CO2 in the KHCO3 solution. Moreover, the FE currents (~40% of the total currents) are still far below the expected FE-s reported for silver catalysts.[27] A similar approach as the one just described would consist of using AEM electrolysis cell configuration with the circulation of a carbonate/bicarbonate solution in the cathode compartment. This approach has been demonstrated to be effective for water electrolysis[51] and could be test-proofed for CO2 electrolysis. Both of these cell configurations are depicted in Fig. 2A. Overall, several drawbacks arise from the use of a neutral immobilized electrolyte configuration. First, the current carrier (K+, HCO3-) has to be supplied by the catholyte. This implies that the cathode interface would again consist of a CO2-saturated liquid electrolyte, and so that the CO2-electrolysis cell would be limited to small current densities (0.01–0.03 A cm-2) even though this limiting current could be increased by working under higher CO2 pressure conditions.[52] The second drawback is related to the high level of purity required for the catholyte, where traces of metal cations at the ppm level could lead to much higher rates of hydrogen evolved at the expense of CO2 reduced.[53] Finally the durability of this configuration might be an issue since continuous operation will ultimately lead to the build up of a pH gradient between both electrodes.

To overcome some of these technical limitations, Delacourt et al. introduced a dual solid electrolyte configuration consisting of an 800 μm thick glass fiber impregnated with 0.5 M KHCO3 and being in contact with the cathode whereas an additional PEM is in contact with the anode. The cathode can be fed with a humidified stream of CO2 whereas the anode is exposed to a liquid aqueous solution for the OER.[27] With this dual solid electrolyte design CO2RR current densities of up to ~0.140 A cm-2 were achieved for the reduction of CO2 to CO on a silver-based GDE.[53] These current densities are at present the highest reported in literature for the CO2RR. However, there are several drawbacks associated with the cell design proposed by Delacourt et al. First, by having the anode and cathode operating under different pH conditions, one introduces an additional loss to the cell voltage (0.059 V per pH unit difference between anode and cathode). The second drawback is related to the overall thickness of the buffer layer. Assuming an ionic conductivity of 10 mS cm-1, the ohmic drop across the 800 μm buffer layer would amount to 1.6 V for a current density of 0.200 A cm-2. This tremendous IR drop would be highly disadvantageous in terms of cell performance. The overall cell efficiency could, however, be significantly improved for instance by replacing the 800 μm buffer layer by a 50 μm thick AEM (such as those used for alkaline fuel cell applications[54]). Another alternative to the glass fiber used by Delacourt et al. would be a OH- or HCO3-doped polybenzimidazole (PBI) membrane, as depicted in Fig. 2B. This membrane, when doped with H2PO4, is typically used in high temperature fuel cells,[55] and some attempts were already made to incorporate KOH into the membrane for alkaline electrolysis of fuel cell operation.[56,57] Such a modified cell design with a dual electrolyte configuration, also enabling straightforward collection of gaseous and liquid products, is foreseen as one of the most promising electrolysis configuration.

An alternative approach for an improved cell design enabling higher CO2RR current densities was developed by Kenis and coworkers (for the detailed description of this cell design the interested reader might refer to refs [28,58–60]). This design is based on a combined (liquid) flow cell and gas diffusion type of reactor where a liquid electrolyte is flushed between two fixed GDEs. This concept of a ‘floating’ GDE is known to enable very fast diffusion rates.[61] Products of the CO2RR (e.g. non-volatile formate) are then released into the liquid electrolyte stream on the inner side of the cathode (Fig. 2A). With regard to the CO2RR, high current densities of 0.130 A cm-2 for HCOO- production[28] and 0.06 A cm-2 for CO production have been reported for this cell design.[62] These results also prove the versatility of this cell design. Not only (volatile) gaseous reaction products (e.g. CO) can be obtained at high current densities but also liquid (non-volatile) products such as formate.

As electrolyte, a highly concentrated aqueous (bicarbonate) could be used. The high solubility of the Cs and Rb salts (up to 25 mol%) can provide a highly concentrated electrolyte with conductivities up to 100 mS cm-1 and allow operation at temperatures above 100 °C at atmospheric pressure.[63,64] It should be kept in mind that since liquid electrolytes are involved in this approach, the same concerns regarding the purity of the electrolytes need to be addressed, as discussed above. Alternatively, also non-aqueous electrolyte solutions might be used in this configuration. Their CO2 solubility is higher than in aque-
ous environments (e.g. acetonitrile shows a CO₂ solubility which is higher by factor 8 compared to water). The same is valid for room-temperature ionic liquids (RTILs). The use of ionic liquids is also attractive due to their ability to capture selectively CO₂ from a diluted gas stream. Their use in such a flow-cell design is, however, restricted to those having a low viscosity. What makes ILs promising electrolytes also for such flow cell devices is their ability to even catalyze the CO₂RR. It was demonstrated that imidazolium-based RTILs dramatically decrease the overpotential for CO₂ reduction particularly in water/RTIL mixtures. Rosen et al. used 18 mol% Emim-BF₄ (1-ethyl-3-methylimidazolium tetrafluoroborate) in water as a catholyte in a flow electrochemical reactor. A few recent works have also demonstrated highly selective CO₂RR toward CO on nanostructured metallic catalysts (Ag, Bi) in RTILs and RTIL/acetonitrile. In this part, we have reviewed all the possible CO₂-electrolysis cell configurations, which would allow closing the gap in terms of operating current density with respect to an alkaline water electrolyzer.

All these arrangements rely on the use of a GDE for an optimal transport of reactant and reaction products in the gas phase. In order to maximize the number of triple phase boundaries (defined as the presence at the same place of an active catalyst site, CO₂ and electrolyte) and to decrease the kinetic overpotential, the next step should consequently be how to design such GDE with the highest possible roughness factors i.e. high cm⁻², values. This part will therefore focus on understanding how CO₂ reduction kinetics could be increased, and in the meantime HER currents be suppressed, when engineering electrocatalysts at the micro- and the nano-scale.

5. Electrode Materials for CO₂ Electrolysis

5.1 Electrodes for Formate Production

The products and rates of CO₂ electroreduction are affected strongly by the nature and structure of catalytic materials as well as electrolyte solution composition. Numerous half- and full-cell studies were performed to elucidate the key factors influencing CO₂ conversion. As we mentioned above, formic acid and CO would be desirable products in CO₂ electroreduction. The catalytic materials selective for formate production are listed in a recent review article and include: metallic Pb, Hg, In, Sn [28,72–77] Pd [78,79] SnO₂ [32,77,80] and metallo-organic complexes. In order to reach sufficient current densities GDEs are used. Fig. 3 demonstrates the plot of operational potentials and corresponding partial current densities for formate and CO production in CO₂ electroreduction on different GDEs. A few data points are given for non-GDEs.

It is rather difficult to compare the performances of different catalyst materials reported by different research groups, as the CO₂ electrolysis was conducted under different conditions (electrolyte, pH, cell configuration). However, we can distinguish certain trends. The highest current densities for formate production, up to ~0.13 A cm⁻², were obtained on unsupported Sn GDEs (solid squares in Fig. 3A). We notice that among s- and p-metals, Sn catalysts seem to be the most promising catalytic material, as it is rather inexpensive, less toxic than e.g. lead, and has a very good selectivity for formate. A few recent studies explored Sn as a catalyst for CO₂ electroreduction and reported better kinetics and selectivity toward formate production at such catalysts as compared to Sn [77,80,82]. However, the stability of SnO₂ under operando conditions (rather negative potential of CO₂ reduction), or any oxide phase in general, is still an issue to be addressed. Rather low overpotentials were found for formate production on Pd [79] and Ru-Pd [83] catalysts (star and pentagon in Fig. 3A) with FEUs to 100% operating potentials approximately 0.5 V below the values observed for Sn catalysts. However, the high price of Pd needs to be considered before implementing such a catalyst in CO₂ electrolysis devices.

Review of the literature data showed that the energy efficiency for formate production on different catalysts as obtained in full-cell studies typically has not exceeded 50% even at current densities ≤0.02 A cm⁻² and dropped with higher current densities. Such energy efficiency is considerably smaller than the expected maximal efficiency calculated above (Fig. 1C), and is not satisfactory yet.

5.2 Electrodes for Carbon Monoxide Production

The reduction of CO₂ to CO (or syngas, CO + H₂) is very attractive, as it can be used as a feedstock for synthetic fuel production via Fischer-Tropsch processes. Electrochemical CO formation from CO₂ is favored by Ag, Au and Zn catalysts. Use of water-free electrolyte solutions such as aprotic solvents and ionic liquids also increases the FE for CO production. Fig. 3B displays the relationship between operating potentials and partial current densities for CO formation on different electrodes taken from various full-cell studies. One can see that GDEs with unsupported Ag NPs display relatively good performance reaching partial current densities up to 0.115 A cm⁻² at E = –0.8 V RHE. A considerably lower performance and FE for CO was found for carbon-supported Ag NPs (40 wt%, dot-centered squares in Fig. 3B), in order to obtain partial current densities of CO production one needed to apply 0.2–0.3 V more negative potential as compared to unsupported Ag NPs (solid squares). However, the use of TiO₂ as a support with 40 wt% loading of Ag (empty squares) allowed reaching similar kinematics of CO₂RR as unsupported Ag NPs (solid squares) but with much smaller silver loading. In general, it is better to avoid a carbon support, as it increases the current efficiency of HER. Due to the high surface area of the carbon support, the contribution of HER in overall cathodic process can be very significant. The energy efficiencies for CO production are 40–60% at partial current densities up to 0.115 A cm⁻², which is 50% higher than the efficiencies for formate production (Fig. 1B). Normally, the FE of HER increases with increasing the cell voltage. However, since hydrogen gas is a component of syngas, total energy efficiencies for CO production are similar to those depicted in Fig. 1C. Importantly, the CO/H₂ ratio can be readily tuned by changing cell voltage and potentially by the right choice of the catalyst system.
A recent review postulated the importance of the catalyst morphology for kinetics and even selectivity of CO$_2$RR.[93] Many examples demonstrated that nanostructured and/or nanosized electrodes could significantly decrease the overpotential of CO$_2$RR as compared to conventional bulk electrodes. The use of such catalysts also allows high current densities to be reached (respective to geometric area and the mass of catalyst material), which is due to not only a large actual surface area, but also a larger number of active sites for CO$_2$RR on nanostructured surfaces.[93] The catalytic effect of metallic nanostructured electrodes can be enhanced by introducing additional foreign metals, forming bimetallic nanostructures, such as alloys, core-shell and thin-film configurations.[94] The catalytic properties of bimetallic catalysts can be tuned by the choice of foreign metals, chemical composition, morphology of the nanostructures (size, shape and configuration) and capping agents, providing intrinsic functionality different from that of monometallic catalysts. Bimetallic catalysts have been studied for many electrochemical reactions, such as oxygen reduction, hydrogen evolution, CO and alcohol oxidation. However, they are scarcely studied on CO$_2$RR to date.

5.3 Electrodes Modified with Ligands and Complexes

Besides metal surfaces and nanoparticles, nitrogen-rich ligands or metal complexes deposited on the electrode surface also showed promising results for electroreduction CO$_2$ to formate or CO (Fig. 4B). For example, FEs close to 100% at 70 mA cm$^{-2}$ were achieved on metal-phthalocyanine complexes M-Pc, where M = Co, Ni, Pd, Ag[81,88,89] (dot-centered rhomb and triangle in Fig. 3B). Promising results were obtained in a flow cell on carbon-support ed, nitrogen-based organometallic Ag catalysts.[89] At the same potential, the current densities of CO formation form CO$_2$ on e.g. silver 3,5-diamino-1,2,4-triazole supported on carbon (AgDAT/C) were similar to those achieved on Ag-based GDEs (star-symbols in Fig. 3B), but comparatively at much lower silver loading.

Alternatively, nitrogen-rich ligands (for example pyridine, bipyridine, benzimidazole and their polymers) and metal complexes with transition metal centers which are dissolved in an electrolyte solution are also promising (co-)catalysts for electrochemical reduction of CO$_2$ to CO or formate (Fig. 4C).[95,96] By tuning the structure of the metal complex/ligand, one can tune the stability of the CO$_2$-adduct which dictates the selectivity of the final product formation. In the past four decades, numerous metal complexes based on the transition metals ruthenium, rhodium, iridium, cobalt, nickel, palladium, silver, copper, iron and manganese (both mono- and dinuclear) were proposed for CO$_2$ electroreduction, which are based on different families of metal complexes with macrocyclic ligands, with phosphine ligands and with polypyridyl ligands in the electrolyte solution.[95] Although some proposed mechanisms suggested such additives acted as homogeneous catalysts for CO$_2$RR, it seems that in the presence of transition metal complexes or nitrogen-rich ligands the efficiency of CO$_2$ reduction also depends on the cathode material. As an example, nickel cyclams chemisorbed on mercury were reported to show an enhanced catalytic activity compared an inert electrode such as glassy carbon.[95,97–99] This fact indicates that the ability of an electrode material to adsorb the organic compounds plays an important role in the CO$_2$ electrocatalytic reduction in the presence of organic ligands or metal complexes. Based on these results, we believe that the use of metal nanoparticles modified with nitrogen-rich metal complexes or ligands (Fig. 4D) might be a promising approach towards the development of effective catalysts for CO$_2$RR with a well-controlled catalyst selectivity and stability.

6. Conclusion

The direct electrochemical conversion of CO$_2$ into more valuable products can be considered as a highly promising approach for the concentration reduction of atmospheric CO$_2$ and at the same time for the storage of a surplus of renewable energy (e.g. from solar and wind sources) in form of a reduced carbon compound. A careful analysis of the estimated production costs and process efficiencies revealed that CO (or syngas) and formate are the economically most favorable reaction products of such CO$_2$ conversion. Their electrochemical generation can be considered as potentially competitive with their conventional and well-established routes of production.

In this critical review we, however, identified a number of challenges which still need to be addressed before CO$_2$ electrolysis can become economically viable. New designs of CO$_2$ electrolyzers need to be developed which allow for much higher current densities (0.2 A cm$^{-2}$) than recently reported for state-of-the-art CO$_2$ electrolyzer set-ups. In conventional electrolyzers where an aqueous environment serves as CO$_2$ source it is the CO$_2$ mass transfer which typically limits the CO$_2$ conversion rate. An improved CO$_2$ mass transfer can be achieved by using non-aqueous electrolytes (e.g. ionic liquids) that reveal a much higher CO$_2$ solubility (one order of magnitude as compared to aqueous media). An alternative and most likely even more promising approach to tackle CO$_2$ mass transfer issues is based on a gas-diffusion type of cell design where the cathode is directly fed with the gaseous CO$_2$ reactant. Concepts of alkaline and acidic water electrolyzers with proton exchange membranes (PEMs) and anion exchange membranes (AEMs) as their key elements can be in part transferred to the design of a more efficient CO$_2$ electrolyzer. These concepts and in particular the membrane design still need to be adjusted to the specific requirements of the CO$_2$ electroreduction reaction. The same is valid for the design and chemical composition of the gas diffusion electrodes. In the case of the CO$_2$ electroreduction there is no need to disperse the electrocatalytically active material on a carbon support since the common catalysts for CO$_2$ electroreduction are abundant and cheap (e.g. Sn for
formate and Zn for CO production). Furthermore, other concepts like (i) increasing the surface area of the catalyst (e.g., metal foams), (ii) use of bimetallic catalysts, and (iii) use of organo-metallic complexes or nitrogen-rich ligands as (co-)catalysts might become more important for the CO₂ electrolysis.

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Storage of Heat, Cold and Electricity

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Abstract: A promising energy storage system is presented based on the combination of a heat pump, a heat engine, a hot and a cold storage. It can be operated as a pure bulk electricity storage (alternative to Pumped-Heat Electrical Storage (PHES)/Compressed Air Energy Storage (CAES)) or as combined storage of heat, cold and electricity. Both variations have been evaluated using a steady state, thermodynamic model and two promising concepts are proposed: A transcritical CO$_2$ cycle for the pure electricity storage and a subcritical NH$_3$ cycle for combined storage of electricity, heat and cold. Parametric studies are used to evaluate the influence of different parameters on the roundtrip efficiency of the storage system.

Keywords: Dual Energy Storage & Converter · Electricity storage · Power-to-Heat · Reversible heat pump

Introduction

Storage technologies are bound to play an important role in the integration of renewable energy sources and in increasing the energy utilization efficiency in the upcoming years. The development of efficient and cost-effective storage technologies in all energy sectors is crucial to this task.[1] Along with the development of innovative electricity, thermal and chemical storage, the establishment of systems that can provide flexibility between energy forms will also gain importance.[2]

A promising storage system based on the combination of a heat pump, a heat engine, a cold and a hot storage is presented (Fig. 1). The system can be designed to serve as pure bulk electricity storage or a combination of heat, cold and electricity storage. The underlying operating principle is that during periods of excess electricity generation, a heat pump is operated to charge a hot and in some cases also a cold storage. In periods of excess electricity demand, the system can be operated in reverse as a heat engine, using the stored temperature difference to generate electricity. This system variation is particularly interesting for bulk electricity storage in a power output range higher than 10 MW. It can be viewed as an alternative to Pumped-Storage Hydroelectricity (PSH or PHES) and Compressed Air Electricity Storage (CAES), with the additional advantages of a higher energy density and the possibility of site-independent installation.

The first reports of this type of storage system can be found as early as 1924[3] and were continued in the 1970s[4] under the term ‘reversible heat pumping’. In recent years, this technology has been the subject of several independent academic and industrial investigations with varying system specifications (working fluid, temperature levels, storing material, etc.). Most investigators named the system differently (e.g. ETES,[5] PTES,[6] CHEST,[7] TEES,[8] and others[9]), making the identification of relevant projects challenging.

The authors propose a thermally open variation of the technology, named Dual Energy Storage & Converter, where the two storage units can be used, not only as a means to store electricity but also to cover heating and cooling demands. This version offers additional flexibility between energy forms (power, heat and cold) and can be implemented in applications which possess a relatively high demand of all three energy forms during the whole year (e.g. food & beverages industry). A thermally open variation of the reversible heat pump has been previously considered for building applications using water storage for the high temperature side but no storage on the low temperature side.[10]

This work presents the evaluation process of different variations of the storage system by means of a simple thermodynamic tool. Two promising systems are selected and are shown in detail in terms of temperature–entropy diagrams.

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Fig. 1. Schematic of the DESC process comprising a heat pump, a heat engine, a hot and a cold storage.
Methods

A simple steady-state thermodynamic tool has been developed for the scanning of different variations of the storage system shown in Fig. 1. The tool is based on Matlab\textsuperscript{[11]} and extracts the thermodynamic properties from the NIST-REFPROP database.\textsuperscript{[12]} It calculates the thermodynamic points describing the basic processes taking place during the heat pump and Rankine cycle (e.g. evaporation, expansion, condensation, etc.). Both the inefficiencies introduced by the machines and the exergy losses during heat exchange are considered but pressure drops and heat losses are neglected. The model was verified using independently calculated values describing the ABB concept with transcritical CO\textsubscript{2}. It was subsequently used to carry out parametric studies of the systems considered and assess variations of the technology (working fluids, number of stages, etc.).

Results and Discussion

The main characteristics of the two system variations selected to be presented in this work are shown in Table 1. ETES is a bulk electricity storage concept developed by ABB\textsuperscript{[5]} while DESC is a combined heat, cold and electricity storage concept developed by the authors.

The first thermodynamic evaluation was performed for the ETES system and can be seen in Fig. 2. The concept is based on transcritical CO\textsubscript{2} as working fluid for thermally closed cycles (see Table 1). The red line represents the heat pump cycle, the blue the Rankine cycle. Water is used for the sensible high temperature storage at 120 °C whereas ice is used for the low temperature storage at 0 °C. As seen in Fig. 2, the maximum operating pressure is 136.3 bar. The temperature levels and storage units are chosen to create an optimum match between the condensation/evaporation processes of the working fluid and the behavior of the storage media (water/ice) during charging/discharging. The ability to utilize water as the storage medium on both sides represents one of the biggest advantages of this variation of the reversible heat pump concept. The model was verified using independently calculated values provided by ABB. After the verification, the model was used to carry out parametric studies examining the influence of different parameters on the roundtrip efficiency of ETES. The parameters considered were: (i) temperature of hot storage, (ii) temperature of cold storage, (iii) ambient temperature, (iv) $\Delta T$ during heat transfer and (v) isentropic efficiencies of the mechanical components. Fig. 3 presents the results of

<table>
<thead>
<tr>
<th>Name</th>
<th>Energy form Input</th>
<th>Energy form Output</th>
<th>Working fluid</th>
<th>Storage units (hot/ cold)</th>
<th>Criteria for choice of T levels</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETES</td>
<td>El.</td>
<td>El.</td>
<td>CO\textsubscript{2}</td>
<td>Sensible / Latent (ice)</td>
<td>High roundtrip efficiency; water as storage material</td>
<td>Bulk electricity storage</td>
</tr>
<tr>
<td>DESC</td>
<td>El., heat</td>
<td>El., heat, cold</td>
<td>NH\textsubscript{3}</td>
<td>Latent / Latent</td>
<td>Optimized for customer-relevant T levels</td>
<td>Heat, cold, electricity and storage, and supply</td>
</tr>
</tbody>
</table>

![Fig. 2. Output of thermodynamic modeling for ETES concept with transcritical CO\textsubscript{2} as described in Table 1.](image1)

![Fig. 3. Surface plot showing the roundtrip efficiency of the transcritical CO\textsubscript{2} system, $\eta_{ret}$ as a function of the $\Delta T$ during the heat exchange and the maximum temperature of the high temperature storage $T_{HST}$](image2)
one parametric analysis showing the evolution of the ETES roundtrip efficiency as a function of the maximum temperature of the hot storage and the $\Delta T$ during heat transfer. As expected, an increase in the heat exchanger $\Delta T$ results in a dramatic decrease in the ETES roundtrip efficiency $\eta_{ETE}$. In contrast, an increase in the maximum temperature of the hot storage results in an increase in the $\eta_{ETE}$.

