## Table of Contents

**Editorial**

3  SCCER Networked Research – Opening up New Opportunities

**Batteries – Advanced Batteries and Battery Materials**

5  Electrolyte Optimization: The Case of Sn Electrode as Negative Electrode for Na-Ion Batteries
7  Novel Nanostructured Electrode Materials for Li-Ion and Na-Ion Batteries
9  Alkali-Ion Rechargeable Batteries
10  Metal-Air/Metal-Water Rechargeable Batteries
11  Influence of Stress Cycling on Li-Ion Battery Cells for Vehicle Applications
13  Manufacturing Technologies and Production Methods for Battery Cells

**Heat – Thermal Energy Storage**

15  High-Temperature Combined Sensible/Latent-Heat Thermal Storage
17  Combined Sensible/Latent Heat Storage – CFD Analysis and Experimental Validation
19  Phase Change Material Systems for High Temperature Heat Storage
21  High Temperature Thermal Shock and Oxidation Behavior of Si-Infiltrated SIC Lattices
23  Aqueous Sodium Hydroxide Seasonal Thermal Energy Storage: Reaction Zone Construction and Assessment

**Hydrogen – Production and Storage**

29  Hydrides for Energy Storage
31  The Origin of the Catalytic Activity of a Metal Hydride in CO₂ Reduction
33  Advances in the Development and Characterization of Water Electrolysis Catalysts at the EPFL
36  Demonstration of a Redox Flow Battery to Generate Hydrogen from Surplus Renewable Energy
39  Hydrogen/Energy Storage and Delivery with the Carbon Dioxide Formic Acid Systems

**Synthetic Fuels – Development of Advanced Catalysts**

43  Catalysts for CO₂ Reduction to Synthetic Fuels
45  CO₂ to Fuels
47  Electrochemical Conversion of CO₂
50  Electrochemical CO₂ Reduction for Syngas Production
Table of Contents

Integration – Interactions of Storage Systems

55  A Uniform Techno-Economic and Environmental Assessment for Electrical and Thermal Storage in Switzerland
59  Applied Power-to-Gas Systems
62  ESI – Energy Systems Integration Platform

Appendix

65  Conferences
66  Presentations
69  Publications
72  Organized
76  Co-Organized Events
One of the major societal challenges is to stop the threat of climate change. In this context it is necessary to reduce the emission of CO$_2$. Roughly 60% of the global anthropogenic CO$_2$ emissions are originating from fossil fuels within the Energy Sector (i.e., coal, oil and natural gas) which defines the necessity to work on a change for sourcing our energy supply.

This is a global challenge, which, however, different countries approach in different ways. Switzerland is one of the states excluding the nuclear energy option in the future and therefore will expand the contribution of renewable energies within the Swiss energy system. Besides hydropower which presently already plays a major role as energy source, the share of photovoltaics and wind power will have to be significantly increased in the years to come. The performance of these sources is considered to be sufficient to provide enough energy to power the country.

However, electricity production from wind and solar energy is by definition subject to considerable temporal fluctuation, which is inextricably linked to the ability of energy storage. Here, both short-term storage in the range of minutes to hours as well as seasonal storage is of significance. The analysis of the energy consumption of modern industrial societies also shows that about half of the primary energy is used to generate heat with a large share for the heating of buildings.

The currently available storage technologies are mainly limited to different types of batteries, pumped-hydro energy as well as water-based heat storage, respectively. It is, hence, necessary to continue to invest into Research & Development of energy storage technologies opening up new opportunities for the energy system.

Within the Swiss Competence Center for Energy Research Heat and Electricity Storage (SCCER H&E Storage) the 23 participating groups from Cantonal Universities, Universities of Applied Sciences and ETH domain institutions are working on different technologies for energy storage ranging from power and heat storage to the storage of energy in gases and synthetic fuels. Through our networked R&D within Switzerland, the SCCER H&E Storage understands itself as a one-stop shop for new developments in energy storage.

Clearly, developing new options for energy storage to help to shape the energy system of the future, all academic members of the SCCER are closely linked through individual joint projects to different industrial partners who see the great technical and commercial potential for energy storage technologies. At this point, we would like to thank all our partners from the academic and private sector for their contributions to the ongoing projects within SCCER H&E Storage.

Our Competence Center just successfully finished its second year of operation. As a publicly funded Center, this Annual Report 2015 is supposed to provide everybody a more detailed insight into our exciting projects and technologies.

So sit back, relax and enjoy reading this summary of our activities!

Prof. Dr. Thomas J. Schmidt
Head SCCER Heat and Electricity Storage
Work Package 1 at a glance

Batteries offer the unique opportunity to directly store and when needed to release electric power with high overall roundtrip efficiencies of $>90\%$, therefore offering high potential for decentralized storage of excess renewable energy from the kilowatt to the megawatt range.

The main topics of research in work package 1 are centered around the development and testing of materials and components for next generations of alkali-ion batteries, i.e., high energy and power Li- and Na-ion batteries.

Specifically the Na-ion based batteries have the potential to overcome challenges related to the scarcity of Li and the expected future high cost of lithium, and are identified to play a key role in future battery technologies.

The research direction pursued by the participating research groups is mainly the synthesis and investigation of nano-structured materials for electrodes and the identification of suitable electrolyte systems for Li and Na type batteries.

Beside the fairly fundamental aspects, research and development on manufacturing as well as on safety and durability aspects are addressed by the SCCER.
Electrolyte Optimization: The Case of Sn Electrode as Negative Electrode for Na-Ion Batteries

Scope of project

Na-ion batteries are considered as the most promising alternative to Li-ion batteries as energy storage system. Recently, a first prototype was shown to deliver 90 Wh/kg for over 2000 cycles [1], even better than the first Li-ion batteries commercialized in 1991 (80 Wh/kg for 1000 cycles). Graphite electrode, commonly used in Li-ion system, shows a poor electrochemical activity in Na-ion system [2]. Thus, new anode materials need to be explored. Theoretically, Sn presents an attractive specific charge of 847 mAh/g by forming reversibly Na$_x$Sn alloy. Even if some works demonstrated good performances over 100 cycles in limited conditions (low loading of the electrodes) [3], Sn electrodes suffer from the volume change exceeding 400% upon cycling. Recently, we have shown that the electrochemical performances of the Sn electrode are strongly dependent on the engineering of the electrode [4]. It was found that micrometer particles associated with a mixture of carbon black / carbon fibers (VGCF) and carboxymethylcellulose (CMC) binder was the best combination while using 1 M NaClO$_4$ in propylene carbonate (PC). We decided to push further our investigations on electrode engineering and have a closer look at the electrolyte. In the present study, the optimized Sn electrodes were tested in NaClO$_4$ based electrolytes with different co-solvent combinations.

Status of project and main scientific results of workgroups

Electrodes were prepared by casting a suspension of 70% wt. Sn powder (325 mesh), 9% wt. Super C65, 9% wt. VGCF and 12% wt. CMC in water onto Al foil. The electrodes were then dried under air, punched and finally dried at 120°C under vacuum. The used solvents for the preparation of the electrolytes are PC, ethylenecarbonate (EC), dimethylcarbonate (DMC) and fluoroethylene carbonate (FEC). Cells were assembled in an argon glove box (O$_2$ and water < 1 ppm) and cycled with an Astrol potentiostat at C/30 rate between 1 V and 0.01 V vs. Na$^+$/Na and, 2h potentiostatic step was added at the end of sodiation.

The Figure 1a displays the galvanostatic curve of the 1st sodiation process of Sn electrode in the different electrolytes. The curves of the PC electrolyte and the mixture EC/DMC are similar with three potential plateaus at 0.2 V, 0.08 V and 0.03 V vs. Na$^+$/Na, typical from Na-Sn reaction mechanisms [3]. For PC/EC and PC/EC/DMC/FEC mixtures, only two potential plateaus can be detected at 0.16 V and 0.05 V vs. Na$^+$/Na. A higher polarization is observed since the first potential plateau is 40 mV lower than in the PC electrolyte. The described phenomenon is even more pronounced for the electrolyte PC/FEC with a first potential plateau at 0.14 V vs. Na$^+$/Na resulting in a difference of 60 mV for the 1st potential plateau with the PC electrolyte. An increase in polarization can be related to a higher resistance (thicker SEI) or from the intrinsic properties of the electrolyte (bad solvation). Due to this higher polarization, the last potential plateau at 0.03 V vs. Na$^+$/Na, visible with PC electrolyte and EC/DMC electrolyte, is not accessible for the electrolyte mixture of PC/FEC, PC/EC/DMC/FEC and EC/PC. Consequently, the specific charge
Batteries

Electrolyte Optimization: The Case of Sn Electrode as Negative Electrode for Na-Ion Batteries

The performances of Sn electrodes with different electrolytes are presented in Figure 1b. Interestingly, the electrolyte combining PC and FEC shows the best electrochemical performances after 27 cycles with a value of specific charge at 350 mAh/g compared to 280 mAh/g in PC electrolyte and to 100 mAh/g in EC/DMC electrolyte. The specific charge for the mixture EC/DMC drops significantly already at the 2nd cycle to reach only 250 mAh/g even if the full sodiated state was obtained at the 1st cycle according to the galvanostatic curve (Figure 1a). The passivation provided by the EC/DMC decomposition is probably not adapted for sustaining volume change upon cycling. A less pronounced decrease is observed for the mixture PC/EC with only 400 mAh/g reached for the 2nd cycle instead of 760 mAh/g for the first one and, after 13 cycles, a value lower than 100 mAh/g is reached. As a comparison, electrolyte containing only PC, reaches a specific charge of 600 mAh/g after the 3rd cycle but certain stability can be achieved with values higher than 500 mAh/g for the specific charge after 15 cycles. It can be assumed that PC is playing a crucial role in the good performance of Sn electrode since mixtures containing another co-solvent than PC are performing badly. The electrolytes containing FEC present the highest reversibility since the specific charge decreases from 650 mAh/g to 550 mAh/g for the PC/FEC mixture between the first and second cycle. FEC is known to provide a good passivation layer in Li [5] and Na-ion batteries, thus after 20 cycles, the specific charge is more stable. As it can be seen in the galvanostatic curves of FEC containing electrolyte (Figure 1a), the full 1st sodiation cannot be reach due to the formation of a thick SEI layer coming from the decomposition of FEC. A longer potentiostatic step at the end of sodiation could leave time to the Na-Sn reaction to take place allowing a better specific charge.

By testing different co-solvent mixture in the electrolyte, we found out that PC and FEC are giving the best electrochemical performances.

References

Novel Nanostructured Electrode Materials for Li-Ion and Na-Ion Batteries

Scope of project

In light of the impending depletion of fossil fuels and necessity to lower carbon dioxide emissions, economically viable high-performance batteries are urgently needed for numerous applications ranging from electric cars to stationary large-scale electricity storage. Sodium-ion batteries (SIBs) are potential low-cost alternatives to lithium-ion batteries (LIBs) because of the much greater natural abundance of Na salts. However, developing high-performance electrode materials for SIBs is a challenging task, especially due to the ~50% larger ionic radius of the Na+ ion compared to Li+, leading to vastly different electrochemical behavior. Herein we summarize our recent work on exploring novel nanostructured conversion-type electrode materials for LIBs and SIBs.

Status of project and main scientific results of workgroups

**Colloidal Bi nanocrystals as conversion-type cathodes for Li-ion batteries**

BiF$_3$ is a highly promising cathode material due to its conversion to Bi$^0$+3 LiF via a three-electron reduction reaction (during discharge), occurring at an average voltage of ~3 V. Due to high specific weight of Bi, the theoretical specific capacity of BiF$_3$ is very high (302 mAh g$^{-1}$), corresponding to an energy density of ~900 Wh kg$^{-1}$, almost two times higher than that of commercial LiFePO$_4$ (one-electron reduction, 169 mAh g$^{-1}$, ~3.5 V and 590 Wh kg$^{-1}$) and LiCoO$_2$ (half-electron reduction, 135 mAh g$^{-1}$, ~3.9 V and 560 Wh kg$^{-1}$). We developed a facile colloidal synthesis of BiF$_3$ nanocrystals (NCs) via thermal decomposition of bismuth(III) trifluoroacetate in oleylamine. The NC size can be tuned from 6 to 40 nm by the adjustment of synthesis parameters. After removal of the capping surfactant molecules, BiF$_3$ NCs were tested as a cathode material for Li-ion batteries. Close to theoretical Li-ion storage capacities of up to 300 mAh g$^{-1}$ at an average voltage of 3 V were obtained at current densities of 50 mAh g$^{-1}$.

**Inexpensive Sb NCs and their composites with phosphorus as Na-ion anodes**

Two Na-ion anode materials – antimony (Sb) and phosphorus (P) – have been recently shown to offer excellent cycling stability (Sb) and highest known Na-ion charge storage capacity (P). In this work we reported on the synergistic Na-ion storage in a P/Sb/Cu nanocomposite, produced by mixing inexpensive colloidal Sb nanocrystals with red P and with copper (Cu) nanowires. In comparison to electrodes composed of only phosphorus, such P/Sb/Cu-composite shows much greater cycling stability providing a capacity of above 1100 mAh g$^{-1}$ after 50 charge/discharge cycles at a current density of 125 mAh g$^{-1}$. Furthermore, P/Sb/Cu-composite also exhibits excellent rate-capability, with capacity of more than 900 mAh g$^{-1}$ at a high charge/discharge current density of 2000 mA g$^{-1}$.

**Metal phosphide NCs as Na-ion anodes**

Metal phosphides such as FeP, CoP, NiP$_2$, and CuP$_2$, remain essentially unexplored as electrode materials for SIBs, despite their high theoretical charge storage capacities of 900–1300 mAh g$^{-1}$. We have developed the synthesis of metal phosphide NCs and assessed their electrochemical properties as anode materials for SIBs, as well as for LIBs. We also compared the electrochemical characteristics of phosphides with their corresponding sulfides, using the environmentally benign iron compounds, FeP and FeS$_2$, as a case study (see Figure 1). We show that despite the appeal-

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**List of abbreviations**

LIB | Lithium-Ion Battery
---|---
NC | Nanocrystal
SIB | Sodium-Ion Battery

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**Figure 1:**
Galvanostatic charge and discharge curves for the first cycle for Na-ion (left) and Li-ion (right) half-cells with working electrodes made of metal phosphides.

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Pyrite (FeS$_2$) nanocrystals as inexpensive lithium-ion cathode and sodium-ion anode materials

Due to its low raw material cost, non-toxicity and potentially high charge-storage capacity pyrite (FeS$_2$) is a highly promising electrode material. We have studied the electrochemical performance of FeS$_2$ NCs as lithium-ion and sodium-ion storage materials. First, we found that nanoscopic FeS$_2$ is a promising Li-ion cathode material, delivering a capacity of 715 mAh g$^{-1}$ and average energy density of 1237 Wh kg$^{-1}$ for 100 cycles, twice higher than for commonly used LiCoO$_2$ cathodes (see Figure 2). Then we demonstrated, for the first time, that FeS$_2$ NCs can serve as highly reversible sodium-ion anode material with long cycling life. As sodium-ion anode material, FeS$_2$ NCs provide capacities above 500 mAh g$^{-1}$ for 400 cycles at a current rate of 1000 mAg$^{-1}$. In all our tests and control experiments, the performance of chemically synthesized nanoscale FeS$_2$ clearly surpasses bulk FeS$_2$ as well as large number of other nanostructured metal sulfides.

Efficient and inexpensive Na-Mg hybrid battery

We have shown a hybrid battery based on a sodium/magnesium (Na/Mg) dual salt electrolyte, metallic magnesium anode and a cathode based on FeS$_2$ NCs presented in previous section (see Figure 3 for the working principle). Importantly, compared to lithium or sodium, metallic magnesium anode is safer due to dendrite-free electrotplating and offers extremely high volumetric (3833 mAh cm$^{-3}$) and gravimetric capacities (2205 mAh g$^{-1}$). Na-ion cathodes, FeS$_2$ NCs in the present study, may serve as attractive alternatives to Mg-ion cathodes due to higher voltage of operation and fast, highly reversible insertion of Na-ions, as demonstrated in previous section. In this proof-of-concept study, electrochemical cycling of the Na/Mg hybrid battery was characterized by high rate capability, high coulombic efficiency of 99.8% and high energy density. In particular, with an average discharge voltage of ~1.0 V and a cathodic capacity of 189 mAh g$^{-1}$ at a current of 200 mA g$^{-1}$, the presented Mg/FeS$_2$ hybrid battery delivers energy densities of up to 215 Wh kg$^{-1}$, comparable to commercial Li-ion batteries and approximately twice as high as state-of-the-art Mg-ion batteries based on Mo$_3$S$_8$ cathodes. Further significant gains in the energy density are expected from the development of Mg/FeS$_2$ electrolytes with broader electrochemical stability window. Fully based on Earth-abundant elements, hybrid Na-Mg batteries are highly promising for large-scale stationary energy storage.

References

Alkali-Ion Rechargeable Batteries

Scope of project

The Fromm group develops 1) LiMnPO4 nanomaterials as cathode, 2) nanoscale transition metal oxide precursors as cathode, and 3) Sn/C composite as anode for alkali (Li+/Na+) ion batteries. And we synthesize silver nanoparticle doped titania nanoparticles and –containers for CO2 reduction in the collaboration with the team working on synthetic fuels (WP4).

Status of project and main scientific results of workgroups

Conventional transition metal oxide materials suffer from the dissolution of transition metal ions in the electrolyte [1]. For safer and high energy Li-ion cathode material, nanosized LiMnPO4 particles were investigated. LiMnPO4 cathodes containing various shapes of nano-LiMnPO4 particles showed that not necessarily the smallest particles of LiMnPO4 have the highest ionic diffusion coefficient but rather the ones with the shortest path length of Li+ diffusion in a particle. Similar analyses are ongoing for nanoscale LiCoO2.

Nanomaterials are known to lead to poor loading of active material in the electrode due to their high volume. We increased the loading of active nanomaterial from 0.2–0.5 mg to 5 mg per cm² via a ball milling process and via controlling the shape of nanoparticles of LiMnPO4. The rate capability test for the best electrode showed 120 and 80 mAh g⁻¹ at C/20 and 1C (Figure 1).

For Li+ and Na+ battery cathode materials, heterometallic single source precursors were explored. For example, sodium phenoxide (NaOPh) reacts with CoCl2 in THF to provide Na0.67CoO2 after calcination at 600°C. However, after washing to remove the residues, the structure of Na0.67CoO2 was destroyed. We are now optimizing the washing conditions and are testing reactions with cobalt sulfate, nickel sulfate, Ni(OH)2, NiBr2, NiI2 and Ni(CH3CO2)2 to obtain new nanoscale mixed oxides.

