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SCCER Networked Research – One-stop Shop for New Developments in Energy Storage

The Swiss Competence Center for Energy Research (SCCER) Heat and Electricity Storage successfully finished its third year of operation in 2016, which in turn also means, the first phase since its implementation in 2014 finally came to its end. Last year, therefore, was dictated by two important aspects, viz. the efforts to demonstrate scientific and technical progress in the final year of the first SCCER funding period and the preparation and submission of the proposal for the second funding period 2017–2020. The latter we successfully submitted and it was finally accepted for funding by the Commission for Technology and Innovation Switzerland (CTI) which enables us now to continue our research and development (R&D) on energy storage until 2020 under the roof of the SCCER Heat & Electricity Storage.

Within the SCCER Heat & Electricity 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 understands itself as a one-stop shop for new developments in energy storage.

This annual report 2016 summarizes all progress achieved by SCCER Heat & Electricity Storage over the last year. Besides lots of remarkable achievements on the more fundamental level of understanding materials and processes, the great progress in building different demonstration platforms should be emphasized at this point.

For instance, the SCCER Heat & Electricity Storage contributed to the construction and operation of the world’s first Advanced Adiabatic Compressed Air Energy Storage (AA-CAES) plant built near Biasca in Switzerland. This plant demonstrated a storage efficiency of > 70% which is in line with values typically seen for pumped-hydro energy storage plants therefore offering potential for better flexibility in grid-scale energy storage.

As a second example, Switzerland’s first Power-to-Methane plant in Rapperswil was operated and characterized further within the last year, enabling important insights into practical operation and applications of the technology as well as in-depth understanding with respect to different operational aspects, e.g., CO2 source or the use of the product gas for grid-injection or mobility applications.

These are only two examples of our demonstrators built within the framework of the SCCER with many equally important ones described in this Annual Report. With this I would like to invite you dive into the world of energy storage while reading our 2016 achievements in the following pages.

Prof. Dr. Thomas J. Schmidt
Head SCCER Heat and Electricity Storage
Work Package "Heat Storage" 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 this work package to tackle materials and systems development for low-temperature seasonal heat storage for building applications and high temperature heat storage for industrial applications.

Low-temperature storage

A central goal of the low-temperature storage activities is the development of a compact, retrofittable seasonal-storage unit for building applications. The solution being investigated by the Institute for Solar Technology at the University of Applied Sciences Rapperswil is a closed sorption heat storage based on water vapour absorption in an aqueous sodium hydroxide solution (NaOH-H₂O) or other aqueous solutions. The key advantage of sorption storage is the significantly higher volumetric energy density compared to sensible hot water storage systems. As part of the EU-financed COMTES project, a NaOH-H₂O prototype with 10 kW output power was designed, built, and operated. For the discharging (absorption) process, however, the measured exchanged power is lower than expected. This has been traced to the poor wetting of the stainless steel tube bundle in the adsorption/desorption unit of the storage and the short residence time of NaOH in the water vapour. Surface modifications and the use of surfactants are being investigated in a dedicated 1 kW test rig in an effort to improve the discharging performance.

At the University of Applied Sciences Lucerne, the interaction of power and heat in combination with thermal energy storage is being investigated through the Dual Energy Storage and Converter (DESC) concept. Their storage system is based on the combination of a heat pump, a heat engine, and two thermal storage units and can be operated either as pure electricity storage or as a combination of heat, cold, and electricity storage. The primary focus is on latent heat storage because of higher energy densities compared to sensible heat storage and because the constant temperatures during phase changes simplify the storage integration. New phase-change materials were identified for temperatures of 93°C and 12°C, allowing efficient coupling with heat pumps and chillers. Laboratory setups were designed to test and evaluate the application potential of these technologies under realistic conditions.

High-temperature storage

For high temperature applications, the efforts have focused on two applications and involved researchers from ETH, EPFL, and SUPSI. The first application is advanced adiabatic compressed air energy storage (AA-CAES). For AA-CAES plants, thermal storage at temperatures of about 550–600°C is the key to raising the cycle efficiency from about 40–50% for diabatic CAES to about 70–75%. These efficiencies are close to those observed in practice for pumped hydro storage, which is one reason why AA-CAES is often viewed as an attractive technology for the bulk storage of surplus electrical energy. The efforts on AA-CAES include simulations and experiments. The simulations, in turn, encompassed 1d, 2d, and 3d simulations of the thermal storage itself as well as simulations of entire AA-CAES plants that include a 1d model of the thermal storage. These simulations were instrumental in the design and operation of the world’s first AA-CAES pilot plant near Biasca, Switzerland, in a close collaboration with Airlight Energy SA/ALACAES SA. Pilot-scale experiments were carried out using both a sensible-only storage based on a packed bed of rocks as well as a combined sensible-latent storage in which the packed bed of rocks was supplemented with a separate latent storage using a metallic phase-change material encapsulated in steel tubes.

The second high temperature application is the development of heat exchangers based on silicon carbide for temperatures up to 1600°C.

Scope of project

The growing share of fluctuating renewable energy sources like wind and solar requires short- and long-term energy storage to guarantee the power supply. Pumped hydro storage is at present the main option for large-scale storage. However, its economic viability is threatened and alternative large-scale storage technologies must be being investigated. One promising alternative to pumped hydro storage is advanced adiabatic compressed air energy storage (AA-CAES). In contrast to the diabatic form of CAES, which has been proven for several decades at the industrial scale with the plants in Huntorf (Germany) and McIntosh (USA), AA-CAES stores the heat generated during air compression in a thermal energy storage (TES). During expansion, the heat is recovered from the TES by the air, leading to an increase of potential round-trip efficiencies from around 45–50 % to more than 70 %. Compared to diabatic CAES, AA-CAES has the additional advantage of not requiring the burning of fossil fuels; during operations, AA-CAES does not emit CO₂.

Status of project and main scientific results of workgroups

In collaboration with industrial partner ALACAES and SUPSI, an AA-CAES pilot plant has been designed and constructed in an unused tunnel near Pollegio (Switzerland). The 10 MWh sensible-heat thermocline TES is placed inside the cavern to prevent large pressure differentials acting on the TES walls, thereby simplifying its design considerably. Multiple charging-discharging cycles were performed with the pilot plant. During charging, compressed air of about 550 °C flows through the TES, releases its heat to a packed bed of rocks, and the cooled air is then stored in the cavern. During discharging, the cold air flows through the TES and leaves the cavern as hot air. To our knowledge, the cycling experiments with the pilot plant represent the first time an AA-CAES pilot plant has been operated worldwide.

To design the experimental schedule for the pilot plant and to predict the performance of large-scale plants, a quasi-one-dimensional heat transfer model [1] was used. This model was extended to include the temperature and pressure evolution inside the cavern [2]. The comparison of the simulated temperature profile inside the TES and the experimental results shows good agreement, see Figure 1. In addition to the sensible-heat storage, a separate latent-heat storage with a capacity of 500 kWh was constructed and tested, see Figure 2. The latent-heat storage contains 296 steel tubes filled with the metallic phase-change material (PCM) Al₆₈.₅Cu₂₆.₅Si₅ (melting temperature of 518 °C). The goal of this storage was to stabilize the discharging outflow temperature of the sensible storage near the melting temperature of the PCM and thus enable higher AA-CAES plant efficiencies.

List of abbreviations

<table>
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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>AA-CAES</td>
<td>Advanced Adiabatic Compressed Air Energy Storage</td>
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<tr>
<td>HTF</td>
<td>Heat Transfer Fluid</td>
</tr>
<tr>
<td>PCM</td>
<td>Phase Change Material</td>
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<tr>
<td>TCC</td>
<td>Thermocline Control</td>
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<tr>
<td>TES</td>
<td>Thermal Energy Storage</td>
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Figure 1 (left): Comparison of temperature distribution inside the sensible-heat TES in Pollegio between 1D model (solid lines) and experiment (symbols) during 40 h of charging.

Figure 2 (right): Latent-heat TES inside the tunnel in Pollegio.

Authors

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In Figure 3, the measured air temperature at the outflow of the latent storage during discharging is presented. The results of the experimental campaign with the sensible and combined sensible-latent storage units are currently being investigated in detail.

The temperature drop during discharging in a sensible-heat TES is a consequence of thermocline degradation. Reasons for thermocline degradation are axial heat conduction, radiation, and poor convective heat transfer. These mechanisms are influenced by the storage geometry, storage material, and the manner in which the TES is operated. Adding PCMs, either on top of the packed bed or in a separate latent heat TES unit (as in the AA-CAES pilot plant), allows the impact of thermocline degradation on the air outflow temperature to be reduced.

An alternative to PCMs is to actively increase the thermocline steepness inside the tank. This approach, referred to as thermocline control (TCC), has two main benefits:

- Higher utilization factor: Storage size and hence material costs can be reduced.
- Lower temperature drop during discharging: More efficient plant operation.

Amongst several TCC strategies, previous work proposed extracting and returning Heat Transfer Fluid (HTF) at certain positions of the thermocline [3]. Simulations with the quasi-one-dimensional heat-transfer model [1] confirmed that this can indeed steepen the thermocline and lead to higher storage utilization, as illustrated in Figure 4. The results shown in the figure were obtained for a packed bed of rocks with air as HTF. The fully charged capacity is 440 MWh. Without TCC, the discharged energy per cycle is only 143 MWh (indicated by the green-shaded area in Figure 4, left), giving a utilization factor of 0.33. With TCC, the discharged energy per cycle increases to 210 MWh (indicated by the green-shaded area in Figure 4, right), resulting in a utilization factor of 0.48, or an improvement of 45% relative to the case without TCC.

References
CFD Modeling of the Pollegio AA-CAES Pilot Plant TES System

Scope of project

The present study aims at modelling, by means of a computational fluid dynamics (CFD) approach, the thermo-fluid dynamics behaviour of the thermal energy storage (TES) system equipped in the first advanced adiabatic compressed air energy storage (AA-CAES) pilot-plant built in Pollegio. The sensible-heat storage system is based on a packed bed of natural rocks. Due to the unusual geometry proposed for the TES under investigation, a detailed 3D computational domain was exploited and time-dependent CFD simulations were performed. According to the CFD simulation results obtained, none relevant three-dimensional effects on the temperature distribution into the packed bed were observed.

Status of project and main scientific results of workgroups

Advanced adiabatic compressed air energy storage (AA-CAES)

Pumped hydro storage (PHS) can be considered as the most exploited solution, at global level, for large-scale electric energy storage (EES) applications [1]. However, its applicability limited to suitable sites and its relatively low energy density are among the major limitations of this EES solution.

A valuable alternative to PHS can be represented by compressed air energy storage (CAES). CAES plants operate on a «decoupled» Brayton cycle in which, depending on the grid availability/request of electric energy, compression and expansion occur at different times. In current CAES plants, during the compression stage a large amount of thermal energy is produced and removed (wasted) from the compressed-air. On the other hand, during the electricity generation stage, an extensive supply of thermal energy is required, currently provided by burning natural gas. This inadequate heat management strategy is among the main factors limiting the overall efficiency of this technology.