The thermodynamic model was modified to describe the behavior of other reversible heat pump variations. Other working fluids were evaluated such as isobutane and ammonia. A promising variation for the combined storage uses NH$_3$ as a working fluid (Fig. 4). Similarly to Fig. 2, the red line describes the heat pump cycle and the blue line the Rankine cycle. Both processes comprise two stages providing the flexibility of charging/discharging the hot and the cold storage separately. Both the produced heat and cold will be stored in latent heat storage units to ensure an optimal match with the temperature profile of the subcritical cycles. The storage temperatures have been chosen at 0 °C and 95 °C because they represent two key temperature levels for industrial process heat and cold. Despite its toxicity, ammonia is a promising natural refrigerant with a very high enthalpy of vaporization. It has been used widely in refrigeration and there are already commercially available heat pumps that can deliver the temperatures required for this DESC variation. One big disadvantage is the high overheating during the heat pump operation which imposes challenges for the lubricant and induces mechanical stress on the components. The expansion processes during the heat engine mode take place in the two-phase region which imposes constraints on the choice of the expander. At the maximum operating pressure of 60 bar, even though not as high as the one demanded by the transcritical CO$_2$ cycle, it could still impose challenges in the component development and operation.

**Conclusions**

A promising energy storage system is presented. It can be operated as a pure bulk electricity storage (alternative to PHES/CAES) or as combined storage of heat, cold and electricity. Both variations have been evaluated using a steady state, thermodynamic model and two promising concepts are being proposed: A transcritical CO$_2$ cycle for the pure electricity storage and a subcritical NH$_3$ cycle for combined storage of electricity, heat and cold. The CO$_2$ system has a maximum operating temperature of 120 °C and can be combined with water as a storage medium on both the hot and cold sides, which offers a valuable simplicity to the ETES system. The NH$_3$-based DESC system on the other hand can be integrated in a large number of industrial applications which require cold at 0 °C and heat at ~95 °C. The high heat of vapourisation of NH$_3$ and high energy density of the latent heat storage units increase system compactness. The developed steady-state thermodynamic tool is suitable for a first scanning/evaluation of different storage systems variations. It can also be successfully used to perform parametric studies and find optimal operation points. For a more detailed estimation of the system potential, the tool has to be extended to capture transient phenomena and to include pressure drops and heat losses.

**Acknowledgments**

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**Fig. 4. Results of thermodynamic evaluation for DESC concept with subcritical NH$_3$ as described in Table 1.**
Phase Change Material Systems for High Temperature Heat Storage

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Abstract: Efficient, cost effective, and stable high-temperature heat storage material systems are important in applications such as high-temperature industrial processes (metal processing, cement and glass manufacturing, etc.), or electricity storage using advanced adiabatic compressed air energy storage. Incorporating phase change media into heat storage systems provides an advantage of storing and releasing heat at nearly constant temperature, allowing steady and optimized operation of the downstream processes. The choice of, and compatibility of materials and encapsulation for the phase change section is crucial, as these must guarantee good and stable performance and long lifetime at low cost. Detailed knowledge of the material properties and stability, and the coupled heat transfer, phase change, and fluid flow are required to allow for performance and lifetime predictions. We present coupled experimental-numerical techniques allowing prediction of the long-term performance of a phase change material-based high-temperature heat storage system. The experimental investigations focus on determination of material properties (melting temperature, heat of fusion, etc.) and phase change material and encapsulation interaction (stability, interface reactions, etc.). The computational investigations focus on an understanding of the multi-mode heat transfer, fluid flow, and phase change processes in order to design the material system for enhanced performance. The importance of both the experimental and numerical approaches is highlighted and we give an example of how both approaches can be complementarily used for the investigation of long-term performance.

Keywords: High-temperature heat storage · Latent heat of fusion · Multimode heat transfer · Phase change materials · Thermal energy storage

1. Introduction

The Swiss industrial sector uses about 50% of its energy for process heat.1 This process heat is provided by fuels (74%) and electricity (26%). Based on the European heat market statistics 40% of that heat is high-temperature heat (>400 °C), thus accounting for an estimated 4.6% of the total end energy consumption in Switzerland. The metal processing and chemical industries are main consumers. The large exergy content of high-temperature heat, the non-continuous industrial processing routes, and the intermittency of some heat sources are drivers to develop high-temperature heat storage systems. Other applications for high-temperature heat storage include concentrated solar power and electricity storage by advanced adiabatic compressed air energy storage (AA-CAES).2 The latter represents one of the main complementing large-scale electricity storage approaches to pumped hydro electricity storage.

The design of thermal energy storage systems highly depends on the application, which defines its temperature level, energy storage capacity, storage duration, and charge and discharge rates. In addition to the technical and performance requirements, long lifetime, low cost, high volumetric energy density, and stable operation are key factors for a practical heat storage system.

Heat can be stored in the form of sensible and latent heat. Latent heat storage systems often use the solid/liquid phase transition due to volumetric constraints. If a material with a well-defined melting point is used (such as pure elements, compounds, or eutectics) then storing heat by means of a phase change makes it possible to stabilize the temperature at which heat is discharged. The downstream processes can subsequently operate stably and optimally at a specified temperature. As sensible heat storage materials tend to be less costly than phase change materials (PCMs), combined sensible-latent heat storage systems are developed to provide stabilized output temperatures at reduced cost.3 An additional challenge of PCMs is the requirements of containment in the molten stage. The stability of the interface between the PCM and the encapsulation is crucial for high and stable long-term performance, especially in high-temperature environments. Complex interlayers can ensure the mechanical and chemical stability while maintaining efficient heat transfer.

A generic latent heat storage system is shown in Fig. 1 utilizing a heat transfer fluid (HTF) to provide and evacuate the high-temperature heat. Heat is transferred from the hot HTF to the solid PCM during charging. The PCM undergoes melting and thus absorbs the latent heat of fusion within a narrow temperature range. When discharging, the reverse process occurs. A part of the heat can be stored as sensible heat in the encapsulation and interlayer, and in the PCM if it is completely melted and further heated above the melting temperature. The material combinations used for the heat storage system (PCM, interlayer, encapsulation) must be chosen carefully. The mechanical stability and good heat transfer performance must be ensured while guaranteeing chemical stability and inertness of the interfaces and interlayers. Detailed analysis of the heat transfer, fluid flow and phase change processes is
required to predict and enhance the system performance while investigating the interactions between the components and at the interfaces are required to predict and enhance the durability, stability, and system lifetime.

2. Phase Change Materials (PCM)

Phase change materials are commonly classified as organic or inorganic.[5] Organic materials are rarely stable above 400 °C making them unworkable for high-temperature heat storage. Among the inorganic materials, salts are often cheaper while metals outperform their counterparts in terms of high thermal conductivity and heat of fusion (see Table 1). Heat transfer enhancement techniques, such as the immersion of mesh layers, have been investigated for salts[5–8] but result in more complex material systems with reduced per volume and mass amount of active PCM material.

The detailed knowledge of material properties, such as melting temperature, heat of fusion, heat capacity, density, thermal conductivity, sub-cooling and thermal expansion coefficient, is of paramount importance when evaluating the performance of phase change materials. Data can be obtained from literature for elements and well known compounds, but are not always readily available or consistent for new PCMs under consideration. Differential scanning calorimetry (DSC), which is typically used to determine phase transformations and associated energies (glass transition temperature, melting temperature, heat of fusion), can be of limited applicability since the properties of bulk PCMs can vary from that of small samples (in the order of mg) used in this technique. The T-history method can be employed to investigate the thermo-physical properties (melting temperature, sub-cooling, specific heat capacity and heat of fusion) of different PCMs by melting and solidifying at controlled environment temperatures.[12] This type of measurement provides a fast and non-destructive way to measure bulk properties for encapsulated systems. A set of assumptions on sample geometry (i.e. cylindrical symmetry and aspect ratio) and heat transfer to the environment have to be verified for the results to be reliable. A typical T-history measurement for Al-12Si is shown in Fig. 2 allowing for the determination of the melting temperature and sub-cooling.

To address the stability of PCM and encapsulation the above-mentioned thermo-physical characterization techniques can be employed in sequence with typical load cycles. In addition, post mortem inspection of encapsulated PCM samples can give insight into degradation mechanisms and extent. In the case of steel encapsulated aluminum alloys an intermetallic reaction product forms at the interface and can be quantified visually after cross-sectioning. The formed iron aluminides are brittle and may deteriorate the mechanical properties of the encapsulation.[13,14]

3. Numerical Simulation

For the development of an optimized, high-performance material system design, the coupled multi-mode heat transfer, fluid flow, and phase change processes have to be understood. Generally, convective heat transfer dominates in the heat exchange between the HTF and the PCM, and conduction the heat transfer within the PCM. However, convection plays a role in the liquid phase of the PCM if a flow is induced and heat conduction is low, and radiative heat transfer from the surface of the opaque encapsulated PCM plays a role at high temperatures. Two main processes limit the charging and discharging rates of encapsulated metallic PCMs; the rate at which heat is transferred between the HTF and the encapsulation (further to the PCM) and the rate of melting. Potentially, evolving or pre-applied interlayers might provide additional conductive resistance due to changes in conductivity or imperfect layer contact. The performance prediction thus requires simulation of conductive, convective, radiative heat transfer, fluid flow, and phase change.

Back-of-the-envelope calculations predict the convective heat transfer between the HTF and the encapsulated metal PCM to be limiting. Indeed, in the experimental campaign (see Fig. 2) it took 20 minutes to transfer 15.12 kJ of heat in order to melt

Table 1. Thermo-physical properties of selected inorganic PCM. Metal alloy conductivities for the solid and liquid phases, salt conductivities for the solid phase.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Compound</th>
<th>Melting temperature [°C]</th>
<th>Heat of fusion [Jg⁻¹]</th>
<th>Thermal conductivity [Wm⁻¹K⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salts</td>
<td>NaNO₃</td>
<td>306[8]</td>
<td>172[8]</td>
<td>0.6[8]</td>
</tr>
</tbody>
</table>

Fig. 1. Generic latent heat thermal energy storage system in its charging state incorporating hot HTF, solid PCM, encapsulation, and stabilizing interlayers.

Fig. 2. Temperature measurement for Al-12Si encapsulated in an AISI 316L steel tube (2.13 cm outer diameter; 2.53 mm wall thickness). Preset oven temperature ramp during heating (charging) is indicated in green. Oven was turned off during cooling (discharging).
27g of Al-12Si. This illustrates the need for material system designs that increase the specific surface per unit mass of PCM such as provided by porous structures.

For the comparison of different material system designs, numerical simulations are the tool of choice. The phase change is attributed to the general class of free boundary problem due to the presence of melting or solidification fronts which evolve and represent a discontinuity in material properties. Early attempts of numerical solution are documented by Voller et al.[15]. The work of Voller led to the enthalpy porosity-method,[16] the state-of-the-art method for phase change simulations implemented in commercial software (ANSYS, COMSOL). While such simulations allow to better understand the physics of multi-mode heat transfer processes, it has been demonstrated,[17] that the requirement for semi-empirical constants has a significant influence on the solution. Due to their weak relation to first principles, their tuning with reference to experiments is necessary and the predictive power of the method is limited. This underlines the necessity of a dual approach, including simulations and experimental validation.

4. Chemical Stability and Performance Losses of PCM in AA-CAES Application

The following illustrates current efforts at our laboratory to develop tailored high-performing and stable high-temperature heat storage material systems. Specifically, we illustrate the effect of chemical degradation on the performance of a heat storage system. For that purpose the chemical stability of an aluminum alloy Al-12Si encapsulated in an AISI 316L steel tube – relevant in AA-CAES application – was investigated experimentally and the results were included in a numerical simulation to assess the impact of chemical degradation on the long-term heat storage characteristics.

4.1 Experimental Data

For the investigation of chemical stability, 20 AISI 316L steel cylinders with 21.3 mm outer diameter, 6 cm height, and 2.53 mm wall thickness were filled with approx. 27 g of Al-12Si and heated in a furnace to 700 °C. After different time periods the samples were removed from the oven and cooled to ambient. Cross-sectioning revealed, in accordance with literature[18,19] that an iron- and aluminum-rich intermetallic interlayer had formed as the PCM reacted with the encapsulation (confirmed by SEM-EDX). The quantified growth of the intermetallic layer thickness is illustrated in Fig. 3 together with an empirical fit. The growth kinetics of the intermetallic layer is generally accepted to be diffusion controlled[19] and monotonic growth over time is expected.[18] Since PCM is consumed to form high melting products ($T_m \geq 1160 ^\circ C$)[13] which act as a sensible heat material, the performance is expected to be altered. At the same time the mechanical stability is affected, as the interlayer is hard (up to 1000 HV[14]) and brittle enough to fracture from thermal stresses upon cooling the sample to ambient conditions.

4.2 Numerical Simulation

The impact of interlayer growth on performance was predicted by applying numerical simulations and using the measured interlayer growth thickness. A one-dimensional model was applied and the enthalpy method was used.[15] No convection was assumed and changes in density of the aluminum alloy were neglected, such that no empirical constants were required as input to the model. For comparison, the same temperature boundary conditions as in Fig. 2 were used and a heat transfer coefficient of 300 W/m²K between surrounding air and cylinder was assumed. The properties of a Fe$_{0.6}$Al$_{0.4}$ interlayer were used and it was assumed that the interlayer grew symmetrically with respect to the initial interface.

Fig. 4 illustrates the amount of sensible and latent heat stored as the cylinder is heated (charged) and cooled (discharged). The simulation was repeated for different interlayer thicknesses to highlight the decrease in performance. As the PCM was consumed, less heat could be stored in the latent heat of the PCM. Instead more heat was stored as sensible heat in the encapsulation and interlayer. The charge and discharge rates remained similar, however, the duration of melting and solidification decreased. For a heat storage system, this effectively means that a full charging cycle stores less heat and the discharge phase at constant temperature becomes shorter as

![Fig. 3. Measured and fitted intermetallic layer growth for Al-12Si encapsulated in an AISI 316L steel cylinder and decrease in discharge time at constant temperature.](image1)

![Fig. 4. Numerical prediction of the stored heat form (sensible – $h_s = \dot{h}(T=300K) = 0$ – and latent) of the AISI 316L steel encapsulated Al-12Si during heating (charging) and cooling (discharging) initially (solid lines) and for different thicknesses of the formed Fe-Al intermetallic layer(dotted lines).](image2)
the chemical degradation advances. Based on our model assumptions, in a material system with an interlayer of 1.6 mm, 19 wt% of the PCM material was consumed and the discharging time at constant temperature was reduced by 10%. The results presented in Figs 3 and 4 can be used to advance the accuracy of computational performance models of combined sensible-latent heat storage systems, such as the type described by Geissbühler et al.,[3] and models of complete AA-CAES electricity storage plants.

5. Conclusions

The development of tailored, encapsulated phase change material systems is crucial for the design of advanced high-temperature heat storage technologies, which are essential for enhancing the efficiency of applications such as industrial high-temperature processes, electricity storage by AA-CAES, and concentrated solar power. Our current research focuses on the challenges of finding appropriate material systems characterized by enhanced heat transfer and stable long-term performance.

We show how combined experimental and numerical methods can be used to quantify performance and degradation, and to provide design guidelines for tailored heat storage solutions guaranteeing high and stable performance over long lifetime at low costs.

Acknowledgements

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Seasonal Solar Thermal Absorption Energy Storage Development


Abstract: This article describes a thermochemical seasonal storage with emphasis on the development of a reaction zone for an absorption/desorption unit. The heat and mass exchanges are modelled and the design of a suitable reaction zone is explained. A tube bundle concept is retained for the heat and mass exchangers and the units are manufactured and commissioned. Furthermore, experimental results of both absorption and desorption processes are presented and the exchanged power is compared to the results of the simulations.

Keywords: Adsorption · Desorption · Falling film tube bundle · Seasonal solar thermal energy storage · Thermochemical heat storage

1. Introduction

Solar thermal energy storage for heating and cooling systems is a priority goal in the renewable energy future.

High thermal losses occurring by the use of sensible thermal energy in materials over the long term, i.e. seasonal storage and a low volumetric energy density (typically, water storages) are drawbacks. Therefore, numerous research groups are applying various approaches that aim to reduce the required tank volume assigned for seasonal thermal storage.1 Phase-change materials (PCM) and thermochemical materials (TCM) are promising approaches with the potential for increased volumetric energy density. In a TCM-based thermal storage system, thermal energy is used to separate the storage medium working pair in its components. Reversing the process releases thermal energy through an exothermal reaction. The storage material composed of two reactants forming a product are usually aqueous salt solutions (NaOH, LiCl, LiBr, etc.). A recent overview of sensible, latent and thermochemical storage concepts indicated the specific advantages and disadvantages.2

The closed sorption heat storage approach (only heat is exchanged with the environment, no exchange of substances) functions as a continuous but not full cycle liquid state absorption heat pump.3 The process operates in the planned temperature and pressure range under exclusion of non-condensing gases. No thermal insulation is required for the storage tanks as long as they are kept at room temperature. In fact, except during the loading/unloading operation, no thermal losses occur over the time as it is the case for conventional water storage.

In a first part of this article, the working principle of the thermochemical storage will be described and focus will be put on the heat and mass exchanger, a central component of the facility. The modelling as well as the manufacture and commissioning of the heat and mass exchanger will be presented in a second part. Experimental measurements and results in both absorption and desorption modes will then be shown in a third part.

2. Thermochemical Storage Concept

2.1 Working Principle

The absorption/desorption storage concept works with a sorbent (in the present study aqueous sodium hydroxide) and a sorbate (water).3 In summer, during the charging process, the solar energy provided by the thermal panels is used in the desorber to increase the sorbent concentration (partial evaporation of water from the sodium hydroxide solution under reduced pressure). The water vapour is condensed and releases its latent heat to the environment (through a ground heat exchanger) and the water is stored at room temperature in its liquid phase.

The concentrated sorbent is separately stored at room temperature until winter, when the storage is discharged through operating in the reverse direction. Then, the sorbate is evaporated under reduced pressure in the evaporator using ground heat at a low temperature level. This vapour flows to the absorber and is absorbed by the concentrated sorbent solution, releasing heat at a sufficiently high temperature level to satisfy the building’s heating requirements.

Thus, this storage design concept is based upon the thermally driven heat pump principle.

The concept of this storage allows a separation of the power unit (heat and mass exchangers) and the energy unit (reactant and product storage tanks) – like in gas or oil burner thermal energy system sources. Furthermore, because of the seasonally separated process steps of desorption in summer and absorption in winter one heat and mass exchange component for desorption/absorption and one for condensation/evaporation can be used.

As aqueous sodium hydroxide is available at low cost and as water vapour absorption in aqueous sodium hydroxide has a considerably higher volumetric energy density compared to sensible thermal storage systems (theoretically up to six times for a concentration decrease from 50 to 25 %wt), Weber et al.3 investigated a closed sorption heat storage based on sodium hydroxide and water. In the present work, the reaction zone of an absorption/desorption concept with sodium hydroxide (NaOH) and water will be highlighted and investigated, focussing on the design of the core components.

2.2 Heat and Mass Exchanger Conception

A compact geometric design of the heat and mass exchangers is essential in order
to keep the high volumetric energy density benefits of the chosen concept and material. Both the heat and the mass exchanges are directly correlated to the transfer area. For this transfer zone, the falling film technology with horizontal tubes\[4\] was chosen because of the large contact area between vapor and the liquid fluid as well as the solution mixing that occurs when the droplets fall from one tube to another. That enables the volume of the heat and mass exchanger area to be decreased.\[5\] In order to facilitate the vapor transfers in the falling film,\[6\] all non-condensable gases are removed from the reaction zone (tube bundles seated in evacuated container, see Fig. 1).

As mentioned above, the sequential running of the heat storage allows a combination of desorption/absorption (A/D) and evaporation/condensation (E/C) processes each confined to one component and an increase of the storage volumetric energy density. However, the challenge in the design of the components is to surmount the different heat and mass transfer rates in the process steps in one component.

A critical point in the design is the homogeneous distribution of the fluids on the outer tube surface to achieve an efficient heat/mass transfer. Therefore, special attention was applied to design the nozzle manifold (in yellow in Fig. 1) that sprays the fluid on the top of the tube bundle. Because of corrosion, stainless steel (DIN 1.4404) is used.

Previous experimental studies on the LiBr-H\textsubscript{2}O absorption system showed that a certain degree of fluid recirculation increases the heat and mass transfer. Deng\[7\] describes that increasing the flow rate (volume flow) per area is favourable for higher heat/mass transfer rates because an improved wetting of the tube surface by a higher volume flow is achieved. Nevertheless, recirculation requires additional electric energy for pumping. To reduce this parasitic energy consumption the challenge is to find a parameter range in which steady state operation can meet the required thermal power without recirculation.

3. Design and Manufacture of the Heat and Mass Exchanger

3.1 Heat and Mass Exchanger Modelling

The modelling of the heat and mass exchanger tries to be representative for the reality of the system in regard of the operation set points. In the simulation, the coupled heat, mass and momentum equations are solved under steady state conditions.