For a high-energy alkali ion battery anode, tin and carbon composites are studied. The theoretical specific capacity of a Sn anode is about 3 times higher than that of commercial graphite anodes [2]. However, Sn suffers from the extreme volume expansion versus Li+ or Na+ insertion. Therefore, the structure morphology is critical. Tin encapsulated carbon composites were synthesized by reverse micelle formation and by the template method. While one nanoparticle of tin is encapsulated in a shell via the reverse micelle formation method, the template method yielded particles containing several Sn-nanoparticles (Figure 2). Further characterization and the carbon shell synthesis are on-going.

In collaboration with the Broekmann group from the University of Berne, we synthesize silver nanoparticle doped titania nanoparticles and –containers for studying the CO2-reduction [3].

References


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List of abbreviations

TEM Transmission Electron Microscopy
THF Tetrahydrofuran

Figure 1:
Rate capability of thin rod shaped nano-LiMnPO4 electrode.

Figure 2:
TEM image of Sn nanoparticles (black dots) and polystyrene particles (large spheres).
Metal-Air/Metal-Water Rechargeable Batteries

Scope of project

Li-water and Li-O₂ batteries exhibit the potential for offering higher energy density than conventional batteries, such as Li-ion battery (LIB) [1]. This is because lithium metal is used as anode and water or/oxygen as the cathode [2]. The scientific challenges of such rechargeable batteries are the electrochemical reversibility of charge/discharge processes and the generation of selective Li⁺ and O₂/water membranes. For the reversibility, the Fromm group develops aqueous electrolytes as catholyte and ionic liquids as anolyte, while the Park group develops selective membranes.

Status of project and main scientific results of workgroups

During discharge, the pH value increases due to the formation of LiOH, destroying membrane materials and decreasing the solubility of O₂. We could show that acid additives could buffer the high pH and improve the O₂ solubility. In the anolyte part, room temperature ionic liquids are considered as thermally and chemically stable electrolytes [3,4]. We advanced the synthesis of functionalized benzo-15-crown-5 and dibenzo-18-crown-6 to high yield (Figure 1). For the membrane part, a stacked layer structure of graphene oxide was obtained. Controlling the gap of the interlayer will allow the selectivity of Li⁺, water and O₂ as a membrane. The Li⁺ diffusion coefficient of GO membrane was 7.18×10⁻¹² m²s⁻¹ using LiCl aqueous solution (Figure 2).

In order to assemble all components, a Swagelok cell was manufactured and being optimized for assembly. In a first step, carbon black was used as cathode in a full cell assembly while the membrane from Park’s group was under development. The electrodes containing carbon black in a current collector showed pulverization due to the gas evolutions of O₂ and H₂ during discharge. When the current density increased, the amount of gas evolution increased and the adhesion between the current collector and the electrode and the adhesion between the particles in the electrode needs to be strong enough to avoid the pulverization. We are thus optimizing the paste condition for increasing this adhesion.

References

Influence of Stress Cycling on Li-Ion Battery Cells for Vehicle Applications

Scope of project

The development of batteries with high energy densities, long cycle life, and high safety was triggered in the last years due to the growing energy demand, the tendency to use renewable energies, and because of ecological reasons. Today, Li-ion batteries have a large impact on the global market of portable and mobile applications. For optimal usage of Li-ion batteries, management systems as well as charging strategies have to be developed and optimized, requiring an understanding of ageing mechanisms as well as charge transport phenomena in Li-ion cells and their components. According to this we studied the influence of stress cycling on high power A123 AHR32113M1 battery cells made for hybrid power trains [1]. Electrochemical impedance spectroscopy (EIS) measurements [2] and density functional theory (DFT) calculations [3] have been performed, and a more general statistical approach to charge transport was implemented [2] to get an insight on the Li-ion transport in the LiFePO4 cathode material.

Status of project and main scientific results of workgroups

To investigate the influence of stress cycling the following four different cycling strategies have been applied:

- In the first case a power profile, derived from a light vehicle speed profile (WLTC driving cycle class 3), is applied to stress the cell.
- For the other three cases standard discharge-charge (DC-C) cycles have been performed with different state of charge ranges using the average (dis)charge power of the WLTC cycle.

Considering the loss of cell capacity, the DC-C cycles where much more stressful compared to the WLTC cycles. The reduction of the state of charge (SOC) range slowed down the loss of capacity. We can conclude that a driving distance of about 195 000 km could be reached until 20% of the cell capacity is lost by taking into account a full battery, consisting of 70 cells, [1].

EIS measurements have been performed during the stress cycling in the range of 1 mHz to 10 kHz at different SOC. Using an adequate equivalent circuit with constant phase elements (CPE) we were able to model the frequency dependence of the impedance and extract transport parameters with valid physical meaning (circuit and example fit shown in Figure 1) [2]. The charge transport in the cathode was related to the response at low frequencies (1–10 mHz), which appears as a straight line at the right end of the Nyquist plot. In contrast to common assumptions, the slope of this line differs from 45° and changes with the SOC (Figure 2), which we showed is related to the type of charge transport in the systems [2].

From these results we conclude that the Li-ion transport in the cathode is sub-diffusive (trapping of Li-ions occurs) and it depends strongly on the amount of Li present in the...
Influence of Stress Cycling on Li-Ion Battery Cells for Vehicle Applications

LiFePO₄ cathode. With stress cycling a decrease of the angle was observed at the same SOC, indicating a change of the transport properties further away from a diffusive process towards an insulating regime. Moreover, our measurements revealed a correlation between this angle and the capacity of the battery. Thus, this angle can serve as indicator of the quality of lithium transport in the cathode, which is related to cathode structure and degradation.

The transport properties of the cathode are often linked to the state of health (SOH). Therefore a next step will be to evaluate whether the impedance spectrum can be measured on the fly by the battery management system (BMS) in mobile and stationary applications and – based on calibrated data – can be used to monitor the SOH.

In order to understand the origin of the Li-ion transport DFT model calculations have been reviewed. Using a quantum mechanical formalism DFT allows calculating ionic transition states in solids. Diffusion constants can thus be determined without empirical parameters. The cathode material LiFePO₄ exhibits one dimensional Li-ion diffusion channels. Experimental data have been explained by taking into account, e.g., cross channel hopping [3]. At Fe impurities that block 1D lithium diffusion channels, the cross channel hopping appears to be enhanced. It is evident that the limiting factor of the Li diffusion in this material is not the in channel hopping rate. In a next step the influence on stability and ageing of diffusing metal ions and Li-Li correlations will be investigated more deeply.

Microscopic studies on the A123 AHR32113M1 cells using FEI Helios NanoLab Ga-FIB/SEM dual beam and Zeiss Orion He-FIB microscopes gave an insight on the microstructure of the battery components. The isolating three layer separator could be visualized. Dense inclusions containing enhanced amounts of carbon and certain nanoscale features have been identified using these techniques with energy-dispersive X-ray spectroscopy (EDX) analysis (Figure 3) [1]. Further investigations are ongoing.

To conclude, stress cycling, electrical impedance spectroscopy, physical diffusion modelling, statistical charge transport approaches as well as microscopic investigations were combined to identify, characterize and quantify the ageing behavior of Li-ion battery cells. The present results serve as base to establish substantiated selection criteria and design rules for reliable, safe and cost efficient battery systems and their tailored online state of health monitoring.

Figure 3: EDX analysis of a dense inclusion [1]. The line scan, indicated with the yellow bar, revealed an enhanced carbon content in the feature.

References
Manufacturing Technologies and Production Methods for Battery Cells

Scope of project

The research group manufacturing technologies for battery production focuses on the development of innovative, sustainable and cost-effective production technologies for high performance battery cells. Our aim is to support Swiss battery industry such as battery production and equipment suppliers from Swiss machine industry as well as suppliers for electro-chemicals. The purpose is to share machine and process knowledge from a holistic approach to support even smaller firms with deeper process knowledge. With this base additional functionality and value for the battery industry can be created. Further we like to connect the Swiss excellence in electro-chemical research with the production line at the shop floor by demonstrating production at our pilot line.

Status of project and main scientific results of workgroups

As a result of the various mobile and stationary applications, there are different production tendencies which are focused mainly on lithium-ion, sodium-ion or redox-flow batteries. Not only different types of batteries, it is also possible to manufacture them in different sizes and designs. The prime focus lies on lithium based cells. According to their package layout they are grouped commonly as cylindrical, prismatic and pouch cells and are available for miscellaneous utilization purposes.

The conventional lithium-ion battery production is based on two main stages, which are electrode and cell manufacturing. Battery cell manufacturing begins with a drying step and targets to remove residual water from the electrodes. Considering the case type there are different processing methods available. For pouch cell type, cell manufacturing includes cutting, stacking and assembly steps. At this phase there is big improvement potential in terms of process parameters and technologies such as positioning accuracy, cutting tool, cutting speed etc.

It is predicted that, with cooperation of different disciplines such as automation technology, control engineering, data communication and data management, the research studies in this field will pave the way for the smart manufacturing process in an «Industry 4.0» environment. For that reason, at the BFH, a research group is implementing a pilot production line which is based on battery cell manufacturing. Therefore the pouch cell design as a future-oriented case type was decided for this production.

At the first stage of this project it is planned to establish an assembly line that includes cutting, handling and stacking steps for electrodes and separator. It should be mentioned that the production line is aimed for the experimental purposes of research groups, industrial partners and also for demonstrating the battery cell assembly. For the cell chemistry it is forseen to use first lithium-ion and later sodium-ion technology.

The team cooperates with research groups at BFH Energy Storage Research Center ES-Rec at the InnoCampus Biel. Simultaneously it supports the know-how-transfer between research units – such as ETHZ, PSI, University of Freiburg – for the development of new, suitable as well as cost-efficient manufacturing technologies of battery cells.

References


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Work Package 2 at a glance

In Switzerland, nearly 50% of the total energy is consumed in the form of heat. The consumption can be classified into 60% for space heating, 27% for process heat, and 13% for warm water. Several projects are ongoing within work package 2 to tackle materials and systems development for low-temperature seasonal heat storage for building applications and high-temperature heat storage for industrial applications.

The seasonal storage concept is based on the absorption and desorption of aqueous sodium hydroxide. For high-temperature storage, material-systems development focuses on phase-change materials such as aluminum-silicon encapsulated in steel and silicon-infiltrated silicon-carbide lattices. A specific target application of high-temperature storage is advanced adiabatic compressed air energy storage, which is investigated with simulations and will also be assessed with pilot-scale experiments.
High-Temperature Combined Sensible/Latent-Heat Thermal Storage

Scope of project

Thermal energy storage (TES) at high temperatures (> 300°C) is relevant to the Swiss Government’s Energy Strategy 2050 for two main applications. One is advanced adiabatic compressed air energy storage (AA-CAES), where a TES recovers the thermal energy generated by compressing air to high pressures and resupplies it when the compressed air is expanded to run a turbine and generate electricity. Energy efficiencies of AA-CAES can be as high as 70–75% [1], which makes it competitive with pumped hydro energy storage [2]. The second application comprises industrial processes where TES can be used to recover waste heat. This application is important because process heat accounts for about 50% of the total energy use in Swiss industry.

Status of project and main scientific results of workgroups

The overall focus of our work is the development and demonstration of an efficient and cost-effective thermocline TES. Previous work has shown that a TES consisting of a packed bed of rocks (sensible heat storage) and air as heat transfer fluid (HTF) can yield 95% overall (charging-discharging) energy efficiency [3]. However, one drawback of sensible-only TES is the HTF outflow temperature drop during discharging. Simulations and experiments showed that replacing a small amount of rocks (1–5% by volume) with an encapsulated phase-change material (PCM) is sufficient to stabilize the outflow temperature during discharging [4].

In the second year of this research project we extended the numerical analysis of combined sensible/latent TES, with emphasis on the assessment of exergy efficiency and material costs of sensible and combined storage units. Furthermore, the quasi-one-dimensional heat-transfer model was extended to predict the behaviour of an AA-CAES pilot plant that is being built by Airlight Energy SA in Pollegio, Switzerland.

The heat-transfer model was validated with laboratory-scale experiments [2, 4]. The validated model was used to compare sensible-only and combined TES for two industrial-scale storages after steady cycling conditions were reached [4]. The parameters of primary interest were exergy efficiency and specific material costs. The exergy analysis includes the pumping work that cannot be neglected for large storages.

Figure 1 shows the exergy efficiency as a function of the maximum temperature drop during discharging for TES systems of 1000 MWh discharge capacity. To reduce the temperature drop during discharging with sensible-only storages, the TES must be oversized. Due to the larger storage sizes of the sensible-only TES, the pumping work dominates the exergy losses through thermal losses and internal heat transfer.

In contrast, the total size of the combined storage can be kept constant and lower temperature drops are reached by replacing more rocks with PCM, leading to higher exergy efficiencies. In addition, due to the smaller volume of the combined storage, specific material costs are lower than

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**Figure 1:** Exergy efficiency and exergy loss breakdown as a function of the maximum temperature during discharging for a 1000 MWh storage.

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**List of abbreviations**

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<tr>
<th>Abbreviation</th>
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<tr>
<td>AA-CAES</td>
<td>Advanced Adiabatic Compressed Air Energy Storage</td>
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<tr>
<td>CFD</td>
<td>Computational Fluid Dynamics</td>
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<td>HTF</td>
<td>Heat Transfer Fluid</td>
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<td>PCM</td>
<td>Phase Change Material</td>
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<td>TES</td>
<td>Thermal Energy Storage</td>
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Heat for the sensible-only storage for a given maximum temperature drop during discharging. With specific material costs of $5–7/kWhth and exergy efficiencies above 96%, the combined storage exceeds the goals of the U.S. Department of Energy’s SunShot Initiative (costs < $15/kWhth and exergy efficiencies above 95%).

The 1D heat-transfer model was also compared to 2D computational fluid dynamics (CFD) simulations [5]. Figure 2 shows the temperature distribution of the laboratory-scale storage predicted by the 1D and 2D models. The results of the 2D model confirm that radial gradients are significant in this storage. Nevertheless, the overall agreement of the 1D model with experimental data is good [4]. It can therefore be applied with confidence to larger storages where radial gradients are known to be less significant.

One application of the 1D model is to the AA-CAES pilot plant in Pollegio (see Figure 3). A tunnel is used as a cavern to store the compressed air and a TES will be used for the heat recuperation. The system will be tested at pressures up to 33 bars. The 1D heat-transfer model was extended to simulate the cavern pressure and temperature also. The extended model is being used for the design of the experiments that will be performed with the pilot plant. Figure 3 also shows the simulated temperature profile in the packed bed of rocks and the insulation of the pilot-plant storage.

Future work will focus on the experiments with the AA-CAES pilot plant, planned for April 2016. The results will be used to further validate the model at high operating pressures. Furthermore, different techniques for steepening the thermocline inside the TES will be studied because this allows further decreases of the storage size and material costs without sacrificing performance.

**References**


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**Figure 2:** Temperature distribution of the 1D (left) and 2D (right) models for a laboratory-scale storage.

**Figure 3:** TES for AA-CAES pilot plant in Pollegio, Switzerland: Photograph (left) and simulated temperature distribution in °C (right).
Scope of project

The development of reliable and cost-effective thermal energy storage (TES) systems is among the main technical challenges to realize the long-term energy policy (Energy Strategy 2050) developed by the Federal Council. In the field of high-temperature TES, packed beds with low-cost filler material can be considered as representative solution for sensible heat storage and even the most suitable for air-based systems such as advanced adiabatic compressed air energy storage (AA-CAES). However, an intrinsic drawback of this solution is the decrease of the heat transfer fluid (HTF) outflow temperature, towards the end of discharging. This drawback can be mitigated if a latent TES is exploited instead. However, the high cost of the phase change material (PCM) is among the limiting factors on its integration into an AA-CAES plant. For this reason, the idea of adding a small amount of PCM on top of a packed bed was proposed, and experimentally evaluated [1, 2], with the aim of stabilizing the HTF outflow temperature during discharging limiting, at the same time, the increment of the overall TES system cost.

The present study aims at modelling, by means of time-dependent 2D computational fluid dynamics (CFD) simulations, the behaviour of an experimental lab-scale combined sensible/latent heat storage which uses air as HTF.

Status of project and main scientific results of workgroups

**Experimental combined sensible/latent heat storage**

A schematic of the 42.3 kWh combined TES prototype is reported in Figure 1. A packed bed of gravel was exploited as sensible heat storage. AlSi12 alloy was selected as suitable PCM material for high temperature applications. It was encapsulated in steel tubes positioned on top of the packed bed. Pebbles and encapsulated PCM were located into a 1.68 m high cylindrical stainless steel tank, 0.4 m external diameter.

As depicted in Figure 1 (right), the prototype is equipped with several thermocouples (TCs). During charging, hot air is fed through the TES from top delivering its thermal energy to the PCM and rocks leaving then the system from the bottom. Conversely, during discharging, the energy is recovered by reversing the air-flow direction with the HTF entering the TES from the bottom and leaving it from top.

**CFD model**

A CFD-based approach was applied to evaluate the thermo-fluid dynamics behaviour of the TES prototype accounting for the effect of channeling, i.e. radial variation of the void-fraction. The axisymmetric characteristic of the prototype was exploited to build a 2D computational domain. Grid-independent results were obtained with a grid of about 360,000 quadrilateral cells. The packed bed and the bank of tubes were modelled exploiting the porous media approach [3]. Local thermal non-equilibrium between solid matrix and fluid phase was assumed. Thermal energy losses were also considered.

**Sensible heat section**

In the case of randomly packed homogeneous spherical particles, the void-fraction in the bulk region ranges between 0.36–0.42 [4]. Near the containing wall, the arrangement of the particles is sensibly modified for a distance of approximately 5dₚ from the wall. In this near-wall region, the void-fraction follows a damped oscillatory variation, from a value close to unity at the wall to a minimum of 0.2 at a distance of about dₚ/2 from the wall. In the case of packed beds of rough 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 rather

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<td>Computational Fluid Dynamics</td>
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<td>Differential Scanning Calorimetry</td>
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<td>FVM</td>
<td>Finite Volume Method</td>
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<td>Heat Transfer Fluid</td>
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<td>LTNE</td>
<td>Local Thermal Non-Equilibrium</td>
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<td>Phase Change Material</td>
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<td>Thermocouple</td>
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**Figure 1:** Schematic of the pilot-scale combined TES (left) and TCs position (right).