To overcome this limitation of conventional CAES plants, the concept of advanced adiabatic compressed air energy storage (AA-CAES) has been proposed: a thermal energy storage (TES) is exploited to store the thermal energy produced during compression to be recovered prior to expansion.

Although the AA-CAES concept is still in the research and development stage [2], the expected round-trip efficiency is in the order of 70% [3] comparable to PHS. Other advantages of AA-CAES such as limited environmental impact and lower estimated capital costs make this technology attractive as a potential alternative to PHS for achieving the long-term energy policy developed by the Swiss Federal Council (Energy strategy 2050).

Pollegio AA-CAES pilot plant

To evaluate the feasibility and applicability of the AA-CAES concept, a pilot plant was built in Pollegio, in the framework of a project sponsored by BFE and involving, among others, ALACAES and ETHZ.

A 120 m long section of a tunnel of the Alptransit project not in use anymore was exploited as air reservoir. A thermocline TES system with a packed bed of natural rocks was selected as suitable solution for storing the thermal energy produced during compression. A schematic of the TES system under investigation is reported in Figure 1.

The volume of the packed bed is equal to about 44 m³ with average particles diameter and void-fraction of 20 mm and 0.342 respectively. The Pollegio AA-CAES prototype is designed to operate with charge...
Heat and discharge cycles of 2.75 h each, with a pressure variation of the reservoir between 31.5 bars and 33 bars. Since the compressors train exploited in the pilot-plant is equipped with intercoolers, to replicate the effect of air temperature increment during compression, a 260 kW electric heater is installed between compressors train and TES system to heat up the air up to 823 K.

CFD simulation results and conclusions

Since the TES system is a key component of AA-CAES technology, an extensive CFD analysis was performed with the twofold aim of evaluating its thermo-fluid dynamics behaviour and characterizing its performance. The CFD simulation, performed with ANSYS Fluent 15.0, was mimicking a 38 h thermal pre-charging, intended to rapidly reach steady working conditions, followed by five consecutive charge/discharge cycles. The packed bed was modelled exploiting the porous media approach [4] assuming local thermal equilibrium between solid and fluid phases.

Figure 2 shows the air outflow temperature at the bottom of the TES during charging and on top during discharging. According to the results obtained, the air outflow temperature at the end of discharging decreases by about 50°C with respect to the reference charging temperature, following the same temporal evolution for all the five cycles analysed. Conversely, the air outflow temperature at the end of charging (bottom of the TES) reduces with consecutive cycles reaching 40°C at the end of the 5th charge phase.

Figure 3 shows the temperature distribution into the packed bed as a function of the height, monitored on a line lying between the airflow inlet and outlet regions on the symmetry plane (see r.h.s. of Figure 3). The temperature into the packed bed at the end of charging and discharging is almost the same for all the five cycles indicating that the TES, thanks to the pre-charging, is operating in a repeatable working condition.

From a graphical standpoint, Figure 4 shows the contours of static temperature of the TES system at the end of the first charging.

Another interesting result obtained is, that despite the unusual shape of the TES under investigation no relevant three-dimensional effects on the temperature distribution into the packed bed should be expected. Therefore, the TES system can be accurately analysed with a simplified 2D approach reducing substantially the computational time.

References


Figure 2 (left): Air outflow temperature during charge and discharge phases.

Figure 3 (right): Temperature distribution into the packed bed, as a function of the height, for the five cycles analysed.

Figure 4: Contours of static temperature on different planes. Temperature values are [K].
Performance Evaluation of a Packed Bed TES System Exploited in Compressed Air Energy Storage Technology

Scope of project

In the field of large-scale electric energy storage, advanced adiabatic compressed air energy storage (AA-CAES) technology can be considered as valuable alternative to the most exploited solution of pumped hydroelectric energy storage. In this technology, a thermal energy storage (TES) is exploited to store the thermal energy produced during air compression stage to be recovered prior to expansion. The TES is therefore a key component for a successful exploitation of AA-CAES technology. In this work a thermocline TES, based on a packed bed of rocks, was proposed as suitable and reliable TES solution. A CFD-based approach was then followed to characterize the thermo-fluid dynamics behaviour of the TES system demonstrating the potential feasibility and reliability of its implementation in a real-scale AA-CAES plant working under realistic grid load conditions.

Status of project and main scientific results of workgroups

Reference CAES plant and TES characteristics

The TES system was designed according to the operating condition of the 321 MW Huntorf plant [1] assumed as reference CAES plant for the purpose of this study. This plant is designed for a peak power generation of 2 h at full load of the turbines while the compressors train is dimensioned to charge the air reservoirs in 8 h. During normal plant operations, the pressure range of the air reservoirs is between 46 bars and 66 bars. The nominal air mass flow rate during charging and discharging is equal to 108 kg/s and 417 kg/s, respectively. In order to maximize the storage capacity of the reservoirs and to avoid environmental issues, compressed air is stored at a maximum temperature of 50 °C. After the compression stage, the high-pressure air reaches a temperature of about 500 °C. Calculations showed that, based upon the aforementioned Huntorf CAES plant operating conditions, a total of about 3500 m³ of rocks are required to store the thermal energy produced during air compression stage, i.e. charging phase. A truncated cone shape of the tank, 22 m high, 18 m and 10 m for the upper and the lower diameters respectively, was exploited to prevent thermal ratcheting, i.e. plastic deformation of the tank due to different thermal expansion coefficients.

CFD simulations results and conclusions

A 2D axisymmetric slice of the TES packed bed was selected as computational domain, so to minimize computational costs of the numerous «time accurate» simulations required. Mass, momentum and energy conservation equations were solved using ANSYS Fluent 16.2. Due to the large packed bed volume, a division of the total storage volume in different tanks connected in parallel (2-tanks and 4-tanks) was proposed. The packed bed was modelled exploiting the porous media approach [2] and local thermal equilibrium between solid and fluid phases was assumed. Variable pressure conditions of the TES, according to the pressure level in the air reservoirs during charging and discharging, were also accounted for.

Figure 1 shows the CFD simulation results, of the 20 consecutive charge/discharge cycles analysed, in terms of air outflow temperature from the bottom during charging (l.h.s.) and from top during discharging (r.h.s.) for the three different tank arrangements proposed. According to the results obtained, dividing the overall storage volume in different tanks has a minor influence on the TES performance. Concerning the charging, a maximum air outflow temperature of 150°C was found after a stable thermal stratification into the packed bed was

List of abbreviations

AA-CAES
Adiabatic Compressed Air Energy Storage
CFD
Computational Fluid Dynamics
TES
Thermal Energy Storage

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Figure 1: Air outflow temperature for the 1-tank, 2-tanks and 4-tanks configurations during of some charging (l.h.s.) and discharging (r.h.s.).
Performance Evaluation of a Packed Bed TES System Exploited in Compressed Air Energy Storage Technology

References

Figure 2:
Air outflow temperature during charging:
- a) 22:00 – 6:00;
- b) 7:30 – 12:30;
- c) 13:50 – 20:00;
and during discharging:
- d) 6:00 – 7:30;
- e) 12:30 – 13:50;
- f) 20:00 – 22:00.

attained around the 20th cycle. On the other hand, during discharging, despite the large air outflow temperature reduction, after almost 10 cycles the air temperature was found matching the requirements of the power block during the whole discharge phase.

The TES behaviour was also analysed assuming realistic operating conditions of the CAES plant according to likely real grid load conditions. Therefore, starting from a completely charged TES at the beginning of the day (6:00), two partial charge (7:30–12:30 and 13:50–20:00) and discharge (6:00–7:30 and 12:30–13:50) stages are considered. Then, the stored energy is released in a full discharge run (20:00–22:00), followed by a complete charge process until the next morning (22:00–6:00). A total of 31 consecutive cycles were simulated and the results obtained, in terms of air outflow temperature during charging and discharging, are reported in Figure 2.

Looking at the curves of the 8 h charging overnight (Figure 2a), it can be observed that in the first day the air outflow temperature, at the bottom of the TES, increases up to 415 °C. This undesirable temperature increase is due to the 6 h pre-charging considered which leads to a TES overcharging. In particular, after 6–7 days a stable thermal stratification into the packed bed is attained with a maximum air outflow temperature that does not exceed a thermal threshold of 185 °C. On the other hand, in the two partial charge periods of 5 h (Figure 2b) and 6.2 h (Figure 2c) lower air outflow temperatures are obtained. Focusing on the air outflow temperature during the three discharging periods, in all these cases it is above 480 °C, matching the requirements of the power block from the first discharging. A detailed analysis of the two partial discharge periods (Figure 2d and 2e) reveals that almost no air outlet temperature decrease occurs. The obtained thermal behaviour in both charging and discharging periods allow to conclude that the proposed TES tank is valid not only for a continuous complete charge and discharge operation, but also for a partial charge and discharge cycling condition. Furthermore, the performed analysis has demonstrated that the TES behaviour during charging and discharging is only slightly dependent on the particular operation strategy.
Phase Change Material Systems for High Temperature Heat Storage

Scope of project

The development of technologies for high temperature 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). Here, we focus on high temperature heat storage (above 300 °C) and on metal PCMs due to their advantage in terms of heat transport characteristics, energy density, and high temperature application. The development of an advanced, reliable computational model of a high temperature heat storage system and its coupling to various industrial techno-economic process models is crucial for the design of tailored high temperature heat storage systems and for the assessment of the performance and economic benefit of high temperature heat storage in industrial processes.

Status of project and main scientific results of workgroups

High-temperature heat storage model: Coupled conductive-radiative heat transfer

We focused on the understanding of the coupling between radiative and conductive heat transfer in our porous heat storage media in order to provide guidance on when coupling effects can be neglected.

At high temperatures, radiative heat transfer can dominate the heat transfer. However, the extent of domination highly depends on the material characteristics of the contributing bulk phases (their conductivity, extinction and absorption coefficients). The multiple scales present in porous media used as heat storage system further contribute to the challenge of assessing such systems (micro scale of the porous media and macro scale for the heat storage system). We used our direct pore-level simulation framework to assess the coupling effects between conductive and radiative heat transfer modes. The term «coupling effects» is used to highlight the naturally occurring interaction between the modes. We quantified the coupling effect for an example porous geometry consisting of two phases (stagnant HTF and PCM). We varied their bulk material properties in order to provide material-independent guidance on when to neglect coupling effects. We identified that coupling effects, assessed as being the ratio between the sum of the radiative and conductive heat fluxes of the uncoupled and the coupled case (ζ), can reach up to 15 % (Figure 1). The ratio of the thermal conductivities, kf/ks, and the optical thickness, κL, were identified as key parameters contributing to the importance of the coupling. Coupling effects in the range of 4 % are expected for specific HTFs and PCMs considered in our heat storage solutions (air and aluminum alloys). The model de-
Heat

Phase Change Material Systems for High Temperature Heat Storage

development and the results of this study have been submitted for publication to an international journal.