The present model considers only one vertical tube column of a falling film heat exchanger and the scaling of the power is done linearly (fluid distribution inside and outside of the tubes in parallel). For each tube (or horizontal tube row with index $n$ in the scaling, see Fig. 2a), the temperature is calculated inside and outside of the tube, and on the tube surface with the same index as shown in Fig. 2. The heat exchange coefficient ($h_i$) inside of each tube is calculated according the Sieder and Tate or Colburn correlation depending on the flow regime.\[7\] For the heat exchange coefficient calculation outside of the tube ($h_e$), the model convergence was studied using different kinds of correlations. The calculations showed that the prediction of the heat transfer coefficients at low mass flow rates has limited accuracy. For the desorber/absorber sizing, it was therefore.

**Fig. 1. CAD cross-sectional view of the E/C unit (manifold and tube bundle).**

**Fig. 2.** (a) Tube bundle model schematic with the indicated variables used in the modelling; (b) mass flow rate (right vertical axis), average temperatures and solution concentration (right vertical axis) development in the desorber in function of the tube number $n$. 
decided to use a linear regression based on the experimental data gathered at low mass flow rates by Lee\cite{10} instead of applying the correlations established by Owens\cite{10} and Hu and Jacob\cite{11,12}.

In the design process a multi-parameter problem has to be solved according to the set boundary conditions. This comprises the definition of the tube bundle geometry: number of tube columns and tube rows, tube length \((L)\), outer and inner tube diameters \((D_1, D_2)\) as well as tube spacing.

Desorber modelling results are shown in Fig. 2b: the development of temperatures \((T)\): fluid temperature outside of the tube; \(T_m\): wall temperature; \(T_e\): fluid temperature inside of the tube), of the sodium hydroxide concentration \((wt)\) and of the mass flow rate inside of the tubes \((m_i)\) and of the mass flow rate outside of the tubes \((m_e)\) are depicted over a 4x16 tube bundle arrangement in function of tube number \(n\) (with bottom-up method enumeration, \(n=1\) is the lowermost tube of the tube bundle). The heat transfer fluid inside the tubes of this counter current heat and mass exchanger, cools down while solar thermal panels heating up this fluid. Outside the tubes, the sorbent is fed by the fluid manifold nozzles with a temperature lower than its saturation temperature. Therefore, \(T_e\) raises rapidly until the saturation temperature is reached in uppermost tubes of the tube bundle. Then, partial evaporation occurs, the sorbent concentration \((wt)\) increases and its temperature follows the mixture saturation temperature. As the heat transfer coefficient inside of the tube is higher than outside (see Table 1), the wall temperature \(T_m\) is closer to \(T_e\) than to \(T_f\).

Table 1 shows that for the desorber/absorber combined heat and mass exchanger unit, the required heat flux \((Q)\) of about 12 kW for the desorber and 8 kW for the absorber is reached with a tube bundle geometry of 4 columns and 18 rows (tube length \(L=300\) mm and outside tube diameter of \(D_2=10\) mm). This tube bundle geometry also minimizes the auxiliary energy consumption of the circulating pump because of moderate pressure losses (calculation inside of the tubes).

In the same way, the tube bundle configuration of the evaporator/condenser unit was determined: 16 columns of 12 rows (same tube diameter \(D_1\), tube length \(L=700\) mm). In order to increase the heat transfer coefficient outside the tubes, fluid recirculation is planned for the operation of this unit.

### 3.2 Heat and Mass Exchanger Manufacture and Commissioning

A modular concept (each component is easily dismountable) as well as a limited number of vacuum sealing gaskets were other challenges in the vacuum envelope design. As showed in Fig. 3, two inspection windows allow a view to the top of the tube bundles, which are installed directly under the feed manifold. Except for the both fluid outlets at the bottom of the containers and a temperature sensor feed through in the A/C envelope, all connections and feed throughs are located on the tube bundles flanges (in blue in Fig. 3). These connections enable the feed of the tube manifolds with caustic soda solution on the A/D side and water on the E/C side. Two other feed through connections placed on the flanges are for the evacuation of the containers and the operation pressure measurement. The manifolds are integrated into the flanges for the inlet and outlet of the tube bundles heating and cooling fluid and further feed through are for the temperature sensors measuring the heating and cooling fluid temperature inside the tube bundle tubes as well as outside these tubes (outside tube wall temperatures).

For process and handling reasons as well as for fluid separation, both A/D and E/C units are placed in different containers (Fig. 3). The vapour feed through connects both units, enabling the required exchange of vapour in both directions (evaporator to absorber or desorber to condenser). On one hand the vapour pressure loss through the feed through should be as low as possible (a value between 50 and 120 Pa is expected depending on the pressure level inside of the reaction zone) and on the other hand the feed through should avoid the transfer of liquid splashes from one container to the other. Additionally, the vapour feed through should only act as mass transfer unit and therefore form a thermal infra-red barrier. A nickel plated and bent metal sheet is implemented for this task and will predominantly form a radiation shield (radiative disconnection due to the high reflectivity of nickel in the infrared).

The manifolds placed at the top of the tube bundle should ensure a homogeneous fluid distribution above the tubes, taking advantage of the experimental results obtained with a preliminary test rig. Particularly tricky was the manufacture of the nozzles in DIN 1.4404 stainless steel alloy. In preference to several other possible designs, a version with nozzles directly machined in a stainless steel nozzles plate was retained. With this version a high flexibility of the nozzle geometry is reached, enabling a good liquid distribution. A drawback of the chosen design is its high price.

Special attention was paid to the fluid distribution on the absorber/desorber tube bundle unit as this heat and mass exchanger is used without fluid recirculation. In the preliminary experimentation test rig, the caustic soda mixture enters the

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**Table 1. Modelling of the desorber/absorber unit under the worst working conditions: principle quantities.**

<table>
<thead>
<tr>
<th></th>
<th>Desorber</th>
<th>Absorber</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m_i) (\text{[kg/s]})</td>
<td>0.300</td>
<td>0.100</td>
</tr>
<tr>
<td>(T(1)) (\text{[°C]})</td>
<td>95</td>
<td>14</td>
</tr>
<tr>
<td>(T(N+1)) (\text{[°C]})</td>
<td>80.5</td>
<td>33</td>
</tr>
<tr>
<td>(h_i) (\text{[W/(m}^2\text{*K}]})</td>
<td>7932</td>
<td>2733</td>
</tr>
<tr>
<td>(P_e) (\text{[Pa]})</td>
<td>7050</td>
<td>590</td>
</tr>
<tr>
<td>(m_i(N+1)) (\text{[kg/s]})</td>
<td>0.0094</td>
<td>0.0048</td>
</tr>
<tr>
<td>(m_i(1)) (\text{[kg/s]})</td>
<td>0.0056</td>
<td>0.0080</td>
</tr>
<tr>
<td>(T_e(N+1)) (\text{[°C]})</td>
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<td>18.0</td>
</tr>
<tr>
<td>(T_e(1)) (\text{[°C]})</td>
<td>79.3</td>
<td>43.0</td>
</tr>
<tr>
<td>(h_e) (\text{[W/(m}^2\text{*K}]})</td>
<td>984</td>
<td>514</td>
</tr>
<tr>
<td>(Q) (\text{[kW]})</td>
<td>12.21</td>
<td>7.95</td>
</tr>
</tbody>
</table>

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**Fig. 3. CAD drawing of the reaction zone with both A/D (left) and E/C unit (right).**
top of the manifold from both sides of a perforated feed tube. The expected pressure losses through the perforation holes are 3 to 5 times higher than those due to the fluid flow along inside the tube, ensuring an equalised fluid distribution between both ends of the manifold. Furthermore, a fluid film formation is aimed on the bottom plate of the manifold (the plate with the nozzles) ensuring a homogeneous fluid distribution on the manifold nozzles plate on each side of the feed tube. Fig. 4 (left) shows the proper working of the manifold with water as working fluid: the droplets are correctly falling under the nozzles and hit the uppermost tubes of the tube bundle on their total length. An optical method developed to quantify the wetting of the heat and mass exchanger tube arrangement (see Fig. 4, right) also enabled us to validate that the influence of the temperature sensors mounted outside of the tubes (film temperature measurement $T_e$) on the fluid flow is small.

4. Measurements

4.1 Absorption Process

The first non-isothermal experiment campaign shows that the exchanged power during the discharging process (absorption) is quite a lot lower than expected; only a small concentration decrease of the initial 50wt% sodium hydroxide solution is reached at the outlet of the absorber unit. Therefore, instead of emulating annual operation of a building, it was decided to run measurements in steady state conditions in order to characterize the heat and mass exchangers and to compare the experimental results with those obtained from the numerical modeling. The aim is to find out the weak points of the heat and mass exchangers to further increase the exchanged power value for the absorption process. The measurement points presented in Fig. 5 are averaged values obtained during 30 minutes steady state experiments.

An optical inspection shows that during the discharging process only a fraction (about 50–60%) of the absorber tube bundle surface is wetted. Besides the dependence of the exchanger power on the temperature difference between the evaporator and the absorber (Fig. 5, left), it was also noticed that this power depends on the so-

![Fig. 4. Side view picture of the falling film on the A/D tube bundle heat and mass exchanger (left) and of the A/D heat and mass heat exchanger during the fluid distribution tests (right).](image)

![Fig. 5. Development of the power ($\Phi$) in function of the temperature difference ($\Delta T$) between both absorber and evaporator chamber during discharging process (left) and of the absorption power in function of the linear mass flux ($\Gamma$) arriving on the absorber (right).](image)

![Fig. 6. Development of the power ($\Phi$) in function of the temperature difference ($\Delta T$) between both desorber and condenser chamber during charging process (right).](image)
Dihydrogen oxide mass flux flowing over the absorber (Fig. 5, right). An increase of the sodium lye mass flux leads to a better tube wetting, showing that this parameter is a limiting factor for the exchanged power on the absorber side.

4.2 Desorption Process

During the charging process (sorbent desorption with an initial sodium hydroxide concentration of 30wt%), it seems that the exchanged power only depends on the temperature difference between the desorber and the condenser (Fig. 6), a higher temperature difference leads to a higher pressure difference between both units and therefore an increased vapour transfer rate.

The wetting of both tube bundle surfaces as well as the exchanged power on both desorber and condenser are appropriate. For a temperature difference of 60 K (similar to the boundary conditions taken for the modeling), a power of 9.5 kW (about 25% less than predicted) can be reached.

5. Conclusion

According to this first comparison between the experimental and the simulation results, it looks like that under low sorbent flow rates the modelling accuracy is limited, especially for the absorption process. As the discrepancy between the real extracted power and the expected value is much higher for the absorption process than for the desorption process, the combination of the absorber and desorber unit can be questioned. Nevertheless, the evaporator/condenser unit works well, probably due to the fluid recirculation and in desorption modus, the A/D tube bundle under-performs the simulation by only 25%.

In the near future, more extensive comparisons between the modelling and experiments will be carried out. In parallel, for the absorber heat and mass exchanger, the wetting should be optimised and/or a new concept should be found. One step towards this target is performing measurements on a down-scaled experimental set-up.

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Challenges towards Economic Fuel Generation from Renewable Fuel: The Need for Efficient Electro-Catalysis

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Abstract: Utilizing renewable sources of energy is very attractive to provide the growing population on earth in the future but demands the development of efficient storage to mitigate their intermittent nature. Chemical storage, with energy stored in the bonds of chemical compounds such as hydrogen or carbon-containing molecules, is promising as these energy vectors can be reserved and transported easily. In this review, we aim to present the advantages and drawbacks of the main water electrolysis technologies available today: alkaline and PEM electrolysis. The choice of electrode materials for utilization in very basic and very acid conditions is discussed, with specific focus on anodes for the oxygen evolution reaction, considered as the most demanding and energy consuming reaction in an electrolyzer. State-of-the-art performance of materials academically developed for two alternative technologies: electrolysis in neutral or seawater, and the direct electrochemical conversion from solar to hydrogen are also introduced.

Keywords: Electrochemical water splitting · Energy storage · Hydrogen · Oxygen evolution reaction

1. Introduction

The current global energy supply system, mainly based on fossil fuels and nuclear power, will change dramatically in the next decades. The accelerated depletion of non-renewable energy resources and ecological consequences associated with their use are a major concern for both policy makers and the general population. In a recent review of different possible scenarios for the Swiss electricity system until the year 2050, renewable sources of energy are forecasted to be deployed on a large scale after a transition period based on natural gas-powered generation.[1] In addition to reducing the climate impact from fossil fuels, enhanced utilization of renewable energy is expected to help bring electricity to the 1.6 billion people in the world currently without access to energy, meeting the energy demand of a growing population and ensuring stable and secure energy access for all nations.[2]

Globally, renewable energy can be extracted from a few key available resources: hydroelectric (0.5 terawatts (TW), available at maximum), from all tides & ocean currents (2 TW), geothermal integrated over all of the land area (12 TW), globally extractable wind power (2–4 TW), and solar energy illuminating the earth (120,000 TW).[3] In total, the maximum energy that can be converted from these sustainable sources substantially exceeds the energy consumed by humans on earth today, (ca. 600 EJ per annum corresponding to an average consumption rate of 17 TW), and also the predicted usage rate for 2050 and 2100 (40.3 and 48.8 TW respectively).[4] Additionally, it is also striking that the conversion of only 0.05% of the solar energy (or 0.5% considering solar cells with 10% conversion efficiency) would be sufficient to secure the energy demand for the next century.

However, the major limitations towards expanded use of renewable energy sources in the global energy portfolio are currently their availability and intermittency.[5,6] These drawbacks can be overcome through the conversion and storage of renewable energy into a stable but accessible form allowing energy use when needed.[6] Energy storage is especially needed to accommodate the disaccord between the times of energy peak production and of peak consumption as well as transporting energy from where it is harvested to where it is used.[11] Additionally, Fig. 1 shows an example of the discrepancy between the load on the electric network and the energy generated from renewable sources (wind, solar and wave) in the Pacific Northwest of the U.S.[7] All data, originating from both real and simulated sources, show the daily average for each category through the year 2008 (pu: penetration units defined as the ratio of the peak load to the peak generation within the year). The load, solar, and wave data sets exhibit both diurnal and seasonal variability, while the wind generation appears to be less seasonally correlated.

Wind and wave data also show a large disparity in power generated each day, in contrast to the load. Notably the largest load values are in the end and beginning of the year (the winter months), which is the same time when solar output is negligible. This set of data demonstrates the necessity of storing the energy from renewable sources on a short timescale (i.e. daily to accommodate wind / wave variability and night / day divergence in generation and usage) and on a longer period—on the time scale of a year for solar or wave energy, for example.

Chemical storage, i.e. storing energy in the bonds of molecules such as hydrogen or simple carbon-based compounds (e.g. methane, methanol or formic acid), is particularly attractive as this method does not exhibit limitation to the storage time. Indeed there are potentially very few losses during the storing period (depending on the stability of the compounds) compared to electrochemical energy storage (e.g. in Li-ion batteries). Moreover, H₂ or carbon-based fuels could be integrated to existing distribution systems for fossil gas or oil.[8]

One potential way to form these chemical energy storage vectors from electricity...
is to use an electrochemical cell, where a difference in electric potential (voltage) drives a non-spontaneous reaction. In an electrochemical cell the overall reaction is ically reduced at the cathode to make $H_2$ at distinct sites in the cell: the oxidation reaction at the anode and the reduction reaction at the cathode. In order to produce $H_2$ via electrolysis is 5–10 times greater than hydrogen produced by society as, in part, the price of the hydrogen splitting is an attractive route for storing renewable energy, a hydrogen-based energy system has comparable efficiencies and operate at similar temperature (50–100 °C) and pressure (<30 bars).[9,10] Alkaline water electrolysis is widely recognized as the most mature and the most widespread technology. It offers the possibility to use large area electrodes but its large-scale deployment is restricted by the maximum current density and the purity of the hydrogen generated (99.5–99.9%).[11,12] PEM electrolyzers have a slight advantage in terms of gas purity (>99.99%), efficiency and produced-hydrogen cost but suffer from poor stability.[9] The operating principles of an alkaline electrolyzer and a PEM electrolyzer are illustrated in Fig. 2a and 2b respectively.

The main differences between the two types of electrolyzer are the electrolyte and the membrane separating the two electrodes. While in an alkaline electrolysis cell, the two electrodes are separated by a gas-tight diaphragm submerged in a liquid electrolyte, a solid proton-conducting membrane is used to isolate the oppositely charged electrodes in a PEM cell (typically Nafion™). The higher permeability to gas of the diaphragm as compared to a PEM reduces the efficiency of the alkaline system due to oxygen diffusion on the cathodic side.[12]

The electrolyte used for a alkaline electrolyzer is highly basic, usually a 20–40 wt% aqueous solution of potassium hydroxide (KOH), which is preferred over sodium hydroxide (NaOH) due to its higher ionic conductivity. In contrast, in a PEM electrolyzer, high purity water (<1 μS cm⁻¹) is required for the cell to operate at high efficiency, increasing the cost of this technology.[11] The difference in the employed pH results in different chemical processes occurring on the electrodes.

In the alkaline system, water is reduced at the cathode according to Eqn. (1), evolving hydrogen and generating hydroxyl anions. These hydroxyl groups migrate through the ion-permeable diaphragm to reach the anode side, where they are oxidized (Eqn. (2)) to generate oxygen and extract the four electrons required for the reduction.

$$\text{Alkaline / Cathode: } 4\text{H}_2\text{O} + 4e^- \rightarrow 2\text{H}_2 + 4\text{OH}^- \quad (1)$$

$$\text{Alkaline / Anode: } 4\text{OH}^- \rightarrow O_{2p} + 2\text{H}_2\text{O} + 4e^- \quad (2)$$

In the PEM system, water is oxidized at the anode, generating four protons and transferring four electrons to the external electric circuit. Protons are transferred to the cathodic side through the proton exchange membrane and react with the four...
electrons from the electric circuit, resulting in the formation of hydrogen gas. These reactions are summarized in Eqn. (3) and Eqn. (4):

\[
\text{PEM / Cathode: } 4H^+ + 4e^- \rightarrow 2H_2(g) \\
\text{PEM / Anode: } 2H_2O \rightarrow O_2(g) + 4H^+ + 4e^- 
\]

The same overall reaction occurs in both systems, which corresponds to the water dissociation reaction:

\[
2H_2O \rightarrow O_2 + 2H_2(g) 
\]

Typical electrochemical characterization (shown in Fig. 2c) of water splitting anodes (red) and cathodes (blue) is usually performed in a three-electrode (potentiostatic) setup, to probe specifically one of the electrodes for research development. The potential of the working electrode (the electrode under test) is varied against a reference electrode, whose potential is fixed in the electrolyte. This current generated by the reaction occurring on the working electrode is transferred to a third electrode (the counter electrode) which adapts its potential according to the current and the resistivity of the electrolyte. This method enables isolating the process at the working electrode and disregards the losses related to the reaction occurring on the counter electrode.

When the applied potential reaches a certain potential below the reduction potential of water, i.e., 0 V vs. the reversible hydrogen reference electrode (RHE), water molecules or protons can start to react on the cathode, resulting in a negative measured current (i.e., electrons moving from the electrode into the electrolyte). This current increases in magnitude when shifting the potential cathodically as the driving force for reduction is enhanced. We define here the overpotential for reduction, \( \eta_{\text{red}} \), as the difference of potential between that which is applied and the thermodynamic reduction potential of water to reach a certain current density (e.g., \(-10 \text{ mA cm}^{-2}\)) in our example in Fig. 2c). Analogously, when probing the anode as the working electrode, a positive current can onset once the potential exceeds the thermodynamic potential of water oxidation (1.229 V vs RHE), when water molecules or hydroxyl anions are converted to \( O_2 \) on the anode material. The overpotential for water oxidation, \( \eta_{\text{ox}} \), is therefore defined as the difference of between the potential applied and the potential of water oxidation, to reach a certain current density (+10 mA cm\(^{-2}\)) in our example).

The overall voltage required, shown in Fig. 2c, corresponds to the voltage needed to operate an electrolyzer with a certain current density (e.g., \( 10 \text{ mA cm}^{-2}\)) ignoring the ohmic losses in the electrolyte or membrane. It equals the sum of the reversible potential for water reduction and oxidation (1.229 V) and the overpotentials for the reduction and oxidation reactions. This overall voltage must be minimized in order to increase the energy conversion efficiency, consequently decreasing the price of the storage. While additional overpotential can arise from ohmic losses due to the electrolyzer geometry, bubble formation, or ion conduction in the membrane and in the electrolyte, these can be reduced through cell engineering. Indeed the most significant losses come from the overpotentials required to kinetically activate the electrochemical reactions. The charge transfers between the chemical species and the electrodes requires overcoming an energy barrier that depends strongly on the catalytic properties of the electrode materials. Usually, the anodic half-reaction requires a much higher activation overpotential than the cathodic half-reaction due to the complex multi-electron transfer route required to form molecular \( O_2 \).[11,14] The next sections will thus accordingly focus on the catalytic properties of materials developed as water splitting electrodes, with particular emphasis on those used for the most energy demanding reaction, water oxidation.

3. Electrode Materials for Alkaline Electrolysis

The requirements to select electrode materials for alkaline water electrolysis include good corrosion resistance, high electronic conductivity and high catalytic activity with regard to the two reactions of interest (the hydrogen evolution reaction, HER; at the cathode and the oxygen evolution reaction, OER, at the anode). As mentioned before, the overall water splitting reaction is mainly limited by the slow kinetics of the OER at the anode.[11,14] Therefore tremendous research efforts have been dedicated to the search of a low-cost and efficient electrocatalyst for oxygen evolution.