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short distance [5]. The average void-fraction in the packed bed is also affected as long as the vessel-to-particle diameter ratio is lower than 25–30 [6, 7]. Since the lab-scale TES is characterized by a diameter ratio of about 12.5, the radial void-fraction distribution is included in the model [8].

**Latent heat section**

The effective heat capacity method [9] was exploited to model the phase transition of the PCM. With this approach, the phase transition is modeled as sensible process, i.e. non-explicit phase change tracking, with the latent heat of fusion combined into the specific heat of the material. PCM and encapsulation were modeled as a single material with equivalent thermo-physical properties. Radiation from the top plate to the topmost tube row was accounted for by adding a source term that was extracted from the results of a 1D model [10].

**Conclusions**

A 2D CFD model of a lab-scale combined sensible/latent heat storage was validated with experimental data. The overall agreement between the simulations and experimental results is fairly good. Further effort is still required to improve the model accuracy in replicating the behavior of the lab-scale prototype during discharging. Figure 4 and Figure 5 show the temperature contours into the TES prototype during charging and discharging respectively; the importance of channeling on the heat transfer into the packed bed can be easily noticed by the resulting thermal gradients in the radial direction.

References

Phase Change Material Systems for High Temperature Heat Storage

Scope of project

The development of technologies for energy storage has been intensified in recent years driven by the disparity between energy availability and demand. Latent heat storage by means of phase change materials (PCMs) has proven to be an attractive heat storage technology. Such a heat storage system consists of an encapsulation, a phase change medium contained in the encapsulation and the heat transfer fluid (HTF). Multi-mode heat transfer will transfer the heat from the HTF through the encapsulation into the storage medium, and vice versa. The design of the storage system (dimensions, architecture, etc.), the material choices and combinations (metals, ceramics, etc.), and the operating conditions (mass flow rate of HTF, pressure, temperature, etc.) determine the performance of the system. The heat storage medium should have a high heat of fusion, such that high energy densities can be achieved, and a high conductivity, such that high charging and discharging rates can be achieved. The encapsulation guarantees mechanical and chemical stability. The specific choice of the component’s material is challenging and requires a careful evaluation.

Aluminium ($T_{\text{melt}} = 600 \, ^\circ\text{C}$) or aluminium alloys ($T_{\text{melt}}$ range $460 - 670 \, ^\circ\text{C}$) encapsulated in steel using air as HTF are two promising combinations that are experimentally and numerically evaluated.

Status of project and main scientific results of workgroups

Figure 1 illustrates the melting process of Al-12Si encapsulated in AISI 316L steel calculated in a 2D simulation domain.

A hollow cylinder of outer diameter 21.3 mm and wall thickness 2 mm is simulated in a laminar flow of air at 10 m/s and 727 °C, 148 °C above the melting temperature of Al-12Si, flowing from left to right. The PCM and encapsulation were initially at 578 °C, the liquid fraction is illustrated after 16 s of physical time. The melting process was simulated using the enthalpy method [1], implemented in an in-house code using unstructured meshes in collaboration with Dr. Haselbacher.

The results show that no melting front exists. Instead the melting is homogeneous and the range of liquid fractions is between 3.57% and 3.61%, larger closer to the encapsulation. The deviation from radial symmetry is close to negligible in this case although for different HTF temperatures and heat transfer rates the asymmetry might be more pronounced.

Currently, an implicit scheme is implemented in order to circumvent computational limitations in the current explicit scheme. This novelty will allow for three dimensional analysis. This code additionally already allows simulating the radiative heat transfer in complex geometries [2]. In the longer term it will be possible to simulate real systems including the effect of all modes of heat transfer.

The enthalpy method was chosen based on good agreement of simulation results with measurements.

For validation purposes, two experimental campaigns were run utilizing different PCMs:
- 99.99% pure aluminium contained in an aluminium oxide crucible, and
- Al-12Si alloy in an Al-Si 316L steel container.

The PCM was melted and solidified representing one charging and discharging cycle. Up to 10 consecutive cycles were conducted.

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Authors

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Sophia Haussener¹

¹ EPFL
Phase Change Material Systems for High Temperature Heat Storage

In the future, larger numbers of consecutive cycles will be tested in combination with an accelerated aging protocol to assess and quantify degradation and lifetime of these heat storage systems.

Results of the first campaign

The aluminium was contained in a crucible of 19 mm outer diameter and 1.5 mm wall thickness and heated up to 460°C in an electrical furnace before being cooled down to 227°C by controlling the surrounding air temperature. The temperature was measured in the centre of the PCM using a K-type mineral insulated thermocouple. The measured temperature history is illustrated in figure 2 and compared to numerical results. The measurement clearly shows that the phase change processes occur isothermally for the case of pure aluminium. For the numerical simulation radial symmetry was assumed, such that it could be performed in one dimension. The enthalpy method [1] was used. Aluminium properties were taken from [3]. The radiative heat exchange between the oven wall and the crucible was taken into account using analytical formulas for two concentric cylinders [4]. The numerical and experimental results are in good agreement with the largest deviations observed when the sample is completely melted and further heated. The simulations show that radiation dominates conductive and convective heat transfer.

Similar results have been obtained for Al-12Si [5]. In addition to model validation, the developed coupled experimental-numerical methodology allows for a general characterization and quantification of encapsulated PCM systems, their performance (energy density, charging and discharging rates), and their material properties (melting temperature, temperature range over which a material is melting, latent heat of fusion). More challenging material combinations will be investigated in the future such as copper (T\text{\text{melt}} = 1085°C) in a SiC enclosure.

Besides mechanical and chemical stability, the main criteria for judging the heat storage system design is optimal heat transfer from the HTF to the PCM; fast charging and discharging; high energy density. Different rates of heat transfer will be required depending on the application. Different designs (tube dimensions, number of tubes, etc.) are expected to turn out to be optimal depending on the PCMs and encapsulations. One important value is the size of the tube or tube-like structures containing the PCM. Our 2D simulations showed that the heat transfer between a fluid flowing around large cylinders turns out to be too low for practical applications, such that using porous materials will be an interesting option (figure 3). In a next step, different material combinations will be numerically tested to specifically match the requirements given by several industrial applications such as in the cement or glass industry.

The long term goal is to derive simplified models based on the results of the full three dimensional simulations to allow a full assessment of different designs and materials, from a technical, economic and ecological point of view.

Acknowledgement

The financial support of CTI Swiss Competence Centers for Energy Research (SCCER Heat and Electricity Storage) and the National Research Program «Energy Turnaround» (NFP70) of the SNFS is kindly acknowledged.

References


Figure 2:
Temperature in the center of aluminium contained in an Al2O3 crucible during melting and solidification; measurement and simulation.

Figure 3:
Heat storage solutions: from hollow cylinders to porous materials.
High Temperature Thermal Shock and Oxidation Behavior of SI-Infiltrated SIC Lattices

Scope of project

Open-celled cellular ceramics are attractive structures for high temperature applications such as heat exchangers, recuperators, solar receivers and heat storage systems [1]. Si-infiltrated SiC is considered as a desirable material for these structures due to its enhanced thermal and mechanical properties at high temperatures (above 1000°C).

Because of the demanding conditions, these structures are often subjected to thermally induced stresses. These can induce local crack formations followed by local failure of the structure. Besides, in presence of air, both Si and SiC oxidize in either passive or active mode. Passive oxidation results in formation of a protective SiO$_2$ layer while active oxidation forms volatile SiO causing material gradual weight loss [2, 3]. This work analyses both phenomena in two different environments at 1400°C.

Status of project and main scientific results of workgroups

Experiments

3D printed templates with five different geometrical structures were ceramized using replica technique followed by silicon infiltration in 1450°C (EngiCer SA, Balerna, CH). Figure 1 depicts the SiSiC Lattices with relative densities ranging 0.08–0.18. Three sets of experiments were designed to observe the behavior of porous structures in two different oxidative environments at temperatures up to 1400°C.

A group of samples was thermally shocked in a porous burner (group A), as shown in Figure 2, while the other group (group B) was oxidized in the steady state condition of an electric air oven. Samples’ microstructure and mechanical behavior were then characterized.

Optical microscopy

After the tests, it was observed that approaching to 1400°C, silicon was out-melted from the structures (Figure 4). Beads as large as 4 mm in diameter were found on some samples. Group A specimens had different colors on their surfaces, likely due to different SiO$_2$ thickness in each region. Group B samples were all gray, showing a thicker homogeneous SiO$_2$ scale (Figure 3).

Oxidation

Both passive and active oxidation modes were found in thermally shocked samples. Scanning electron microscope (SEM) analysis showed the
Heat

High Temperature Thermal Shock and Oxidation Behavior of SI-Infiltrated SIC Lattices

presence of whiskers-like SiO₂, which were in a ring shape (Figure 6) around some struts. Group B instead went through a homogeneous passive oxidation. All the samples had a weight gain showing that passive mode was the dominant oxidation mode for both groups. The bead formation is likely due to oxidation of Si and SiC in the microstructure and formation of SiO₂ and thus forcing the melted Si out of the microstructure [4].

**Conclusions**

The samples survived the thermal shock test in the porous burner. Si exudation is believed to be the main reason for low strength in samples of group B. The phenomena can be due to penetration of SiO₂ inside the microstructure, which squeezes out the molten silicon. Samples of group A were heavily oxidized on the bottom part where the temperature was at maximum (1400°C). This can be due to presence of water vapor in the fluid flow, which reacts with both Si and SiC phases of the material much faster than oxygen.

**Damage and mechanical strength**

To examine the extent of damage, all samples were mechanically tested in a compression configuration and were compared with as produced specimens. As shown in Figure 7, thermally shocked samples didn’t show any decrease in their strength. However, group B had a strength drop off which can be due to silicon exudation from the microstructure.

References


Figure 3 (left): Gray surface of samples group B, right: Various colors coming from different oxidation thickness on surface of samples group A.

Figure 4 (right): Beads of molten silicon inside and outside of structure.

Figure 5 (left): SEM analysis from a fractured surface of thermally shocked lattices (group A).

Figure 6 (right): Ring shaped Silica layer on a strut of a sample of group A.

Figure 7: Compression strength results for 45 samples with five different structures.
Aqueous Sodium Hydroxide Seasonal Thermal Energy Storage: Reaction Zone Construction and Assessment

Scope of project

In the frame of the EUFP7 project «Combined development of compact thermal energy storage technologies – COMTES», the falling film absorption and desorption technology was identified as a promising technology for developing a seasonal thermal energy storage.

With the concept of separating
• the power – the reaction zone (absorption & desorption and evaporation & condensation) and
• the capacity – storage of sorbent and sorbate in individual tanks,
a power and capacity scaling can be done separately. The heat and mass exchanger modelling having been carried out [1], the results were used to size, design and manufacture the unit. Once done, the last year the heat and mass exchanger was commissioned and experimentally assessed [2, 3].

Status of project and main scientific results of workgroups

Heat and mass exchanger manufacturing

The components of the heat and mass exchanger are shown in Figure 1. Two challenging design concepts were used: modularity (each component is easily dismountable) as well as a limited number of vacuum sealing gaskets for the vacuum envelope.

For processing and handling reasons as well as for fluid separation, both A/D (Absorber/Desorber) and the E/C (Evaporator/Condenser) units are placed in different containers (Figure 1). The vapour feed connects through both units, enabling the required exchange of vapour in both directions. Additionally it should only act as mass transfer unit and, therefore, should create a thermal infrared barrier. Thus, a nickel plated and bended metal sheet was implemented. It will predominantly form a radiation shield (radiative disconnection due to the high reflectivity of the 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 challenging was the nozzles manufacturing from 1.4404 stainless steel alloy. From the other possible designs, a version with nozzles directly machined in a stainless steel plate was selected. Using this solution, a high flexibility on the nozzle geometry is reached, enabling a good liquid distribution.

Experimental results obtained with the demonstrator

The first non-isothermal experiments campaign showed that the exchanged power during the discharging process (absorption) is quite lower than expected. Only a small concentration decrease from the initial 50 wt% sodium hydroxide solution is reached at the outlet of the absorber unit. Therefore, instead of emulating yearly operating of a building, measurements were run in steady state conditions in order to characterize the heat and mass exchangers and to...
Aqueous Sodium Hydroxide Seasonal Thermal Energy Storage: Reaction Zone Construction and Assessment

The wetting of both tube bundles 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 modelling), a power of 9.5 kW can be reached. Figure 3 (right) shows that the desorber modelling is relatively accurate in terms of power, especially around the nominal power value. In this point, the measured power differs from the predicted value with less than 25% of relative error.

Further work will be carried out at lab scale in order to improve the low heat transfer encountered during the absorption process. Thus, the wetting [4] between the viscous fluid (sodium hydroxide at ambient temperature and high concentration) and the heat and mass exchanger has to be increased. The use of surfactants [5] as well as surface texturing and coating are currently investigated. An increase of the heat and mass transfer interface area is also considered (use of metallic fibres for example).

Figure 2:
Discharging process: development of the power ($\Phi$) in function of the temperature difference ($\Delta T$) between both absorber and evaporator chamber (left) and of the absorption power in function of the linear mass flux ($\Gamma$) arriving on the absorber (right).

Figure 3:
Charging process: development of the power ($\Phi$) in function of the temperature difference ($\Delta T$) between both desorber and condenser chamber (left) and comparison of the measured exchanged power with the modelling results (right).

References
**Low Temperature Pumped Heat Energy Storage (LT-PHES)**

**Decentralized Heat Supply and Electricity Storage with Combined Heat Pump and Power Cycle Process**

**Scope of project**

The process as sketched in Figure 1 uses water as storage medium due to its non-toxic features and its abundant availability. It is further envisaged to use this medium in a range which can be handled with techniques already well established in domestic application, i.e. at ambient pressure and with temperature changes limited between 0°C and 100°C. On the other side the working fluid to be used is a refrigerant. The inherent problem of a storage medium with sensitive heat (no phase change) and a working fluid with latent heat, resulting in large temperature differences in the heat exchangers, is addressed by varying the pressure level of the working fluid during charging and discharging. By this more or less the same temperature differences in the heat exchangers can be ensured, as shown in Figure 2 for charging (heat pump process).

**Status of project and main scientific results of workgroups**

Besides the considerable advantages due to the media to be used, potential difficulties have to be faced in view of the turbomachinery. These are

- wide range in pressure ratio;
- wide range in volume flow (for adaption of power demand/availability);
- high Mach numbers (due to low speed of sound of refrigerant);
- expansion into a two-phase region (when overheating is not envisaged to avoid additional heat storage).

All this goes along with efficiency penalties. The high variability in pressure and volume flow range is to be addressed by the use of variable shaft speed and variable stator vanes (or nozzles, resp.). The amount of wetness due to expansion into a two-phase region strongly depends in the refrigerant to be used and the aerodynamic efficiency of the turbine. For a given refrigerant, the wetness at the end of the expansion is higher the higher the aerodynamic efficiency is (Figure 3). The wetness causes additional losses (so-called wetness losses). Such losses are more or less well known for water steam and in combination with axial turbines, but not for refrigerant and the completely

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**List of abbreviations**

- CHP: Combined Heat and Power
- LT-PHES: Low Temperature Pumped Heat Energy Storage
- PV: Photovoltaics
- TES: Thermal Energy Storage

**Figure 1 (left):** Components of LT-PHES (Low Temperature Pumped Heat Energy Storage).

**Figure 2 (right):** Charging process at begin (top, from 5.9 to 16.4 bar) and end (bottom, from 3.4 to 27.9 bar).

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Heat

Different flow path in a radial turbine. On the other hand, with a low aerodynamic efficiency the wetness content is inherently lower and therefore also the wetness losses are lower. These two effects have to be weighted in order to ensure sufficiently high over-all efficiency over the entire process.

For some refrigerants Figure 4 shows the maximum polytropic efficiency as function of gradient of saturation line for several refrigerants.

Table 1:
Scenarios considered for generation of Pareto curves with respect to levelized cost of energy vs CO\textsubscript{2} emissions.

<table>
<thead>
<tr>
<th>Scenario</th>
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For some refrigerants Figure 4 shows the maximum aero-dynamic efficiency that still allows an expansion taking place in the gaseous phase. According to this for R134a, e.g., starting from 20 bars, one would opt for efficiencies not higher than 80%.

Alstom provided several simulations for the annual need of electricity and heat (respectively cold) for a representative block of buildings, when this need was covered by (see Table 1)

- electricity from photovoltaics (PV), combined heat and power (CHP) or wind in combination with fossil heating (scenario 1);
- batteries are added for storage (scenario 2);
- instead of batteries a heat pump is used (scenario 3);
- or a heat pump plus a storage for heat (TES) (scenario 4);
- or – on top of this – a power cycle is implemented (PHES) (scenario 5);
- or instead of the power cycle again batteries are used (scenario 6).

Scenario 5 represents the present LT-PHES process.

For these scenarios Pareto curves were evaluated for the levelized cost of energy in €/MWh against CO\textsubscript{2} emissions (specific CO\textsubscript{2} emissions in kg CO\textsubscript{2}/MWh).

The result (see Figure 5) shows that scenario 5 is equivalent to scenario 6, meaning that the proposed PHES-process has a very high potential. The advantage of the PHES-process is, however, the usage of existing and well established technologies.
Hydrogen is an inherently clean energy vector provided the gas is produced from renewable sources or with the help of renewable energy. The partners in work package 3 are focusing on the one hand on the production of hydrogen via water electrolysis as well as via a combined redox-flow cell/catalytic reactor. On the other hand, storage of hydrogen gas is addressed by developing advanced hydrides with increased storage capacities and the hydrogen storage in formic acid reaction cycle.
Hydrides for Energy Storage

Scope of project

The hydrogen cycle allows for storing hydrogen produced by renewable energy and does not contain carbon (CO₂ neutral). Hydrogen exhibits the greatest combustion energy by mass of all known materials [1]. Hydrogen can be produced in large quantities from water by electrolysis using renewable energy. Finding a material that allows for storing hydrogen with high hydrogen density and fast hydrogen sorption kinetics [2, 3] is requested by most applications, and, therefore, several options are under consideration. Liquefied hydrogen, pressurized hydrogen in tanks, metal hydrides and complex hydrides have been intensively investigated.

Status of project and main scientific results of workgroups

The challenge is to understand the interactions of the hydrogen molecules or atoms with solid materials or surfaces on an atomic level in complex hydrides in order to develop the ideal materials for the application. The identification of the decomposition reaction pathways of complex hydrides, the determination of the intermediate species in dehydrogenation reactions, the emission of side products and the role of catalysts are the subjects of the ongoing research [4] that require the most advanced characterization instruments and a profound knowledge of the chemical physics of gas-solid interactions.