High-temperature process modeling: Techno-economic model of aluminum production

Aluminum is produced more than any other non-ferrous metal at present. There are two ways to produce aluminum: primary aluminum smelting and secondary aluminum melting.

According to the International Aluminum Institute, the primary aluminum smelting energy consumption is 690'170 GWh p.a. in Europe in 2014 [1]. Typical aluminum melting temperatures are around 650 °C to 700 °C and offer a high potential to reduce the energy consumption when operating in batch by utilizing high temperature heat storage. An optimization study of such a batch process (Figure 2, top) showed that the cost of aluminum production in terms of operational expenditure (OPEX) can significantly be reduced (in the best case by almost a factor of two) when introducing high temperature heat storage solutions (Figure 2, bottom).

The competition between sensible (SHS) and latent heat storage (LHS) in terms of cost and performance points to the optimal solution: combining both. If combined optimally, sensible and latent heat storage can preserve the advantages of both technologies: high storage capacity and discharge at constant temperature for latent options and low cost for sensible options.

High-temperature process modeling: Performance model of direct steam generation

The need for storage in direct steam generation is dictated by the intermittent nature of the provided heat. This intermittency can result from the utilization of renewable energy sources or variation in the process operation. Short scale intermittencies (timescale of sub-seconds) are usually compensated by an active control system activating injections at different locations. Medium scale intermittencies (timescale of minutes) can be compensated for with large heat storage units. For example, phase change materials have a potential to act as a passive control system and reduce the cost and complexity of direct steam generation power plants.

We developed a transient, one-dimensional model of the direct steam generation unit in order to get a preliminary understanding of the benefit of the usage of heat storage units in direct steam generation applications. Our model incorporates multi-model heat transfer (conduction, convection and radiation). The model reveals that there is a significant potential in terms of performance when heat storage options via PCMs are integrated in the steam generation process.

For example for an assumed input energy of 5500 W/m (per
length of the tube), the steam generation operates at an efficiency (ratio of useful energy and input energy) of 78% for the case without storage and of 73% for the case with storage, both at steady state.

The lower efficiency of the storage-case results from the fact that part of the input energy is required to charge the storage.

Once the transients are introduced (for example: 10 seconds operation at 20% of initial heat flux followed by 10 seconds of full heat flux, continued over 3 minutes), the useful energy drops below 36% for a significant amount of the 3 minutes for the case without storage, while the storage case can maintain the useful energy above 67% for the 3-minute intermittency duration. The exact behavior of the direct steam generation unit depends on the amount of incorporated storage, the charging/discharging state of the storage, and the operating conditions.

Conclusions and future work

The transient, multi-dimensional and multi-model heat transfer model of the heat storage unit was reduced and used to assess and quantify coupling effects of radiative and conductive heat transfer. The introduced error for a variety of HTF and PCM material combinations was quantified and, consequently, guidance on the validity and accuracy of simplified conduction-radiation models was provided. The heat storage unit model was mathematically reduced and incorporated into two high temperature industrial process models:

- aluminum processing, and
- direct steam generation.

The aluminum processing model was coupled to an economic model and predicted that operational cost could be reduced by almost a factor of 2 when storage was incorporated. The direct steam generation model focused on the ability of high temperature heat storage to damp and counteract intermittent heat inputs. It predicted that heat storage can maintain the useful energy at a level significantly below the steady state case when exposed to intermittent input energy.

Both process models contribute to the notion that heat storage integration in industrial processes can significantly benefit their performance and cost.

In a next step, we will optimize the industrial processes (in terms of cost and performance) by utilizing tailored high-temperature heat storage units (designed with our advanced heat storage unit model) with desired energy and power densities and storage temperatures.

Acknowledgement

The financial support of CTI Swiss Competence Centers for Energy Research (SCCER Heat and Electricity Storage) is kindly acknowledged.
Tubular SiSiC Structures for High Temperature Applications

Scope of project

Silicon infiltrated Silicon Carbide (SiSiC) is a prevalent ceramic material for applications in harsh environments such as burners, recuperators and heat storage systems. It has wide industrial applications due to its high mechanical and chemical stability at elevated temperatures and its excellent thermal shock resistance. SiSiC is also particularly suitable for near-net-shape production of complex components such as porous structures via melt infiltration of silicon. At temperatures above 1000 °C, three main factors may limit the performance of SiSiC: bead formation due to melting of silicon, severe oxidation especially in presence of water vapor, and high thermally induced stresses. We investigated the first two factors earlier for various SiSiC lattices [1] and here focus on the thermal behavior of SiSiC lattices. This work builds the foundation for future analysis of their thermal stress resistance.

Status of project and main scientific results of workgroups

SiSiC tubes were manufactured from alpha-SiC powders bound within silicon, which was melt-infiltrated at high temperature (EngiCer).

The test rig (Figure 2) was designed and assembled to reach high temperatures (max. 1600 °C) in order to measure heat exchange capabilities of the porous media. A custom-made furnace able to provide high thermal power (up to 3000 W) in a well-defined cylindrical area (of 3 cm in diameter and 10 cm in length) was commissioned from Xerion (Freiberg, D). An expansion

Experiments

The experimental test rig consists of a SiSiC tube, which can be loaded with porous samples such as the one shown in Figure 1. The tube is considerably longer than the samples in order to ensure developed inlet and outlet flow conditions.

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List of abbreviations

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<th>Abbreviation</th>
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<tr>
<td>LTNE</td>
<td>Local Thermal Non-Equilibrium</td>
</tr>
<tr>
<td>SiC</td>
<td>Silicon Carbide</td>
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<tr>
<td>SiSiC</td>
<td>Silicon infiltrated Silicon Carbide</td>
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Figure 1: As received SiSiC random foam sample side view (left) and top view (right).

Figure 2: High temperature measurement apparatus.
chamber was coupled to the extended tube in order to ensure laminar flow at the inlet. Preliminary tests at a temperature of 1280 °C were successfully performed on empty tubes and tubes filled with random foams with air flowing at 13.2 m/s. Namely, we measured the temperature and pressure of air inside the tube at the inlet and outlet. The temperature of the furnace was controlled with a thermocouple embedded inside the furnace between the two heating elements. The temperature on the outer surface of the tube was as well measured using three thermocouples placed on the tube in the middle part (the heating zone).

**Numerical model**

An axisymmetric LTNE (local thermal non-equilibrium) steady-state model was developed and solved using a commercial numerical solver (COMSOL Multiphysics). Similar to the experiments, the tube is filled with a porous medium, modeled by a homogenized medium with effective properties taken from Haussener et al. [2] obtained by direct pore-level simulations.

**Results**

During the preliminary tests neither the tube nor the porous foam showed any remarkable signs of degradation.

The results provide evidence that the heat transfer capabilities of the tube filled with a porous medium are more than two times larger than that of an empty tube (overall thermal efficiency of the empty tube was 33 % while 78 % for porous).

As depicted in Figure 3, samples with smaller cell size show to be more effective in removing heat from the tube (decreasing the nominal pore diameter by an order of magnitude increases the overall heat transfer coefficient by about 20 %). However small pore diameters lead to higher temperature variations in the solid foam (Figure 3, right), which is expected to cause higher thermally induced stresses.

**Conclusions and future work**

A high temperature test rig, designed to operate up to temperatures of 1600 °C, was designed to measure heat transfer effectiveness of ceramic porous media.

Preliminary experiments were successfully performed on empty tubes and tubes filled with porous ceramics made of random foam structures, indicating that the heat exchange efficiency can be almost doubled when introducing the porous media. The experiments are complemented with an advanced LTNE computational model of the system.

The model was used to predict the performance of the porous ceramics and to optimize their structure for best performance. For this purpose, several random lattice structures and dimensions were modeled to verify the effectiveness of these systems and compare with the empty tubes as a benchmark.

Different structures will be designed and manufactured. These samples will be used in the developed test rig and the results will be further used to validate the numerical model and provide guidance for structural engineering for best performance.

**References**


Thermal Absorption Energy Storage

Scope of project

Closed sorption heat storage, for residential applications, based on water vapor absorption in aqueous sodium hydroxide solution (NaOH-H₂O) or other aqueous solutions like LiCl, LiBr, KOH theoretically achieves a significantly higher volumetric energy density compared to sensible hot water storage systems [1].

Status of project and main scientific results of workgroups

Assessment of heat and mass transfer unit

In the frame of the EU FP7 project «Combined development of compact thermal energy storage technologies – COMTES», a NaOH-H₂O prototype with 10 kW output power was designed and built. Operation was carried out in both process modes – absorption and desorption – in steady state boundary conditions [2]. The heat and mass exchanger assessment and the comparison with the results of the initial numerical model used to design the heat and mass exchanger was done.

For the absorption process, it appears that the dilution of the sodium hydroxide (water vapor absorption in the liquid) occurs to a limited extent. For the desorption mode, a full comparison of the experimental and modelling results was carried out [3]. For water vapor desorption from a sodium hydroxide solution over a horizontal tube bundle with smooth tubes, a proposition of a correlation for the Nusselt number is given [4]. Within 25 % of relative uncertainty, numerical and experimental results have a similar order of magnitude for the desorption process. However, for the absorption process, the measured exchanged power is much lower than expected.

Surface wetting of absorbers

The low absorption power can be explained by the poor wetting of the stainless steel (AISI 316L) tube bundle from the absorption/desorption unit [2] and the short residence time of the sodium hydroxide in the water vapor.

As wettability is depending on the solid surface properties (e.g. roughness, surface oxygen content and the polar component) and on the fluid properties [5], different surface modifications (structuring, annealing) and fluid tuning (use of surfactants to reduce the surface tension) were investigated [6].

Higher surface area is obtained by mechanical texturing; by developing structured surfaces, an enhancement of the heat transfer coefficient is aimed as well as a size reduction of the absorber unit. Moreover, annealing in air increases the surface metal oxide content; a better wetting in terms of low wetting times was obtained for all the annealed samples. This can be explained by physical bonding between polar groups from the testing fluid and the surface metal oxide.

The influence of different surface texturing on the wetting with concentrated sodium hydroxide, without/or with surfactant addition was assessed. Compared to the reference case, the surfactant addition leads to a better wetting, decreasing the wetting time. The influence of two main parameters was analyzed:

- the residence time of the sorbent (sodium hydroxide solution) in the water vapor (sorbate) and
- the surface wetting behavior of the heat transfer fluid on the exchanged power.

A 1 kW absorption/desorption unit using the falling film working principle, concentrated sodium hydroxide (aqueous solutions) and water vapor as sorbent/sorbate pair was designed. Optimized tubes and sorbent will be used for the absorber/desorber tube bundle in order to quantify the impact of these technologies on the heat and mass exchanges.