Stainless steel and lead oxide were first identified as inexpensive electrode materials, with relatively low overpotential for the OER, but their chemical stability at sufficiently high voltage in highly concentrated alkaline solutions limit their applicability. Nowadays, \( \text{IrO}_2 \) and \( \text{RuO}_2 \) are considered the benchmark materials for OER in alkaline conditions, presenting overpotentials of 0.32 and 0.29 V respectively for a current density of 10 mA cm\(^{-2}\).[15,16] The activity of iridium-based electrodes towards
Limited stability in alkaline solutions, these precious metals do not show unlimited stability in alkaline solutions,19–21 are costly, and their supply is not sustainable. Therefore, they are not suitable for large-scale TW applications. In order to find a low-cost OER electrocatalyst, researchers are now concentrating their efforts on first-row transition metals and their composites, for instance cobalt phosphate composites, nickel borate, cobalt oxide nanoparticles and manganese oxide thin films.19–22 All these materials offer satisfying OER activity, with overpotentials lower than 0.4 V for a current density of 10 mA cm\(^{-2}\), and significantly lower fabrication costs when compared to ruthenium- or iridium-based materials.

Recently, Jaramillo and coworkers tested a large range of first row transition metals for the OER in both alkaline and acidic conditions.15,16 All electrode materials were electrodeposited on glassy carbon (GC) substrates using a similar protocol for each of them, in order to benchmark the assessment and the performance of anode materials for water oxidation. Due to the highly oxidizing conditions experienced during OER, the electrocatalysts are likely converted to oxides or oxyhydroxides but they are named according to their metal composition for simplicity. Comparison of the electrode activities in 1 M NaOH is shown on Fig. 3. The magnitude of the overpotential required to achieve a current density of 10 mA cm\(^{-2}\) after 2 hours of operation is shown on the y-axis while the same overpotential recorded immediately after immersion in the electrode is shown on x-axis. This type of plot gives valuable information on both electrode performance and short-term stability, i.e. if there is no change in activity, the material is represented on the black dotted 45° line. Except for ruthenium, most catalysts tested in this study can achieve the chosen current density at an overpotential between 0.35 and 0.5 V, which is slightly higher than the target overpotential selected in this study (0.35 V, represented by the dashed blue lines in Fig. 3). However, one can notice the good performance of NiMoFe, the only non-noble metal catalyst able to function at a potential below the target, during initial test and after two hours of operation. This result is even more encouraging taking in account that the active area (real area x roughness factor) was smaller than the one measured for the ruthenium reference electrode, which means that the specific catalytic activity (activity normalized to the active area) was actually higher. Other promising materials that demonstrated overpotentials lower than 0.4 V include Co-P, CoFe, NiCo, NiFe and NiFeCo. It is worth noting that all the aforementioned materials succeed in showing good stability in performance over long term measurements (24 h), except for NiCo and NiFeCo.

From this report, nickel-, iron- and cobalt-based electrodes, especially the ones containing two or three different metals, seem to have the best catalytic properties towards OER in alkaline solution. This was corroborated by recent studies of iron-nickel alloys that showed considerable catalytic performance. Maximum performance was obtained for films or particles containing between 30 and 40% Fe, achieving 10 mA cm\(^{-2}\) at overpotentials below 300 mV.[23,24] The iron incorporation inside the nickel oxide/hydroxide layer has been evidenced to modify the environment of the Ni–O bond, reducing the electrochemical oxidation of Ni(OH)\(_2\) to NiOOH,[24] and activating Ni catalytic centers (probably Ni\(^{2+}\)) throughout the catalytic film.[25] These results are also consistent with the better performance of Ni films after aging, which indicates that previous reports of highly active Ni(OH)\(_2\)–based OER catalysts include Fe impurities.[24,25] Using this material, Lu et al. have recently obtained the highest catalytic activity for non-noble metal electrodes, when electrodeposited NiFe onto a nickel foam mesostructure, with a record current density of 500 mA cm\(^{-2}\) at an overpotential of only 240 mV in 10 M KOH.[26]

Another study of nickel-iron electrodes for oxygen evolution evidenced an additional feature of highly active materials for this application using SQUID magnetometer measurements.[27] This technique allows the detection of extremely subtle magnetic susceptibility inside the material induced by an external magnetizing field (H). Fig. 4 shows the magnetic response of three NiFe electrodes, electrodeposited at a constant current density of either 25 mA cm\(^{-2}\) or 250 mA cm\(^{-2}\) in presence of ammonium sulfate (sample A and C respectively), as well as a reference sample deposited at 105 mA cm\(^{-2}\) without (NH\(_4\))\(_2\)SO\(_4\). The good performance of the electrodeposited samples with the ammonium salt have been correlated to the ferro/ferrimagnetism exhibited by sample A and C at 300 K. In contrast, sample B shows paramagnetic behavior, reflecting the chemical and physical complexity of the catalyst and the slight changes in crystal organization depending on the deposition parameters.

Theoretical modeling and experiments have also evidenced a transition through high spin states in the CaMnO\(_4\) catalytic cluster of Photosystem II during water oxidation.[28,29] Oxygen-activating enzymes have also been characterized with a high-spin heme iron, non-heme iron and copper catalytic sites.[30,31] Therefore, the correlation between the ferromagnetic character and suitable catalytic properties in NiFe electrodes suggest strongly that the high spin states in the catalyst facilitate the electron spin inversion required for oxygen evolution. Further investigations are nevertheless necessary to characterize the desired properties for the catalyst and to fully understand the O\(_2\) formation mechanism. The considerable catalytic performance of nickel iron alloys for the OER reaction renewed the interest in inexpensive and large-scale produced materials.
such as nickel containing stainless steel: AISI 304 (8% Ni, 18–20% Cr), AISI 316 (10% Ni, 18% Cr) and AISI 316L (same as 316, low in carbon). Two recent studies[32,33] show that steel samples require a pretreatment to form an oxide layer at the surface, which acts as the catalyst. Electrooxidation of an AISI 304 metal alloy under particularly harsh conditions (at a current density of 1.8 A cm$^{-2}$ in 7.2 M NaOH for 300 min), results in the formation of an ultrathin film, depleted of Cr on the surface and composed of 67% Ni / 33% Fe. Catalytic performance of such film (named Elox300) is compared to untreated AISI 304 alloy in Fig. 5. The surface-modified metal sample exhibits remarkable current voltage characteristics, achieving 10 mA cm$^{-2}$ at an overpotential of 270 mV in 0.1 M KOH, and 12 mA cm$^{-2}$ at only 212 mV in 1 M KOH.[31] These surface-oxidized steel samples proved to be inert. Moreover, X-ray photoelectron spectroscopy (XPS) performed on this film suggest that γ-NiOOH constitutes the catalytic active species on the surface of the electrode, consistent with the negative current wave observed at potential 1.2–1.42 V vs. RHE (Fig. 5), which is attributed to the Ni(III)/Ni(II) redox couple.

Nickel enrichment of the steel surface was also obtained upon aging a film of AISI 316L in 5 M LiOH electrolyte at 0.8 V vs. Hg/HgO reference electrode (ca. 1.7 V vs. RHE) for 250 h.[30] The metallic surface composition was found to be 83% Ni, 10% Fe and 7% Cr and Ni(OH)$_2$, NiOOH, FeOOH as well as CrO$_2$ were detected in the oxide layer with XPS. Such film shows high electrocatalytic activity towards OER after an induction time of 250 h and stable performances over 3000 h of operation.

The increase in OER activity for the aged and pretreated steel films have been rationalized with the increase in roughness and a synergetic effect (hypo-hyper d-orbital interbonding effect) due to the presence of dispersed Fe and/or Cr in the oxide layer. These recent results, especially those concerning the stability of the samples, hold significant promise for high-performance OER catalyst in the future and should be further studied to uncover the full potential of low cost steel electrodes.

In addition to the development of conventional alkaline electrolysis cells operating at temperatures below 100 °C, researchers are also exploring high-temperature electrolysis (keeping concentrated KOH as the electrolyte). Increasing the operating temperature over 100 °C modifies the thermodynamics of the system (reducing the potential required) and enhances electrode performance by accelerating kinetic processes. Particularly, ionic conductivities of NaOH and KOH solutions are increased significantly when the temperature reaches 200–250 °C.[34] For the electrolyte to remain in the liquid phase, it is necessary to apply high pressure (30–100 bars)[35] or to immobilize the electrolyte in porous material such as strontium titanate (SrTiO$_3$).[36] Moreover, the relative volume of the formed hydrogen or oxygen gas bubbles is also lowered with increasing pressure, which subsequently decreases losses in the catalytic area of the cell (ohmic losses).[37] The effect of temperature has been shown to be more pronounced on the oxygen evolution reaction than the hydrogen evolution reaction: for a current density of 0.25 A cm$^{-2}$ applied on polished Ni electrodes, the anodic overpotential decreases from 0.53 V to less than 0.05 V, whereas the cathodic was reduced from –0.43 to –0.19 V by increasing the temperature from 80 to 264 °C.[38] In terms of cathode materials, nickel alloys (Ni-Ti, Ni-Co and Ni-Mo) have demonstrated slightly better performance than pure nickel at high temperature.[35,39,40] For anodes, spinel and perovskites structured materials, such as Co$_3$O$_4$, NiCo$_2$O$_4$, LaNiO$_3$, and La$_{0.5}$Ni$_{0.5}$CoO$_3$ were shown to provide the lowest overpotential as compared to pure nickel electrodes.[35,41,42] However, the increased thermal degradation at high temperature may be problematic for large-scale application.

4. Electrode Materials for PEM Electrolysis

Historically, alkaline electrolyzers have been the first widely developed devices for water electrolysis and still make up most of the electrolyzers that can be found on the market nowadays. As discussed before, the design of such cells, see Fig. 2, offers several advantages, including an inexpensive microporous ceramic diaphragm and electrodes that can be made of relatively simple and cheap materials such as nickel,
stainless steel or other first row transition metal oxides.\cite{12,43,44,46,47}

However, this technology presents at least three major drawbacks.\cite{12,43,46,47}

1. The output current density is relatively low (typically 0.2–0.4 A cm$^{-2}$). This is mostly due to large ohmic losses across the electrolyte and thick diaphragm (typically between 500 nm and 1 µm to efficiently prevent gas diffusion).

2. It is impossible to operate at high pressure. This prevents the creation of a compact system, and forces the post-compression of hydrogen for storage.

3. It has a very low partial-load range, because under low load (usually <40% of the nominal load), the oxygen production rate is low enough that the small amount of hydrogen diffusing through the diaphragm (independent of the load) can create an explosive mixture (>4% H$_2$ in O$_2$)\cite{12,43,44} in the system. This makes alkaline electrolyzers less suitable for the dynamic requirements of storing the highly variable renewable energy.

To address these issues, a different design has been proposed as a promising alternative: the proton-exchange membrane (PEM) electrolyzer. The configuration of a PEM electrolyzer is depicted in Fig. 2. In this design, water circulates through the anode, while the hydrogen is produced in a dry environment at the cathode. Similarly to the alkaline design, the anode and cathode are coated with electrocatalysts for the OER and HER respectively. Nevertheless, a major difference with alkaline electrolysis lies in the presence of a solid electrolyte: a very thin (20–300 nm) humidified acidic membrane (typically Nafion$^\text{®}$)\cite{46,47} transports protons from the anode to the cathode, where they directly recombine with electrons from the external circuit to yield gaseous hydrogen. This proton-exchange membrane is also responsible for the acidic environment in which the electrodes are required to function. PEM electrolyzers possess several advantages compared to their alkaline counterparts. First, they can operate at much higher current densities (typically higher than 2 A cm$^{-2}$)\cite{48,49} which allows operational cost reduction. This improvement comes from the much lower thickness and much higher conductivity of the PEM compared to the alkaline diaphragm, which in turn reduces ohmic losses between the electrodes. Second, it can operate under much higher pressures (up to 350 bar),$\text{12,43}$ and even under differential pressure, where only the cathode size is pressurized to extract hydrogen without producing dangerous pressurized oxygen on the anode side. Finally, and perhaps most importantly, the PEM has an extremely low permeability to hydrogen.$\text{10,50,51}$ This ensures a very high purity of the output hydrogen stream, while removing the safety issues associated with gas mixing. Moreover, it allows the electrolyzer to function under a wide range of partial load and even potentially under overload. This makes the system very dynamic as it can adapt to large input current variations. On the other hand, PEM electrolyzers still present one big drawback compared to the alkaline alternative: they are much more expensive due to the very acidic operation regime imposed by the membrane. Indeed this prevents the use of most metals – which would quickly corrode during operation, especially under the oxidative conditions at the anode – and forces the use of more expensive materials for the electrodes (typically titanium-based alloys) and the electrocatalysts, as will be developed further in this section.

Despite its higher cost, the PEM electrolyzer design is very attractive when it comes to running the device with a renewable source of electricity. Indeed, the intermittency of wind and, especially, solar energy makes them very hard to use efficiently with an alkaline electrolyzer that has to be shut down under 40% partial load for safety reasons.$\text{12}$ On the other hand, PEM electrolysis can be performed under almost any fraction of the nominal load (although the range does decrease with increasing pressure).$\text{47}$ This ability, coupled with the very quick response of electrochemical reactions and proton transport to changes in current density (contrary to the much more inert ion transport in liquid electrolytes), makes the PEM electrolyzer a very attractive candidate for the renewable production of highly pure and already-compressed hydrogen gas (e.g. in a PV + electrolyzer configuration).

The first report of a PEM electrolyzer goes back to 1973 and already produced much higher current densities than state-of-the-art alkaline electrolyzers (1 A cm$^{-2}$ for an applied voltage of 1.88 V) that were reported to be stable for over 15000 h.$\text{12}$ Unfortunately, due to the previously mentioned tendency of most metals to corrode in acidic conditions, the authors had to use platinum black as the HER catalyst and iridium as the OER catalyst. Since this first report, the very high cost of catalysts based on the platinum group metals (PGM) has remained one of the biggest obstacles to the development of cost-efficient PEM electrolyzers. Indeed, even in more modern commercial electrolyzers, PGM catalysts still represent a significant portion of the overall material cost,$\text{52}$ despite their relatively low loading: ca. 2 mg cm$^{-2}$ for the Pt at the cathode, and ca. 6 mg cm$^{-2}$ of Ir at the anode. Moreover, and perhaps even more importantly, beyond the cost of these PGMs, their scarcity (especially for Ir) completely prevents their use on the global scale associated with a hydrogen-based economy. This is the reason why research laboratories have been and are still looking for alternative catalytic materials able to completely replace the current generation of PGM catalysts. In the next paragraph, we will therefore present the progress made over the last four decades in catalyst optimization for the HER and OER in acidic conditions.

The highly acidic environment created by the membrane is favorable to HER catalysis, since it is typically easier to reduce protons to hydrogen when they are present at high concentration. Platinum is well known for being an extremely efficient catalyst for water reduction, with an overpotential ($\eta_{\text{red}}$) lower than 0.05 V to produce a current density of 10 mA cm$^{-2}$ in 1 M H$_2$SO$_4$. In fact, to date, it is still the best monoatomic catalyst available for HER. As such, it has been traditionally used at the cathode of PEM electrolyzers developed at the laboratory scale, but its scarcity prevents a realistic use on a large scale. Still, its performance is usually used as the benchmark for alternative catalysts that should approach. In addition to its prohibitive cost, platinum suffers from being very easily poisoned by trace amounts of metallic contamination in the feed water. Metallic ions will indeed undergo underpotential deposition (UPD) and completely cover the surface of the platinum, seriously decreasing its catalytic performance. For these reasons, a considerable amount of work has been dedicated to designing and optimizing robust earth-abundant electrocatalysts able to compete with the efficiency of platinum. Typically non-noble metal catalysts are constructed around Fe, Ni, Cu, Co, Mo and W, which are orders of magnitude more abundant than Pt in the Earth’s crust, with Fe and Ni being the most abundant among them. Since none of these elements is a good HER catalyst by itself, it is necessary to combine them with others to produce competitive materials. Recently, molybdenum disulfide (MoS$_2$) has received a lot of attention. For a long time, it was considered to be completely inactive towards the HER. While this is true for bulk crystalline MoS$_2$, it was predicted in 2005$\text{53}$ and shown in 2007$\text{54}$ that MoS$_2$ was actually very active under its nanocrystalline morphology. More specifically, the edge sites of MoS$_2$ nanoflakes have been demonstrated to be responsible to this catalytic behavior. Since then, MoS$_2$ has been extensively studied, and has been reported with very good performances in acidic electrolyte: a current of 10 mA cm$^{-2}$ was obtained for $\eta_{\text{red}} <$ 0.2 V with chemically exfoliated MoS$_2$.\text{55,56} Interestingly, amorphous molybdenum sulfide, MoS$_3$, also produces very good catalytic water reduction, with a reported current of 15 mA cm$^{-2}$ at $\eta_{\text{red}} = 0.2$ V.\text{57} In another work, a nickel-molybdenum nitride cata-
lyst was reported to produce ca. 4.5 mA cm\(^{-2}\) at \(\eta_{\text{red}} = 0.2\) V.\(^{[58]}\) Nickel phosphide (Ni\(_2\)P) and cobalt phosphide (CoP) have also been recently reported with excellent catalytic abilities. Nanostructured Ni\(_2\)P was measured to produce 20 mA cm\(^{-2}\) at \(\eta_{\text{red}} = 0.13\) V.\(^{[59]}\) and was measured, by a different group, to be stable for more than two days.\(^{[60]}\) On the other hand, CoP has been reported to produce 10 mA cm\(^{-2}\) at \(\eta_{\text{red}} = 85\) mV.\(^{[61]}\) Other efficient catalysts reported in the recent literature are listed in a review from 2015 by Zou and Zhang.\(^{[62]}\) A more direct and accurate comparison of the performances of different HER catalysts in acidic conditions has been recently published by Jaramillo and coworkers (Fig. 6).\(^{[63,64]}\) In this study they benchmark the currents produced by several materials under identical conditions. Unsurprisingly, platinum remains the best HER catalyst, but interestingly, several alloys, such as NiMo, CoMo, NiCoMo or NiW come very close in performance, and also display very good stability. Overall, a variety of very good alternative materials have been proposed to replace Pt as HER catalyst in acidic conditions. Moreover, given the scalable deposition of most of these materials, it seems like they could be easily applied on an industrial scale.

Unfortunately, replacing PGM as catalyst for OER is a much tougher challenge. Indeed, as mentioned before, most metals are easily corroded under oxidative conditions in acid. Since the oxidation of the metal is easier than the oxidation of water, the catalyst oxidizes and since most metal cations are soluble in acid the electrode dissolves into the electrolyte. State-of-the-art OER acid catalysis has been achieved with iridium or iridium oxide since the very early work on PEM electrolysis. Despite the large amount of work produced in the field since these first reports, and contrary to the success encountered with earth-abundant HER catalysts, no viable replacement has been found so far. Iridium being the rarest element in the Earth’s crust, replacing it with any other element would already represent progress. Ruthenium has been found to be more active than iridium, but it has also been found to corrode after some time.\(^{[65,66]}\) On the hand, Ir-Ru binary mixtures show very good catalytic properties and stability,\(^{[65,66]}\) for an Ir content as low as 20 mol\%. However, ruthenium is almost as scarce as iridium and does not really represent a viable replacement for large-scale applications. Other works reported that diluting Ir in even more abundant elements, such as Nb,\(^{[67]}\) or Sb\(^{[68]}\) was also a viable approach to reduce Ir content in the catalyst. An interesting study described a mixture of SnO\(_2\), TaO\(_2\), and IrO\(_2\) that performed efficiently even at low Ir content (15\%).\(^{[69]}\) Unfortunately, in the past decades, no alternative metal or metal oxide has been found to come anywhere close to iridium, or ruthenium, in performances, as illustrated in Fig. 6.

Overall, PEM electrolysis seems to be the most promising short term option for the large-scale production of high-purity hydrogen, especially in the context of the development of renewable energy sources. Indeed, the PEM technology is better adapted to deal with the intermittent current typically provided by these sources, as it can very quickly adapt to any change in input current, without creating explosion hazards in the system. However, the material cost of PEM devices remains high, and electrocatalyst coatings—although they represent a tiny fraction in mass—still represent a significant fraction of the overall cost. More precisely, while cheap HER catalysts have been developed in recent years, and seem very likely to be introduced in industrially produced electrolyzers, there is still no viable replacement for iridium-based electrocatalysts at the anode. Finding an earth-abundant OEC (Oxygen Evolution Catalyst) able to operate in acidic conditions would accelerate significantly the development of the water electrolysis technology, and as such, remains a critical field of research.

5. Water Splitting in Other Conditions: Sea Water / Neutral pH

As previously discussed, extreme pH and high purity water systems are efficient for water electrolysis but the cost of such systems with, for example expensive ion-selective membranes or catalysts may be limiting large-scale application. Moreover, impurities in the water feedstock can dramatically decrease the lifetime of electrochemical cells. As such, water splitting electrocatalysts have been studied in neutral pH conditions. Neutral pH media are promising systems since they are less corrosive toward active materials (for example catalysts) and other system components (for example: piping).\(^{[70]}\) However, no efficient and safe electrolysis in a sustained pH-neutral environment has yet been developed. Therefore, taking advantage of the large amount of water on earth, it is crucial to study systems that are sustainable and do not require expensive equipment for water electrolysis. Most of the time, depending on the source, seawater contains many species such as Na\(^+\), Cl\(^-\), Mg\(^{2+}\), Ca\(^{2+}\), K\(^+\), SO\(_4^{2-}\), Br\(^-\), CO\(_3^{2-}\). The latter chemicals might interfere with the water reduction (hydrogen evolution) and/or water oxidation (oxygen evolution).