In the materials under consideration, the quantitative targets for hydrogen capacities vary significantly depending on the different applications, e.g. the gravimetric and volumetric density is crucial for mobile applications, whereas in stationary systems, the gravimetric hydrogen density plays a minor role [5, 6] (see Figure 1). Therefore, for each specific application, the targets related to volumetric density, thermodynamics, kinetics, cost and safety are different.

The focus of our research activities is on hydrogen in solid compounds, is on complex hydrides which can store up to 20% wt. of hydrogen. Most of the known complex hydrides are too stable for mobile or even stationary applications and require high temperatures of several hundred °C to desorb the hydrogen. However, several complex hydrides exist, which are liquid at room temperature, e.g. Al(BH₄)₃ and Ti(BH₄)₂, and spontaneously desorb hydrogen around room temperature. Little is known about the properties of these compounds, because due to
the low stability the compounds tend to decompose during the experiment. The goal of our work is to investigate unstable complex hydrides and to develop methods to stabilize the materials. Furthermore, it is of fundamental scientific interest how the stability correlates with the melting temperature and the surface properties of the complex hydrides.

Liquid complex hydrides are a new class of hydrogen storage materials with several advantages over solid hydrides, e.g. they are flexible in shape, they are a flowing fluid and their convective properties facilitate heat transport. The gas-phase molecules of Ti(BH4)3 decompose rapidly after formation in inert atmosphere [7]. The physical and chemical properties of a gaseous hydride change when the molecules are adsorbed on a material with a large specific surface area, due to the interaction of the adsorbate with the surface of the host material and the reduced number of collisions between the hydride molecules.

We can report now the synthesis and stabilization of gaseous Ti(BH4)3. The compound was successfully stabilized through adsorption in nanocavities. Ti(BH4)3, upon synthesis in its pure form, spontaneously and rapidly decomposes into diborane and titanium hydride at room temperature in an inert gas, e.g. argon. Ti(BH4)3 absorbed in the cavities of a metal-organic framework is stable for several months at ambient temperature and remains stable up to 350 K under vacuum. The adsorbed Ti(BH4)3 reaches approximately twice the density of the gas phase. The specific surface area (BET, N2 adsorption) of the metal-organic framework (UiO-66) decreased from 1200 m$^2$g$^{-1}$ to 770 m$^2$g$^{-1}$ upon Ti(BH4)3 adsorption [8] (see Figure 2).

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### References

T. Frankcombe, Chem. Rev., 112, 2164 (2012);

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**Figure 2:** Impregnation of Metal Organic Framework UiO-66 with the volatile complex hydride Ti(BH4)3 (top) and the analysis of the desorption products.
The Origin of the Catalytic Activity of a Metal Hydride in CO₂ Reduction

Scope of project

To secure future energy supplies and to limit anthropogenic carbon dioxide emissions, a sustainable energy society is to be based on a closed energy material cycle. Renewable energies need to be stored in energy carriers such as synthetic hydrocarbons with the energy density comparable to fossil fuels (e.g. petrol). The raw materials base by using carbon dioxide (instead of crude oil) needs to be expanded in the chemical industry. In the short term, carbon dioxide (flue gas) is captured from the various point sources such as fossil fuel power stations and factories. In the long term, carbon dioxide is captured from the atmosphere to close the material cycle for energy (artificial photosynthesis). To store renewable energy in synthetic hydrocarbons, the reduction of carbon dioxide, as well as the capture of carbon dioxide, are the major challenges. [1]

Status of project and main scientific results of workgroups

Carbon dioxide can be reduced to hydrocarbons by binding hydrogen via the following heterogeneous catalytic reactions:

\[ \text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O(g)} \] (the Sabatier process, \( \Delta H^{\circ}_{\text{298K}} = -165 \text{ kJ/mol} \)),

\[ \text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O(g)} \] (reverse water-gas-shift reaction (RWGS), \( \Delta H^{\circ}_{\text{298K}} = 41 \text{ kJ/mol} \)).

The Fischer-Tropsch process delivers diverse hydrocarbon products in the range of 1 to >20 carbon atoms. The direct and indirect hydrogenation of carbon dioxide and carbon monoxide leads to several reactions, depending on the kinetics and thermodynamics, towards the production of hydrocarbons. For the hydrogenation, a surface of metal with high solubility of hydrogen is of particular interest, in view of control of the reaction (Figure 1).

The catalytic activity of the metal hydride ZrCoHₓ was analysed as a function of the hydride composition ZrCoHₓ (\( x = 0, 0.1, 1.2, 2.9 \)) (Figure 2). The samples were loaded into a fixed-bed tubular flow reactor. Carbon dioxide, hydrogen and helium (carrier gas) were admitted into the reactor. In a mixture of hydrogen and carbon dioxide, methane was markedly formed on the metal hydride ZrCoHₓ in the course of the hydrogen desorption and not on the pristine intermetallic.

The surface analysis was performed by means of near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS), for the in situ analysis (Figure 3), and time-of-flight secondary ion mass spectroscopy (ToF-SIMS). The aim was to elucidate the origin of the catalytic activity of the metal hydride. For the metal hydride, the hydrogen desorption leads to a complete reduction of cobalt. This suggests the origin of the catalytic activity of the metal hydride,
with respect to the reactivity of hydrogen, and the hydrogen molecules impinging on the surface of metallic cobalt can readily dissociate into hydrogen atoms.

The atomic hydrogen flux from the metal hydride is crucial for the reduction of carbon dioxide and surface oxides, especially at grain boundaries or adlination sites, while at the initial stage, the dissociation of hydrogen molecules from the gas phase is hindered by the high activation barrier on the oxidised surface. The higher the hydride composition, the higher the concentration of active sites and hence, the better the activity that increases with metal hydride composition. It is expected that this effect be found also for various supported and unsupported bulk catalysts, composed of hydrogen-absorbing materials [5].

**Figure 2:**
The formation of CH₄ on ZrCoHₓ (x = 0, 0.1, 1.2, 2.9) in the flow of CO₂, H₂ (H₂/CO₂ = 5), and He (carrier gas). The ion current ratio m/z = 2(H₂⁺) to m/z = 4(He⁺) vs. temperature (5°C/min) (top). The ion current ratio m/z = 15(CH₃⁺) to m/z = 4(He⁺) vs. temperature (5°C/min) (bottom). For both, the intensities at 150°C are the background levels.

**Figure 3:**
The Co 2p XP spectra of ZrCoHₓ measured in the atmosphere of hydrogen at 1.0 mbar and at the temperatures of 25°C and 240°C, respectively, and the reaction mechanism. Initially, the surface is covered with surface oxides. The hydrogen desorption, namely, the atomic hydrogen flux from the metal hydride, leads to reduction of cobalt oxide and carbon dioxide. Hydrogen can spill over to formate, resulting in formation of methane and water. [5]

**References**
Advances in the Development and Characterization of Water Electrolysis Catalysts at the EPFL

Scope of project

The development and characterization of novel electrodes for water electrolysis are central objectives of the new catalyst testing platform facilities in LIMNO at EPFL, which successfully opened this year thanks to the SCCER. This competence lab, shown in Figure 1, aims to build expertise in the assessment of heterogeneous catalysts for both water oxidation and reduction, the analysis of produced gases, as well as in the advanced electronic characterization of (photo-) electrodes and processes. A non-exhaustive list of equipment currently available includes apparatus for solution-processed thin film deposition (Sol Gel, Spin Coating, Spray Pyrolysis), electrodeposition, and ovens able to provide annealing under controllable atmosphere. Electrode characterization techniques available in-house include X-Ray Diffraction (XRD), Raman spectroscopy, electrochemical performance assessment (Potentiostat), transient and frequency modulated techniques (EIS), a homemade solar simulator and monochromatic LED illumination setup.

Status of project and main scientific results of workgroups

Within this framework, we have pursued our investigations on 2-D transition metal dichalcogenides (TMD, e.g. WS₂ or WSe₂), which are globally considered as promising catalysts for both oxygen evolution reaction (OER, water oxidation) and hydrogen evolution reaction (HER, water reduction).

We have recently shown that these compounds can be exfoliated into 2-D nano to micron sized flakes and assembled with a controllable and cost effective technique, opening new horizons for this family of materials as catalysts for the water reduction reaction [1]. Future work optimizing the flake dimensions and understanding structure-function relations are underway in our facilities.

In addition, we are also pursuing the development of catalysts for the water oxidation reaction. The oxygen evolution reaction is considered as a bottleneck in the development of inexpensive systems for (photo-) electrochemical production of hydrogen, due to its sluggish kinetics and the high overpotentials required.

Moreover, while recent techno-economic studies of water electrolysis have evidenced that the major contribution to the price of hydrogen produced in an electrolyzer comes from the price of the electricity [3, 4]. This contribution corresponds to 60–90% of the hydrogen cost and raises to 97% when the electrolyzer is associated with Si photovoltaic modules [5]. The most likely path to reduce electrolyzer system cost is to reduce the cost of the stack (50–60% of both PEM and alkaline systems) and simplify the systems to make them better suited for mass production [4].

The cost breakdown of an alkaline electrolyzer, the current leading technology on the market, evidenced that 25% of the stack cost is related to the anode material, mostly composed of expensive metal oxides (IrO₂ or RuO₂). Iridium is not only considered an issue by stakeholders due to its

List of abbreviations

- EIS: Electrochemical Impedance Spectroscopy
- HER: Hydrogen Evolution Reaction
- OER: Oxygen Evolution Reaction
- PEM: Proton Exchange Membrane
- TMD: Transition Metal Dichalcogenide
- TRL: Technology Readiness Level
- XRD: X-ray Diffraction

Figure 1: Competence center for the development of water electrolysis catalysts in EPFL LIMNO.
Advances in the Development and Characterization of Water Electrolysis Catalysts at the EPFL

Figure 2: Gibeon electrode performance before/after 5 hours of oxidation and after stability test.

Figure 3:

b) Summary of performance (overpotential measured at 10 mA cm\(^{-2}\)) for the studied electrodes before, during and after oxidation.

Indeed, alloys based on abundant metals, Ni and Fe, have been recently identified as promising catalysts for this reaction [2] but little is known on the most effective composition and the mechanism involved on the bimetallic surface. To study the role of metal composition on the water oxidation kinetics, we used the Gibeon meteorite that is composed of approximately 92% Fe and 7.5% Ni. This material is composed almost uniquely of the two metals of interest and offers unique microstructures due to the slow cooling rate (1°C/1000 y) the material experienced after colliding with the earth crust. These distinctive properties make it an attractive substrate to study the composition and microstructure effects on the catalysis properties (we note that the characterization of the meteorite is in collaboration with the team working on synthetic fuels in WP4). Moreover, the metal composition can be altered on surface with different etching treatments or during oxygen evolution at high current density due to the different stability of the metal atoms in solution. This material was also compared to different grades of stainless steel (AISI 304L and 316L types), which are mass produced and have a high Ni content, in addition to other elements such as Cr, Mn or Mo.

A summary of the methods and results are as follows: All electrodes (ca. 0.5 mm thick) underwent the same experimental procedure. After cleaning and polishing, the electrode performance was tested (current density, \(J\), extracted against applied potential, in 1M NaOH) before and each hour during highly oxidizing conditions (5 hours in total at 500 mA cm\(^{-2}\)).

Figure 2 shows the positive effect of the oxidation on the Gibeon surface as the OER current is cathodically shifted by more than 100 mV (reduced energy loss). To quantify the energy losses related to the reaction catalysis, we consider the overpotential, i.e. the potential applied against the standard potential of water oxidation (1.23 V vs. RHE),
required to extract a current density of 10 mA cm\(^{-2}\) that corresponds to 10% Solar-to-Hydrogen efficiency when the additional energy is provided by a solar cell.

Figure 3 shows that a similar positive effect is observed on the stainless steel electrodes after surface treatment, with the overpotential decreasing and stabilizing below the 0.35 V threshold set by McCrory et al. [2] after 2–3 hours of oxidation. The achievement of this performance is surprising and completely unprecedented for the operation of a naturally-occurring metal alloy. One can also notice that despite an increase in the reaction overpotential after operating the electrodes 2 hours at 10 mA cm\(^{-2}\), potentially due to metal dissolved redepositing on the electrode, it remains below the threshold.

Cyclic voltammograms recorded during the oxidation process evidenced one oxidation and one reduction peak in the 1.2–1.4 V vs. RHE range, which has been attributed to Ni(II)/Ni(III) couple (Figure 4). Therefore, the catalytic improvement of the studied electrode is attributed to the enrichment of the metal electrodes surface in Nickel, due to the selective dissolution of other metallic atoms in highly oxidative environment [7]. Further investigations of the surface modification are ongoing using X-ray photoelectron spectroscopy to determine the modification of the metal composition on surface.

Overall, these initial results will undoubtedly help determine the ideal composition and structure of the NiFe catalyst and understand the synergetic role of the metal atoms on surface. When reproduced synthetically in the laboratory, the development of such catalyst will benefit for the development of inexpensive energy-to-fuel conversion systems.
Demonstration of a Redox Flow Battery to Generate Hydrogen from Surplus Renewable Energy

Scope of project

The present demonstration project finds its roots in a concept developed in our laboratory, which primarily aims at increasing the energy density of redox flow batteries (RFBs) and, as a consequence, its energy storage capacity. The system is extensively explained elsewhere [1, 2, 3], but, in a few words, the idea is to use the RFB in its typical electrochemical mode except when a surplus of (renewable) energy is available and the battery is already fully charged. In this particular case, a secondary circuit (see Figure 1) made of two catalytic beds enables an external chemical discharge of both electrolytes.

On the negative side (right circuit in Figure 1), the catalytic chemical discharge reaction is the reduction of protons by the V(II) species present in the electrolyte, generating hydrogen and regenerating the discharged V(III) species. The catalyst for this reaction is molybdenum carbide, which was chosen for its low price, its stability and its clear activity for the reaction of hydrogen evolution in an acidic V(II) solution. On the positive side (left circuit in Figure 1), catalysts such as iridium dioxide (IrO₂) or ruthenium dioxide (RuO₂) are able to activate the oxidation of water by the Ce(IV) ions, generating oxygen and protons – that can cross the membrane and re-equilibrate the proton concentration on the negative electrolyte – and regenerating the discharged Ce(III) species.

Both chemically discharged electrolytes return then to the RFB, which can be charged further, storing thus surplus energy in the form of hydrogen. This increases the RFB energy density and capacity. The efficiency of this system in chemical discharge mode is calculated by comparison of the chemical energy capacity corresponding to the hydrogen produced and the electrical energy used for charging the V–Ce RFB. Using a bench-scale system, this efficiency was close to 50%.

Status of project and main scientific results of workgroups

This secondary circuit for hydrogen and oxygen evolution is meant to increase the energy density and capacity of RFBs and do not compare to electrolyser in terms of productivity (due to the currently relatively lower current densities at the electrodes in RFBs). However, the indirect, or mediated, water electrolysis process exhibits several significant advantages over classical water electrolysis, such as the decoupling in space and in time of both gas evolution half-reactions and it avoids all the issues related with the electrode stability under gas evolution conditions. The electrochemical process is basically independent from the chemical process of hydrogen evolution. This leads to a higher purity of hydrogen and allows the use of less catalytically active, but more stable and less expensive (so more catalyst can be added) catalysts for both gas evolution reactions. The conditions for the chemical formation of hydrogen can also be different than in the electrochemical cell in terms of pressure and temperature, for instance. In this system, one electrochemical cell is used for two processes: the storage of electrochemical energy in the battery and additionally, the production of hydrogen on demand. On the contrary, a conventional electrolyser coupled to a RFB requires more costly equipment, as a state-of-the-art electrolyser alone would not easily adapt to the highly variable power profile associated to renewable energy production.
Demonstration of a Redox Flow Battery to Generate Hydrogen from Surplus Renewable Energy

It should first be noted that the V- Ce RFB can be replaced by an all-vanadium RFB, as it is the most advanced type of RFBs and they are commercially available. However, this involves changing the reaction for the chemical discharge of the positive electrolyte. The prerequisites for this reaction are that it must consume one proton per V(V) reduced in order to keep the overall proton balance of the dual-circuit system. Moreover, the oxidised product of the reaction should be easy to separate from the electrolyte – ideally it is a gas or a solid, and it should not modify its initial composition, i.e. it should not modify in any way the operation of the RFB.

In our demonstration system, a commercially available 10 kW/40 kWh all-vanadium RFB was installed in 2014 with the aim of validating the feasibility of the dual-circuit concept at a larger scale. As a first step, the battery was fully characterised by various analyses of the charge and discharge curves. Moreover, the chemical discharge of the negative electrolyte, that is the reaction of hydrogen evolution, was already scaled-up to a medium-scale on the basis of a first reactor design. These two aspects were discussed in the last report and published last year [3, 4].

A first advance reported here is an improvement of the design of the hydrogen evolution reaction. Indeed, the previous design was not satisfying enough in terms of electrolyte flow resistance and of the efficiency of the liquid-gas separation process. The horizontally-shaped catalytic reactor was therefore replaced by a vertical, segmented configuration (Figure 2). This allows a more controlled and efficient separation of the hydrogen from the electrolyte during the reaction itself, without blocking the flow of electrolyte in the reactor. The flow rate of electrolyte in this reactor can reach 1 L/min, allowing the discharge of the fully charged negative electrolyte of the battery in 17 h (equivalent to 2.4 kW discharge, 540 A electrolysis). However the rate of the chemical discharge can easily be increased by adding several such reactors in parallel with the first one.

The second aspect to be discussed here is the chemical discharge of the vanadium based positive electrolyte. As water oxidation cannot be performed using the V(V) electrolyte, the oxidation reactions of N₂H₄, SO₂ and H₂S were investigated [3]. The corresponding products of the reactions are N₂, SO₄²⁻ and S, respectively. Nitrogen is readily separated from the electrolyte as a gas when it is produced. The reaction is based and exothermic, it needs therefore to be performed under controlled conditions (slow flow rate and/or addition of a cooling system), making the oxidation of H₂S a potentially viable approach. The separation of solid sulfur from the discharged electrolyte before it returns to the battery is also easily achieved by filtration for instance. The separation of soluble sulfate ions from the electrolyte is however less evident. Two processes were tested. In the first case, the chemical oxidation of the SO₂ in the electrolyte (no catalyst) is followed by the extraction of sulfate by dialysis. In the second case, a fuel cell was built, in which the first half-reaction is the oxidation of SO₂ and the second half-reaction is the reduction...
Demonstration of a Redox Flow Battery to Generate Hydrogen from Surplus Renewable Energy

of V(V). In this case, sulfate is produced in the stream separated from the positive electrolyte stream, but this reaction needs a catalyst, especially for the reaction of SO₂ oxidation. The energy efficiency of these reactions was calculated and is given in [3].