References


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Storages for Flexibility of Power and Heat

Scope of project

The aim is the advancement of novel storage technologies used at the intersection of power-to-heat(-to-power) in the framework of the project Dual Energy Storage & Converter (DESC). In this context, various models of thermal storages as well as their combination with heat pumps for both domestic and industrial applications have been further developed and verified within 2016. The models were used to evaluate and optimize existing systems as well as to design new ones. New phase change materials were identified and implemented in novel thermal storage technologies at key temperatures to be efficiently combined with heat pumps and chillers. Laboratory setups were designed to test and evaluate the application potential of these technologies under realistic conditions.

Status of project and main scientific results of workgroups

All the defined milestones for phase I were successfully reached. This report summarizes the work conducted by the Thermal Energy Storage (TES) group at Lucerne University of Applied Sciences (HSLU) during the year 2016.

Simulation and experimental characterization of high-power, latent heat storage

In 2015, a computational model of a latent heat storage based on tube bundle heat exchangers was successfully developed and verified by HSLU within the framework of SCCER HaE [1]. Due to the low heat conductivity of phase change materials (PCM), finned heat exchangers (HEX) are often utilized as alternative to tube bundle heat exchangers.

In an extension of previous modelling work, the solidification in a commercial Sunamp Heat Battery using a finned HEX was modelled and experimentally characterized [2]. The enthalpy based method was used as the most suitable approach to predict the heat transfer rate between the PCM and the heat transfer medium. A comparison between the heat flow of the storage as a function of time and the model predicted values are presented in Figure 1. The model can be used to optimize the HEX design regarding production costs and heat transfer rate.

Simulation of thermal storage for residential heating systems with heat pump to increase flexibility in smart grids

Integrating large shares of variable renewable energies requires high flexibility from the major consumers to balance energy consumption and production. Ideal candidates for this balance are heat pumps due to their high efficiency and the energy demand for space heating.

To decouple heat production and consumption for residential heating, the impact of additional thermal storage systems as well as the building inertia was investigated (see Figure 2). The impact of different heat pump capacities, thermal storage systems and building types was studied with Matlab/Simulink simulations based on detailed and experimentally verified models for the individual components [3].

The integration of thermal storages enables an increase of the flexibility (fraction of the day with blocked heat pump activity) at the expenses of a lower efficiency. In particular,
Storages for Flexibility of Power and Heat

Figure 2: Overview of modelled components and motivation for enabling flexibility by increased exploitation of thermal storages and building inertia.

References

Development of novel PCM storage technologies

Concept based on PCM slurries

In this concept, similarly to ice slurries, only a part of the phase change material changes phase during charging/discharging of the storage, enabling pumping of the storage medium. Such systems promise higher energy densities both as refrigerants and as storage media while presenting better heat transfer characteristics than conventional latent heat storage technologies. This technology is expected to deliver high thermal power and high temperature stability in a compact design that can operate with conventional components (heat exchangers, pumps, etc) [6].

For the retrofitted old building, a substantial increase can be achieved. The integration of a storage element is vital to compensate the efficiency losses acquired by enabling flexibility [4, 5].

Concept based on direct contact heat exchange

In this project, a novel latent heat storage system based on a direct contact between the heat transfer fluid (HTF) and the PCM was developed, to drastically increase heat transfer in latent storage systems. These systems preserve the high energy density associated with latent heat storage while avoiding complicated and cost-intensive heat exchangers. Additionally, the ability to generate large heat exchange surface area at the interface of the HTF bubbles and the PCM can result in high thermal power output. A proof of concept test-rig has been built and evaluated in HSLU (see Figure 3). The first results show that such a system can achieve a heating power up to 25 kWm⁻³ at a logarithmic temperature mean of 2.5 K, while the power output can be controlled directly via the mass flow. [7]

Novel PCM research – esters

In this work, unbranched, saturated carboxylic esters were evaluated with respect to their suitability to be used as storage media for latent heat storage applications. Therefore, important thermophysical properties were gathered both by means of literature research as well as by experimental measurements. Additionally esters were critically evaluated against other common phase change materials in terms of their environmental impact and their economic potential. The experimental investigations were performed for eleven selected ester samples with a focus on the determination of their melting temperature and their enthalpy of fusion using differential scanning calorimetry. Both experimental results and literature data revealed that the highest potential of esters against other phase change materials lies in low temperature applications where the main alternative is using salt hydrates [8].

Figure 3: Laboratory test-rig for the investigation of direct contact heat exchange concept.
One of the options to store electrical energy is the use of batteries. This direction was investigated within this work package of this SCCER.

Along the rather exploratory phase I, the main efforts were dedicated to gaining basic knowledge on prospective battery systems, with the goal to identify the most promising ones for the development of future technologies.

Three main directions were pursued for material related activities, and all partners were involved in the different topics. Under the lead of Maksym Kovalenko from ETHZ and Empa the search for high-energy negative electrodes for lithium-ion batteries was going on in phase I, in order to outperform current commercial battery systems. Strong efforts were also made on alternative realistic systems, more specifically on sodium-ion batteries, an activity under the lead of Claire Villevieille from PSI. Also, under the lead of Katharina Fromm from the University of Fribourg, there was a search for alternative energy storage concepts being possibly important in the far future, like the lithium-air and lithium-water chemistries. The main focus was however on both Li-ion and Na-ion research where all three groups provided their core expertise and demonstrated collaboration in research, and applied for joint projects.

Of course, the production processes for the new materials as well as the electrodes thereof needed to be understood. Challenges expected during the production of real sized battery cells under real economic conditions needed to be identified and feedback given to the material developers. The underlining question is how to produce batteries in a cost effective way. These activities are under the lead of Axel Fuerst from Berner Fachhochschule (BFH) Biel.

Also, the activities at Empa formerly under the lead of Urs Sennhauser (retired) and now under the lead of Corsin Battaglia are currently being integrated into this work package dealing with all aspects of batteries.

**Li-ion batteries**

The research activities focusing on Li-ion batteries included highly exploratory search for novel materials as well as very practical tasks raised by the Swiss industry (Belenos Clean Power Holding). The leitmotif was the development of anode materials (nanoscale materials composed of Sn, Sb, SnSb alloys, and metal phosphides). Initially these nanomaterials were synthesized using new, often costly but precise methods. The preparation of selected materials, such as antimony, was then further followed, yielding low-cost synthesis that had been scaled-up with the help of Belenos to 100 g scale. The materials were then tested at the premises of the industrial partner Belenos. The first results from Li-ion and also Na-ion full-cell laboratory experiments, using LiCoO_2 and Na_1.5VPO_4.8F_0.7 as cathodes, indicate stable cycling performance of SnSb nanocrystals with respective lithium- and sodium-ion anodic specific charge of 600 mAh/g (up to 3.0 V) and 400 mAh/g (up to 2.7 V). The voltage in parentheses is the average one during cell discharge.

Within both Li-ion and Na-ion batteries research domains, experimental studies were supported with a computational structure prediction work.

**Sodium based batteries**

Due to the low abundance of lithium and thus projected increasing cost, cheaper alternatives based on other alkali metals were investigated.

The main focus was on sodium which is a bigger and heavier cation compared to lithium, thus the specific energy of a sodium-based battery is lower. This drawback can be compensated by higher voltage cathodes and higher specific charge anodes. For the latter, the alloy/conversion reaction of Sn as a model element was investigated but the volume change close to 400% resulted in particle fractures and strong capacity fading.
Thus, we switched to stabilized Sn-based materials (MnSn₂, FeSn₂, and CoSn₂) as the inactive transition metal combined to an active element mitigates the volume changes. With an appropriate engineering of the electrode, >400 mAh/g was obtained for MnSn₂ during 100 cycles. However, in a full-cell, too much Na was consumed for solid-electrolyte interphase (SEI) formation.

Thus, the activities were re-focused on the development of low cost, bio-waste based negative electrodes. Nut shells from almonds were identified as a source of promising carbonaceous material and a specific charge of 270 mAh/g was demonstrated during more than 200 cycles. Regarding the positive electrode, the layered oxide P2-Na₂₀·₆₇(Mn₀·₆Fe₀·₂₅Co₀·₁₅)O₂ was investigated, where a part of the Co has been substituted by Al. The Al-based materials demonstrated a specific charge of >130 mAh/g. Now, the next step will be to combine the bio-waste negative electrode material with a low cost positive electrode material.

In the frame of material research activities in the long run, a concept of SnO₂@C-Nanorattles was tested, in which the active material can expand and shrink inside a conductive shell material. Also, heterometallic single source precursors were synthesized with different equivalents of sodium alkoxides, to get after combustion the phase Na₈₀·₆₇CoO₂₆ as a prospective material for sodium-ion batteries. Electrolytes based on different types of imidazolium- as well as pyrrolidinium-based ionic liquids were synthesized and their inflammability, thermal and electrochemical stabilities were examined. Pyrrolidinium-based ionic liquids based on a benzo-15-crown-5 core showed one-dimensional channel in the solid state, promising excellent Li-ion transport properties.

Further, for possible future battery chemistries, a buffer of an aqueous electrolyte for a dual-electrolyte Li-air battery was optimized. A full cell assembly of a Li-air battery system was tested.

**Battery production**

In parallel, steps towards a production line for small series of battery cells were taken. A technology screening was finalized and a test plant to optimize the critical system parameters for slitting and welding processes is in place. Demonstration of prototype production of battery electrodes on newly developed processing machinery is working, tested as proof-of-concept with nanosized LiCoO₂ cathodes.

For the battery production work a new research group was founded at BFH, focusing on the development of innovative and cost-effective production technologies and process optimization.

The aim is to support Swiss battery industry and battery production equipment suppliers from Swiss machine industry, as well as suppliers of electrode materials. The purpose is to share machine and process knowledge from a holistic approach to offer support with deeper process knowledge and to identify potential for process optimization.

Further, BFH aims to connect Swiss excellence in electrochemical research with the production at the shop floors, inter alia, due to a pilot line for testing and demonstration (cf. Figure 1).

**Battery testing**

Finally, a unique 500 kW battery testing facility was built at Empa, equipped with temperature, gas, and flame sensors, enabling aging experiments and stress cycling of cells and batteries. Worst case scenarios such as fire and explosion are contained by a sand extinguisher and pressure relief panels. Failure mechanisms of commercial batteries were investigated and identified using electron microscopy and focused ion beam techniques and, to facilitate the interpretation of data, a theoretical statistical model for electrochemical impedance spectra of batteries was developed.
Development of Nanostructured Electrode Materials for Li- and Na-Ion Batteries

Scope of project

Lithium-ion batteries (LIBs) with higher energy and power densities are actively sought to increase the competitiveness and widespread deployment of electric cars and stationary energy storage units, and for enabling new portable electronic devices. Great hopes have been extended to conceptually similar sodium-ion batteries (SIBs) due to the much greater natural abundance of Na and the possibility of replacing copper anode current collectors with aluminum foils. The eventual success of SIBs will require this technology to have the same energy density as LIBs.