In seawater, the large numbers of chlorine ions can be preferably oxidized (instead of H\(_2\)O oxidation) because of the lower overpotential for chlorine evolution. Two main reactions can occur: chlorine evolution reaction (Eqn. (6)) and water oxidation reaction (Eqn. (7)):

\[
2\text{Cl}^- \rightarrow \text{Cl}_2(g) + 2e^- \tag{6}
\]

\[
2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2(g) + 4e^- \tag{7}
\]
One approach to overcome the chlorine evolution is to insert a selective ion membrane in the electrochemical cell. The use of a cation-selective membrane was shown to be very beneficial in enhancing the oxygen evolution at the TiO$_2$/Ti electrode as an anode.[7] The surface of the latter electrode was modified by a perm-selective polymer (Nafion), which hinders chloride ion transport to the electrode surface and, as a result, suppresses chlorine evolution and increases oxygen evolution reaction by a factor of 2. Another study on the effect of ions contained in seawater was reported recently.[2] The hydrogen evolution rate was observed to vary depending on the nature of ionic species. Especially in the presence of MgCl$_2$ species, the hydrogen evolution rate was drastically lowered. For example, to overcome the problem, magnesium ion can be suppressed from seawater by polyelectrolyte multilayer membrane so that hydrogen evolution rate could be expected to increase.[3] But the use of such additional membrane may increase the overall cost of production of water splitting. Another study focused on manganese-tungsten oxide for iridium oxide electrodes in a 0.5 M NaCl at pH 8.0.[4]

Studies of oxygen-evolving catalysts in neutral and natural waters are important to lower the cost of hydrogen-based energy storage.[5] Research of oxygen-evolving catalysts has been recently focused on active catalysts under neutral conditions. A facile method for deposition of a cobalt oxygen-evolving catalyst (Co-OEC) has been studied under pH 7. The Co-OEC has shown high current density (100 mA cm$^{-2}$) at an overpotential of 442 mV in near neutral conditions (pH 9.2)[6] and in natural waters and seawater.[7] Modest overpotentials at 1 mA cm$^{-2}$ were observed with the Co-OEC compared to a standard Ni electrode in natural water and seawater. Nocera and co-workers also investigated an alternative to the Co-OEC by developing a nickel-borate oxygen-evolving catalyst that is stable under near neutral conditions (pH 9.2). Ni-based oxide films evolves oxygen with a current density of 1 mA cm$^{-2}$ at an overpotential of 425 mV.[8] Another study showed an alternative with a silver oxygen-evolution catalyst (Ag-OEC) reaching an overpotential of 318 mV at 1 mA cm$^{-2}$.[9] More recently, a Janus cobalt-based catalyst was developed for water splitting in neutral conditions. It is the first time non-noble metal catalysts have been developed for both reduction and oxidation of water. The modest overpotentials achieved for both oxygen and hydrogen evolution are promising for photocatalysis systems and for lowering the cost of electrochemical systems.[10]

6. Photoelectrochemical Water Splitting

A simpler approach to convert renewable energy into a transportable fuel is to directly interface a semiconductor able to absorb light with an electrolyte to perform the water photolysis. This route could potentially reduce costs of building two separate devices and eliminate the losses related to the electricity transport between where the renewable energy is harvested and the electrolyzer, where it is converted into a fuel.[7]

Absorption of a photon in a semiconductor will promote an electron from the valence band to the conduction band, generating subsequently an electron-hole (or hole) in the valence band. These charge carriers can be separated spatially by the space charge field (an electric field produced by the equilibration of the semiconductor Fermi level and the electrolyte upon contact). With appropriate semiconductor band-edge positions (i.e., with a valence band lower in energy than the water oxidation potential and a conduction higher than the water reduction potential), the free photogenerated hole is then able to oxidize water while the electron can reduce water on the other side. This has been first demonstrated by Fujishima and Honda in 1972 using TiO$_2$ in an aqueous electrolyte at pH 4.7,[8] TiO$_2$ offers excellent stability under the harsh conditions of water splitting but suffers from its semiconductor band gap energy (3.2 eV) that limits the maximum solar-to-hydrogen (STH) conversion efficiency to less than 2%. Tremendous efforts have been deployed to find a material with high light absorption (low band gap), and electronic bands that straddle the water redox couples (band gap should be about 1.7–1.8 eV to account for overpotentials). Unfortunately, this ideal material has not been developed yet.

This drawback can be addressed using two semiconductors in tandem to generate sufficient energy and also optimize the fraction of solar energy collected. A scheme representing the operational principle of a tandem cell using a n-type semiconductor as a photoanode and a p-type semiconductor as a photocathode is shown in Fig. 7a. The shorter wavelengths photons are absorbed in the first material (photoanode in our example), generating a hole that can oxidize water. Longer wavelengths, which have not been absorbed, are transmitted to the second electrode (photocathode), where the photogenerated electrons can reduce water. Both majority carriers (elec...
tron in a n-type photoanode and holes in a p-type photocathode) drift into the bulk of the semiconductor and recombine in order to close the electric circuit.

Specific performance of a typical photoanode and photocathode are shown in Fig. 7b, in red and blue respectively. The onset of the photocurrent appears below the energy of the respective redox couple (at potentials cathodic to +1.229 V vs. RHE for the photoanode and anodic to 0 V vs. RHE for the photocathode), as the reaction is performed by the minority charge carriers (holes in the photoanode and electrons in the photocathode). The potential of an electrode being defined by the bulk Fermi level, that corresponds to majority carriers. In both cases, the photocurrent plateaus, depending on the conversion efficiencies and the light absorption of each material, before the onset potential of the dark current (sharp rise in current due to reaction with majority carriers).

Unlike the case for (dark) electrolysis electrode and photocathode is defined for a photoelectrode as the difference between the quasi Fermi level of the minority carriers and the redox energy level (see Fig. 7a). The operating potential and operating current of the cell is defined by the intercept of the photoanode current–voltage characterization with the inverse of the photocathode one (see Fig. 7b). The inverse of the cathodic current is used as the cathodic current is generally considered negative (electrons entering the electrode) whereas the anodic current is positive (electrons are extracted from the anode. This current will correspond to the amount of gas produced according to Eqs (1) and (2) in case of alkaline electrolyte (Eqs (3) and (4) in acidic conditions) and described in section 2.

For a tandem cell, as depicted in Fig. 7, calculations have predicted a maximum 7th conversion efficiency of 21.6% assuming 1.0 eV losses per photons (charge thermalization) using optimum band gap values of 1.89 and 1.34 eV for the first and second separator respectively.[79] This corresponds to a certain improvement as compared to the 12.7% resulting from calculations performed for a single semiconductor assuming similar losses.

There is a large number of literature reviews concerning the development advances of materials that can be used in photoelectrochemical tandem cells.[81-84] Amongst the most promising photoanode materials, one can cite the long-studied FeO₂ (stable in a long range of pH 4–14),[85] WO₃ that operates in acidic conditions,[86] and BiVO₄ that can be used around neutral pH.[87] Hematite and tungsten trioxide have been tested in a tandem cell configuration, using a dye-sensitized solar cell instead of a photocathode to promote electrons at an energy sufficient to reduce water on a platinum counter electrode but performances were limited by the late photocurrent onset of the photoanode.[88] BiVO₄ has also been used in a tandem cell, in combination with a Cu₂O photocathode[89] or with a Si solar cell.[90] However, these studies evidenced routes for improvement as they showed instability due to detachment of the CoPi catalyst and restricted current originated from bismuth vanadate limited absorption of the solar spectrum.

In terms of photocathode materials, recent studies demonstrated the potential of using CuO, which showed relative stability and current densities of up to ~7.6 mA cm⁻² at 0 V vs. RHE.[91] Si, GaP or GaAs are other materials vigorously developed in the field but suffer from poor stability in water and require careful protection with overlayers.[92] p-type GaInP has also been investigated for water photoreduction and reached a record STH efficiency of 12.4% in a stand-alone monolithic device, exhibiting however rapid degradation.[93]

Overall while the development of an integrated PEC water splitting device offers a simple way to directly convert our most abundant renewable energy source directly to a chemical storage vector, or solar fuel, considerable efforts are needed to increase the device stability and decrease the cost in order to be economically competitive with traditional solar-to-hydrogen conversion methods (i.e. PV + electrolysis).

7. Conclusion and Outlook

Efficient energy storage is required to enable a global energy economy based on renewable energies. For this purpose, chemical storage offers attractive possibilities as it can store the electricity produced from any kind of renewable energy into the bonds of chemical compounds, which themselves can be stored indefinitely and/or transported. Hydrogen and simple carbon-containing compounds (e.g. formic acid, methane, and methanol) are examples of promising energy carriers that can be formed from electricity through electrolysis.

Today, two major technologies lead the market of electrolyzers: the Alkaline and Proton Exchange Membrane types. Alkaline electrolyzers operate in very basic conditions, which offer several advantages, including an inexpensive microporous carbon-containing membranes that can be made of relatively simple and cheap materials. Its main drawbacks are the low current density achievable, mostly due to the oxygen diffusion from the anode to the cathode, and significant voltage losses originated from poor oxygen evolution catalysis on the anode. Recent progress however showed that reasonable current can now be achieved at less than 300 mV overpotential using inexpensive materials like steel or NiFe. Unfortunately alkaline electrolyzers are poorly suitable for the dynamic requirements of storing the highly variable renewable energy due to the low partial-load range. In contrast, PEM electrolyzer do not suffer from dynamic load limitations or limited maximum current densities as the proton exchange membrane is a better gas diffusion blocker. The highly acidic environment engendered by the membrane helps the facile catalysis of HER but limits the choice of material for the OER catalysis to expensive and rare metals such as Ir or Ru. This is the main disadvantage for this technology and hindered its expansion on the market. The identification of an inexpensive and stable water oxidation catalyst for use in PEM electrolyzers would be a major breakthrough for these devices.

As an alternative to conventional electrolyzers, research is also focusing on developing systems able to function in natural water – mostly at neutral pH – and seawater, but demonstrated performances remain quite low in this area. Another direction explored by researchers is the direct conversion of solar energy into a transportable fuel, through photoelectrochemical water splitting. Despite recent progress in the domain, these systems still suffer from poor efficiency and/or poor stability that hinders a large scale application. Further efforts are still needed in order for semiconductor-based devices to compete with already commercialized technologies.

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Experimental and Numerical Investigation of Combined Sensible/Latent Thermal Energy Storage for High-Temperature Applications

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1. Introduction

The fluctuating nature of intermittent renewable energy sources such as wind and solar requires short- and long-term energy storage to guarantee the power supply. At present, pumped hydro storage (PHS) is the main option for short-term large-scale storage. Market conditions threaten the economic viability of PHS, however. Compressed air energy storage (CAES) is an alternative technology that has been proven at industrial scale.[1] Because CAES plants waste the heat generated during compression, it must be resupplied prior to expansion, leading to cycle efficiencies of about 40–55%. In advanced adiabatic compressed air energy storage (AA-CAES), the heat produced during compression is stored in a thermal energy storage (TES), resulting in projected cycle efficiencies of 70–75%, which are comparable to PHS’s cycle efficiencies.[2] Advantages of AA-CAES compared to PHS are lower estimated capital costs[3] and smaller land requirements. For these reasons, AA-CAES is potentially an attractive alternative to PHS for Switzerland. Because the high efficiencies of AA-CAES plants are due to the integration of a TES for temperatures of up to 650 °C, this study is focused on the experimental and numerical investigation of TES for high-temperature applications. The results presented are relevant as well to waste heat recovery in industrial processes and concentrated solar power plants.

Thermocline TES represents an efficient and cost-effective way of storing thermal energy.[4] In prior work, a packed bed of rocks as sensible heat storage material and air as heat transfer fluid (HTF) was experimentally shown to yield 95% overall (charging-discharging) efficiency.[5–7] A drawback of thermocline TES is the decreasing HTF outflow temperature during discharging, which can reduce the cycle efficiency of AA-CAES. This drop can be reduced by oversizing the storage or increasing its height-to-diameter ratio at the expense of higher pressure drops[8] and/or increasing material costs. Another way of avoiding the temperature drop is through latent TES based on phase-change materials (PCM). Because the phase change occurs at constant temperature, latent TES can, in principle, stabilize the HTF outflow temperature during discharging. Among a large number of potential PCMs, metals are attractive because they offer high heats of fusion and high thermal conductivities.[8] However, intermetallic layers can form between the encapsulation and the PCM, impacting their performance.[9] Another drawback of PCMs is that they are expensive compared to sensible heat storage materials. For these reasons, our interest has centered on combined sensible/latent TES with the twofold aim of stabilizing the HTF outflow temperature during discharging compared to sensible-only TES and reducing costs compared to latent-only TES. The combined storage concept was investigated experimentally and numerically at the laboratory scale in previous work.[10–14]

For the numerical analysis of TES, 1D models are often used, especially for parametric studies, because the computational cost is much lower than for 2D or 3D models. The simplification to 1D can be justified if the tank-to-particle-diameter ratio is large, which means that radial gradients are small over the entire cross section except near a small annular region close to the storage walls. In that region, where the length scales of the flow and heat transfer are comparable to the particle diameter, 1D models are not valid. This means that 1D models are more accurate for large-scale than laboratory-scale TES. Therefore, the objectives of this article are: (i) to validate a 1D model of a lab-scale combined sensible/latent heat storage and (ii) to compare 1D and 2D simulations of that storage.

Abstract: Combined sensible/latent heat storage allows the heat-transfer fluid outflow temperature during discharging to be stabilized. A lab-scale combined storage consisting of a packed bed of rocks and steel-encapsulated AlSi12 was investigated experimentally and numerically. Due to the small tank-to-particle diameter ratio of the lab-scale storage, void-fraction variations were not negligible, leading to channeling effects that cannot be resolved in 1D heat-transfer models. The void-fraction variations and channeling effects can be resolved in 2D models of the flow and heat transfer in the storage. The resulting so-called bypass fraction extracted from the 2D model was used in the 1D model and led to good agreement with experimental measurements.

Keywords: Packed bed · Phase change material · Simulation · Thermal energy storage · Thermocline
2. Modelling

2.1 1D Model

The 1D heat-transfer model\cite{14,15} is formulated separately for the sensible and latent heat sections and the storage structure with the insulation. Fluid, solid, and molten phases are considered and convective, conductive, and radiative heat transfer mechanisms are included. The description below assumes that the PCM is encapsulated in tubes and is restricted for brevity; a more detailed description can be found in refs \cite{14,15}. Time integration is performed implicitly and spatial derivatives are approximated with second-order accuracy. The enthalpy method\cite{16} is used to solve the equations of the PCM.

2.1.1 Sensible Heat Section

The energy conservation equations for the fluid and solid phases are given by Eqsns (1) and (2), where the symbols are defined in the nomenclature. Temperature-dependent rock and air properties are implemented and are taken from refs \cite{6,13,17}. The volumetric heat-transfer coefficient \( h_{\text{v,rocks}} \) is determined from Eqn. (3) for the convective heat-transfer coefficient per unit area \( h_{\text{v,rocks}} \) with \( h_{\text{v,rocks}} = a \cdot \frac{d}{\sqrt{d_j}} \). The lateral wall convective heat-transfer coefficient \( h_{\text{w,conv}} \) is taken from ref. \cite{19} and the conductive-radiative wall heat-transfer coefficient \( h_{\text{w,cond-rad}} \) is taken from ref. \cite{20}. The effective axial conductivity \( k_{\text{eff}} \) is calculated according to ref. \cite{21}. The term \( \phi_{\text{interface,rad}} \) represents the radiative heat transfer between the last row of tubes and the top of the packed bed of rocks. Because of the small value of the tank-to-particle-diameter ratio, a bypass fraction of 10% of the small value of the tank-to-particle-transfer between the last row of tubes and is restricted for brevity; a more detailed description can be found in refs \cite{14,15}. Time integration is performed implicitly and spatial derivatives are approximated with second-order accuracy. The enthalpy method\cite{16} is used to solve the equations of the PCM.

Further details of the model of the latent heat section are available in refs \cite{14,15}.

2.1.3 Storage Wall and Insulation

The radial and axial temperature distribution in the storage wall and the insulation is determined from Eqn. (8), where \( q_{\text{boundary}} \) represents the heat transfer at the boundary-interfaces of the wall and the insulation. At the inner boundary, convective heat transfer to the heat transfer fluid and convective-radiative heat transfer to the packed bed are accounted for, see the last terms in Eqns. (1), (2), and (5). Free convection heat transfer is assumed at the outer boundary.\cite{17} At the height of the topmost tube row, measured insulation temperatures in each material are imposed as boundary conditions.

2.2 2D Model

The primary purpose of the 2D model is to quantify channeling, i.e., the radial variations in the flow and heat transfer due to variations of the void fraction. As stated in the introduction, these variations are important because the tank-to-particle-diameter ratio for the lab-scale storage is small. To reduce the computational cost, the 2D model is based on the assumption of axisymmetry of the flow and heat transfer in the storage. The model solves the mass, momentum, and energy conservation and turbulence transport equations using ANSYS Fluent 15.0. Turbulence effects are accounted for with the realiziable \( k-\epsilon \) model\cite{23} with enhanced wall treatment.\cite{24} Grid-independent results were obtained with 360 000 quadrilateral cells. The packed bed and the tube rows are modelled using the porous media approach.\cite{25} As in the 1D model, the solid and fluid phases are assumed to be in thermal non-equilibrium. The solid-to-fluid heat-transfer coefficient is computed with Eqns. (3) and (6) for the packed bed and the tube bundle, respectively. Air is assumed to be an ideal gas.

Further details of the model of the latent heat section are available in refs \cite{14,15}.

2.1 Modelling

2.1.1 Sensible Heat Section

The energy conservation equations for the fluid and the encapsulation are given in Eqns (4) and (5). A volumetric air-to-tube heat-transfer coefficient \( h_{\text{v,rocks}} \) is used to compute \( q_{\text{eng}} \) and is calculated from a correlation (Eqn. (6)) for the convective heat-transfer coefficient per unit area \( h_{\text{v,rocks}} \) with \( h_{\text{v,rocks}} = a \cdot \frac{d}{\sqrt{d_j}} \). The gas Prandtl number evaluated at the temperature of the solid, \( Pr_{\text{s}} \), is the gas Prandtl number evaluated at the temperature of the gas, \( Pr_{\text{g}} \), and \( Pr_{\text{g}} \) is used in the correlations given in Eqns. (4) and (5) for the sensible heat transfer coefficient. The maximum interstitial velocity \( u_{\text{max}} = S_{\text{inj}} / (5 - d_{\text{inj}}) \). The term \( h_{\text{top,rad}} \) accounts for the radiative exchange between the perforated plate (Fig. 1) and the topmost row of tubes. An energy conservation equation (Eqn. (7)) is solved for each row of encapsulated PCM.

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with temperature-dependent properties.\cite{17} Temperature-dependent properties of solid materials are also implemented.\cite{6,13,17} Thermal losses by convection and radiation are considered assuming a surrounding temperature of 20 °C and a convective heat-transfer coefficient of 5 W/m²K. The PISO and PRESTO methods were used to couple the velocity and pressure fields and to solve the pressure-correction equation. Convergence was considered to have been achieved when the mass, momentum, and turbulence residuals were below 10⁻⁵ and the energy residual was below 10⁻⁴.

2.2.1 Sensible Heat Section

For randomly packed spherical particles of uniform diameter, the void fraction in the bulk region ranges between 0.36–0.42.\cite{27} The packing structure is affected by the tank wall for a distance of approximately 5d. In this near-wall region, the void fraction distribution follows a damped oscillatory variation, from a value close to unit at minimum of approximately 0.2 at a distance of about d/2 from the wall. For a distance greater than about 5d from the wall, the void fraction approaches the value in the bulk region. For packed beds of non-spherical and non-homogeneous particles, the variation of the void fraction in the radial direction is better described by an exponential decay affecting the packing structure for a distance of about 2–3d.\cite{28} The near-wall void fraction variation leads to channeling, which is important if the tank-to-particle diameter ratio is lower than 25–30.\cite{29,30} Since the lab-scale storage is characterized by a diameter ratio of about 12.5, the radial void-fraction distribution is included in the 2D model,\cite{31} see Eqn. (9), where \( C_s = 1.2 \) and \( C_v = 2.0.\)\cite{32} An effective thermal conductivity, \( \lambda_e \), implemented in Fluent through a user-defined function, was used to account for the conduction- and radiation-driven heat transfer in the packed bed.

2.2.2 Latent Heat Section

The effective heat-capacity method,\cite{34} was used to model the phase transition of the PCM. This method allows the phase transition to be modeled without the need for explicit tracking of the phase boundary by combining the latent heat of fusion with the specific heat. This so-called effective heat capacity was defined as a piecewise linear function of the temperature. The PCM and encapsulation were modeled as a single material with equivalent thermophysical properties. A sensitivity analysis was performed to ensure that the time step did not affect the phase transition. Radiation from the top plate to the topmost tube row was accounted for by adding a source term that was extracted from the 1D model.