The chemical reactions of SO₂ and H₂S were also observed to be fast and they are particularly interesting for gas desulfurization, for instance in petrochemical industries or for the removal of H₂S from a raw biogas stream. Therefore, in the present state, the all-vanadium RFB can be discharged chemically on both sides, producing hydrogen and being able to completely remove sulfur species from a gas stream. This is a significant advance in the demonstration of the feasibility of the system, but also for the discussion of the integration of the system into specific energy networks.

In terms of perspectives, studies for the chemical discharge of a cerium based positive electrolyte (oxygen evolution) are still undergoing and an overall characterization of the dual-circuit RFB performance for various energy production and consumption profiles will be performed based on the reactions discussed in this report. In a longer term view, the scale-up of the chemical discharge of the V(V) electrolyte based on the Westinghouse process as well as the production of hydrogen under pressure will be studied over the next years. The former process is based on the SO₂ oxidation to sulfuric acid by V(V), which can be reduced to SO₂ again in presence of heat, generating oxygen and, in an overall view, consuming only water. SO₂ is therefore cycled back to discharge the battery. This cycle allows discharging the positive electrolyte at low costs, it keeps the proton balance and it presents synergies with the application of sun energy through the use of a solar concentrator for instance.

References
Hydrogen / Energy Storage and Delivery with the Carbon Dioxide Formic Acid Systems

Scope of project

Hydrogen storage is one of the great current challenges, and the on-demand decomposition of formic acid into hydrogen and CO₂ represents a cunning solution. We have developed the first example of a first row transition metal catalyst that efficiently and selectively performs formic acid dehydrogenation under mild conditions in aqueous solution.

Various renewable energy sources (e.g. wind and solar) have seen large-scale applications over the last decade and capacities are steadily increasing. In terms of energy distribution and storage, hydrogen is considered one of the ultimate energy vectors to connect a decentralized grid of power generators to various end users for «mobile applications». Particularly in combination with fuel cell technology, hydrogen has the potential to provide mobile application with an efficient and (locally) emission-free energy source. A hydrogen/energy storage-and-release cycle based on formic acid decomposition and carbon dioxide hydrogenation can be envisioned that could solve the inflexibility of decentralized power generation. The simplicity and elegance of the combination of formic acid and H₂/CO₂ as a reversible hydrogen storage system certainly sounds appealing, since the hydrogenation of CO₂/HCO₃⁻ over homogeneous catalysts has been achieved with excellent activities.

Status of project and main scientific results of workgroups

Quantitative aqueous phase formic acid dehydrogenation using Iron(II) catalysts

An ideal energy storage cycle would combine carbon dioxide with H₂ from renewable resources, or reduce CO₂ electrochemically with solar/wind-powered electricity to generate formic acid. Formic acid production is even possible in acidic media, under base-free conditions, as our group demonstrated recently. Stocks of formic acid then would be used as transportable fuels for on-demand remote power generation or even for mobile applications. Other research groups have also investigated the formic acid/CO₂ couple using different metal salts as precatalysts, such as ruthenium, iridium, or even their combination in bimetallic systems. Usually homogeneous catalysts offer greater selectivity towards the dehydrogenation reaction, although progress is being made with certain gold or palladium nanoparticles supported on various media, or the use of non-metal catalysts such as boron. With the intent to combine the advantages of both homogeneous and heterogeneous catalysts, immobilization of the highly active and stable Ru(II)-mTPPTS catalyst on ion exchange resins, in polymers, on silica and zeolites was carried out in our group earlier.

Now we have investigated the homogeneous catalytic hydrogen production aqueous phase formic acid dehydrogenation using non-noble metal based pre-catalysts. This required the synthesis of m-trisulfonatedris[2-(diphenylphosphino)ethyl]phosphine sodium salt (PP₃TS) as a water soluble polydentate ligand. New catalysts, particularly those with iron(II), were formed in situ and produced H₂ and CO₂ from aqueous formic acid solutions; requiring no organic co-solvents, bases or any additives. Manometry, multinuclear NMR and FT-IR techniques were used to follow the dehydrogenation reactions, calculate kinetic parameters, and analyse the gas mixtures for purity. The catalysts are entirely selective and the gaseous products are free from CO contamination. To the best of our knowledge, these represent the first examples of first row transition metal based catalysts that dehydrogenate quantitatively formic acid in aqueous solution.

Calorimetric and spectroscopic studies of solvent/formic acid mixtures in hydrogenation storage

Solvents play a crucial role in many chemical reactions and additives can be used to shift the reaction equilibrium towards the product side. Herein we have assessed different solvents (water, organic solvents) and basic additives (amines, aqueous KOH) for carbon dioxide hydrogenation and formic acid dehydrogenation by determining the enthalpy of mixing with formic acid. From an efficiency perspective any heat evolving during these exothermic processes has to be reinvested to produce free...
formic acid. In both scenarios, the addition of basic chemicals causes higher costs and reduces therefore the chances of a successful economic application.

The highest formic acid concentrations in direct catalytic carbon dioxide hydrogenation under acidic conditions were reached in dimethyl sulfoxide (DMSO). This solvent exhibits considerably stronger interactions with formic acid than water as it was revealed in calorimetric measurements. This difference can be ascribed, at least partly, to stronger hydrogen bonding of formic acid to DMSO than to water as it was revealed in calorimetric measurements. Furthermore, the investigation of the DMSO/formic acid and water/formic acid systems by $^1$H- and $^{13}$C-NMR spectroscopy revealed that only 1:1 aggregates are formed in the DMSO solutions of formic acid in the broad concentration range, while the stoichiometry and the number of the formic acid–water aggregates depend on the concentration of the aqueous solutions essentially.

We quantified the enthalpy of mixing for water and several organic solvents with formic acid by heat flow calorimetry. The heat of mixing for water and formic acid showed an unexpected behavior by reacting most exothermically at a certain mole fraction ($X(\text{water}) = 0.7$) and not in the beginning when the pure chemicals were combined as was observed for the other tested solvents. The enthalpies of mixing, collected under realistic conditions, are valuable information when it comes to developing a hydrogen battery since they demonstrate how effectively the solvent sequencers produced formic acid or formate and also to estimate the energy, which is necessary for hydrogen evolution under these circumstances. Mixtures of DMSO or water with formic acid were explored by spectroscopic measurements (multinuclear NMR and infrared ATR) and we identified different types of adducts in both systems, whose presence depends on the concentration. These data were further corroborated with quantum chemical calculations and finally used to draw mutual DMSO–formic acid and water–formic acid structures (Figure 1).

Acknowledgement

We thank the Swiss Competence Center for Energy Research (SCCER), the Commission for Technology and Innovation (CTI) and the École Polytechnique Fédérale de Lausanne for their financial support.
Although CO$_2$ is an energetically very stable gas, pathways to convert the molecule into a synthetic fuel are very attractive as they offer the potential to close the CO$_2$ cycle, i.e., developing overall CO$_2$ neutral processes.

In work package 4 two general routes are followed to produce synthetic fuels: On the one hand, homogeneously and heterogeneously catalyzed pathways are followed in order to produce high value fuels and chemicals. On the other hand, a direct electrochemical reduction pathway (co-electrolysis) is followed to produce chemical feedstock. In both routes, the focus is centered around the development of highly active and selective catalyst systems.
Catalysts for CO₂ Reduction to Synthetic Fuels

Scope of project

Our research focuses on the synthesis of ionic liquids, defined as salts with a melting point below 100°C, and their application as catalysts, co-catalysts or as active solvents for biphasic catalysis. Ionic liquids (ILs) combined with homogeneous or heterogeneous catalysts, or used in pure form, are potent catalysts for CO₂ applications, and particularly for the reduction of CO₂ into synthetic fuels such as methanol or methane.

Reducing CO₂ directly often requires harsh conditions because of the high thermodynamic stability of CO₂. In three key projects we are attempting to develop so-called <soft> organic/homogeneous approaches to produce fuels (it should be noted that these studies are still in an early stage). The most efficient catalysts currently used to hydrogenate CO₂ to afford methane or methanol are based on heterogeneous metal-based materials which operate under high pressures and temperatures. Although it is not yet possible to say whether the soft approaches under evaluation will be more cost effective than the currently used systems. They will operate under milder conditions and, therefore, if these new catalysts are sufficiently stable, they may offer economic advantages. The synthesis of dimethylcarbonate (DMC) is more advanced than that of MeOH (see below), and is currently made on an industrial scale from carbon monoxide. We would like to demonstrate the synthesis of this compound on a medium scale in the next 12 months and have already had a preliminary discussion with Lonza in this regard.

Status of project and main scientific results of workgroups

In the first approach we proposed to overcome the thermodynamic barrier to CO₂ reduction by first incorporating CO₂ into a diol to form a carbonate. Further hydrogenation/hydrogenolysis of the carbonate yields methanol and recovers the diol, i.e. the diol can be considered as a co-catalyst (Figure 1). Due to the low-basicity of imidazolium ionic liquids that can potentially catalyze the first step, we were interested in alternative ion-pairs for the reaction of diol and CO₂ to carbonates. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)-based ILs show promising activity, although so far the yields remain modest and further studies to improve the efficiency of the reaction are in progress. The hydrogenation of propylene carbonate to regenerate the diol and form methanol is currently being studied using transition-metal nanoparticle catalysts, again this challenging reaction requires further optimisation and in situ spectroscopic studies are in progress to determine the reaction mechanism, which should facilitate the rational design of superior catalysts.

In the second related approach we are attempting to by-pass the direct reduction approach of CO₂ by the reductive functionalization of amines with CO₂ to generate the corresponding formamide. Hydrogenolysis of the N-C formyl bond may be performed under mild conditions with various catalysts. We recently discovered an inexpensive organo-catalyst for the first step, i.e. formation of the formamide from CO₂, and very recently we have improved on this catalyst with the development of an exceptionally active catalyst. Work on the hydrogenolysis step to close the cycle will start in 2016.

The third <soft> approach under investigation was inspired by previous work on imidazolium-based polymers that has led us to design suitable cross-linked ionic polymers for CO₂ applications [1]. Imidazolium salts are potent catalysts...
Catalysts for CO₂ Reduction to Synthetic Fuels

for the cycloaddition of CO₂ to epoxides, but show low activity for the one-pot production of DMC from CO₂, epoxides and diols. DMC is produced yearly on multi-ton scale from CO₂ and has important applications as a fuel additive. We designed ionic polymers with functionalized linkers that provide favourable interactions with the substrates, and allow the production of carbonates from CO₂ and epoxides under mild conditions (Figure 2). The one-pot formation of DMC suffers from side-reaction, in particular with the formation of ethers from the ring-opening of the epoxide by MeOH, and we are continuing to develop improved catalysts for this reaction.

The electrochemical reduction of CO₂ to CO, ideally using renewable electricity, is another excellent method to achieve the twin objectives of carbon recycling and fuel generation. Carbon monoxide is a key starting material for the production of important commodities, such as acetic acid, methanol, and other liquid hydrocarbons, and is therefore an extremely valuable product [2]. It was recently shown that the addition of certain imidazolium-based ionic liquid co-catalysts, such as 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF₄], resulted in a significant decrease in the overpotential required for the electrochemical reduction of CO₂ on silver electrodes [3]. Through the systematic evaluation of structure-activity relationships, we have ascertained an important interaction between the imidazolium cation and CO₂, which contributes to the observed catalytic behavior of imidazolium-based salts (Figure 3).

Furthermore, we have designed and synthesized novel ionic liquids that enhance this interaction, resulting in the development of a co-catalyst (compound 4 in Figure 1), which selectively produces CO with high Faradaic efficiencies. We are in discussions with a company to see if they are interested in exploiting the superior co-catalyst.

References

Scope of project

The conversion of CO₂ to fuels can be carried out via various processes, depending on the type of catalysts: homogeneous, heterogeneous and electro-catalysts, including photo and electrocatalysts. Each type displays its own advantages and disadvantages, but they all require major improvement towards a possible industrial use. In addition, there is a need of accurate data to improve all catalytic systems. Our laboratory has developed expertise in the synthesis of supported single-site catalysts, immobilized homogeneous catalysts and supported nanoparticles. Our goal here is the development of heterogeneous catalysts for the conversion of CO₂ using immobilized homogenous hydrogenation catalysts, supported Cu nanoparticles for the catalytic hydrogenation and electro-reduction of CO₂ into hydrocarbons, and supported Ni particles for dry reforming (CO₂ to syngas). Our ultimate aim is a predictive approach towards the design of functional materials with the conversion of CO₂ to fuels and to provide data to compare all systems.

To this end, we have worked on four topics within a collaborative network:
1.) the immobilization of homogeneous catalysts for the CO₂ hydrogenation to improve their stability and recyclability (Project A),
2.) the understanding of Cu-based CO₂ hydrogenation to develop in a more rational way CO₂ to methanol hydrogenation catalysts (Project B),
3.) the synthesis of carbon supported Cu nanoparticles and alternative oxide-based support to improve electrocatalyst stability (Project C),
4.) the development of robust methanation and dry reforming catalysts (Project D).

Status of project and main scientific results of workgroups

**Project A: Immobilized homogeneous hydrogenation catalysts**

Several homogeneous catalysts display unprecedented performance for the hydrogenation of CO₂ to formate derivatives, but suffer from the difficulty to separate the catalysts from the products. Here our effort has been directed at developing the corresponding immobilized equivalent towards the development of a continuous process.

People involved:
I. Thiel (SCCER/DAAD), H.K. Lo (SNF), A. Fedorov (ETHZ)

Collaborations:
P. von Rohr (ETHZ, High-Pressure) and exchange of best practices and materials with EPFL (P. Dyson)

This year, we have confirmed the high activity of homogeneous Ru and Ir-based molecular catalysts and identified the optimal linker(s) and ligands. Novel hybrid materials have been obtained, and the associated immobilized catalysts towards hydrogenation of CO₂ to formic acid derivatives are underway. The synthesis of such materials involved many synthetic steps, and an important parameter to evaluate this technology will be the potential scale up of the synthesis of such materials.

**Project B: Hydrogenation of CO₂ with supported Cu nanoparticles**

Supported Cu nanoparticles have been promising CO₂ hydrogenation catalysts, but they suffer from the lack of selectivity through the competitive conversion of CO₂ into CO, in place of methanol. This year, we have shown the key role of the support towards the selective formation of methanol, and developed highly active, selective and stable hydrogenation catalysts based on Cu/ZrOₓ/SiO₂ (selectivity = 94% at 5% conversion; productivity = 2.3 g CH₃OH/gCu/h) by comparison with the industrial catalysts Cu/ZnO/Al₂O₃, which are associated with a low methanol selectivity (selectivity = 8%) and productivity (0.05 g CH₃OH/gCu/h) under the same reaction conditions. In particular, we have demonstrated the key role of zirconia interface in close vicinity to Cu for the selective production of methanol. We are currently investigating the exact role of ZrOₓ by combining experiment and computation, and we use the aforementioned information to further improve the catalysts.
People involved:
Collaborations:
A. Urukawa (ICIQ, Spain) and C. Mueller (ETHZ, D.MATV).

**Project C: Electro-reduction of CO₂ to fuels**

The electro-reduction of CO₂ to fuels faces several challenges, such as the selective transformation of CO₂ to one or a selected number of fuels and the stability of the supports for the complementary oxygen reduction reaction (ORR) and oxygen evolution reaction (OER).

We have thus been developing methodology to prepare small Cu nanoparticles on carbon and stable oxide catalysts to replace carbon for electrocatalysts. For Cu nanoparticles, robust preparation methods were developed to obtain Cu colloids with various sizes and capping agents. In parallel, precipitation deposition methods were shown to be difficult to control Cu particles size on carbon. Current research efforts aim at controlling the formation of small and narrowly dispersed carbon supported Cu nanoparticles through the functionalization of carbon supports to control the dispersion.

In parallel, we plan to investigate by computational approach the key parameters for selective electrocatalytic reduction of CO₂ to fuels; this study will focus on the effect of the morphology of the nanoparticles and on dopants. In parallel, we have developed robust methods to prepare conductive oxide nanoparticles for ORR and OER. These approaches allowed the formation of highly conductive, stable and high surface area supports. The current work focuses on the development of the deposition of Pt metals on these supports.

People involved:
E. Oakton (CCEM/SCCER), D. Lebedev (Swiss Electric Research), H.J. Liu (CCEM).
Collaborations:
T.J. Schmidt (PSI) and C. Mueller (ETHZ – D-MATV).

**Project D: Dry reforming and methanation catalysts**

Another important research theme devoted to the conversion of CO₂ to fuels is the reforming of CO₂ and the related Water Gas Shift and Methanation reactions.

These processes require stable supported Ni-based catalysts, which typically suffer from sintering and coke formation. In the past year, we have developed highly stable Al₂O₃ and MgAl₂O₄-supported Ni catalysts, prepared via a molecular approach. This approach has allowed the formation of small and narrowly distributed Ni particles, which display high reforming stability. Detailed mechanistic studies in combination with computational chemistry have shown that the interface is essential for the activation of CO₂. In addition, it has been shown that the addition of Fe to Ni improved significantly the stability of 8 nm Ni nanoparticles, while it has little effect on very small (2 nm) nanoparticles. Detailed operando XAS study in combination with complementary methods revealed that the role of Fe, present as FeOₓ, is to remove coke from Ni. Further work in this field is directed at understanding further the role of each component in the catalysts composition.

People involved:
Collaborations:
C. Mueller (ETHZ, D.MATV) and F. Ribeiro (Purdue University).

**Financial supports**

CCEM, DAAD, ETHZ, JSPS, Unicore, SCCER, SNF (Synergia) and Swiss Electric Research.
Electrochemical Conversion of CO₂

Scope of project

The electrochemical reduction of CO₂ to hydrocarbon is a promising pathway for the recycling of this greenhouse gas. Nevertheless, the electrochemical reduction of CO₂ suffers from a low faradaic efficiency (it is kinetically more favorable to evolve hydrogen in the hydrogen evolution reaction (HER) from water than to reduce CO₂), and from a poor and/or uncontrolled yield of valuable products such as methanol or methane. In this work package, strategies will be employed in order to:

- design tailored Cu electrocatalysts to increase selectivity in the CO₂ reduction towards desired C₂ products.
- monitor the oxidation state changes of SnO₂ that accompany CO₂ reduction by in operando Raman Spectroscopy.