Status of project and main scientific results of workgroups

Anode materials – tin-antimony alloys

We have developed a simple and inexpensive colloidal synthesis of SnSb nanocrystals (NCs) and demonstrate their utility as lithium- and sodium-ion anode materials [1], see Figure 1.

In particular, SnSb NC Li-ion anodes deliver capacities of ~890 mAh g⁻¹ for 100 cycles at a current density of 200 mA g⁻¹ and show excellent rate capability, reaching 90% and 80% of the theoretical capacity at current densities of 1000 and 5000 mA g⁻¹, respectively.

Similarly, SnSb NCs show also outstanding Na-ion storage properties with only ~5% capacity loss over 100 cycles at a rate of 5000 mA g⁻¹.

Full-cells can be constructed with SnSb anodes and state-of-the-art cathodes, achieving anodic capacities of 600 and 400 mAh g⁻¹ with an average discharge voltage of 3.0 and 2.7 V for lithium- and sodium-ions, respectively.
Development of Nanostructured Electrode Materials for Li- and Na-Ion Batteries

Cathode materials – iron(III) fluoride

With the demands placed on batteries constantly increasing, new positive electrode materials are desired with
• higher energy density,
• satisfactory power density,
• long-term cycling capabilities,
• composed of highly abundant low-cost elements.

One such low-cost cathodic material is iron(III) fluoride – FeF₃. Its theoretical capacity for single-electron reduction, accompanied with the insertion of Li⁺ ions, is 237 mAh g⁻¹. Herein we have developed a new synthesis for nanocrystalline FeF₃ using inexpensive iron trifluoroacetate as a molecular single-source precursor [2], see Figure 2.

We also extended this simple chemistry to several transition metal difluorides (M = Fe, Co, Mn).

With FeF₃, high capacities of 220 mAh g⁻¹ were attained at moderate current densities of 100 mA g⁻¹ (~0.5 C). In addition to high capacity, we find a strong evidence for high rate capability. Capacities of up to 155 mAh g⁻¹ were observed with 1 minute (10 Ag⁻¹) charge-discharge ramps, and at least 88% of this capacity was retained after 100 cycles. When tested as a sodium cathode, FeF₃ exhibits capacities of up to 160 mAh g⁻¹ at a current rate of 200 mAh g⁻¹.

References

Figure 2:
(a) Photograph of a vial containing iron(III) trifluoroacetate («Fe(TFA)_3»);
(b) Powder XRD pattern of «Fe(TFA)_3» before and after decomposition to FeF₃ (PDF 033-0647) with an asterisk indicating a minor impurity of small FeF₂ (its (110) reflection (PDF 045-1062));
(c) TEM images of FeF₃;
(d),(e) HRTEM images of FeF₃;
(f) Selected-area electron diffraction (SAED) indexed with ReO₃-structure of FeF₃;
(g),(h) SEM images of FeF₃.
**Scope of project**

Due to the abundance of sodium in the Earth’s crust, Na-ion batteries could be a more economical alternative to lithium-ion batteries. However, one has to consider the lower energy density of this technology and thus, Na-ion batteries could be applicable for stationary energy storage. While there’s a wide array of choice for cathode materials, the choice for a stable anode material is limited to disordered carbons [1] as graphite is not suitable to the sodium-ion system. Disordered carbon materials are generally synthesized out of industrial products such as sucrose and polyacrylonitrile [2]. These compounds, however, can be replaced by biowaste materials which present the advantage of further decreasing the cost of the electrode materials. In this study, shells from almonds were used as a source of carbonaceous materials and used as negative electrode for sodium-ion batteries. Various atmosphere were used for the synthesis and the impact on the carbon properties was investigated by means of galvanostatic cycling, X-ray diffraction (XRD), scanning electron microscopy (SEM). Based on this material, a full cell with layered oxide \( \text{P}_2\text{Na}_0.67(\text{Mn}_{0.6}\text{Fe}_{0.25}\text{Co}_{0.15})\text{O}_2 \) , where a part of the Co had been substituted by Al, on the positive electrode was investigated.

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

After establishing a careful guideline to optimize the electrode engineering in conversion based materials (Sn, MnSn\(_2\), FeSn\(_2\), CoSn\(_2\), Figure 1) [3] and the electrolyte formulation both of which strongly influence electrochemical cycling performance, we developed new materials (negative and positive electrodes) for cheap Na-ion batteries.

For the former, the most common binder used in Li-ion batteries, polyvinylidene difluoride, was found to be unsuitable for Na-ion batteries due to its decomposing to form NaF [4]. Additionally, a systematic investigation of particle size, binder and conductive additive ultimately led to an optimized electrode composition consisting of 70\%wt micron-sized active material, 18\%wt carbon black and 12\%wt sodium carboxymethyl cellulose (Na-CMC) binder [5] (Figure 1).

For the latter, we have developed a new research direction to drastically reduce the cost of the Na-ion batteries by making carbonaceous materials (negative electrodes) based on biowaste.

**Experimental**

Almond shells were first ground using mortar and pestle and then soaked in 10\%H\(_2\)SO\(_4\) solution for 24 h. Removal of the acid was subsequently done by washing with deionized water until reaching neutral pH. The shells were dried at 80°C for 12 h prior to size reduction using ball milling. Carbonization was then operated in a tubular oven at 1000°C under different atmospheres \([\text{Ar, } \text{N}_2, \text{Ar }+ 5\% \text{H}_2 \text{ (AWS)}]\). Finally, the resulting carbonaceous samples were named as \(\text{Ar}_x\), \(\text{N}_x\), and AWS. Galvanostatic cycling was performed in...
a half-cell with sodium metal as counter electrode and 1 M NaClO₄ in propylene carbonate used as the electrolyte. The electrode was composed as such 85:5:10 (active material: Super C65:CMC).

**Results**

The SEM images (Figure 2) reveal similar morphological features among the carbonaceous samples whatever the atmospheres used. The primary particles are very small below the micrometre range even if some of them can be very large with several microns as can be seen in the case of the N₂ sample. As expected from the ball milling procedure, the particle size distribution is also very broad. We noticed that the particles tend to form big agglomerates of several tens of micrometres.

The XRD patterns of the carbonized samples reveal characteristic broad peaks at 2θ values ca. 22° and 44° corresponding to the (002) and (100) planes, respectively. A minor impurity (CaS) was detected at 32° and 45° in the patterns of the carbonaceous materials and originated most probably from the calcination of CaSO₄ present in the almond shell.

The cycling performance of the different materials is shown in Figure 3. Initially, both Ar and N₂ have specific charge values at ca. 325 mAh/g with a Columbic efficiency of ca. 70% for the first cycle. The sample AW5 exhibits the lowest specific charge at ca. 200 mAh/g for the first cycle and the lowest Coulombic efficiency ca. 50%.

On succeeding cycles, the samples synthesized under Ar and N₂ present stable specific charge values at ca. 265 mAh/g whereas the one synthesized under AWS delivers only 100 mAh/g. The relative low electrochemical performance obtained for AWS could be linked to the higher level of graphitization obtained from Raman spectroscopy analysis.

Surprisingly, the specific charge of the N₂ sample increases accompanied by a decrease in Columbic efficiency. This may be attributed to the electrolyte decomposition upon cycling. Further optimizations are ongoing to verify the electrochemical performance.

**Full Cell Testing**

The new anode material was tested in combination with the also developed new cathode materials based on the 20 most abundant elements in Earth crust [6].
Development of Low Cost Na-Ion Batteries

On the positive electrode we investigated the layered oxide P2- Na 0.67(Mn0.6Fe0.25Co0.15)O2, where a part of the Co had been substituted by Al, combined with the negative electrode based on the carbonaceous biowaste material described above. The electrochemical performance of the materials is presented in Figure 4 (left) at different cycling rates. The Al-based materials demonstrated higher specific charge at ca. 140 mAh/g at 1.6C, compared to 115 mAh/g for the reference material NaMFC. After 50 cycles, a specific charge higher than 130 mAh/g is still provided for the Al-based compounds whereas only 80 mAh/g is reached in the case of NaMFC.

Conclusion
Disordered carbons have been successfully synthesized using biowaste materials i.e. almond shells.

The inert atmosphere used during synthesis has a significant impact on the physical and electrochemical performance of the disordered carbons. Carbons synthesized out of Ar and N2 have similar specific surface area, pore size distribution and electrochemical performance despite a probable different surface composition. Thanks to this approach, we obtained a specific charge of 259 mAh/g.

Meanwhile, carbons synthesized under a reducing atmosphere (AWS) resulted to poorer electrochemical performance compared to the ones synthesized under an inert atmosphere.

Finally, the target is to generate full-cell Na-ion batteries combining bio-waste negative electrode materials with low cost positive electrode materials. As indicated in Figure 2 (right) some issues still need improvement to maintain the stable specific charge and this will be the challenge of the next SCCER period for the Na-ion batteries.

References
Development of Anodes, Cathodes and Electrolytes for Alkali Metal Ion Batteries and Li-Air Batteries

Scope of project

Electricity storage is an important contribution to the plans in energy turnaround. Stand-alone devices are expected to store electricity overproduction within short times of charging and releasing it when needed. This requires higher energy densities, less toxic and more abundant materials, better electrolytes and improved electrodes. Together with the teams of Maksym Kovalenko and Claire Villevieille, we contribute to the development of new cathode and anode materials, new electrolytes and test them in coin cells.

Status of project and main scientific results of workgroups

Development of ionic liquids as an electrolyte for rechargeable alkali metal ion batteries

Different types of imidazolium- as well as pyrrolidinium-based ionic liquids were synthesized with crown ether based moieties. Their inflammability, thermal and electrochemical stabilities were examined.

The imidazolium ionic liquids with benzo-15-crown-5 showed the best thermal stability up to 400 °C, while the others are stable until 320 °C. The electrochemically most stable ionic liquids were the ones with a butyl-substituted imidazole ring (Figure 1). Pyrroldinium-based ionic liquids based on a benzo-15-crown-5 core showed one-dimensional channel in the solid state, promising excellent Li-ion transport properties. The purification and upscaling are ongoing and first ionic liquids are under testing for sodium ion batteries at PSI (collaboration C. Villevieille).

Development of anode materials for rechargeable alkali metal ion batteries

While providing higher capacities than commercial graphite, alkali metal alloys undergo large volume changes during insertion/extraction of alkali metal ions, causing cracks in the electrode and capacity drops.

Nanorattles, in which the active material can expand and shrink inside a conductive shell material, have been designed to prevent these drawbacks. Core-shell particles of Sn@SiO₂ are formed by the reverse micelle microemulsion method. They are coated by carbon and chemically etched to form Sn@C. After this process, tin was found inside and outside of the shells (Figure 2) and the electrochemical tests of this material with lithium showed a rate capability of 590 mAh/g at C/10 after 10 cycles. We will further optimize the carbon shell size, the shell shape and the loading of Sn by slight synthesis modifications.