3. Experimental Setup

The combined sensible/latent heat lab-scale TES consists of encapsulated AlSi₁₂ on top of a packed bed of rocks in an insulated cylindrical tank. A schematic with dimensions and the locations of the thermocouples is shown in Fig. 1. The inlet temperature of the air above the topmost tube row was measured by a shielded thermocouple. A radiation correction was applied to the measured temperature, see ref. [15]. The packed bed consisted of rocks with an average diameter of 32 mm and a total mass of 245 kg. The average void fraction of the bed was measured to be 0.4.\cite{13} AlSi₁₂, was chosen as the PCM due to its melting temperature being suitable for AA-CAES and CSP applications as well as due to its high heat of fusion, high thermal conductivity, and comparatively low cost.\cite{9} The encapsulation was made of AISI 316 steel tubes with an inner diameter of 16 mm and a wall thickness of 1 mm. Four rows of 17 tubes each were stacked at angles of 45°. The masses of the PCM and encapsulation were 9.27 kg and 13.17 kg, respectively. Thermal conductivities, heat capacities, and densities of the PCM and the encapsulation are given in ref. [14]. The heat of fusion of the PCM is 466 kJ/kg with a melting range of 4 K.\cite{13} The formation of an intermetallic layer between encapsulation and PCM was neglected, but is under investigation in a companion project.\cite{9} The tank was made of 3 mm thick stainless AISI 304 steel and was insulated with Microtherm®, felt, and rockwool. The thicknesses of the insulation layers as well as the thermophysical properties of the tank and insulation materials are given in ref. [14]. Two perforated steel plates of 20 mm thickness were used for flow transpiration at the top and the bottom of the storage. The storage was charged with air at up to 595 °C from the top and discharged with air at room temperature from the bottom. The total capacity of the combined storage is 42.4 kWhₑ.

4. Results

Two experimental runs under identical conditions were performed to obtain the temperature measurements at all desired positions, as only 26 thermocouple ports could be used in each run. To check reproducibility, 9 of the 26 thermocouples were connected in both runs. For these thermocouples, it was found that the mean temperature differences between the runs did not exceed 8 K or 1.4%. Figs 2, 3, and 4 show comparisons of the measured and simulated temperature distributions at the end of charging. The 2D model results clearly show the substantial radial gradients caused by the small values of the tank-to-particle diameter ratio.

5. Conclusions and Outlook

Simulations with 1D and 2D models of a lab-scale combined sensible/latent heat storage were validated with experimental results. Radial gradients were significant because of the small tank-to-particle diameter ratios and were represented well by the 2D model. The 2D simulations were used to extract the bypass fraction that was employed to represent the unresolved radial gradients in the 1D model. For larger tank-to-particle diameter ratios, as encountered in industrial-scale storage units, the
effect of radial gradients will decrease significantly and the validated 1D model can therefore be applied with confidence. Future work includes improved modeling of radiation effects in the 2D model and incorporation of correlations for the evolution of intermetallic layers between the PCM and the encapsulation.[9]

Nomenclature

Latin characters

- \( a \) Surface area per unit volume \([m^2/m^3]\)
- \( c \) Heat capacity \([J/kgK]\)
- \( d \) Diameter \([m]\)
- \( e \) Specific internal energy \([J/kg]\)
- \( f \) Area fraction \([-]\)
- \( h \) Specific enthalpy \([J/kg]\)
- \( h_v \) Volumetric heat-transfer coefficient \([W/m^3K]\)
- \( h_v \) Volumetric heat-transfer coefficient \([W/m^3K]\)
- \( k \) Thermal conductivity \([W/mK]\)
- \( m \) Mass \([kg]\)
- \( N \) Number of layers / units \([-]\)
- \( q \) Volumetric heat flux \([W/m^3]\)
- \( r \) Radius \([m]\)
- \( S_s \) Transverse pitch between tubes \([m]\)
- \( T \) Temperature \([K]\)
- \( t \) Time \([s]\)
- \( u \) Interstitial velocity \([m/s]\)
- \( u_s \) Superficial velocity \([m/s]\)
- \( V \) Volume \([m^3]\)
- \( x \) Axial coordinate \([m]\)

Greek characters

- \( \varepsilon \) Emissivity \([-]\)
- \( \rho \) Density \([kg/m^3]\)
- \( \mu \) Dynamic viscosity \([kg/ms]\)
- \( \sigma \) Stefan-Boltzmann constant, \(5.6704 \times 10^{-8}[W/m^2K^4]\)
- \( \varphi \) Volume fraction \([-]\)

Dimensionless numbers

- \( Nu \) Nusselt number, \(hd/k\) \([-]\)
- \( Pr \) Prandtl number, \(\mu c_p/\kappa\) \([-]\)
- \( Re_s \) Superficial Reynolds number, \(\rho u_s d / \mu\) \([-]\)
- \( Re_{max} \) Reynolds number for tubes, \(r u_{max} d_{abs} / \mu\) \([-]\)

Subscripts

- \( 0 \) Undisturbed flow
- \( \infty \) Surroundings
- \( c \) Charging
- \( cond \) Conductive
- \( cont \) Contact
- \( conv \) Convective
- \( d \) Discharging
- \( eff \) Effective
- \( enc \) Encapsulation
- \( epcm \) Encapsulation and PCM
- \( g \) Gas
- \( max \) Maximum
- \( p \) Particle
- \( rad \) Radiative
- \( s \) Solid
- \( str \) Storage wall and insulation
- \( v \) Volumetric
- \( w \) Wall
Acknowledgments

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Scientific Basis for Regulatory Decision-Making of Nanomaterials
Report on the Workshop, 20–21 January 2014, Center of Applied Ecotoxicology, Dübendorf

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In this article (\textit{CHIMIA} 2015, 69, 52–56), the name of author Etienne Vermeirssen is corrected.
Low-Valent Iron: An Fe(i) Ate Compound as a Building Block for a Linear Trinuclear Fe Cluster


The cluster structure of polynuclear iron compounds can determine the characteristics of (multi-)redox processes, enable cooperative reactivity, and allow the precise adjustability of magnetic properties. Lichtenberg, Grützmacher and co-workers present a low-valent trinuclear iron complex with an unusual linear Fe(i)–Fe(i)–Fe(i) unit. The metal complex is prepared by a rational approach using a salt metathesis reaction between a new anionic Fe(0) containing heterocycle and FeCl3. Its electronic structure was studied by single crystal XRD analysis, EPR and Mössbauer spectroscopy, and magnetic susceptibility measurements.

Combined Operando X-ray Diffraction–Electrochemical Impedance Spectroscopy Detecting Solid Solution Reactions of LiFePO4 in Batteries

M. Hess*, T. Sasaki*, C. Villevieille, and P. Novák, Nat. Commun. 2015, 6, 8169. PSI Villigen

Lithium-ion batteries are widely used for portable applications today. Unfortunately, they often suffer from limited recharge rates. Hess, Sasaki and collaborators report a combination of high-resolution operando synchrotron X-ray diffraction and electrochemical impedance spectroscopy to directly track non-equilibrium intermediate phases in lithium-ion battery materials. This technique uses a bulk exposure of X-rays on battery materials similar to the bulk exposure on standard photo cameras. LiFePO4, for example, is known to undergo phase separation when cycled under low-current-density conditions. Operando X-ray diffraction under ultra-high-rate alternating current and direct current excitation reveals a continuous but current-dependent, solid solution reaction between LiFePO4 and FePO4. This study changes the understanding of the intercalation dynamics in LiFePO4.

Solid-State Reversible Nucleophilic Addition in a Highly Flexible MOF


In this paper, Lanza, Macchi and co-workers describe a flexible and porous MOF based on CoII connectors and benzotriazolide-5-carboxylato linkers. The MOF reacts selectively with guest molecules trapped in the channels during the sample preparation or after an exchange process. Upon mild compression or cooling, the Co atoms are able to extend their coordination binding the nucleophilic guest molecules. The transformation involves all Co atoms with methanol as guest, whereas only part of them with the larger dimethylformamide. The addition is reversible and upon decompression or heating, the initial phase is reobtained. This peculiar example of chemisorption may have enormous implications for gas storage, selective sieving and potentially for catalysis. Further study is ongoing in the same research group.

Enantioselection on Heterogeneous Noble Metal Catalyst: Proline-Induced Asymmetry in the Hydrogenation of Isophorone on Pd Catalyst

L. Rodríguez-García, K. Hungerbühl, A. Baiker, and F. Meemken*, J. Am. Chem. Soc. 2015, 137, 12121. ETH Zürich

In the (S) proline-mediated asymmetric hydrogenation of isophorone (IP) on supported Pd catalyst, excellent enantioselectivity is achieved, with an enantiomeric excess of up to 99%. The role of the heterogeneous catalyst has been the subject of a controversial debate. Meemken and collaborators investigated the enantioselectivity-controlling steps on the metal surface using attenuated total reflection infrared spectroscopy. The results demonstrate the existence of two competing enantioselective processes leading to opposing enantioselection. Depending on surface coverage of the Pd catalyst, the reaction is controlled either by kinetic resolution ((S)-pathway) or by chiral catalysis ((R)-pathway). The unravelled (R)-reaction pathway emphasizes an intriguing strategy for inducing chirality in heterogeneous asymmetric catalysis.
Deep UV-LED Based Absorbance Detectors for Narrow-Bore HPLC and Capillary Electrophoresis

Duy Anh Bui and Peter C. Hauser*

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Keywords: Capillary detection · CE · Deep UV-LED · HPLC · UV photodiode

The most common detection method for the analytical separation techniques of HPLC and capillary electrophoresis (CE) is absorbance measurement in the deep-UV range (below 300 nm) as a large number of organic species absorb in this wavelength region. Conventional UV detectors are based on deuterium discharge lamps coupled to a monochromator for wavelength selection. Light-emitting diodes (LEDs) for this wavelength range have been produced in recent years. They have bandwidths of typically 30 nm, which makes them well suited for direct absorbance measurements of molecules without requiring a monochromator. Only UV-photodiodes and a log-ratio amplifier integrated circuit for emulating Lambert-Beer’s law are required to complete the electronic circuitry.

Narrow-bore HPLC has primarily been developed for use with mass-spectrometric detection, for which only small amounts of analytes are sufficient. However, the savings in eluent consumption makes this approach also attractive for use with optical detection when ultimate sensitivity is not required. In CE narrow channels are essential to limit the Joule heating associated with the ionic current along the separation path.

The design of LED-based detectors for these narrow gauge methods is more challenging than for standard HPLC. Due to the small available volumes, the construction of dedicated Z-shaped flow cells is not possible and the measurement has to be made transverse to the flow path. The narrowness of the necessary apertures requires careful attention to efficient light coupling and avoidance of stray light. High mechanical stability is also required in order to minimize noise due to mechanical fluctuations. Despite these hurdles excellent performance with regard to baseline noise (low μAU range), reproducibility of peak areas (~1%), and linearity of calibration curves (correlation coefficients >0.999) could be obtained with LEDs of the commonly used wavelengths of 255 and 280 nm for both, narrow-bore HPLC (250 mm ID) and CE (50 mm ID).

The inexpensive LED-based devices display a capability comparable to standard commercial detectors. Their compact size and low power requirements make them also suitable for portable battery-powered instruments.

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The detector cell for capillary electrophoresis.

Detection of aromatic acids in capillary electrophoresis using a 50 µm ID capillary with a 255 nm LED.

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Effect of Experimental Parameters on Water Splitting Using a Hematite Photoanode

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Abstract: Many studies designate hematite as a promising material for direct water splitting into hydrogen and oxygen. For a real outdoor application, it is important to consider hourly and seasonal conditions like temperature and sunlight intensity. The performance of an undoped hematite thin-film photoanode was tested in a photoelectrochemical cell under varying conditions of temperature and light intensity. Both parameters show a positive effect on performance under outdoor conditions.

Keywords: Hematite · Light intensity · Photoelectrochemical cell · Temperature · Water splitting

Introduction

The production of hydrogen from renewable intermittent energy sources provides a solution for storage of clean energy. This enables the production of liquid fuels such as methanol, which can be used in existing infrastructure. Solar-induced water splitting using a hematite (α-Fe₂O₃) photoanode in a photoelectrochemical (PEC) cell is one of the most promising technologies. α-Fe₂O₃ is an inexpensive material with high chemical stability in alkaline conditions. The band gap of about 2.0–2.2 eV provides good absorption in the visible spectrum up to 590 nm with a theoretical conversion up to 20% of incident solar energy into hydrogen. However, several factors limit the practical performance of hematite for solar water splitting, such as high rate of carrier recombination, poor charge transport and short lifetime of minority carriers. The phenomena that occur in a PEC cell are not yet fully understood, but it is clear that the semiconductor/electrolyte interface holds a great importance for the performance.[1]

For commercial application, it is important to consider hourly and seasonal conditions such as variation of sunlight intensity and temperature in outdoor conditions. Several simple models have been proposed to predict the behavior of a PEC cell as a function of temperature and light intensity. The Gartner model describes the electron/hole formation in the space-charge layer of the semiconductor:[2]

\[
I_{ph} = q\phi \left(1 - e^{-\alpha W} \right) \left(1 + \frac{\alpha L}{1 + \alpha L} \right) \tag{1}
\]

where, \(I_{ph}\) is the photocurrent, \(q\) is the charge of the electron, \(\phi\) is the photon flux, \(\alpha\) is the absorption coefficient, \(W\) is the width of the space-charge layer and \(L\) is the carrier diffusion length (2–4 nm for α-Fe₂O₃). The Gartner model assumes that every hole contributes to the photocurrent. This model predicts a linear relationship between the luminous flux and the photocurrent.

The temperature dependence can be explained in several ways. Carrier diffusion length is defined as:

\[
L = \sqrt{D\tau} \tag{2}
\]

where \(D\) is the diffusion coefficient and \(\tau\) is the minority carrier lifetime, which are two temperature-dependent parameters. The carrier lifetime (\(\tau\)) is weakly dependent on temperature.[3] Carrier diffusion coefficients \(D_e\) (for electrons) and \(D_h\) (for holes) are related to minority carrier mobility (\(\mu\)) and temperature by the Einstein equation:[1,4]

\[
D_i = \frac{k_b T}{q} \mu_i \tag{3}
\]

Finally, the empirical Varshni equation gives the band gap variation as a function of temperature:

\[
E_g(\tau) = E_g(0) - \frac{AT^2}{T+B} \tag{4}
\]

where \(A\) and \(B\) are fitting parameters of a given semiconductor and \(E_g(0)\) is the band gap at zero kelvin.[10]

Experimental Part

Photocurrent measurements were performed in a ‘cappuccino’ photoelectrochemical cell with a standard three-electrode configuration. The hematite photoanode[5] was used as working electrode (WE), a platinum foil electrode (Metrohm ref 6.0305.100) as counter-electrode (CE) and an Ag/AgCl KCl 3M (Metrohm ref 6.0733.100) as reference electrode. The cell was filled with about 20 ml of electrolyte aqueous solution of 1.0 M NaOH (pH = 13.6) prepared with Milli-Q water. Only 0.28 cm² of the photoanode was in contact with the electrolyte and was exposed to sunlight. To obtain the photocurrent density-voltage (J-V) curves, an external potential bias is applied between the working electrode and the counter electrode at a scan rate of 10 mV s⁻¹ by a Bio-Logic SP-50 potentiostat. The potential (\(E_{\text{RHE}}\)) was measured between the working electrode and the reference electrode and reported against the reversible hydrogen electrode (RHE) according to the Nernst equation:

\[
E_{\text{RHE}} = E_{\text{WHE}} + E_{\text{AgCl}}^0 + 0.059 \text{pH} \tag{5}
\]

with \(E_{\text{AgCl}}^0 = 0.210\) V at 25 °C. The temperature dependence of about 1 mV/°C is neglected. The photoanode was illuminated with a Xenon short arc lamp (Osram XBO R 180/45C) with integrated parabolic reflector and IR short pass filter (Thorlabs
FEL0800, cutoff 800 nm). The incident illumination power was measured with a calibrated photodiode (Thorlabs S120VC) and adjusted with the lamp power supply (Lumina Power XLB-300).

The PEC cell was placed in a thermostatic box. The temperature was measured by a thermocouple immersed in the electrolyte and is controlled with a Peltier element.

**Effect of Sunlight Intensity**

Power density was varied from 30 to 100 mW cm\(^{-2}\) which corresponds to an illumination of 0.3 to 1.0 sun equivalent. The electrolyte temperature is kept constant at 26 °C. The J-V curve shows a characteristic curve with a saturation region between 1.4 and 1.7\(V_{	ext{RHE}}\) as a flat area (plateau)\(^{[5]}\) defined by an inflection point \(J_{\text{pl}}\) (Fig. 1).

![Fig. 1. Photocurrent density-voltage (J-V) diagram of the hematite photoanode at different light intensities from about 0.3 to 1.0 sun equivalent.](image1)

The current density observed at 1.23\(V_{\text{RHE}}\) or at \(J_{\text{pl}}\) (plateau) follows a nearly linear relationship (Fig. 2) in accordance with Eqn. (1). No saturation effect is observed with increasing illumination. The non-linearity for higher illuminations can be explained by the increased hole recombination rate observed with higher generation rate.\(^{[6]}\)

![Fig. 2. Linear relationship between light intensity in sun equivalent and the generated photocurrent density.](image2)

**Effect of Temperature**

The temperature varied from 25 °C to maximum 50 °C to prevent evaporation of the electrolyte. The electrolyte was replaced at each experiment (Fig. 3).

![Fig. 3. Photocurrent density-voltage (J-V) diagram of the hematite photoanode at various temperatures from about 25 °C to 50 °C.](image3)

The temperature has an effect on position of the inflection point defined in the photocurrent saturation region. The photovoltage show a consistent shift to lower potential. The photocurrent increases with temperature but we can see a saturation effect beyond about 35 °C (Fig. 4). The photocurrent increase is mainly due to the improved minority carrier mobility and therefore the carrier diffusion length. This fact is weakly countered by the minority carrier lifetime which typically decreases slightly with temperature.\(^{[7]}\)

![Fig. 4. Drift of inflection point (\(J_{\text{pl}}\)) as function of temperature.](image4)

**Conclusion**

This study shows a positive effect of sunlight intensity and temperature on a photoelectrochemical cell for water splitting with hematite photoanode. The photocurrent increases linearly with sunlight without significant saturation effect. The advantageous temperature effect avoids the loss of efficiency due to PEC cell overheating. For a commercial application, the photoelectrochemical cell does not require a cooling system under conventional operating conditions.

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\(^{[3]}\) P. Dias, T. Lopes, L. Andrade, A. Mendes, *J. Power Sources* 2014, 272, 567.


Platform for a Technological Leap in Antibiotics
Elisabeth Heinzelmann, science + technology journalist

Abstract: NTN Swiss Biotech™ brings together the Swiss Biotech Association SBA, which is involved in regulatory, financial and legal issues, and biotechnet Switzerland, which is active in translational R&D, to provide a technology base for joint projects. Biotechnet aims to push promising domains by creating topic-oriented platforms that enable academia and industry to work together to produce R&D results of major importance to society and the economy. The first activity initiated by biotechnet is the Antibiotics Platform that has now been launched.

Keywords: Antimicrobial-resistant organisms · Gram-negative bacteria · Klebsiella pneumoniae · Multidrug-resistant strains · Pathogenesis of tuberculosis

Antimicrobial-resistant organisms are insidious: their rapid spread around the world in recent years represents a great risk for humanity. It seems that we can keep Gram-positive pathogens in check for the time being, but the increasing incidence of antibiotic-resistant Gram-negative infections is forcing us to accord high priority to combating this type of bacterial resistance.

A Clear Objective in Mind

“For multidrug-resistant (MDR) strains, in particular, there is often a lack of treatment options as they have become resistant to virtually all available antibiotics”, explains Prof. Markus Seeger, research group leader in the Institute of Medical Microbiology at the University of Zurich. “Gram-negative bacteria are generally much less permeable to antibiotics and thus generally less susceptible to naturally occurring antibiotics. This renders the discovery of novel antibiotics very challenging but at the same time rewarding.” He is the head of the Antibiotics Platform created by the NTN Swiss Biotech™ to combine the expertise of outstanding scientists from academia and industry in common projects supported by the Commission for Technology and Innovation (CTI). The reason for this step is that – following a period of stagnation – research and development in antibiotics are today globally in full swing. A key role in this domain is played by Switzerland with some highly innovative SMEs and start-ups that were unfortunately not well networked in the past. This has now changed with the Antibiotics Platform that involves all specialists within the sector to drive things forward both rapidly and efficiently.

In this close-knit network most industry partners have a clear emphasis on the discovery of antibiotics for the treatment of Klebsiella pneumoniae, Pseudomonas aeruginosa, Acinetobacter baumannii and Escherichia coli. These pathogens have become a major problem in the context of hospital-acquired (nosocomial) infections. In addition to these Gram-negative bacteria, multidrug-resistant Mycobacterium tuberculosis (MDR-TB) – the causative agent of most cases of tuberculosis – has become a global threat. Members of the Antibiotics Platform from industry – among them BioVersys – and from academia – such as the microbiologist Stewart Thomas Cole, Head of the Cole Laboratory at EPFL – are working on the development of drugs to treat MDR-TB. In a joint start-up meeting in Bern in early autumn 2015, partners from academia and industry explained their views and objectives in forging plans for a common Antibiotics Platform.

Everyone Contributes Individual Excellence

The Center of Organic and Medicinal Chemistry (ZHW Wadenswil) places particular emphasis on the design and synthesis part of the drug discovery process. In order to improve the potency, selectivity and pharmacokinetic profiles of modulators of validated drug targets, the group rationally designs and synthesizes novel scaffolds and focused libraries based on X-ray data of co-crystal structures. “Our iterative process of computational design, organic synthesis and biological testing leads to detailed structure-activity relationships for therapeutically relevant drug targets”, explains Prof. Rainer Riedl, head of the Center. “Our medical chemistry expertise allows for the development of clinical drug candidates for the treatment of bacterial infections.”