Status of project and main scientific results of workgroups

CO₂ electroreduction on Cu-based catalysts

Polycrystalline Cu catalysts show a superior activity of CO₂ conversion towards C₂ products (ethylene, ethane etc.). However, the selectivity towards a certain desired C₂ product is still rather low.

One promising approach to further increase the product selectivity is a tailored design of the surface morphology which turned out to be a crucial parameter for the catalyst design besides its chemical composition.

We make use of a galvanostatic Cu electrodeposition from an acidified Cu plating under harsh conditions (J = -3 A/cm²) where the Cu electrodeposition process is superimposed on a massive hydrogen evolution reaction (HER). Hydrogen bubbles formed at the electrode surface serve as structural template for the Cu electroplating thus resulting in a highly porous catalyst material whose porosity can be fine-tuned by various parameters such as plating time, applied current density and the Cu ion concentration in solution.

A particularly new aspect of the electrosynthesis of this type of Cu foam catalysts makes use of particular Cu plating additives (provided by BASF SE) that were originally designed for advanced Damascene plating processes. The use of these polymeric additives provides another important degree of freedom to control the desired catalyst performance not only by influencing its morphology but also by its chemical composition through the embedding of trace amounts of foreign elements (N, O, C). An example of the impact of plating time and the choice of the additive package on the resulting foam morphology is given in Figure 1.

We could prove that the selectivity of the Cu foam catalyst (Cu black, 40 s deposition time, additive package 1) towards ethylene and ethane is strongly enhanced compared to a planar Cu wafer substrate (Figure 2). Furthermore, it turned out that the product distribution is strongly depending on the given mean pore diameter (Figure 3). CO₂ conversion does not take place on a planar solid/liquid interface but instead inside the pores...
Synthetic Fuels

Electrochemical Conversion of CO₂

Figure 2: Product analysis based on online gas-chromatography. The 1 h electrolysis was carried out under potentiostatic conditions from a CO₂ saturated 0.5 M NaHCO₃ electrolyte. A blanket Cu wafer coupons is compared to a given Cu black catalyst (deposition time 40 s, additive package 1).

Figure 3: Dependence of the C₂ and CO FEs on the mean pore diameter of the Cu black catalyst.

of the catalyst. Local changes of the pH as well as the trapping of gaseous intermediates and by-products (CO, H₂) are discussed to play a key role for the resulting potential-dependent product distribution, analysed by online gas-chromatography (DC) and ion exchange chromatography (IC). Faradaic efficiencies (FEs) for ethylene and for ethane are found to be above 35% [1].

Next steps of the Cu catalyst development involve the additive-assisted electrodeposition of Cu-based binary and ternary alloy films and foams. In the focus of our development are alloys in which the Cu matrices are modified by more abundant metals (Co, Ni, Sn). These co-alloyed metal components undergo partial surface oxidation under experimental conditions relevant for the CO₂ electroreduction thus leading to metal/metal oxide type of composite catalysts. Catalysts were so far deposited on blanket wafer coupons. The next steps also involve the transfer of these electrodeposition processes onto (primary) porous Cu skeletons. This new approach would then allow for the use of these functional foams under electrolyte flow conditions. This would allow for a better control of the pH inside the catalyst and the residence time of reaction intermediates (CO, H₂) inside the catalyst. In operando Raman- and IR-spectroscopy will be applied to discover mechanisms of product selection control inside the foam catalyst.

CO₂ electroreduction on reduced graphene-oxide supported SnO₂-nanoparticles: An in-operando Raman spectroscopy study

A major concern of electrocatalysis research is to assess the structural and chemical changes that a catalyst may itself undergo in the course of the catalysed process. These changes can influence not only the activity of the studied catalyst, but also its selectivity towards the formation of a certain product.

An illustrative example is the electroreduction of carbon dioxide on tin oxide nanoparticles (NPs). Sub-10 nm SnO₂-NPs (cassiterite-type) were synthesized directly on a reduced graphene-oxide (rGO) support by a wet chemical approach. Under the operating conditions of the electrolysis (that is, at cathodic potentials) the rGO-supported SnO₂-NP catalyst undergoes structural changes which in an extreme case involves its reduction to
Metallic tin. This results in a decreased Faradaic efficiency (FE) for the production of formate (HCOO\(^-\)) that is otherwise the main product of CO\(_2\) reduction on SnO\(_2\) surfaces.

In this study we utilized potential and time dependent in operando Raman spectroscopy in order to monitor the oxidation state changes of SnO\(_2\) that accompany CO\(_2\) reduction. Investigations were carried out at different alkaline pH levels, and a strong correlation between the oxidation state of the surface and the FE of HCOO\(^-\) formation was found (Figure 4). At moderately cathodic potentials SnO\(_2\) exhibits a high FE for the production of formate, while at very negative potentials the oxide is reduced to metallic Sn and the efficiency of formate production is significantly decreased. Interestingly, the highest FE of formate production is measured at potentials where SnO\(_2\) is thermodynamically unstable. However, its reduction is kinetically hindered. The complete reduction to metallic Sn takes place at potentials more negative than what the Pourbaix diagram of the system predicts; at this potential range the intensity of the SnO\(_2\)-related A1g mode (fingerprint for the presence of SnO\(_2\)-NPs) is dramatically decreased.

Next steps of our in-operando study deal with the reversibility/irreversibility of the oxide electroreduction. Preliminary in-operando Raman studies suggest that the electro-reduction of the rGO-supported SnO\(_2\)-NPs followed by their re-oxidation involve a significant change in the size-distribution of the NPs, thus tremendously altering the FEs towards formate production.

References
**List of abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tr>
<td>CO₂RR</td>
<td>CO₂ Reduction Reaction</td>
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<tr>
<td>FE</td>
<td>Faradaic Efficiency</td>
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<tr>
<td>GDL</td>
<td>Gas Diffusion Layer</td>
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<tr>
<td>MEA</td>
<td>Membrane-Electrode Assembly</td>
</tr>
<tr>
<td>MS</td>
<td>Mass-Spectroscopy</td>
</tr>
<tr>
<td>PBI</td>
<td>Polybenzimidazole</td>
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<tr>
<td>PEM</td>
<td>Proton-Exchange Membrane</td>
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**Synthetic Fuels**

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**Electrochemical CO₂ Reduction for Syngas Production**

**Scope of project**

The electrical power produced by renewable energies can be chemically stored as hydrogen and other fuels via electrolysis. CO₂, together with H₂O, can be used in this context as a feed in order to produce valuable chemical products, such as CO, CH₄, C₂H₄, HCOO⁻, or CH₃OH. This process will not only allow storing excess energy but also to close the CO₂ cycle, i.e., recycling of this greenhouse gas. The main challenges of the CO₂ reduction reaction (CO₂RR) are related to reduce its overpotential, increasing overall faradaic efficiency and better control product selectivity. Different aspects are studied at PSI’s Electrochemistry Laboratory:

- development of analytical tools for online and operando detection of reaction products in the electrochemical reduction of CO₂;
- definition of the origin of selectivity for specific electrode materials;
- design electrocatalyst systems with high selectivity in the CO₂ reduction towards valuable products such as syngas, methanol or methane;
- development of polymer electrolyte based electrochemical cell.

In this report the focus is made on the development of polymer electrolyte electrochemical cells.

**Status of project and main scientific results of workgroups**

**Importance of cell level development and short economic analysis**

CO₂RR kinetics and products identification and quantification are mostly studied in half cell configurations using liquid electrolytes. This fundamental approach of studying CO₂RR is limited by the low solubility of CO₂ in water, the maximum CO₂ reduction current being in the range of 0.01–0.02 A/cm². In order to overcome the solubility problem and to reach higher operating current densities, CO₂ reduction needs to be carried out in a co-electrolysis system where pure or diluted gaseous CO₂ is used. To make a co-electrolysis system economically feasible, efforts have to be concentrated on design of highly efficient cells, development of catalysts and their incorporation into an efficient co-electrolyser designed for high-current-density operation.

A recent economic analysis from our group has identified that the electrochemical production of CO and formate from CO₂ shows the most promising perspective [1]. CO production costs ranging from 0.27 to 0.48 $/kg are below the current market price of 0.65 $/kg. CO in combination with H₂ (syngas) serves as an important chemical precursor for a significant number of industrial processes (e.g. Fischer-Tropsch synthesis). Another interesting product of CO₂RR is formic acid. The estimated production cost for this product is a factor of 2–4 below the current market price for formate/formic acid (0.34 vs. 0.8–1.2 $/kg). The analysis is based on an operating current density of 0.2 A/cm² and the same electrolyzer capital cost as for commercial alkaline water electrolyzers.

Based on this economic study, at this stage of the project, the studies are focused on CO production. The catalytic materials selective for CO production from CO₂ are Ag, Au and Zn [2]. Gold was selected as a benchmark catalyst for these studies since it can be used in different pH ranges without major chemical stability issues.

In our cell development, we chose an approach using gas diffusion electrodes allowing to reduce mass transport losses related to the relative low solubility of CO₂ in water under ambient conditions (ca. 0.033 mol/L) and enabling the cell to operate at high current densities, similar as it is used for membrane water electrolysis systems.

**Experimental**

The electrochemical cell and the experimental setup are similar to that used for fuel cell studies [3]. Two membrane-electrode assembly (MEAs surface 1 cm²) configurations were tested. The first one consists in an electrochemical cell with a proton exchange membrane as unique core electrolyte and the second consists in a modified electrochemical cell with a pH-buffer layer of aqueous KHCO₃ between the cath-
Electrochemical CO$_2$ Reduction for Syngas Production

ode catalyst and the proton exchange membrane. A schematic representation of the modified electrochemical cell is given in Figure 1A. The proton exchange membrane used was a Nafion® XL 100 and the buffer layer was composed of an aqueous electrolyte supported in glass fibres (Whatmann® paper GF/D, 2.7 µm pore size).

Regardless of the cell design, the catalyst used at the cathode side was gold black (Sigma Aldrich) spray coated on a carbon gas diffusion layer (SGL 24 BC). At the anode side spray coated Pt/C (47 % wt. Pt on carbon TEC10E50E TKK) on gas diffusion layer (GDL) was used with a loading of 0.4 mgPt/cm$^2$.

The cathode was operated using nitrogen (electrolysis mode) or using carbon dioxide (co-electrolysis mode). At the anode side pure hydrogen gas was used and this electrode was employed as a reference electrode for the system ($U_{\text{anode}} = 0$ V vs RHE at pH 0). The outlet of the cathode compartment was connected to a mass spectrometer in order to identify the CO$_2$RR products (the experimental setup used in this study is shown in Figure 1B). In all measurements the cathode flow was set to 10 mL/min, whereas at the anode side the hydrogen flow was set to 50 mL/min. The cell was operated at 40°C, under full humidification conditions and ambient pressure. The polarization curves were measured galvanostatically. For each data point, the cell current was stabilized for 2 minutes before measurement.

Results and discussion

**PEM configuration**

When MEAs based on the proton-exchange membrane (PEM) was used and fed with CO$_2$, no gaseous CO$_2$-reduction products were detected by mass-spectroscopy. This result is in agreement with another study reported in the literature [4] and shows that this cell configuration is not suitable for co-electrolysis systems under the test conditions used here. The acidity of the membrane shifts the cathode selectivity to hydrogen evolution. Hence, for operation in co-electrolysis mode, the pH value of the cathode needs to be modified.

**Modified PEM configuration - Proof of principle**

A cell with a buffer layer (aqueous 0.5 M KHCO$_3$ solution imbibed in glass fiber) was used for CO$_2$ reduction. The IR polarization curves are shown in Figure 2 and the results are compared to available literature data with good agreement. One of the targets could be readily achieved, namely the co-electrolyzer operation at current densities >0.2 A/cm$^2$. The CO$_2$ reduction products were detected by mass-spectroscopy (MS).
As illustrated in Figure 3, the reduction of CO$_2$ resulted in the expected evolution of H$_2$ (m/z = 2) and consumption of CO$_2$ (m/z = 44), along with an increase in m/z = 28 that points at the production of carbon monoxide. The faradaic efficiency (FE) for CO production calculated from the mass spectrometer signal was approx. 10%. A first approach to increase the CO faradaic efficiency is related to the way of engineering the electrodes.

More efforts are needed in this domain. Several directions are proposed for the next time frame and they are going to be realized in collaboration with other groups involved in the project:

- increasing the gold active site distribution on the GDL (reduce carbon content),
- synthesis of gold nanoparticles or
- substituting the GDL/catalyst layer structure with Au mesh.

However, these first results prove the setup feasibility developed in our laboratory during the first project year.

**Outlook**

Up to date, the buffer layer cell configuration is only a proof of concept. The cell stability being a major issue in this case, new stable buffer layers are needed. Exchange of the glass fiber based buffer layer with an intermediate layer of poly-benzimidazole (PBI) showed first improved results and will be further developed in the next steps.

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**References**

Integration
Interactions of Storage Systems

Work Package 5 at a glance

Work package 5 can be considered as our <door towards the applications> since different application- and system-near projects are combined. Different aspects of energy storage systems are studied in techno-economic and environmental analyses with the focus Switzerland, as well as applied power to gas systems. This work package is very important as it does and will be in the future the SCCER’s platform combining projects in the highest technology readiness levels.
A Uniform Techno-Economic and Environmental Assessment for Electrical and Thermal Storage in Switzerland

Scope of project

The aims of the task «Integrated Assessment of Storage» are to develop a uniform techno-economic, environmental and social assessment method for electrical and thermal storage and apply this method to different energy storage technologies and applications. This report describes the work undertaken at the University of Geneva (UniGE), at Paul Scherrer Institute (PSI) and at Hochschule Luzern (HSLU) in 2015. UniGE and HSLU focus on techno-economic assessment and PSI performs environmental assessments applying life cycle assessment (LCA). All institutions contribute as a team to the development and assessment of different energy storage (ES) technologies and applications.

Status of project and main scientific results of workgroups

The research in progress and related outputs refer to the analysis of different ES technologies for the Swiss Energy transition.

Techno-economic and environmental assessments of power-to-gas (P2G) systems

Power-to-gas systems generating hydrogen and/or methane can be used for linking the heat and mobility sectors, which are traditionally high carbon intense, with renewable energy supply. P2G systems can act as ES by counterbalancing intermittent electricity generation and energy demand. A thorough analysis of the implications of operating P2G systems considering various boundary conditions is key for understanding the performance, economic and environmental benefits of P2G plants.

We quantify both economic and environmental impacts of power-to-gas systems using a dynamic power-to-gas model. The proposed methodology assumes that power-to-gas systems participate in the Swiss wholesale electricity market and considers four services in addition to low carbon gas generation. These saleable services offer potential revenue streams which can considerably improve the economic viability. Both techno-economic and life cycle assessments are utilized to determine key performance indicators, namely system energy consumption, levelised cost, greenhouse gas emissions and further environmental indicators.

As shown in Figure 1, the modelling results indicate that technical and economic benefits increase with the electrolyser rating but those improvements are more substantial for systems on the kW scale while levelling off for larger systems.

Figure 1:
(a) life cycle system efficiency and (b) levelised cost (CHF/MWht) as a function of the electrolyser rating for P2H and P2M depending on the electrolyser technology (alkaline and PEM). The horizontal axis is represented in logarithmic scale. The discount rate was assumed to be equal to 8%.

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A Uniform Techno-Economic and Environmental Assessment for Electrical and Thermal Storage in Switzerland

Integration

(MW scale). Besides, higher capacity factors (by approximately 11%) are needed for proton-exchange membrane (PEM) electrolyser compared to alkaline electrolyser in order to minimise the levelised cost.

LCA shows that potential mitigation of greenhouse gas (GHG) emissions by using P2G mainly depends on the type of electricity generation and the source of CO₂. Additionally, the methodological approach for dealing with CO₂ capture and supply in LCA is important – system expansion is recommended (Figure 2).

Techno-economic assessment of battery storage for single home photovoltaics (PV) units and demand management

The use of batteries in combination with PV systems in single homes is expected to become a widely applied energy storage solution. Since PV system cost is decreasing and the electricity market is constantly evolving there is marked interest in understanding the performance and economic benefits of adding battery systems to PV generation under different retail tariffs. The performance of lead-acid (PbA) and lithium-ion (Li-ion) battery systems in combination with 3 kWp PV generation (standard size) for a single home in Switzerland is studied using a time-dependent analysis. The performance and economic benefits are analysed as a function of the battery capacity, from 2 kWh to 20 kWh. Firstly, the economic benefits of the two battery types are analysed for three different types of tariffs, namely a dynamic tariff based on the wholesale market (one price per hour for every day of the year), a flat rate and a time-of-use tariff with two periods. Secondly, the reduction of battery capacity and annual discharge throughout the battery lifetime are simulated for PbA and Li-ion batteries. It was found that although the levelised value of battery systems reaches up to 28% higher values with the dynamic tariff compared to the flat rate tariff, the levelised cost increases by 94% for the dynamic tariff, resulting in lower profitability. The main reason for this is the reduction of the number of equivalent full cycles performed with battery systems with the dynamic tariff. Economic benefits also depend on the regulatory context and Li-ion battery systems achieved an internal rate of return (IRR) up to 0.8% and 4.3% in the region of Jura (Switzerland) and Germany due to higher retail electricity prices (0.25 CHF/kWh and 0.35 CHF/kWh respectively) compared to Geneva (0.22 CHF/kWh) where the maximum IRR was equal to −0.2%. This latter result is shown in Figure 3.

Figure 2: Life cycle GHG emissions from P2G systems using wind or PV electricity for electrolysis and different sources of CO₂. The synthetic natural gas is used for driving a passenger vehicle. System expansion approach applied for CO₂ capture. The functional unit 1 kWh of electricity corresponds to 664 m, i.e. the distance one can drive with the amount of synthetic natural gas generated by 1 kWh of electricity input to electrolysis.
Assessment of energy storage technologies for different storage time scales

The objective of this analysis is to benchmark large scale electricity storage systems for different time scales corresponding to different applications. The methodology applied considers the technical, economic and environmental performance of storage and includes multi-criteria decision analysis (MCDA) as an integrated assessment approach. Specifically, pumped hydro storage, compressed air energy storage (CAES), battery and power-to-gas are compared for different storage time scales corresponding to short-, medium- and long-term (seasonal) storage. The criteria matrix in MCDA will include the levelised cost of stored energy as indicator for the economic performance, while life cycle GHG emissions, acidification, particular matter, etc. will represent the environmental performance. Life cycle assessment is applied as the methodology for environmental assessment.