Development of cathode nanomaterials

Using the precursor method, we have prepared nanoscale LiCoO₂ of different particle and crystallite sizes, which are currently being tested in half and full cell systems. These materials can be obtained in multi-gram scale. In analogy, NaCoO₂ was made from similar precursors. While for the lithium
Development of Anodes, Cathodes and Electrolytes for Alkali Metal Ion Batteries and Li-Air Batteries

Development of Li-air batteries with dual electrolytes system

The aim of dual-electrolyte Li-air battery is to obtain reversible electrochemical reactions with high capacity. We found that a buffer solution in aqueous electrolyte increased the O₂-solubility and lowered its alkalinity.

The challenge of the full cell assembly was to seal the lithium metal tightly and to exclude CO₂ entering the cell from outside. After managing the sealing and optimizing the aqueous electrolyte, new MoS₂-electrodes from Prof. H.G. Park, ETHZ (collaboration within an NRP-70 project) were tested in full cell setups.

The cyclic voltammograms showed reversible redox reactions at the scan rate between 0.1 and 1 mV/s. While the first charge capacity provided promising 800 mAh/g at 10 μA, the capacity dropped rapidly to 70 and 20 mAh/g (Figure 4). We will investigate in-depth electrochemical analysis and characterization to understand the electrochemical behavior and to improve the capacities.

Development of TiO₂ as photocatalysts

In collaboration with the work package on CO₂-reduction, TiO₂ nanocapsules were synthesized.

They were found to be more active for water splitting than commercial TiO₂. The presence of different amounts of ca. 20 nm silver nanoparticles (AgNPs) in and on the TiO₂ nanocapsules had no positive effect on the catalysis, which is why we are now studying the size effect of the AgNPs (Figure 5). The CO₂-reduction was shown to yield among other products also methanol.

um compounds, the structures of the precursors have been mostly identified, they remain unknown for the sodium precursors.

For the olivine LiMnPO₄, several crystallite sizes and shapes at the nanoscale were synthesized, their preferred Li-ion diffusion pathways identified [1] and the samples are now being tested in full cells (Figure 3).

Figure 5 (bottom):
TEM and SEM pictures of (A) TiO₂-NC, (B) TiO₂-NS, (C) Ag/TiO₂-NC and (D) Ag/TiO₂-NS.
Discovery of Fundamental Relations Between Impedance Spectra and Charge Transport Mechanisms

Scope of project

Impedance spectroscopy is a widely used technique for the investigation of charge- and mass-transport, as well as the associated degradation, in complex systems. It has become a key analytical tool for any group pursuing Li-ion battery research and development. Being a non-invasive method, it can provide valuable information from batteries under actual working conditions. However, there are still great challenges in this field, mainly related to the interpretation of impedance measurements.

Status of project and main scientific results of workgroups

Until recently, most models used in the parameterization of impedance data were based on the assumption that the transport is diffusive. For instance, the bulk impedance resulting from Li-ion intercalation, as ions are injected into the cathode through the solid-electrolyte interface, has been always modelled with the Warburg element, $Z \propto (i\omega)^{-1/2}$. However, experimental evidence indicates that not all data can be explained with circuits made of resistors, capacitors, inductors, and Warburg elements. Then, models have been proposed, which include constant-phase elements (CPEs), $Z \propto (i\omega)^{-n}$, where the phase is $-n\pi/2$, and the exponent $0 < n < 1$ that has no clear meaning.

In a previous work [1], we found that the general CPE can be understood based on a fundamental and more general formulation of the transport, which contains diffusion as a specific case. Within this framework, we showed that the constant-phase behaviour displayed by the impedance of battery parts have a universal statistical origin and that the value of the phase characterizes the type of transport in the system. Ion transport in the electrodes is in general non-diffusive, and this is characterized by the corresponding CPE exponent.

It was also shown that there are correlations of practical importance between $n$, the cell state of charge, and capacity loss. The new approach also links $n$ with the dependence of the cell capacity on the charging rate. Larger deviations in the behavior from the diffusive limit will result in stronger rate-dependency of the capacity.

Applications in the analysis of battery performance and charge relaxation in ion conductors and dielectrics

As a continuation of this work, we were able to show that the laws that we previously applied to the transport of ions (involving hopping) can be extended to describe the orientation of localized dipoles [2]; a model meant to describe polymers widely used in electrochemistry.

This led us to discover universal constraints to the form of dielectric response spectra. In this extension of the work, phase exponents also play the essential role of characterizing the type of relaxation taking place in complex systems, allowing a clear identification of fast (exponentially) relaxing systems and slow (algebraically) relaxing ones.

The classification into slow and fast, based on the low-frequency behavior of the dielectric function, has a general mathematical origin and applies not only to dipolar systems but also to materials with moving ions such as electrodes. The conductivity relaxation in the diffusive limit is equivalent to the relaxation function of a dipolar system that satisfies Debye’s model. Non-diffusive transport has a relaxation similar to dipolar glasses. The relevant exponents for dipolar systems correspond to the rising and lowering slopes of the loss-peak and can be extracted within a standard measurement of dielectric losses.

These results are being applied not only in our battery research, but also in the field of dielectric polymers for energy harvesting and actuators [3, 4].

References


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Manufacturing Technologies and Production Methods for Battery Cells

Scope of project

The focus of the team at the Bern University of Applied Sciences is on manufacturing technology and offers services to battery production industry, equipment manufactures for battery production and battery material suppliers in Switzerland. Emerging materials, e.g. developed by the partners within the SCCER, might benefit or even require prospective manufacturing technologies. Consequently, the focus lies on battery configurations and also on investigations regarding new battery components. The team combines machinery and process knowledge with holistic approach undertaking cooperation between industry and research studies for know-how transfer.

Status of project and main scientific results of workgroups

The Swiss government has decided to exit nuclear energy production until 2050. Changing the actual energy production completely to renewable requires energy storage since wind and sun is not constantly available. For instance the photovoltaic electricity production needs storage for night consumption.

This project is embedded in the Swiss Competence Center for Heat and Electricity Storage to make stationary battery storage more attractive from an economic point of view and to speed up the Swiss energy transition. Although the battery electro-chemistry is already available and constantly improving, resulting in high expectations, batteries need to be manufactured at extreme low cost and, for safety reasons, at very high quality level. Further, the productions of batteries depend on the design and therefore on the application.

A highly optimized and flexible battery production is needed to produce a wide range battery configuration according to different requirements and in different sizes and designs. The application of the ideas of the next industrial revolution will enable such production technology.

Currently, the activities concentrate on implementing a pilot production line for battery manufacturing. At this first stage the pouch cell design was chosen with industry partners as a common application of Li-ion battery. Specifically for the pouch cell type the cell manufacturing includes cutting, stacking and assembly. These are three important steps which have big improvement potential concerning the process parameters such as positioning and cutting accuracy, cutting speed etc. including particular quality control for self-adjusted process control.

Coming back to the photovoltaic application: For a system with uninterrupted power supply, the daily electricity demand needs to be stored and a high current needs to be provided, requiring more conducting surface and cross sections compared to a base load use.

As a first part of the project a laser cutting unit for electrodes has been installed, cf. left side of the picture in Figure 1. Optimization studies for the operational parameters regarding to the demanding quality of the electrode cuts are ongoing. This requires some more work especially for copper foils, since the laser light is highly reflected by plain copper.

After the electrode cutting, anode and cathode sheets are assembled with a separator. Z-folding is one of the assembling methods [4] in which the separator foil is continuously folded surrounding anode and cathode sheets. As a second step for the pilot line the Z-folding module is initialized. Its assembly has begun in September 2016. As shown in Figure 1, at the current stage of this project the main structure of the Z-folding unit was established and building a handling system between two units is continuing in parallel.

The status of the project is shown at the following graph (Figure 1). The orange colored part shows the major steps for electrode production which will be studied in future. The current activities are focused at the blue part: the battery cell manufacturing and specifically cutting and stacking.

The whole line was evaluated with Failure Modes and Effects Analyses (Process FMEA) in the recent months. The boundary conditions were checked against the specifications and the question how the manufacturing process can be improved in a safe manner.

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As a conclusion, this pilot line helps to get deeper understanding and serves as a showcase for industry partners and research groups. With the aid of modelling a virtual production line and integration of smart sensors to the system it will ensure an «Industrie 4.0» environment for the future applications and their developments.

References


Figure 1: Lithium-ion battery production steps and pilot production line (current state).
### Hydrogen Production and Storage

#### Work Package "Hydrogen" at a Glance

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 this work package 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.

The large scale use of hydrogen for the storage of renewable energy requires large scale production of hydrogen, preferably in a dynamic process and large scale storage of hydrogen in an economic and dense form.

The production of hydrogen was investigated by a new approach based on the chemical discharge of the active material in the electrolyte of a redox flow battery. This method has several advantages: the redox flow battery tolerates a highly dynamic charge and discharge and is able to buffer the electrical energy from a fluctuating renewable source e.g. photovoltaic or wind. The new catalytic reaction developed allows to chemically react the charged electrolyte with water and directly produce hydrogen. The reaction products are recycled and returned into the redox flow battery. Since the reaction does not require any electrochemical installation it has a great potential for scaling up.

#### Electrolysers

Two types of electrolysers are commercialized today:

- the polymer electrolyte membrane (PEM) electrolyser and
- the alkaline electrolyser.

The main challenge is the large scale efficient electrolysis in the power range of >1 MW. Alkaline electrolysers exist since more than 30 years with a power of >4 MW and exhibit operational times of >10 years before major revision is necessary. They reach efficiencies of >80% at a rather low current density of only 200 mA/cm². The resistance is due to the membrane and the overpotentials for the oxygen evolution reaction (OER).

New electrocatalytically active materials have been developed and investigated for the overpotential of the OER. Especially Co_{0.11}Fe_{0.33}Ni_{0.55}, a compound found in the Gibeon meteorite that landed 13'000 years ago in Western Africa. The unique microstructure and composition turned out to show a very low overpotential for the OER and is characterized as a model system within the SCCER HaE.

#### Hydrogen storage in complex hydrides

Hydrogen storage in complex hydrides allows to store hydrogen up to 20 mass% and 150 kg/m² in the host material. Many of the complex hydrides turned out to be rather stable compounds that release hydrogen only at elevated temperatures far above room temperature. However, with the development of a thermodynamic model to describe the stability of complex hydrides without the need to know the structure nor to synthesize the compounds and measure, it was possible to find many interesting new complex hydrides that are much less stable than the known ones – and some of them are even liquids at room temperature. The challenge is to handle and to investigate these compounds and to find new ways to stabilize complex hydrides. We have successfully stabilized Ti(BH₄)ₓ, by infiltration in a metal organic framework (MOF). The hydride, which spontaneously desorbs hydrogen at room temperature, became stable over several months by infiltration. This method offers a great advantage in order to investigate these compounds.