Prof. Stewart T. Cole is Director of the Global Health Institute at EPFL. As the Scientific Coordinator of three successful large-scale EC Framework projects he has a track record of bilateral cooperation with academic institutions, SMEs and pharmaceutical companies. His world-class research unit is dedicated to TB drug discovery, unravelling the pathogenesis of tuberculosis and studying the phylogeography of leprosy. “I see a decisive trend towards more microbiome analyses and bioinformatics as well as sequence-driven research”, says the microbiologist. “There is a major need in the context of rapid diagnostics. We could contribute to industrial partners of the platform the use of biosafety level III facilities that already exist at EPFL, in Bern and at UZH.”

At the Laboratory of Molecular Evolution, University of Basel, the group working with Dr. Marc Creus is analyzing the
evolution of resistance to antibiotics in Gram-negative bacteria by means of next-generation sequencing. As an example he cites a detailed clinical case report of a patient infected with a strain of *Klebsiella pneumoniae*, which developed multidrug antibiotic resistance during hospital treatment in Switzerland. In collaboration with an industrial partner, the Creus group has also applied similar sequencing technology to explore the potential adaptation of Gram-negative pathogens to a novel siderophore antibiotic that is currently undergoing clinical trials. “Exploring the evolution of resistance in the laboratory even before an antibiotic is marketed may be extremely informative in understanding the mechanism of action of the drug and may also help to minimize the evolution of resistance later on in the clinical setting.”

The Institute for Chemistry & Bioanalytics at the FHNW Muttenz is particularly active in the research fields biochemistry, bioanalytics & diagnostics, bio-nanotechnology and organic synthesis & chemical engineering.

The bioanalytics group contributed to BioVersys’s CTI projects by providing kinetic binding parameters as indicators for lead identification and optimization. The crystallization of drug-target complexes increases understanding of the binding pocket and allows the development of strategies towards the synthesis of better binders. Together with the organic synthesis group at the Institute, this comprehensive expertise in characterizing highly specific drug-target interactions using both kinetic and thermodynamic binding parameters with cutting-edge methodology forms a good basis for running integrated drug discovery projects. All the members of the organic synthesis group worked for many years in the pharmaceutical industry and thus provide very sound experience in medicinal chemistry, which has enabled the Institute to successfully run various projects in lead discovery and lead optimization both with small biotech and big pharmaceutical companies. In addition to this line of investigation, Prof. Eric Kuebler, whose focus is DNA analysis and mutagenesis, recently started a project with BioVersys to investigate potential resistance mechanisms related to BioVersys’s anti-mycobacterial compounds.

The biotechnet has for several years had a close relationship with the Laboratory of Molecular Microbiology and Biotechnology run by Prof. Anna Maria Puglia at the University of Palermo.

**Rapid Exchange of Know-how**

SNSF Professor Markus Seeger is interested in the structure and function of antibiotic efflux. In particular, tripartite efflux such as the well-studied Acr/AcrB/TolC protein complex from *Escherichia coli* are major contributors to the drug-resistance in Gram-negative ESKAPE pathogens. But ABC transporters, which pump antibiotics out of the cell at the expense of ATP hydrolysis, are also mediators of intrinsic antibiotic resistance, mainly in Gram-positive cells. “We want to understand the molecular details of the pumping mechanisms that lead to antibiotic efflux”, explains Markus Seeger. “For this purpose, we use X-ray crystallography, antibiotic binding and transport studies and mutational analysis of residues lining the antibiotic efflux tunnel.” Crystal structures determined by him and his group feature tunnels inside the protein and imply a ‘peristaltic mode’ of drug transport which could account for the wide substrate specificity observed.

Prof. Vincent Perreten at the Institute of Veterinary Bacteriology, University of Bern, performs epidemiological studies of antibiotic resistance using microarray technology and next-generation sequencing. This involves clinical samples from companion and food-producing animals, with monitoring of samples from healthy animals at the slaughterhouse and food samples of animal origin, i.e. meat.

**A Platform of ‘Give and Take’**

For years, Laves Arzneimittel GmbH in Schötz has concentrated on the exploration and development of preparations based on the *Escherichia coli* strain discovered in 1931 by Dr. Wolfgang Laves. Hans-Dieter Grimmecke, Head of R&D, wants to under-
stand the biofilm of the gut: “Probiotic bacteria of the future will probably originate from the gut microflora”, he says. “A promising field of application for probiotics is the animal industry, in particular in the context of reducing or even banning antibiotics in livestock production.”

As long ago as 2004, Actelion Pharmaceuticals Ltd. initiated a research programme in antibiotics, focusing on novel chemical scaffolds with new mechanisms of action against established targets. Goals are the intravenous treatment of severe hospital infections and oral antibiotics for community-acquired infections. “Drug transport – influx and efflux – is particularly interesting in the context of Gram-negative bacteria”, explains Daniel Ritz, head of Anti-Infectives Biology. “They are much more difficult to treat than Gram-positive bacteria, mainly because of the presence of the outer membrane and the action of tripartite efflux pumps.”

“Networking with experts in the field of bacterial infections is crucial for the advancement of antibacterial research and the development of novel antibiotics”, says Dr. Juerg Dreier. He is group leader Biochemistry & Screening and project leader of pre-clinical antibacterial projects at Basilea Pharmaceutica International Ltd. Basilea is focusing on the development of antibiotics, antifungals and oncology drugs. The company has a portfolio of commercial-stage drugs as well as a pipeline of innovative early-stage anti-infective and oncology product candidates. Through the integrated research, development and commercial operations of its Swiss subsidiary Basilea Pharmaceutica International Ltd., the company focuses on providing innovative pharmaceutical products in the therapeutic areas of bacterial infections, fungal infections and oncology, targeting the medical challenge of rising resistance and non-response to current treatment options.

BioVersys AG in Basel develops small chemical molecules that switch off drug resistance on a gene-regulatory level within bacteria, known as TRICs (Transcriptional Regulator Inhibitory Compounds). “We are working on an anti-tuberculosis project and several approaches to treating Gram-negative infections. We want to collaborate in the areas of X-ray crystallography and in silico modelling and obtain access to strain collections”, says Dr. Michel Pieren, Group Leader Drug Discovery. “We have recently developed a novel technique to create targeted gene deletions in clinically relevant Gram-negative pathogens without the use of antibiotic markers. This is very useful when generating knockouts in multidrug-resistant Gram-negative bacteria.” This method is of potential interest for other platform members.

Remain Modest, Be Powerful!

The platform members will now work out common areas of interest that are not affected by intellectual property issues. A priority seems to be the establishment of general methods to study plasma protein binding. “There is a strong commitment from academia and industry”, Markus Seeger concludes. “We are not seeking to grow in terms of members, but want to realize a lean, effective organization with clear targets to produce visible results that receive international attention.” For Prof. Daniel Gygax, President of biotechnet Switzerland, the clear aim is to increase competitiveness by creating interactive value: “Our focus is on linking the core competencies of companies with the scientific knowledge and experience of academia. We have to ‘plug the holes’ in know-how and technology along the entire value chain!”

Homepage: www.biotechnet.ch

Received: November 2, 2015
Chemical Landmark 2015 – Designation of the Former Institute of Chemistry of the University of Fribourg

Leo Merz

On the 13th of October, the Swiss Academy of Sciences SCNAT designated the former institute of chemistry of the University of Fribourg as «Chemical Landmark». The award ceremony took place in the course of the «Fribourg Chaim Weizmann Lecture». The combined festivities attracted an audience of more than 200 participants.

Prof. Dr. Katharina Fromm (SCNAT, Uni FR) moderated the program and welcomed the guests. Dr. Jürg Pfister, secretary general of SCNAT, briefly introduced SCNAT and the «Chemical Landmark» program, Prof. Dr. Andreas Zumbühl presented the Fribourg Chemical Society, and Beat Vonlanthen (Conseil d’État FR) proudly conveyed the congratulations of the cantonal government of Fribourg.

In his laudation, Prof. em. Dr. Alexander von Zelewsky provided an insight into the history of the institutes. The university was founded upon the initiative of the conseil d’état Georges Python in 1886. Shortly after, in 1896 the faculty of science was opened. Chemistry was installed in a former wagon factory, which had been used as an arsenal for the artillery. Already the first institute of chemistry was from the beginning committed to bilingualism. The first appointed chemistry professor was A. Bistrzycki from Germany. The first associate professor René Thomas-Mamert was called from France. The academic career ladder was different at that time: Thomas-Mamert started in Fribourg in 1896, finished his doctorate in 1897 and was subsequently promoted to full professor. Bistrzycki already had a group of eleven students whom he brought with him to the new and unknown University of Fribourg. Among them was Chaim Weizmann, eponym of the «Fribourg Chaim Weizmann Lecture», who later became the first president of Israel, co-founded the Hebrew University of Jerusalem, and founded the research institute that was later called Weizmann-Institute.

In the early 20th century, a descendant from an old Fribourg family, Henri de Diesbach, was appointed professor for chemistry. Working in his group, Edmond von der Weid was the first to publish the synthesis of phthalocyanine. Amazed about the stability and colourfulness of the molecule, they offered it to the chemical industry in Basel, who was not interested at that time. The technological importance of phthalocyanine was not yet recognised, and the use and mass production started a couple of years later in England. Even today, it plays an important role. In 2000, more than 10’000 tons of phthalocyanines were produced, and 25% of all artificial organic pigments are phthalocyanine derivatives. In honour of this discovery, the «Chemical Landmark» plaque was anodized turquoise with a phthalocyanine dye.
Von Zelewsky, who himself had worked in the old chemistry institute, flavoured his laudation with several anecdotes. He told stories about chemists using chemical tricks to enter the building during holidays to do their research and of (photo-)reactions that could be accomplished in the laboratories in Basel but not in the dark laboratories in Fribourg.

The unveiling of the commemorative plaque concluded the «Chemical Landmark» part of the event. The plaque was attached at an entrance of the original building and is now visible to the public.

The second part of the festivities was the Chaim Weizmann Lecture by Nobel laureate Prof. Alan Heeger, from the University of California, Santa Barbara.

At the concluding apéro the audience had the opportunity to talk to the Nobel laureate Alan Heeger, the ambassador of Israel Y. Caspi, the conseil d’état B. Vonlanthen and of course the researchers.

Additional information on the «Chemical Landmarks» may be found at chemicallandmarks.ch.

Additional information about the «Platform Chemistry» and its activities may be found at chemistry.scnat.ch.

Received: October 28, 2015

SCS Spring Meeting 2016 – Registration open!

Topic: «Green Chemistry»

Date: April 22, 2016, 09.30–17.00
Location: University of Zurich, Department of Chemistry
Irchel Campus, Winterthurerstrasse 190, 8057 Zürich

The Swiss Chemical Society Spring Meeting is a one-day symposium and provides a high quality program with national and international speakers. It is also the platform for the Werner Price Ceremony and the Werner Award Lecture.

As a general rule the Society holds its general assembly during the lunch break.

Registration
Free admission. However, a registration is required via the online form on http://scg.ch/springmeeting/2016/

Program
09.30 Welcome coffee, registration
10.00 Opening, welcome
   Prof. Roger Alberto, Prof. Greta Patzke
10.05 Prof. Martyn Poliakoff, University of Nottingham
11.00 Prof. Paul T. Anastas, Yale University
12.00 Ceremony Werner Prize 2016
12.50 Lunch / Commercial Exhibition
13.30 SCS General Assembly 2016
14.00 Dr. Thomas Güttinger, Process Development Specialty Chemicals at BASF
15.00 Prof. Walter Leitner, RWTH Aachen
16.00 Prof. Paul J. Dyson, EPF Lausanne
17.00 Closing remarks
Apéro and networking event

Supporters

European Photochemistry Association: Call for Nominations from Members

The Porter Medal 2016
Deadline for nominations: 31st January 2016
The Porter Medal is awarded every two years to the scientist who, in the opinion of the European Photochemistry Association, the Inter-American Photochemistry Association and the Asian and Oceania Photochemistry Association has contributed most to the subject of Photochemistry.

Named for the late George Porter FRS, Nobel Laureate, the Porter Medal is awarded to the scientist who in the opinion of the judges, has contributed most the science of Photochemistry with emphasis on more physical matters, thus reflecting George Porter’s own interests.

More details on the webpage: www.portermedal.com

EPA Prize for Best PhD Thesis in Photochemistry
Deadline for nominations: 31st December 2015
The Fifth EPA Prize for the best PhD thesis in Photochemistry will be attributed during the CECP 2016 Meeting in Bad Hofgastein, Austria. (February 13th to 18th). The prize is 1000 €, plus travel costs to Bad Hofgastein (within the limit of 300 €), and ONE FREE YEAR of EPA membership.

More details on the webpage: www.photochemistry.eu/phd_price.php

A WARM WELCOME TO OUR NEW MEMBERS!


Nikos Agorastos, Thalwil – Carlo Perotto, Adliswil – Carl Philipp Rosenau, Zürich.
Registration

Registration is now open for the sixth EuCheMS. You can enjoy early-bird discounts if you register now. You can be connected to all the news and updates with the Congress newsletter and see all services included and registration possibilities.

Plenary Speakers Confirmed

Outstanding speakers have already confirmed their attendance. 6 Nobel Laureates will participate in the Congress offering plenary lectures. Ada Yonah, Richard Schrock, Aaron Ciechanover, Harold Kroto and Jean-Marie Lehn will be plenary speakers at 6th EuChems in Seville.

Avelino Corma, Spain’s most awarded chemist and 2014 Prince of Asturias award for Technical and Scientific Research, the most prestigious in this country, has also confirmed his assistance and joins these spectacular group of plenary lecturers.

The European Chemistry Congresses (ECC) are the most prominent events for the European chemistry community. They constitute a joint endeavour of the national chemical society and the EuCheMS Divisions and Working Parties. Chemists from all parts of Europe come together to present and discuss the latest achievements in cutting edge chemical sciences. There is no other occasion where chemists from different countries, different areas of chemistry and different professional backgrounds can converge in one place. The ECC are unique forums to foster transnational dialogue and collaboration, to encourage the dialogue between the different branches of chemistry, to bring academia, industry and decision makers together and to emphasize the impact of chemistry and chemical research on our society. Special attention is given to all activities that help promote the careers of young scientists. A high level Scientific Committee ensures the highest possible quality of the scientific contributions with a regionally and thematically balanced program of exciting cutting edge chemistry.


6th EuCheMS is less than a year away

Countdown has started for 6th EuCheMS Congress, now less than a year away to take place in Seville, Spain next 11–15 September, 2016. Following, you will find some of the major Congress milestones.

Call for abstracts OPEN

The Call for abstracts process is already available. Guidelines, information for authors, submissions and important dates as well as online submission form are available in the congress website

The online abstract submission deadline is April 1st, 2016.

Topic Conveners

Topic Conveners have been recently appointed. Thus, every topic is already assigned to a European convener specialised in the issue. You can review their background and experience.

Merry Christmas

Hoping many happy moments will find their way to you, leaving lovely memories you’ll treasure all the year through.

We wish you a Merry Christmas and a Happy New Year.

Your team from the Head Office

Sarah & David
SCS Prize Winners 2016

It's our pleasure to announce the winners of the 2016 SCS awards. We would like to sincerely congratulate all prize winners and are looking forward to the ceremonies that will take place at one of our events during the next year.

Paracelsus Prize 2016
CHF 20,000 and medal in gold.
The Paracelsus Prize is awarded to an internationally outstanding scientist for his or her lifetime achievements in chemical research. It is awarded every two years;

The Swiss Chemical Society awards the Paracelsus Prize 2016 to

Prof. Michael Graetzel, EPF Lausanne,

for his invention and development of the dye-sensitized solar cell.

Professor at the Ecole Polytechnique de Lausanne, Michael Graetzel directs the Laboratory of Photonics and Interfaces. He pioneered the use of mesoscopic materials in energy conversion systems, in particular photovoltaic cells, lithium ion batteries and photo-electrochemical devices for the splitting of water into hydrogen and oxygen by sunlight. He discovered a new type of solar cell based on dye-sensitized nanocrystalline oxide films (Picture and portrait text from http://lpi.epfl.ch/graetzel).

Paracelsus Award winners since 2002
2014: Prof. Richard R. Schrock, MIT, USA
2012: Prof. Bernd Giese, University of Basel and Fribourg
2010: Prof. Steven V. Ley, Cambridge, U.K.
2008: Prof. Ben L. Feringa, Groningen, NL
2004: Prof. George M. Whitesides, Cambridge, USA
2002: Prof. Martin Quack, Zürich

All winners on http://scg.ch/awards

Werner Prize 2016
CHF 10,000 and medal in bronze.
The Werner Prize is awarded to a promising young Swiss scientist or scientist working in Switzerland for outstanding independent chemical research. At the time of the award the candidate may not be a tenured professor or someone in a higher position in industry, and should be younger than 40. The prize is awarded annually.

The Swiss Chemical Society awards the Werner Prize 2016 to

Prof. Maksym Kovalenko, ETH Zurich,

for his innovative studies in the chemistry, physics and applications of inorganic nanostructures.

Maksym Kovalenko has been an assistant professor (tenure-track) of inorganic functional materials at ETH Zurich since July 2011. He is also affiliated with Empa - the Swiss Federal Laboratories for Materials Science and Technology. The research activities of his group are carried out at both institutions (portrait text from http://www.old-lac.ethz.ch/kovalenkolab.html).

Werner Prize Winners since 2010
2015: Prof. Gilles Gasser, University of Zurich
2014: Prof. Clémence Corrinboeuf, EPF Lausanne, Prof. Jérôme Waser, EPF Lausanne
2013: Prof. Cristina Nevado, University of Zurich, Prof. Clément Mazet, University of Geneva
2012: Prof. Nicolai Cramer, EPF Lausanne
2011: Prof. Dr. Xile Hu, EPF Lausanne, Prof. Dr. Reto Dorta, University of Zürich
2010: Prof. Sandrine Gerber, EPF Lausanne

All winners on http://scg.ch/awards

Sandmeyer Prize 2016
CHF 10,000 for individuals or CHF 20,000 for groups
The Sandmeyer Prize is awarded to a group for outstanding work in industrial or applied chemistry. The work must be completed in Switzerland or with the involvement of a Swiss national. The prize is awarded annually.

The Swiss Chemical Society awards the Sandmeyer Prize 2016 to the team comprising researchers from Sika Technology AG, ETH Zürich and the University of Colorado Boulder, namely

Dr. Martin Weibel, Sika Technology AG
Dr. Thomas Müller, Sika Deutschland GmbH
Dr. Ratan K. Mishra, ETH Zurich
Prof. Robert J. Flatt, ETH Zurich
Prof. Hendrik Heinz, University of Colorado Boulder

for their experimental and modelling studies of new commercial organic additives for the grinding of inorganic solids.

Sandmeyer Prize Winners since 2011
2015: Actelion Pharmaceuticals Ltd, Hochschule für Technik und Architektur Fribourg and Swissi Process Safety
2014: Syngenta Crop Protection Münchwilen AG
2013: Clarient Group R&D and CNRS-Université de Strasbourg
2012: Solvias AG
2011: BASF Schweiz AG

All winners on http://scg.ch/awards

Dr. Max Lüthi Award 2016
CHF 1'000 and medal in bronze
The Dr. Max Lüthi Award is presented for an outstanding diploma thesis in Chemistry conducted at a Swiss University of Applied Sciences. The prize is awarded annually.

The Swiss Chemical Society awards the Dr. Max Lüthi Prize 2016 to

Mr. Flavio Gall, ZHAW Wädenswil,

for his Bachelor Diploma studies on the design and synthesis of cyclic metalloprotease inhibitors.

Dr. Max Lüthi Prize Winners since 2010
2015: Yvan Mongbanziama, HEIA Fribourg
2014: Yannick Stöferle, ZHAW Wädenswil
2013: Peter Elmiger, ZHAW Wädenswil
2012: Lucie Sägesser, ZHAW Wädenswil
2011: Michael Brand, Zürich
2010: Benjamin Otter, FHNW

All winners on http://scg.ch/awards
**Weiterbildung Analytik**

**Trenntechnik**

**Analytische Anwendungen**

**Methoden der Life Sciences**

**Qualitätssicherung**

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Einzelmitglieder der folgenden Fachverbände können unsere Kurse zum vorteilhaften Mitgliedertarif besuchen:

- Fachverband Laborberufe (FLB), Gesellschaft Deutscher Chemiker (GDCh), Gesellschaft Österreichischer Chemiker (GÖCH), Schweizerische Arbeitsgemeinschaft für Spektrometrie und Elementaranalytik (SASP), Schweizerische Chemische Gesellschaft (SCG), Schweizerische Chemie- und Pharmaberufe Verband (SCV), Schweizerische Gesellschaft für Lebensmittel- und Umweltchemie (SGLUC), Schweizerische Gruppe für Massenspektroskopie (SGMS) und Schweizerischer Verband Diplomierter Chemiker (SVC).

Falls Sie sich für unsere Veranstaltungen interessieren, erreichen Sie uns unter Telefon 058 765 52 00 oder Fax 058 275 58 01 oder mailen Sie an infodas@eawag.ch. Online-Anmeldung im Internet unter: www.scg.ch/kurse

InCompany Training – Individuelle Beratung und Schulung

Im Rahmen des Weiterbildungsprogramms organisieren oder erarbeiten wir gemeinsam mit Ihnen InCompany-Schulungen und -Trainings nach Ihren Vorstellungen und Bedürfnissen. Profitieren Sie davon, dass wir für Sie

- Inhalte an firmenspezifische Anforderungen und Wünsche anpassen
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- praktische Übungen gegebenenfalls an Ihren Geräten durchführen
- Trainings bei Bedarf auch in französischer oder englischer Sprache durchführen

Ein weiterer Vorteil der InCompany-Trainings: für Ihre Mitarbeiterinnen und Mitarbeiter fallen keine Reise- und Übernachtungskosten an!