To consolidate the results, a sensitivity analysis is carried out investigating uncertainties in terms of technology and environmental performance as well as costs. Based on the results, conclusions on the performance of the considered storage technologies for different time scales are drawn. A sample result of cost comparison is shown in Figure 4. It is shown that the operational cycle of the energy storage is an important differentiating factor with regards to the applicability of different technologies.

A review of community energy storage (CES)

The energy system is experiencing an energy transition in which both renewable energy (RE) and energy storage (ES) technologies are expected to contribute to assure a decarbonised and affordable energy supply. Given the modularity of RE technologies and their increasing penetration in the consumption centres, there is increasing interest for ES located very close to consumers which is able to raise the amount of local RE generation consumed on site, provides demand side flexibility and helps to decarbonise both the heating and transport sectors. We are in progress performing a holistic review of community energy storage (CES) in order to understand its potential role and challenges as a key element within the wider energy system. Some novel aspects included in this review are the analysis of the whole spectrum of applications and technologies which can serve as CES systems with a strong emphasis on end user applications; a multidisciplinary assessment of CES including techno-economic, environmental and social analyses; and the review of the CES outlook from a customer, utility company and policy maker perspective. Some interesting findings of this review are: CES can be more effective in (dynamically) balancing local supply and demand than ES located in the distribution system as well as more cost-effective than ES located in single dwellings; PbA.
batteries are more competitive at the moment than Li-ion batteries for demand load shifting (battery capacity sized according to peak demands loads) while Li-ion batteries are more competitive for PV energy time-shift (battery capacity sized according to surplus PV generation); and the community approach serves as a catalysis for implementing RE technologies, energy efficiency in addition to ES technologies, i.e. grass-root initiatives involving the community members.

**Analysis of the impact of the penetration of renewable energy and low carbon technologies in distribution grids**

This an ongoing collaboration with the SCCER-FURIES (ZHAW and EPFL). Given the expected penetration of PV energy, wind energy and other low carbon technologies in the context of the Swiss energy transition, this collaboration aims at analysing different technological options from a techno-economic point of view.

The first study investigates
- the techno-economic benefits of battery storage systems on distribution grids with high penetration of PV respect to its size and location in the network; and
- how battery storage systems compare with PV curtailment.

Specifically, batteries installed next to the PV systems (i.e. individual dwellings) are compared with a single large battery installed next to the distribution transformer from cost and value perspectives.
Applied Power-to-Gas Systems

Scope of project

Power-to-gas is a process for storing the energy from renewable electricity from summer to winter in the form of chemical energy as hydrogen or methane. The required technologies and the main infrastructures required for its implementation already exist today. New and improved technologies from research laboratories and start-up companies will appear on the market in the next few years. The Institute for Energy Technology (IET) has used the funds from the SCCER to build up a group of experts in the domain of the practical application of power-to-gas plants. One important activity is the building and operating of the first power-to-methane plant in Switzerland as a pilot and demonstration plant.

Status of project and main scientific results of workgroups

Pilot and demonstration plant power-to-methane

The main goals of the plant are:
- Measurements of performance and development of ideas for improvement and good system design.
- For IET to learn on all aspects of power-to-gas plants and to build up a team of experts.
- Demonstration and communication of power-to-gas to the public and to experts.
- Since no quantitative results are available on any of the existing power-to-gas plants in Switzerland and in Germany, the publication of quantitative results was also a main goal.

The plant uses sunlight, water and air to produce methane. An aerial view of the plant is shown in Figure 1. It has the following characteristics and key-values:

- Location: Gaswerkstrasse 1, Rapperswil-Jona.
- Electric input power (without CO₂-extraction from atmosphere): 31 kW renewable electricity kindly provided by Elektrizitätswerke Jona-Rapperswil (EWJR).
- Photovoltaic panels with a peak power of 7 kW.
- Source of CO₂:
  - Gas bottles.
  - Extracted from the atmosphere using a prototype from Climeworks.
  - Raw biogas (60% methane, 40% CO₂) from a wastewater treatment plant.
- Output Methane: 1.00 m³/h, 92% methane, 3% hydrogen, 4% CO₂.
- Operating time to fill one methane tank of the car: 20 hours.
- Resources to fill one tank of the methane car:
  - 100 litres of water.
  - 40 kg CO₂.
  - 620 kWh electrical energy.
- Coefficient of performance = (Power output using upper heating value of the output gas) / (electric power input) = 35%.

Normal conditions: 0°C, 1.01325 bara.
A field report was published on the operation of the plant [1] including the chart of energy flows presented in figure 2. The report also sheds light on practical aspects not well known in the industry like start-up procedure, shut down procedure, hot-standby and safety aspects.

Analysis of sources of CO₂

The project «Renewable Methane for Transport and Mobility» funded by the Swiss National Fund as part of National Research Programme «Energy Turnaround» (NRP 70) started in November 2015. The goal of the project is to look at the value chain starting from renewable electricity – the power side – through the power-to-gas plant to the gas grid and further to the application in renewable mobility for fleets. Sources of CO₂ are also included in the project. Their analysis including their geographical distribution is one important result of the first project year.

Figure 3 shows the flows of carbon through Switzerland in the form of a flow diagram. It is structured in four layers, the topmost being the atmosphere, where carbon is emitted in the form of CO₂. The flows of carbon are colour coded according to the origin of the carbon: green for biological origin, grey for geological origin and yellow for fossil origin. The CO₂ stems from various processes in the second layer: from combustion processes for heating, from engines in cars, busses and airplanes, from industrial processes, from waste incineration plants, from cement factories, from animals and humans as well as from biogas plants. These processes get carbon from different storages in the third layer, which are filled from different resources.

• Partner: Erdgas Obersee AG, Erdgas Regio AG, Forschungs- und Förderungsfonds der Schweizerischen Gasindustrie (FOGA), Elektrizitätswerk Jona-Rapperswil (EWJR), Audi AG, Climeworks AG.

All fossil carbon is imported. Geological carbon is extracted from the ground in the form of limestone and used for cement production.

From the data in the figure, the following conclusions were taken:

• CO₂ from biological origin can be used for the production of renewable methane in a power-to-gas plant. It is available in biogas plants and waste incineration plants and accounts for 2.4% of Switzerland’s manmade CO₂-emissions.

• As long as Switzerland decides to burn the waste that cannot be recycled, and as long as Switzerland wants to continue building concrete structures, the CO₂ emissions from the 30 waste incineration plants and 6 cement factories are unavoidable. They account for 13% of Switzerland’s manmade CO₂-emissions. There is no alternative to these emissions. Therefore, it has a positive impact on the environment, if part of this CO₂ is used in the production of methane even if the carbon is of geological or fossil origin. This could be done in large power-to-gas plants, which could be erected directly at the CO₂ sources. The limiting factor is no longer CO₂ but the renewable power used in the electrolyser.

Complementary activities

In order to promote power-to-gas and enable the practical application, complementary activities have been conducted. Publications, presentations...
and conferences are listed in the Appendix of this Annual Report:

- Since the opening more than 500 people have visited the plant. A public event was organised on 27 June 2015 where the population of Rapperswil-Jona was invited.

- A steering committee has been formed giving advice and input to the activities at IET. The committee consists of representatives from politics (two national councillors), industry and science. Two meetings were held on 25 March, 10 September and 27 November 2015.

New projects started in 2015:

- Revision of the Guideline G13 from Schweizerischer Verein des Gas- und Wasserfaches (SVGW) concerning the injection of renewable gas into the gas grid.

- Utilisation of raw biogas from a waste incineration plant for direct methanation.

- Injection of gas produced from the power-to-methane plant into the natural gas grid.

New industrial co-operations in 2015:

- Climeworks AG, Zürich, www.climeworks.com
- Audi, Ingolstadt, Germany, www.audi.ch
- Amag, Zürich, www.amag.ch
- Swissgas, Zürich, www.swissgas.ch
- VGOZT (Verband der Gaswirtschaft der Ostschweiz, der Zentralschweiz und des Tessins, Zürich.

The existing academic co-operations have been continued.

References


Scope of project

The Energy Systems Integration (ESI) Platform at the Paul Scherrer Institute (PSI) [1] provides a basis for research and technology transfer activities for the SCCERs «Heat and Electricity Storage» (HaE) and «Biomass for Swiss Energy Future» (BIOSWEET).

The ESI project covers technology development activities linked to the hardware infrastructure available on the platform, and cross-cutting scientific topics such as catalysis research (synthesis and characterization), process diagnostics tools (sampling, analysis, process validation) and energy system modeling (energy scenarios, technology assessment, life cycle analysis). The interplay of the different components in the system will be one of the primary issues studied. This provides insights into architectural details for future storage systems in terms of dimensioning, system dynamics and cost. Due to the modular configuration, a large flexibility is given for testing of a variety of components.

In the current project phase (2014–2016) the realization of the platform hardware infrastructure was the main focus of the activities. The basic platform infrastructure (support structure for individual sub-systems, supply of media – gases, (cooling) water – and electricity, safety system & controls) is currently being finalized and the commissioning phase will start shortly.

Full operation of the individual sub-systems should be achieved by June 2016.

Status of project and main scientific results of workgroups

The container based sub-systems currently placed on the ESI platform consist of a water electrolysis system, a fuel cell system, a hydrothermal process and a thermochemical process for methane production.

**Electrochemical Systems**

The electrochemical systems (electrolyser, fuel cell) are based on polymer electrolyte membrane (PEM) technology and resemble the backbone of the so-called «Hydrogen Path» of the ESI platform which allows to study (electric) power-to-(electric) power schemes for electric energy storage in chemical form (i.e. hydrogen) and its subsequent re-electrification.

To serve this purpose the platform houses a gas cleaning & drying system and pressure tanks for hydrogen (H₂) and oxygen (O₂). The PEM electrolyser splits water into H₂ and O₂ at elevated pressure (up to 50 bar) and thus provides both product gases readily pressurized to be stored without additional compression needs. The fuel cell system chosen can be operated on H₂/O₂ feed gas (instead of H₂/air) which makes good use of the available oxygen and this way offers a significantly improved electric efficiency (up to 70%).

**SNG production routes**

Both synthetic natural gas (SNG) production routes realized on the platform use different types of (biomass) feedstocks for methane (CH₄) generation.

The hydrothermal process converts wet biomass slurries (e.g. sewage sludge, algae solutions, manure) whereas the thermochemical process is based on methane synthesis from synthesis gas (CO/H₂), biogas (CH₄/CO₂) or carbon dioxide (CO₂) from industrial processes.

Interplatform network

Virtual links (via an inter-platform control system with embedded optimization algorithms) can be established with other related demonstration platforms in the ETH domain (at Empa, ETH Zurich and – possibly – EPF Lausanne).
Operating modes

The operating modes which can be realized with the currently selected components/sub-systems do comprise the operational schemes of individual sub-systems such as:

- Synthetic natural gas (SNG) from wood-derived syngas or biogas;
- SNG/synthetic fuels/chemicals from wet biomass feedstock (algae, sewage sludge, manure);
- Methane synthesis from (industrial) CO₂ (captured from industrial plants or ambient air);
- Power-to-gas (hydrogen and/or SNG);
- Power-to-power/mobility (via fuel cell systems) as well as highly integrated/dynamic modes such as:
  - dynamic power-to-gas (hydrogen and/or SNG) w/o intermediate gas storage,
  - frequency control (via electrolysis and fuel cell systems).

First experiments

In a first series of experiments detailed component/system characterization will be performed, addressing component/system efficiencies at various load points, dynamic system response (load ramps) and operational limits of systems/components.

All components/sub-systems of the ESI platform are aiming towards a power scale in the range of 100 kW. In this way it is envisioned that the results to be achieved in the current project phase are suitable as a basis for a final single scale-up step towards (pre-)commercial MW scale systems.

Outlook

In the next project phase (2017–2020) extended capabilities of the ESI platform hardware are being planned for.

The future expansion targets the integration of heat sources & sinks and calls for 2nd gen technologies which embody improvements based on recent findings. Additional benchmark technologies – such as additional energy conversion technologies like gas turbines/internal combustion engines – are being considered for complementation of the test infrastructure.

Besides a versatile intra-platform operation control scheme, the over-arching control & optimization of integrated energy systems services will be an integral part of the future operating schemes.
Appendix
Conferences

- Swiss Syposium Thermal Energy Storage, 16.1.2015, Luzern, HSLU.
- Power to Gas in der Mobilität, 25.02.2015, Dübendorf, Empa.
- EuroTech Winter School «Integrated Approaches to Energy Systems», 2.2.2015, Lausanne, EPFL.
- Symposium Power-to-Gas, 13.2.2015, Rapperswil, HSR.
- Lectures newly initiated:
  «Energy Storage Systems» at HSLU.
Presentations

WP 1

- K.M. Fromm, Science slam, NRP 70 and 71 kick-off meeting, April 24, 2015, Luzern, Switzerland.
- N.H. Kwon, Swiss Chemical Society Fall meeting, Sept. 4, 2015, EPFL, Lausanne, Switzerland.
- H. Yao, «Ionic liques for rechargeable Li-O₂ and Li-water batteries». Graduate Student Symposium 2015, Sept. 7–8, University of Bern, Bern, Switzerland.
- S. Maharajan, «Sn/C composite anode material for high energy batteries». Graduate Student Symposium, Sept. 7–8, 2015, University of Bern, Bern, Switzerland.
- N.H. Kwon, «Aqueous catholyte for rechargeable Li-O₂ and Li-water batteries». Swiss Chemical Society Fall Meeting, Sept. 4, 2015, EPFL, Lausanne, Switzerland.
- N.H. Kwon, «Aqueous catholyte for rechargeable Li-O₂ and Li-water batteries». Site visit NRP 70, Nov. 18, 2015, University of Fribourg, Fribourg, Switzerland.
- H. Yao, « Ionic liques for rechargeable Li-O₂ and Li-water batteries» Site visit NRP 70, Nov. 18. 2015, University of Fribourg, Fribourg, Switzerland.
- M. Deng, «Li⁺ and water permeable membrane for Li-water batteries». Site visit NRP 70, Nov. 18. 2015, University of Fribourg, Fribourg, Switzerland.
- C. Villevieille, «A combined experimental and theoretical study of sodiation and desodiation reactions of tin: Interface and bulk processes». MRS Conference, April 6, 2015, San Francisco, USA.
- C. Villevieille, «Approche expérimentale et théorie pour étudier les mécanismes réactionnels de matériaux à base d’étain pour les batteries Na-ion». GFECl, March 16, 2015, Autrans, France.
- C. Villevieille, «Understanding the Interaction of the Carbonates and Binder in Na-ion Batteries: a combined bulk and surface study». Societe Francaise de Chimie, July 6, 2015, Lille, France.
- C. Villevieille, «MSn₂ (M=Co, Fe) intermetallics: anode materials for Na-ion batteries». Lithium Battery Discussion (LiBD), June 22, 2015, Arcachon, France.
- C. Villevieille, «Bulk analysis of Sn-electrodes in sodium ion batteries using XRD and first principle calculation». Lithium Battery Discussion (LiBD), June 22, 2015, Arcachon, France.
- K.M. Fromm, «Precursors for and performance of nanoscale battery materials». GDCh-Vortrag, Jan. 22, 2015, University of Ulm, Germany.
- N.H. Kwon, «Li-ion Battery: the ionic diffusivity of LiMnPO₄ in preferred shape nanoparticles». International Center for Theoretical Physics (ICTP), Workshop on materials science for energy storage (smr 2758), May 11, 2015, Trieste, Italy.
- C. Villevieille, «Opportunities and Risks of Nano-LiMnPO₄: ionic diffusivity and life cycle assessments». Lithium Battery Discussion (LiBD), June 21, 2015, Arcachon, France.

WP 2

- P. Gantenbein, «Aqueous sodium lye seasonal thermal energy storage». IEA Task 42 Experts Meeting, Feb. 9, 2015, TU Wien, Vienna, Austria.
Appendix

Presentations

WP 3

- E. Callini, «Stabilization of gas species via incorporation in porous solids». Hydrogen-Metal Systems – Gordon Research Conferences, July 12, 2015, Stonehill College, Easton, MA, USA.
- H.H. Girault, «Different forms of electrochemical energy storage systems». Eurotech Winter School, Feb. 2–13, 2015, Lausanne, Switzerland.
- V. Amstutz, «Two levels energy storage: redox flow battery and hydrogen». Conference to Association pour l’innovation et la recherché énergétique (RIE), April 30, 2015, Martigny, Switzerland.
- P. Peljo, «Electrochemical energy storage». Academy Club for Young Scientists, Finnish Society of science and Letters, May 18, 2015, Helsinki, Finland.
- V. Amstutz, et al., «Nouvelle technologie de batterie et influence sur la distribution électrique». Conférence à ESR (Energie Sion Région), June 12, 2015, Sion, Switzerland.
- H.H. Girault, «New Chemistries for electricity storage in fluid phases». 11th ECHEMS, June 15–18, 2015, Bad Zwischenahn, Germany.
- C.R. Dennison et al., «Ongoing Work in Redox Flow Batteries». Abengoa Research Inauguration, July 8, 2015, Sion, CH.
- V. Amstutz et al., «Fast e-Fuelling Stations». SCCER Mobility Annual Conference 2015, August 26–27, 2015, Zürich, CH.
- H.H. Girault, «Redox Flow Batteries and Hydrogen Production for e-mobility». Seminar at Fudan University, Sept. 27, 2015, Shanghai, China.
- V. Amstutz et al., «Strategies for enhancing the energy density of redox flow batteries». ISE Satellite Meeting, Oct. 1–3, 2015, Hong Kong, China.

WP 4

- C. Copéret et al., «Interface effects in the case of dry reforming – CO2 activation on Ni-supported γ-Al2O3 and Ni-nanoparticles vs ideal Ni(111) surface». Swiss Chemical Society Fall Meeting 2015, Sept. 4, 2015, Lausanne, Switzerland.
- C. Copéret et al., «A Simple One-Pot Adams Method Route to Conductive High Surface Area IrO2-TiO2-Materials». Swiss Chemical Society Fall Meeting, Sept. 4, 2015, Lausanne, Switzerland.
- C. Copéret, «Cu Particle Size and Supported Effect on CO2 Hydrogenation to MeOH over Supported Cu Catalysts». ISHHC 17, July 12, 2015, University of Utrecht, Utrecht, Netherlands.
- C. Copéret, «Cu Particle Size and Supported Effect on CO2 Hydrogenation to MeOH over Supported Cu Catalysts». SCS Fall Meeting 2015, Sept. 4, 2015, Lausanne, Switzerland.
• T.J. Schmidt, «The Swiss Competence Center for Energy Research Heat & Electricity Storage: Background, Topics and Contributions from Paul Scherrer Institute». Joint Center for Energy Storage Research (JCESR), Argonne National Laboratory, Oct. 19, 2016, Argonne, IL, USA.