#### Hydrogen storage in liquids

Hydrogen storage in liquids has many advantages over solids, since a liquid can be pumped and any diffusion limitations can be overcome by convection. Beside the storage of hydrogen in Dibenzyltoluol (or Carbazol) the storage of hydrogen in formic acid only uses CO₂ and water and allows to store >5 mass% of hydrogen. Non-noble metal based pre-catalysts have been developed for aqueous phase formic acid (FA) dehydrogenation. This required the synthesis of m-trisulfonated-tris[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 FA solutions, requiring no organic co-solvents, bases or any additives. 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.

Illustration: Jeff Kubina
Scope of project

For heterogeneous hydrogenation reactions, for example, ammonia synthesis and reduction of carbon dioxide for energy storage (Figure 1), atomic hydrogen on the surface of a metal with high hydrogen solubility is of particular interest. [1] Ammonia is a transport form of hydrogen (17.8 wt% H₂, 121 kg H₂ m⁻³ for liquid), especially for medium to long term hydrogen trading and storage [2]. The hydrogenation of CO₂ is an alternative way for storing large quantities of hydrogen in hydrocarbons. This enables the utilization of carbon dioxide as a raw material and can be further expanded in the chemical industry. [3]

Status of project and main scientific results of workgroups

One of the simplest hydrogenation reactions is the formation of water from oxygen and hydrogen. In the atmosphere with an excess of hydrogen, the formation of water on palladium is dominated by the transport of atomic hydrogen between the surface and the bulk, which was shown by using a molecular-beam relaxation technique under ultra-high vacuum conditions. [4]

In heterogeneous catalysis, palladium is one of the most important hydrogenation catalysts. However, it is generally not clear whether the formation of the metal hydride is important for industrially applied supported catalysts.

By using advanced in situ surface analysis methods, near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS), we have elucidated the origin of the catalytic activity of a metal hydride: since at the initial stage the dissociation of impinging hydrogen molecules is hindered by a high activation barrier of the oxidised surface, the atomic hydrogen flux from the metal hydride is crucial for the reduction of carbon dioxide and surface oxides at interfacial site.

The evolution of the oxidation state was analysed in detail by NAP-XPS in situ, with respect to the equilibrium hydrogen desorption pressures at different temperatures (Figure 2). To analyse hydrogen in the topmost layers of a solid surface, ToF-SIMS is a powerful tool (Figure 3). For ammonia synthesis, we further applied in situ ToF-SIMS surface analysis (in the course of hydrogen desorption) to investigate the formation of NH₃ adsorbates on a metal hydride, in situ in gas (Figure 4). [5] While the industrial Haber-Bosch processes require high pressure (>100 bar) and high temperature (>400°C), under our experimental conditions (at low pressure and low temperature), the formation of NH₃ intermediates are thermodynamically possible, as we experimentally demonstrated [5]. In order to control heterogeneous catalytic reaction, metal hydride catalysts have great potential for various hydrogenation reactions.

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List of abbreviations

NAP-XPS Near-Ambient Pressure X-Ray Photoelectron Spectroscopy
ToF-SIMS Time-of-Flight Secondary Ion Mass Spectroscopy

Figure 1:
Left: A metal hydride catalyst: during the hydrogen desorption, the metal hydride can deliver hydrogen to carbon dioxide at the surface, which is catalytically active in the reduction of carbon dioxide and formation of hydrocarbons.
Right: The pressure-composition isotherms (pcT) at three different temperatures (T₁ < T₂ < T₃).
Hydrogen

Metal Hydride Catalyst for Energy Storage

Figure 2:
Left: The Co 2p XP spectra of ZrCoHx measured in the atmosphere of a mixture of hydrogen (0.3 mbar) and nitrogen (0.6 mbar) at 23°C, 100°C and 240°C, respectively.
Middle: The schematic representation of the surface reduction. When the hydrogen equilibrium pressure (red) exceeds the hydrogen partial pressure, the hydrogen desorption markedly occurs, leading to the reduction of cobalt and the formation of hydroxyl groups on zirconia.
Right: The Zr 3d XP spectra of ZrCoHx.

Figure 3:
A metal hydride catalyst: TheToF-SIMS chemical images of ZrCoDx powder, taken at 2 × 10^-8 mbar and 25°C. The distributions of ZrO- /CoO- (left) and D-/H- (right) on ZrCoDx are shown by labelling the hydrogen isotope. The distribution of deuterium correlates with that of zirconium oxides. [1]

Figure 4:
The ToF-SIMS spectra of H3^+, O^- and NH4^+ taken in the atmosphere of nitrogen (at 1 × 10^-4 mbar). Above 60°C, the recombination of hydrogen and the formation of NHx proceed on the surface of ZrCoHx. [5]

References
Recent Activity for the Advances of Water Electrolysis Catalysts

Scope of project

The competence center dedicated to new water electrolysis catalyst testing, which opened last year in LIMNO at EPFL, has been fully equipped for electrode preparation (solution processable techniques, spin coater, electrodeposition setup, annealing under controllable atmosphere), characterization (XRD, Raman, microscopy) and catalytic performance assessment (potentiostats, transient/frequency modulated techniques). Several new equipment items, including a setup for ageing multiple electrodes under operating conditions, and novel skills, notably in metal electrodes preparation and atomic composition characterization, have been successfully added this year, enlarging the scope of potential materials and electrodes to inspect.

Status of project and main scientific results of workgroups

The first project of our group has been to study electrocatalysts for the water oxidation reaction (or oxygen evolution reaction). This process remains a technological challenge, considering the high overpotential required to drive this 4-electrons reaction, which limits the performance of an electrolyzer.

However, recent investigations on abundant 3d transition metal electrocatalysts, in particular NiFe, FeCo or NiCo, have shown impressive reduction of overpotentials and demonstrated cooperative function of the different metals when alloyed. Thus, we reported the electrocatalytic function of an iron-based Gibeon meteorite for the oxygen evolution reaction (OER) in alkaline medium in collaboration with the group of Paul Dyson. [3] This meteorite originates from sub-saharan Africa and has the largest strewnfield known with pieces discovered over 20 000 km² in Namibia and a total collected mass exceeding 21 tons. Examining this particular type of minerals is of interest for energy conversion applications given their unique atomic composition and formation history.

After 10 hours ageing under operational conditions in an alkaline electrolyte, an activity matching or possibly slightly superior to the best performing OER catalysts emerges, with stable overpotentials as low as 270 mV (for 10 mAcm⁻²) and Tafel slopes of 37 mVdecade⁻¹ (see Figure 1a). The Faradaic efficiency for OER was quantified as unity and no deterioration in performance was detected during the 1000 hours of OER operation tested at 500 mAcm⁻².

Spectroscopic analyses suggest an operando surface modification involving the for-

Figure 1:

- a) Gibeon meteorite [1],
- b) Widmanstätten texture in the surface of an etched meteorite from the Gibeon cluster, Namibia [2].

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Hydrogen

Recent Activity for the Advances of Water Electrolysis Catalysts

References


Figure 2:
a) Summary of the change in overpotential measured at 10 mA cm\(^{-2}\) (left axis) and Tafel slope (right axis) with OER operation time at 500 mA cm\(^{-2}\) in 1 M NaOH
b) Examples of cyclic voltammograms of a Gibeon electrode measured at 10 mV s\(^{-1}\) after different oxidation periods.
c) Atomic composition profile obtained via XPS of a Gibeon sample before (top) and after 50 hours of OER operation.

mation of a 3D oxy(hydroxide) layer with a metal atom composition of Co\(_{0.11}\)Fe\(_{0.33}\)Ni\(_{0.55}\), as indicated by Raman and XPS studies and trace Ir as indicated via elemental analysis. The growth of the catalyst layer was self-limiting to < 200 nm after ca. 300 hours of operation as indicated through XPS depth profiling and cyclic voltammetry, as shown on Figure 2 b and c. The unique composition and structure of the Gibeon meteorite suggest that further investigation Co-Ni-Fe systems or other alloys inspired by natural materials for water oxidation are of interest.

Indeed, metal electrodes based on nickel and manganese containing stainless steel also evidence the in situ formation of a highly catalytic layer for OER in alkaline electrolyte, with overpotentials recorded below 250 mV. The formation of this layer is induced by selective dissolution of metal ions in solution and results in a porous, layered double hydroxide type structure. The composition of the active layer is shown to be enriched in nickel and manganese while iron and chromium contents are drastically decreased as compared to the initial stainless steel composition. Remarkably, the final composition shows little or no dependence on the initial composition and highlights the synergetic function of different metal atoms. These results emphasize and rationalize the potential use of inexpensive and earth abundant metals for alkaline OER catalysis.

The further characterization of the optimized atomic composition will give deep insights into the origin of the benchmark performance and offer routes for further improvement. These studies are underway in our laboratories.
Demonstration of a Redox Flow Battery to Generate Hydrogen from Surplus Renewable Energy

Scope of project

Redox flow batteries (RFBs) can be used in energy storage for stationary applications due to the independence between the power output and the energy capacity, which leads to a flexible design, but also due to their long lifetime (>15,000 cycles claimed by suppliers), their easy maintenance and recyclability, and their secured operation. However, it is considered that RFBs suffer from a low energy density compared to alternative battery systems. In addition, their electrochemical energy efficiency remains still relatively low (80–85%) compared to other batteries. Therefore, a large amount of research is conducted at the levels of the chemistry of the electrolytes, the materials of the electrodes, the design of the cells and the strategy of operation. Different directions of research for the increase of energy density of RFBs were explored during these last four years in the frame of the SCCER funding in our laboratory.

Status of project and main scientific results of workgroups

In a first direction, a demonstration system was developed for the production of hydrogen directly from a redox flow battery.

This allows a significant extension of the energy capacity (which depends on the capacity of the associated hydrogen storage) of a standard RFB system, while keeping a reasonable installation size. Indeed, hydrogen exhibits a much higher energy density than a RFB. Indirectly, this system therefore allows to increase the energy density of the RFB. Moreover, it provides on demand two products in one installation: electricity and hydrogen. Both products can also be obtained simultaneously.

The concept, called dual-circuit redox flow battery, is based on the production of hydrogen from the at least partially charged negative electrolyte of a RFB with a suitable electrochemistry. It is extensively described elsewhere [1–3], but, in a nutshell, 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 proton 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. 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%. When the V–Ce RFB is replaced by an all-vanadium RFB, as it is the most advanced type of RFBs and they are commercially available, it involves changing the reaction for the chemical discharge of the positive electrolyte.