Experten stehen Ihnen für eine persönliche Bedarfsabklärung und Beratung gerne zur Verfügung.

Sie erreichen uns über

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Überlandstrasse 133, 8600 Dübendorf
Telefon 058 765 52 00
E-Mail: infodas@eawag.ch
www.scg.ch/kurse
Information

CONFERENCES IN SWITZERLAND

01.01. – 30.04.2016

14th Swiss Snow Symposium 2016 by SYCA
22.01.2016–24.01.2016
Panorama Hotel Alphubel, Saas-Fee
Science meets Snow! Symposium for young chemists up to 36 years with an interesting combination of science, networking, fun & sports.

20th SASP 2016
Sunstar Parkhotel Davos, Davos
The Symposium on Atomic, Cluster and Surface Physics (SASP) is one in a continuing biennial series of conferences (the last one was held in Obergurgl, Austria in 2014) that promotes the growth of scientific knowledge and exchange of information among scientists in the field of atomic, molecular, and surface physics.
http://icbc.zhaw.ch/de/science/institute-zentren/icbc/sasp-2016.html

23rd International Academic Conference on Development in Science and Technology (IACDST)
11.02.2016
Hotel Allegra, Kloten
IACDST aims to bring together leading academic scientists, researchers and research scholars to exchange and share their experiences and research results about all aspects of Development in Science and Technology. It also provides the premier interdisciplinary forum for researchers, practitioners and educators to present and discuss the most recent innovations, trends, and concerns, practical challenges encountered and the solutions adopted in the fields of Development in Science and Technology.
http://academicsworld.org/Conference/Switzerland2016/IACDST/

23rd International Conference on Environmental Science and Development (ICESD)
12.02.2016
Hotel Allegra, Kloten
ICESD aims to bring together leading academic scientists, researchers and research scholars to exchange and share their experiences and research results about all aspects of Environmental Science and Development. It also provides the premier interdisciplinary forum for researchers, practitioners and educators to present and discuss the most recent innovations, trends, and concerns, practical challenges encountered and the solutions adopted in the fields of Environmental Science and Development.
http://academicsworld.org/Conference/Switzerland2016/ICESD/

LS2 Annual Meeting 2016
Amphipôle, University of Lausanne, Lausanne
At this meeting, LS2 will bring together Swiss Life Scientists from academic backgrounds as well as our industry partners with researchers from all across Europe to explore the large spectrum of ‘Interdisciplinary Sciences’; listen in on the exciting findings in the field of Chemical Biology over Synthetic Biology to Proteomics and ‘Classic’ Molecular and Cell Biology (and many more), discuss opportunities and challenges of the Swiss Research funding system and the life beyond academia in non-academic professions, and be a part of the emotional debate on careers of men and women in the Life Sciences.
http://ls2-annual-meeting.ch

Research breakthroughs and social impact: Young scientists debate synthetic biology
16.02.2016
Amphipôle, University of Lausanne, Lausanne
This event is part of the LS2 Annual Meeting 2016. Emerging technologies have the potential to offer new solutions for society’s challenges but also raise concerns about safety and ethical implications. Synthetic biology is a maturing discipline aiming to modify, rebuild and design biological systems. Possible applications include production of biofuels in microalgae, synthesis of therapeutics in yeast cells or removal of pollutants’ from the environment using bacteria.

Swiss Symposium on Lab Automation 2016
17.03.2016
Hochschule für Technik, Institute for Lab Automation and Mechatronics, Rapperswil
The Institute for Lab Automation and Mechatronics (ILT) annually invites to the Swiss Symposium on Lab Automation, where presentations are given by and for experts in the field of automation and instrumentation in the medical and life science sector. In 2016, the Symposium’s focus is on Labor 4.0: modern technologies and the smart lab of the future. Alongside the presentation, the exhibition provides an ideal networking platform and gives companies and institutions the opportunity to present their skills and working areas.
https://www.ilt.hsr.ch/index.php?id=14274

36th International Conference on Environment and Natural Science (ICENS)
04.04.2016
Hotel Allegra, Kloten
The idea of the conference is for the scientists, scholars, engineers and students from universities all around the world and industry to present ongoing research activities, and hence to foster research relations between academia and industry. This conference provides opportunities for delegates to exchange new ideas and application experiences face to face, to establish business or research relations and to find global partners for future collaboration.
http://iserd.co/Conference/Zurich-Switzerland/ICENS/
SCS Spring Meeting 2016
22.04.2016
University of Zurich, Irchel Campus, Zurich
Symposium topic: «Green Chemistry»
The SCS Spring Meeting is a one-day symposium and provides a high quality program with national and international speakers of a certain topic. It is also the platform for the Werner Prize Ceremony and the Werner Award Lecture.
http://scg.ch/springmeeting/2016

Lectures
01.01.16 - 28.02.2016

University of Bern, Anorganische, Analytische und Physikalische Chemie
Department of Chemistry and Biochemistry, Lecture hall S 379
05.02.2016
11.00 h Prof. Horst Köppel, Universität Heidelberg, Germany
Title to be announced

University of Fribourg
Main auditorium, Chemistry Department
28.01.2016
09.30 h Prof. Petra Swiderek, University of Bremen, Germany
The intriguing world of electrons: Auroras, radiotherapy, nanofabrication and more
10.15 h Prof. Michael Allan, University of Fribourg
Free electrons and molecules – a lifelong passion
11.00 h Prof. Luisa de Cola, University of Strasbourg, France
Title to be announced
12.00 h Prof. Peter Belser, University of Fribourg
Energy Transfer - Everywhere
14.00 h Prof. Frank Neese, Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany
Ab initio Ligand Field Theory for d- and f-elements. A powerful link between theory and experiment
14.45 h Prof. Claude Daul, University of Fribourg
The amazing power of simple ideas
15.45 h Prof. Roman Fasel, University of Bern
Carbon nanomaterials
16.30 h Prof. Titus Andreas Jenny, University of Fribourg
Carbon: a life-long love-story

University of Geneva, Chimie Organique
Sciences II, Auditoire A. Pictet A100
21.01.2016
16.30 h Prof. Vincent Gandon, Université Paris-Sud, France
Title to be announced
18.02.2016
16.30 h Prof. Konrad Tiefenbacher, Department of Chemistry, Technische Universität München, Munich, Germany
Enzyme-like Catalysis in Self-Assembled Aromatic Cavities

University of Geneva, Société Chimique de Genève
Sciences II, Auditoire A. Pictet A100
18.01.2016
17.30 h Prof. Philippe Reymond, Department of Molecular Biology, University of Lausanne
Plant defenses against insect attack

ETH Zürich, Laboratory of Inorganic Chemistry
Hönggerberg HCI, J7
12.01.2016 Dr. Aleix Comas-Vives, ETH Zürich
The role of interfacial water on water desalination, hydrates management, and oil & gas production

The complete and updated lecture calendar is available on www.scg.ch/lectures
Countdown for Seville starts

A lot has happened in the organisation of the 6th EuCheMS Chemistry Congress which will take place in Seville (Spain) on 11 to 15 September 2016.

Themes and topics
Organisers and the scientific committee announced eight congress themes and 29 topics that cover a comprehensive range of chemistry aspects (see next page).
http://euchems-seville2016.eu/euchems-themes

Exhibition
The exhibition floor plan is available on the website. Both sponsors and exhibitors are quickly reserving spaces so organisers recommend early booking.
http://euchems-seville2016.eu/exhibition-booking-form

Plenary speakers
Outstanding speakers have already confirmed their attendance. Five Nobel Laureates and Avelino Corma, Spain’s most awarded chemist, will serve as plenary speakers.
http://euchems-seville2016.eu/euchems-plenary-speakers

Sponsors support the congress
Some major chemical and engineering companies as well as one of Europe’s major chemistry societies have already confirmed their support of the EuCheMS Chemistry Congress. The Compañía Española de Petróleos (Cepsa), the Royal Society of Chemistry, Repsol, Dow Chemical and Técnicas Reunidas have all declared their sponsorship. All sponsors are highlighted on the congress website and in communication materials.

Promotion
The congress organisers and the chair of the scientific committee have visited some of the major chemical societies to engage their commitment and support for the congress. Last June the organisers also attended Achema 2015 in Frankfurt (Germany) to advertise the congress to the 166,000 participants and 3,813 exhibitors of the chemical, pharmaceutical and food industry. In July the congress was also featured at the XXXV Biannual Congress of the Spanish Royal Society of Chemistry in A Coruña (Spain).

Congress newsletter
Up to now two issues of the EuCheMS Congress newsletter have been prepared and distributed among major stakeholders, preregistered attendees and the chemical community in general.
http://euchems-seville2016.eu/euchems-latest-newsletters

Press room
Interviews with congress organisers and major chemical societies’ leaders are published on an exclusive basis on the congress website’s press room. Among others David Cole-Hamilton, EuCheMS president, and Peter G. Edwards, chair of the scientific committee, share their vision about the EuCheMS congresses, chemistry, education and scientific communication as well as other issues like the present and future of chemistry societies in Europe.

Angela López Berrocal
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Young chemists in Boston
Five years ago, the European Young Chemists’ Network (EYCN) and the Younger Chemists Committee of the American Chemical Society (YCC-ACS) created the Young Chemists Crossing Borders (YCCB) programme. Every second year, YCC-ACS invites six European students and a delegation from the Junghemikerforum (JFC) of the Gesellschaft Deutscher Chemiker (GDCh) to ACS conferences. In return, EYCN brings six American students to a EuCheMS event.

Last year, six young Americans visited the EuCheMS Congress in Istanbul. In August this year, the YCCB 2015 awardees Sophie Carenco (France), Grégory Chatel (France), Thomas McGlone (UK), Madeline Kavanagh (UK), Sebastian Sobottka (Germany) and Bart Verbraeken (Belgium) enjoyed the 250th ACS Meeting and Exposition in Boston. YCCB students participated in symposia and presented their work in poster sessions and oral communications. In addition (and thanks to the organisers at YCC-ACS and the North-Eastern Section of ACS) the students visited MIT, Harvard, the Woods Hole Oceanographic Institute and industries such as Genzyme. Moreover, a variety of social events were organised. EuCheMS president David Cole-Hamilton hosted a traditional New England Clambake, sponsored by EuCheMS, RSC and GDCh.

The organisers also invited Fernando Gomollón Bel (EYCN chair) and Fréderique Backaert (EYCN current past chair) to participate in the exchange programme. They presented their most recent activities to their American colleagues, establishing the foundations for YCCB 2016, which will bring six YCC-ACS students to the EuCheMS Chemistry Congress 2016 in Spain.

Fernando Gomollón Bel, chair@eycn.eu

Participants of the YCCB programme in Boston.
IUPAC General Assembly in Korea

At the 48th General Assembly of IUPAC in Busan (Korea) from 8 to 14 August the council elected the officers for the next biennium and voted for a new intermediate subscription scheme to overcome the exchange rate variations. In his report, Mark Cesa, IUPAC president, explained the changes in the management and the secretariat during the last 18 months. The executive director had left and Lynn Soby was hired as new ED. Also the secretary general René Deplanque had resigned shortly after the last General Assembly and was followed by Colin Humphris in April 2014. As new vice president and president elect Qi-Feng Zhou (China) was elected by the council. Mark Cesa (USA) will be past president when Natalia Tarasova (Russia) becomes president for 2016 and 2017. Colin Humphris (UK) was elected as treasurer and Richard Hartshorn (New Zealand) as secretary general. The six newly elected members of the bureau are Mei Hung Chui (China Taipei), Christopher M. A. Brett (Portugal), Hemda Garelick (UK), Ehud Keinan (Israel), Kew-Ho Lee (Korea) and Pietro Tundo (Italy). The re-elected members are Russell Boyd (Canada), Tavarekere Chandrasekar (India), Christopher Ober (USA) and Kaoru Yamanouchi (Japan).

Michael Dräscherm.droescher@t-online.de

EuCheMS Chemistry Congress 2016: Themes and topics

The EuCheMS Chemistry Congress 2016 will take place in Seville (Spain) on 11 to 15 September 2016. The congress themes and topics are as follows:

**Theme A: Education and society**

*Chair: Evangelia Varella, Greece*

- **Topic A1:** Chemistry education
- **Topic A2:** Chemistry, society and public engagement
- **Topic A3:** Benefits: Wealth creation and society

**Theme B: The environment, energy and sustainability**

*Chair: Inmaculada Ortiz, Spain*

- **Topic B1:** Sustainable energy and air quality
- **Topic B2:** Environment and natural resources management
- **Topic B3:** Sustainable chemistry
- **Topic B4:** Food chemistry

**Theme C: New chemical compounds:**

*Synthesis, methods and industrial processes*

*Chair: Sylviane Sabo-Etienne, France*

- **Topic C1:** Synthesis and reactivity in metal based compounds
- **Topic C2:** Synthesis and reactivity in carbon based compounds
- **Topic C3:** Methods and mechanisms
- **Topic C4:** Catalysis in solution

**Theme D: Catalysis, industry and applications**

*Chair: Bob Tooze, UK*

- **Topic D1:** Chemistry in industry
- **Topic D2:** Industrial processes for the 21st century
- **Topic D3:** Catalysis at interfaces

**Theme E: Materials, devices and nanotechnology**

*Chair: Luisa De Cola, France*

- **Topic E1:** Materials chemistry
- **Topic E2:** Nanomaterials, devices, technology and applications
- **Topic E3:** Analytical techniques, characterisation and properties
- **Topic E4:** Carbon based nanotechnology

**Theme F: Properties of matter**

*Chair: Angela Agostiano, Italy*

- **Topic F1:** States of matter
- **Topic F2:** Properties of materials
- **Topic F3:** Polymers
- **Topic F4:** Innovative computational environments for molecular science

**Theme G: Physical, analytical and experimental methods in chemistry**

*Chair: Günther Gauglitz, Germany*

- **Topic G1:** Analytical and physical methods
- **Topic G2:** Determination of structure and physical properties
- **Topic G3:** Chemical dynamics

**Theme H: Chemistry in the life sciences**

*Chair: Péter Mátéyus, Hungary*

- **Topic H1:** Drug discovery and chemical biology
- **Topic H2:** Bio-macrocolecules
- **Topic H3:** Methods and applications
- **Topic H4:** In-silico methods in life sciences
The EuCheMS Executive Board

The EuCheMS Newsletter introduces the EuCheMS Executive Board members. This issue goes on with Wolfram Koch (Germany), Robert Parker (UK) and Igor Tkatchenko (France).

Wolfram Koch has been the executive director of the Gesellschaft Deutscher Chemiker since 2002. Before that he was for seven years professor of theoretical organic chemistry at TU Berlin, prior to which he was a senior scientist at IBM research facilities in Heidelberg (Germany) and San Jose (California).

During his active time in research Wolfram Koch worked on quantum chemical investigations on properties and reactivity of open shell transition metal compounds as well as on spectroscopic properties of small molecules. He has authored and co-authored ca. 190 papers in peer-reviewed journals and is the senior author of a textbook on density functional theory.

Besides being a member of the EuCheMS Executive Board for more than 15 years, Wolfram Koch is also a member of the IUPAC Finance Committee (until the end of this year), the Administrative Council of the German Copyright Collective (VG WORT) and Chairman of the Advisory Board of the German National Library of Science and Technology (TIB Hannover). He is a Fellow of the Royal Society of Chemistry and an IUPAC Fellow and holds an honorary membership of the Czech Chemical Society. Very recently he was appointed an honorary fellow of the Chemical Publishing Society Europe (ChemPubSoc Europe).

Robert Parker is chief executive of the Royal Society of Chemistry, a learned and professional organisation with 51,000 members. It has major outputs in education, events, policy and publishing. Before taking up the position as CEO he ran the very successful publishing wing of the RSC. Robert Parker has a PhD in chemistry and is a Chartered Scientist, Chartered Chemist and Fellow of the Royal Society of Chemistry as well as being a husband, father of three adult children and keen gardener and motorcyclist.

Igor Tkatchenko is a professor of organometallic chemistry and homogeneous catalysis. After postdoctoral research with Günther Wilke at the Max Planck Institute for Coal Research in Mülheim/Ruhr (Germany) and five years research in industry, he worked in France at the Laboratoire de Chimie de Coordination, CNRS, in Toulouse and at the Institut de Recherches sur la Catalyse, CNRS, in Villeurbanne. He then joined the Institute for Molecular Chemistry at the University of Bourgogne, where he served as research director until his retirement. Igor Tkatchenko serves as the general secretary of the Société Chimique de France. He has been appointed to the EuCheMS Executive Board and has represented ChemPubSoc Europe for many years and was a board member of ChemViews magazine.

EuCheMS at the ACS Fall Meeting in Boston

Nineta Majcen, EuCheMS general secretary, and David Cole-Hamilton, EuCheMS president, attended the ACS Fall Meeting in Boston in August at the invitation of Diane Grob Schmidt, ACS president. Wolfram Koch (GDCh) and Robert Parker (RSC), both EuCheMS Executive Board members, were also present, which allowed various meetings to take place involving EuCheMS and the ACS. One of them involved Nineta Majcen, Robert Parker and David Cole-Hamilton from EuCheMS and Diane Grob Schmidt, Tom Connelly (CEO), Pat Confalone (chair of the Board) and Denise Creech (director, Members & Scientific Advancement) from ACS.

The discussion focussed on how the two organisations might work more closely together. It was agreed that we should investigate possible joint symposia, and that the two organisations would support one another’s main meetings (ACS Fall and Spring Meetings, EuCheMS Chemistry Congresses). There was strong support for the Young Chemists Crossing Borders programme and it was agreed that the two societies should collaborate in the next iteration of an employment survey. ACS have been surveying the employment of chemists in the US for many years. The publication of the recent report on chemist employment in Europe (see R. Salzer, P. Taylor, et al., Chem. Eur. J. 2015, 21, 9921), carried out with the support of the European Chemistry Thematic Network (ECTN) and EuCheMS, indicates that there could be important comparative information to obtain through collaboration.

As part of the Young Chemists Crossing Borders programme, six European students had been selected by the European Young Chemists’ Network to attend the ACS meeting (see article on page 1). An ACS-GDCh student exchange was also taking place, so a day trip involving a visit to Woods Hole Oceanographic Institution and a clam bake on Cape Cod, supported by EuCheMS, RSC, GDCh and ACS, was arranged. This was an excellent opportunity for further networking.

Nineta Majcen
David Cole-Hamilton
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The GDCh Science Forum Chemistry in Dresden

On 30 August EuCheMS president David Cole-Hamilton addressed the audience of the opening ceremony of the GDCh Science Forum Chemistry in Dresden, one of the largest chemistry conferences in Europe this year. He introduced EuCheMS as the single voice of chemistry in Europe and mentioned a number of recent EuCheMS activities, such as the Younger Chemists Crossing Border exchange programme with the American Chemical Society and the first European Employment Survey, coordinated by Reiner Salzer from the local TU Dresden.

The GDCh Science Forum Chemistry with the slogan “Connecting chemistry and chemists” gathered more than 1500 chemists. In the UNESCO International Year of Light, GDCh had chosen physics as partner. Physicist and Nobel prize laureate Stefan Hell (Max Planck Institute for Biophysical Chemistry in Göttingen, Germany) as one of the plenary speakers talked about „Far-field optical nanoscopy: principles and recent advancements“. K. Barry Sharpless (The Scripps Research Institute in La Jolla, USA), Nobel prize laureate 2001, was awarded the August-Wilhelm-von-Hofmann lecture. He talked about „Click chemistry – new directions“.

Events 2016

31 January – 5 February 2016, Bressanone, Italy
18 – 20 February 2016, Florence, Italy
ENERCHEM-1, Chemistry of Renewable Energies www.enerchem-1.it
16 – 18 March 2016, Blankenberge, Belgium
26 – 29 April 2016, Guimarães, Portugal
1st European Young Chemists Meeting http://5pychem.eventos.chemistry.pt

3 – 8 July 2016, Vienna, Austria
16th Conference on Molten Salts and Ionic Liquids
4 – 7 September 2016, Minsk, Belarus
23rd Conference of Isoprenoids
11 – 15 September 2016, Seville, Spain
6th EuCheMS Chemistry Congress http://euchems-seville2016.eu

Events 2017

2 – 5 July 2017, Copenhagen, Denmark
4th EuCheMS Inorganic Chemistry Conference www.eicc-4.dk

EuCheMS at the Heroes of Chemistry dinner in Boston

From left: Rosemary Parker, Nineta Majcen (EuCheMS), Robert Parker (EuCheMS), Diane Grob Schmidt (ACS), Wolfram Koch and David Cole-Hamilton (both EuCheMS) with his daughter Rosie Cole-Hamilton, Neil Burford and Yvoula Tsantrizos (both Chemical Society of Canada) and Tom Connelly (ACS).

On the occasion of the ACS Fall Meeting in Boston (see page 3) EuCheMS representatives Nineta Majcen, Wolfram Koch, Robert Parker and David Cole-Hamilton were invited to attend the Heroes of Chemistry dinner where teams from companies were awarded Hero status as a result of pioneering work they had done for the benefit of humanity.

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Schnelle und einfache Analytik mit Mikrowellen zur Lebensmittel-Qualitätskontrolle

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- Cholesteringehalt
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- Hydroxyprolingehalt/Beife-Wert
- Nährstoff-/Elementgehalte
- Aminosäuren
- Inhaltsstoffe, wie z. B. Glucoside, Alkaloid, Steroide,
- Terpene, Pektine, ätherische Öle, Aromen, Farbstoffe,
- Zytostatika, Glucosinolate etc.
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