• T.J. Schmidt, «Electrolysis and Renewable Hydrogen as Basis for Power-to-Gas». Empa Akademie – Power to Gas in der Mobilität, February 25, 2015, Dübendorf, Switzerland.


• E. Fabbri, X. Cheng, T.J. Schmidt, «Ba0.5Sr0.5Co0.8Fe0.2O3-δ Single Material Electrode towards the Oxygen Evolution Reaction». Symposium on Polymer Electrolyte Fuel Cells 15, 228th ECS Meeting, Oct. 11–16, 2015, Phoenix, AZ, USA.

WP 5

• A. Stamatiou et al., «Combined Storage of Heat Cold and Electricity». Greenstock Conference.

• F. Eckl et al., «Heat flux analysis of a latent heat storage». IRES Conference.

• D. Gwerder et al., «Entwicklung einer optimalen Einheit aus Wärmepumpe und thermischem Energiespeicher». BFE-Wärmepumpen-Tagung.

• J. Worlitschek, «(i) Combined storage of electricity, heat and cold, (ii) Heat flux analysis of a latent heat storage». EUROSOLAR, the European Association for Renewable Energy, March 9, 2015, Düsseldorf, Germany.


• U. Sennhauser, «Kondensatoren – Die wichtigen Helfer in der Elektronik». June 12, 2015, Empa Akademie, Dübendorf, Switzerland.

• M. Patel, «Are batteries the PV energy self-consumption optimisation solution for homes?». Sustainable Energy Technologies, Aug. 25, 2015, Nottingham, UK.


Appendix

Publications

WP 1

- M. Oszajca, K.V. Kravchyk, Marc Walter, F. Krieg, M.I. Bodnarchuk, M. Kovalenko, «Colloidal BiF₃ nanocrystals: a bottom-up approach to conversion-type Li-ion cathodes». Nanoscale, accepted.
- M. He, M. Walter, K.V. Kravchyk, R. Erni, R. Widmer, M. V. Kovalenko, «Monodisperse SnSb Nanocrystals for Li-ion and Na-ion Battery Anodes: Synergy and Dissonance Between Sn and Sb». Nanoscale, 7, 455–459, 2015.

WP 2

Appendix

Publications

WP 3


WP 4


• E. Fabbri, M. Nachtegaal, X. Cheng, T.J. Schmidt, «Superior Bi-functional Electrocatalytic Activity of Ba0.5Sr0.5Co0.8Fe0.2O3-δ/Carbon Composite Electrodes: Insight into the Local Electronic Structure». Adv. Energy Mater. 5 (2015), 1402033, doi: 10.1002/aenm.201402033.


• E. Fabbri, X. Cheng, T.J. Schmidt, «Highly Active Ba0.5Sr0.5Co0.8Fe0.2O3-δ Single Material Electrode towards the Oxygen Evolution Reaction for Alkaline Water Splitting Applications». ECS Trans. 69(17) (2015), 869–875, doi: 10.1149/06917.0869ecst.

WP 5


Edited Work

Organized Events

2nd Annual Symposium, SCCER Heat & Electricity Storage, May 5, 2015

The 2nd Annual Symposium «SCCER Heat & Electricity Storage» was held on May 5, 2015, at Paul Scherrer Institut, Villigen. This was a co-organized event together with the Electrochemistry Laboratory at PSI, and its 31st PSI Symposium on May 6, 2015.

Organizers
Thomas J. Schmidt, Jörg Roth, Ursula Ludgate

Speakers
Prof. Dr. Nigel Brandon, Imperial College London, UK
Dr. Claire Villvieille, PSI
Dr. Dipl.-Ing. Timothy Patey, ABB Schweiz AG
Dr. Maurizio Barbato, SUPSI, CH
Dr.-Ing. Stefan Zunft, Deutsches Luftfahrt Zentrum, DLR, D
Prof. Dr. Kevin Sivula, EPFL, CH
Dr. Peter Broekmann, Uni Bern, CH
Christian von Olshausen, sunfire, D
Dr. Christian Bauer, PSI, Ch
Dr. David Parra, Uni Geneva, CH
Dr. Peter Jansohn, PSI, CH

Oral Presentations
• C. Villevieille, «Na-ion Batteries: New Challenges».
• T.J. Patey, «Li-ion Batteries for Use in Public Transportation Infrastructure».
• M. Barbato, «Modeling and Simulation of High-Temperature TES Systems».
• S. Zunft, «Adiabatic CAES: The ADELE-ING project».
• K. Sivula, «Sustainable Electrocatalysts for Hydrogen Production using Renewable Energy».
• Ch. von Olshausen, «sunfire Power-to-Liquids: Fuels and Chemicals from CO₂, Water and Renewable Energy».
• D. Parra, «Development and First Application of an Assessment Method for Energy Storage».
• P. Jansohn, «The Energy Systems Integration Platform at PSI».

Posters
• C. Marino, L. Vogt, P. Novák, C. Villevieille, «Ni₃SnP as Negative Electrode Material for Na-ion Batteries».
• L.O. Vogt, C.I Marino, C. Villevieille, «MSnₓ (M=Fe, Co) Intermetallics as Anode Materials for Na-ion Batteries».
• N.H. Kwon, H. Yin, T. Vavrova, F. Edafe, K.M. Fromm, «1D Ionic Diffusion Direction vs the Shape and Size of Nano-LiMnPO₄».
• S. Maharajan, N.H. Kwonn, K.M. Fromm, «Sn/C Composite Anode Materials for Lithium Ion Batteries».
• J. van den Broek, S. Ayton, J.L. M. Rupp, «Low Temperature Synthesized-Processed Garnet-Type Fast Li-Ion Conductor, La₁₀Al₈3La₅Zr₂O₁₂, for All Solid State Li-Ion Batteries».
• K.D. Becu, «Legal Aspects in Electrochemical Battery Storage».
• S.R. Binder, S. Haussener, «Encapsulations for Aluminum Alloys in High Temperature Energy Storage».
• D. Perraudin, S. Haussener, «Phase Change Material Systems for High Temperature Heat Storage».
• E. Rezaei, A. Ortona, S. Haussener, «Si-infiltrated SiC composites for High Temperature Applications: A Thermo-Mechanical Analysis».
• L. Geissbühler, M.M. Kolman, G. Zanganeh, A. Haselbacher, A. Steinfeld, «High-Temperature Combined Sensible/Latent Storage for AA-CAES».
M. Barbato, «Modeling and Simulation of High-Temperature TES Systems».


C. Fink, G. Laurenczy, «Hydrogen/Energy Storage in Formic Acid/Carbon Dioxide Systems: Enthalpy of Mixing for Formic Acid under Neutral and Basic Conditions».


X. Cheng, E. Fabbri, T.J. Schmidt, «Study of the Oxygen Evolution Mechanism and Activity of Perovskite La$_x$Sr$_{1-x}$CoO$_3$-based Electrodes in Alkaline Media by Thin Film Rotating Ring Disk Electrode Measurements».


P.J. Dyson, «Two-step Approach for the Conversion of CO$_2$ Into CH$_3$OH».

G. Lau, M. Schreier, M. Grätzel, P. Dyson, «Ionic Liquid-Mediated Electrochemical Reduction of CO$_2$».

S. Tada, M. Schwarzwälder, C. Copéret, «Cu Particle Size and Support Effect on CO$_2$ Hydrogenation to MeOH over Supported Cu Catalysts».


Y. Paratcha, J. Herranz, A. Perymakova, J. Durst, T.J. Schmidt, «ECSA determination of Cu electrodes by Pb under potential deposition. Application for CO$_2$ reduction».


A. Fuerst, B. Begelspacher, A. Haktanir, «Fertigung von Lithium-Ionen Batterien».


Organized Events

- M. Barbato, «Modeling and Simulation of High-Temperature TES Systems».
- C. Fink, G. Laurenczy, «Hydrogen/Energy Storage in Formic Acid/Carbon Dioxide Systems: Enthalpy of Mixing for Formic Acid under Neutral and Basic Conditions».
- X. Cheng, E. Fabbri, T.J. Schmidt, «Study of the Oxygen Evolution Mechanism and Activity of Perovskite La$_x$Sr$_{1-x}$CoO$_3$-based Electrodes in Alkaline Media by Thin Film Rotating Ring Disk Electrode Measurements».
- P.J. Dyson, «Two-step Approach for the Conversion of CO$_2$ Into CH$_3$OH».
- S. Tada, M. Schwarzwälder, C. Copéret, «Cu Particle Size and Support Effect on CO$_2$ Hydrogenation to MeOH over Supported Cu Catalysts».
- Y. Paratcha, J. Herranz, A. Perymakova, J. Durst, T.J. Schmidt, «ECSA determination of Cu electrodes by Pb under potential deposition. Application for CO$_2$ reduction».

Organizers and speakers (from left to right):

Front row
Cordelia Gloor,
Claire Villevieille,
Maurizio Barbato,
Timothy Patey,
Kevin Sivula,
Ursula Ludgate,
Petr Novák,
Stefan Zunft

Back row
David Parra,
Nigel Brandon,
Christian von Olshausen,
Christian Bauer,
Thomas J. Schmidt,
Jörg Roth,
Peter Jansohn
Organized Events

3rd Annual Symposium, SCCER Heat & Electricity Storage, October 26, 2015
Storing Renewable Energy for Future Mobility

Organizers
Thomas J. Schmidt, Jörg Roth, Ursula Ludgate

Speakers
Prof. Dr. Maksym Kovalenko, ETH Zürich, CH
Prof. Matthias Rommel, Hochschule für Technik Rapperswil, CH
Dr. Peter Broekmann, University of Bern, CH
Dr. Andrew Dalebrook, EPFL, Lausanne, CH
Dr. Markus Ehrat, Head Innovation mentor CTI, Bern, CH
Dipl. Ing. Uwe Hannesen, Swiss Hydrogen SA, Biel, CH
Dipl. Ing. Rolf Huber, CEO H2 energy, Zürich, CH
Christian Bach, Empa, CH
Boris Meier, Hochschule für Technik Rapperswil, CH

Oral Presentations:
• M.V. Kovalenko, «Advanced batteries and battery materials».
• M. Rommel, «Thermal Energy Storage for Short and Long Term».
• P. Broekmann, «(Electro) reduction of CO₂: From Fundamentals Towards Applications».
• G. Laurenzcy, «Direct homogeneous catalytic carbon dioxide hydrogenation to formic acid: the reversible formic acid – carbon dioxide/hydrogen cycle».
• M. Ehrat, «Innovation Mentors – The catalyst for Efficient Project Applications».
• U. Hannesen, «Comparison of PEM fuel cells running on Hydrogen/air and Hydrogen/Oxygen».
• Ch. Bach, «Renewable Energies in the Future Energy Supply (RENERG2) A common Project of PSI, Empa, ETHZ, EPFL and ZHAW».
• B. Meier, «Sustainable Mobility with Renewable Gas».

Posters
• M. Walter, K.V. Kravchyk, M. Ibanez, M.V. Kovalenko, «A Sodium/Magnesium-Ion Hybrid Battery Based on a Pyrite (FeS₂) Cathode».
• S. Wang, M. He, M. Walter, K.V. Kravchyk, F. Krumbeich, M.V. Kovalenko, «Monodisperse Co-Sn, Fe-Sn, Co-Sb Alloy NCs for High Performance Li-Ion Battery Anodes».
• L. Vogt, C. Marino, C. Villevieille, «MSn₂ (M=Fe, Co) intermetallics as anode materials for Na-ion batteries: controlling volume expansion through reaction pathway engineering».
• C. Marino, C. Villevieille, «CuSbS₂ vs. Sb₂S₃ as negative electrode for Li-ion and Na-ion batteries».
• C. Marino, C. Villevieille, «Comparative study of Ni₂SnP as negative electrode for Na-ion batteries and Li-ion batteries».
• H. Yao, K.M. Fromm, «Ionic Liquids Based on Crown Ether for Batteries».
• S. Maharajan, N.H. Kwon, K.M Fromm, «Sn/C composite anode materials for lithium ion batteries».
• B. Baichette, K.M. Fromm, «Manufacturing technologies for battery production».
• M. Li, H. Gyu Park, «Optimization of Hybrid Metal Oxide/Carbon Nanotube Supercapacitor Electrodes Prepared by a Pulsed Current Electrodeposition Method».
• E. Stilp, E. Cuervo Reyes, D. Adams, M. Held, U. Sennhauser, «Influence of stress cycling on Li-Ion batteries for light vehicle applications».
• A. Fuerst, A. Haktanir, R. Hannes, B. Löffel, I. Perdana, «Manufacturing technologies for battery production».
• M. Held, D. Adams, D. Bachmann, E. Cuervo Reyes, E. Stilp, U. Sennhauser, «Battery Testing@Empa».
75
Appendix

L. Geissbühler, M. Kolman, G. Zanganeh, A. Haselbacher, A. Steinfeld, «Analysis of industrial-scale high-
temperature combined sensible/latent thermal energy storage».


G. Guidati, B. Ribi, C. Scherrer, F. Tillenkamp, M. Krüttli, «LT-PHES (Low Temperature Pumped Heat Energy
Storage) – Decentralized Heat Supply and Electricity Storage with Combined Heat Pump and Power Cycle
Process».

E. Rezaei, S. Gianella, S. Haussener, A. Ortona, «High temperature thermal shock and oxidation behavior of
Si-infiltrated SiC lattices».

E. Callini, P.Á. Szilágyi, M. Paskevicius, N.P. Stadie, J. Réhault, C.E. Buckley, A. Borgschulte, A. Züttel,
«Stabilisation of gas species via incorporation in porous solids».

A. Züttel, Z.O. Kocabas Atakli, E. Callini, S. Kato, «Catalyzed H sorption mechanism in alanates».

P. Peljo, S. Maye, «Heat-to-Power and Energy Storage with Copper Batteries».

P. Peljo, H. Vrubel, V. Amstutz, C.R. Dennison, A. Santasalo-Aarnio, D. Lloyd, F. Guny, K.E. Toghill, H.H. Gir-
ault, «Scale-up of the All-Vanadium Dual Circuit Redox Flow Battery for Simultaneous Desulfurization and
Renewable Hydrogen Generation».

H. Vrubel, V. Amstutz, P. Peljo, F. Guny, C.R. Dennison, A. Battistel, T. Wu, H.H. Girault, «Fast e-Fueling Sta-
tions».

C. Fink, G. Laurenczy, «Development of a New RAPTA-Type Catalyst for Hydrogen Storage in Formic Acid/
Carbon Dioxide Systems».

M. Montandon-Clerc, C. Fink, A.F. Dalebrook, G. Laurenczy, «Quantitative Aqueous Phase Formic Acid Dehy-
drogenation Using Iron(II) Based Catalysts».

L. Bonorand, L. Gubler, D. Meier, F. Oldenburg, H. Binder, «Swiss Membrane Technology (SMT) – Safe, reli-
able and cost effective Electrical Energy Storage (EES): A PSI Spin-off Initiative».

S. Tymen, M.J. Lozano-Rodriguez, A. Scheinost, «From Pd to PdPt nanoparticles: an interesting evolution
from structure to electrochemical properties».

N. Hérault, K.M. Fromm, «TiO2 and Ag-doped TiO2 nanocontainers as photocatalysts for CO2 reduction».

E. Oakton, J. Tillier, G. Siddiqi, Z. Mickovic, O. Sereda, A. Fedorov, C. Copéret, «Structural Differences Be-
tween Sb- and Nb-doped SnO2 and Consequences for Electrical Conductivity».

S. Tada, M. Schwartzälder, C. Copéret, «Cu Particle Size and Support Effect on CO2 Hydrogenation to MeOH
over Supported Cu Catalysts».

Dioxide to CO and C2H4 on Highly Porous Copper Black Catalysts».

M. Rahaman, A. Dutta, P. Broekmann, «Activity of Cu-Au Alloys NPs towards the Electrochemical Reduction
of CO2: A Compositional Dependence Study».

A. Kuzume, A. Dutta, M. Rahaman, P. Broekmann, «Monitoring the Chemical State of Catalysts for CO2 Elec-
troreduction: An in operando Raman spectrosocopic Study».

Y. Fu, F. Stricker, S. Vesztergom, A. Kuzume, A. Rudnev, J. Furrer, P. Broekmann, «Water-promoted Electro-
chemical Reduction of CO2 in Ionic Liquids».

J. Durst, J. Herranz, Y. Paratcha, A. Perymakova, T.J. Schmidt, «Co-Electrolysis Cell Configurations for CO2
Electrochemical Reduction».

X. Cheng, E. Fabbri, M. Nachttegaal, I.E. Castelli, M. El Kazzi, R. Haumont, N. Marzari, T.J. Schmidt, «The
oxygen evolution reaction on La1-xSrxCuo3 perovskites: A combined experimental and theoretical study of
their structural, electronic, and electrochemical properties».


A. Ammann, R. Schwyter von Buonas, A. Stamatiou, J. Wöriltschek, «Investigation of xylitol as a phase change material for process heat
storage».

D. Parra, M. K. Patel, «The impact of the electrolyser technology and size on the performance and economic benefits of power-to-gas systems».


T. Cutic, A. Omu, K. Orehounig, J. Carmeliet, «Power-to-Gas in the context of urban energy system at the neighborhood scale».

Organizers and speakers
(from left to right):
Andrew Dalebrook,
Matthias Rommel,
David Parra,
Thomas J. Schmidt,
Jörg Roth,
Peter Broekmann,
David Perraudin,
Ursula Ludgate,
Uwe Hannesen,
Leonie Vogt,
Christian Bach,
Elsa Callini,
Markus Ehrat,
Kim Larmier

Organized Events
Co-Organized Events

Co-organized: SCCER Heat and Electricity Storage / Electrochemistry Laboratory at Paul Scherrer Institut

31st PSI Electrochemistry Symposium, May 6, 2015

Electrochemical Energy Storage – A Key for Future Energy Systems

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Co-Organized: SCCER Heat and Electricity Storage / SCCER BIOSWEET / Paul Scherrer Institut

At Paul Scherrer Institut, March 12, 2015

Energy, Climate Change and Sustainability

Speaker: Prof. Dr. Steven Chu
Nobel Laureate in Physics 1997
Secretary of Energy of the United States of America, 2009–2013

Prof. Dr. Steven Chu is the recipient of the Richard R. Ernst Gold Medal.