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. The chemical discharge of the negative electrolyte, that is the reaction of hydrogen evolution, was scaled-up to a medium-scale. The chemical discharge power was equivalent to 2.4 kW, that is the discharge of the whole battery in 17 h (1 L/min flow rate for full chemical discharge), in a specifically designed, vertical, segmented...
catalytic reactor. Concerning the chemical discharge of the vanadium based positive electrolyte, as water oxidation could not be performed using the V(V) electrolyte, the oxidation reactions of N$_2$H$_4$, SO$_2$ and H$_2$S were investigated [3]. The corresponding products of the reactions are N$_2$, SO$_4^{2-}$ and S, respectively. 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.

As a follow-up of the successful demonstration of the feasibility of this concept, a research is aiming at optimising the positive side of the dual-circuit. Different approaches are being studied and evaluated. Using Ce as redox couple in the RFB remains an interesting direction and therefore, the chemistry and electrochemistry of cerium and its chemical discharge in the reaction of water oxidation was studied further. Moreover, a system involving an electrochemical cell to discharge the positive electrolyte of an all-vanadium RFB is also currently being studied.

A third research direction focused on the increase of the energy density of the RFB through the addition of solid particles in the electrolyte tanks. The solid needs to be redox-active in the same range of potential as one of the redox couple of the RFB and needs to be chemically stable and to exhibit a low solubility limit in its both redox states. A screening through solids of different natures was conducted for several redox couples. One specific successful assembly was the redox couple Fe$^{3+}$/Fe$^{2+}$ with a polyaniline (PAN) polymer. Preliminary studies showed that the electrolyte energy density can be increased by a factor of 3 if a suitable amount of stationary solid PAN is added in the electrolyte solution with no decrease for at least 20 charge-discharge cycles. This is a considerable increase of the RFB density at a low cost and involving only little change in a classical RFB.

All in all, these 3 years of SCCER Hae funding allowed a wide range of research on redox flow battery to be conducted, going from fundamental science to applied research, involving the building of a demonstration project and leading to multiple communications and publications and to the initiation of new promising projects for the continuation of this research on electrochemical energy storage and hydrogen storage in our laboratory.
Hydrogen / Energy Storage and Production with the Carbon Dioxide / Formic Acid Systems

Scope of project

The reversible catalytic reduction of CO₂ with hydrogen to formic acid (FA, HCOOH) under mild conditions offers a convenient solution to store H₂ with a comparably high volumetric energy density (4.3\%wt H₂, 7.5 MJ L⁻¹). Formic acid is a moderately toxic [1, 2] liquid at room temperature and used as feedstock chemical for industries. [3, 4] Finally, formic acid can be decomposed to H₂, releasing only CO₂ as the by-product on demand. If the CO₂ is recycled a carbon-neutral hydrogen storage cycle is established. [5–8]

Status of project and main scientific results of workgroups

Recently the successful disproportion of formic acid into methanol, realized at ambient temperatures and in aqueous, acidic media employing an iridium catalyst was published. [9]

Based on literature findings, it became evident that iridium-pentamethylcyclopentadienyl dimers are promising starting materials for efficient catalysis. [10–16]

The combination with bidentate nitrogen donors afforded a series of powerful catalysts for CO₂/bicarbonate hydrogenation and FA dehydrogenation in the past. [12, 15, 17]

Li et al. reported in 2015 on achieving unprecedentedly high formic acid dehydrogenation activity on an Ir complex bearing an N,N’-diimine ligand in water without the addition of bases or additives. [18]

This observation triggered the investigation of a variety of Pentamethylcyclopentadienyl-N,N’-diimine ligand based catalysts with Ir or Rh center with the N,N’-diimine ligand as variable [Cp*MCl₂]₂ (M = Ir or Rh, Cp* = Pentamethylcyclopentadienyl), see Figure 1.

The details of used methods instruments and chemicals can be found in our publication. [19]

¹H NMR spectroscopy was used to follow up formic acid dehydrogenation online. The reaction occurred in sealed

References


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

vessels and was kept at a constant temperature during the whole experiment. Among the 13 investigated N,N′-diimine ligands, the 1,2-Diaminocyclohexane (an aliphatic nitrogen diastereomer) shows by far the highest turnover frequency (3278 h⁻¹) at 90°C in acidic media.

The NMR spectra in Figure 2 show the reaction progress at 60°C. The impact of different temperatures on the dehydrogenation rate is depicted in Figure 3 visualizing the dependency of the reaction rate on the temperature.

Based on temperature variation, the activation parameters were obtained by an Arrhenius plot (Figure 4) and determined an apparent activation energy of $E_a = 77.94 \pm 3.2$ kJ mol⁻¹, which is in good agreement with literature findings such as 76.4 kJ mol⁻¹ for [Ir(Cp*)(2,2’,6,6’-tetrahydroxy-4,4’-bipyrimidine)(H₂O)]SO₄ by Himeda et al. [17] or for the Fe(II)-PP₃/propylene carbonate system by Beller et al. (77 ± 0.4 kJ mol⁻¹). [20]

In conclusion, we synthesized a series of compounds by reacting [Cp*MCl₂]₂ (M = Ir or Rh) with bidentate nitrogen donor ligands and examined their catalytic activity in formic acid dehydrogenation. In most cases, the Rh analogues decomposed quickly and were in all cases less performant than iridium based catalysts. The highest TOF of 3278 h⁻¹ was obtained with the complex featuring 1,2-diaminocyclohexane as the ligand. By investigating the activity of the catalyst at different temperatures, we determined an activation energy of $E_a = 77.94 \pm 3.2$ kJ mol⁻¹ for formic acid dehydrogenation.

A generally observed issue with this type of structure is the instability at increased temperatures and elevated hydrogen pressures, leading to the reduction of the metal central ion and thereby to a partial deactivation of the catalyst.

References


Synthetic Fuels

Development of Advanced Catalysts

Work Package "Synthetic Fuels" at a Glance

Although CO₂ is an energetically very stable gas, pathways to reconvert the molecule into a synthetic fuel are very attractive as they offer the potential to close the CO₂ cycle, i.e., developing overall CO₂ neutral processes.

In this work package 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.

Indeed, a wide and diverse range of approaches are under evaluation within the work package, with the ultimate aim of discovering highly efficient and selective electrochemical and catalytic processes and applying them in demonstra-tors.

Electrochemical approaches to reduce CO₂ are the focus of the groups at PSI and the University of Bern, with contributions from EPFL and ETHZ. Indeed, electrochemical CO₂ reduction reaction (CO₂RR) is a complex reaction which must be carried out in a highly selective and efficient manner and various methods are being explored to develop catalysts with improved reaction selectivity and efficiency. However, CO₂RR kinetics and product identification and quantification are mostly carried out 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 reported in the literature 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 can be carried out in a co-electrolysis system where pure or diluted gaseous CO₂ is used. At PSI, research efforts were focused on the design of electrochemical cells for co-electrolyzer operating at high-current density with high product selectivity. The most promising result was obtained with a bipolar membrane used as a solid electrolyte. The cell consists of two metallic gold-coated flow fields, two electrodes and a bipolar membrane (Fumasep® FBM 130 μm thickness). The alkaline side of the bipolar membrane was used at the cathode to keep a high pH value. Au mesh (Goodfellow®) and Pt/C gas diffusion electrodes were used as cathode and anode, respectively. Humidified CO₂ was fed to the cathode side at 10 mL/min and the anode side was fed with pure H₂ at 50 mL/min. With such a cell configuration both high current densities and reaction product selectivity were achieved. CO and H₂ were the only products obtained in this configuration using Au mesh elec-

At the University of Bern improved carbon-supported oxidic nanoparticles (SnO₂-NPs@rGO) and metal foam catalysts (oxide-derived Cu foams) were developed. Catalyst degradation pathways were also studied under in operando conditions using Raman spectroscopy. The potential-dependent stability of SnO₂-NPs was monitored in operando and correlated to the resulting Faradaic efficiency towards formate production (FEformate). The SnO₂-NPs undergo first a partial electrochemical reduction to transient SnO in the potential regime where the highest FEformate is observed. It may be concluded that the most active catalyst contains both Sn(IV) and Sn(II) species at its interface to the working electrolyte. At most negative potentials the SnO₂ catalyst undergoes a full reduction to metallic tin which is accompanied by a drastic drop of FEformate from 75 % (Sn(IV)/Sn(II) composite) to 25 % at pH 8.5. This complete reduction process to metallic tin also involves an irreversible structural degradation of the NPs. Attempts to recover the SnO₂ catalysts by switching back the potential into the thermodynamic stability regime of SnO₂ indeed leads to the reappearance of SnO₂-NPs, which have a different size distribution to the as synthesized NPs. These smaller SnO₂-NPs show a higher FE towards hydrogen evolution reaction (HER) on the expense of FEformate. Further stability measurements of the SnO₂-NPs demonstrate that their partial reduction to the transient SnO is, in contrast, fully reversible over a number of potential cycles. These in operando degradation studies confining the optimum potential window for operating this type of oxidic NP catalysts with regard to both catalyst stability and Faradaic efficiency.

High-surface area Cu foams obtained by an additive-con-trolled electrodeposition process have been demonstrated as excellent CO₂ reduction catalysts affording C₂H₄ and C₃H₆. Various factors have been characterized as important for the resulting FE₂C₂ such as the annealing pre-treatment in air and the mean surface pore size of the Cu foams. Maximum FE₂C₂ reach values of 55 % under optimum condi-
tions. These Cu foams can be deposited not only on planar surfaces but also on 2D-Cu meshes (Figure 2) or on 3D Cu-skeletons which is important for future applications in flow cell devices.

Catalytic approaches to produce fuels from CO₂ and hydrogen were undertaken at ETHZ and EPFL. At ETHZ, research has been focused on heterogeneous catalysts for the direct hydrogenation of CO₂ and also dry reforming processes. It was shown that in both cases the interface between the copper particles and the support play an essential role in controlling the activity and the selectivity of the processes. In the particular case of supported Cu nanoparticles, ETHZ has been able to explain why zirconia is among the best supports for Cu using a combined computational and spectroscopic approach. In brief, Cu activates H₂ and CO₂ at the interface with Zirconia facilitating hydrogenation; this molecular level understanding of the elementary steps provide new guidelines to develop improved catalysts. This was possible through a collaboration with Prof. Urukawa (ICIQ), who developed in situ IR characterization of reaction intermediates under high pressure. For dry reforming, ETHZ has also shown that supported FeNi NPs show much improved stability over pure Ni catalysts, because the Fe present is continuously oxidized by CO₂ to generate FeO, which subsequently reacts with carbon deposits thus avoiding coke formation. In addition, ETHZ has developed preparation methods to prepare supported Cu NPs on carbon with high loadings, which are currently being evaluated in the electroreduction of CO₂ to methanol (collaboration with PSI and Uni Bern). In parallel, it has been found that the corresponding silica-supported copper NPs display very high selectivity in the semi-hydrogenation of alkynes.

In addition, a hybrid material for the conversion of CO₂ to organic compounds (collaboration with EPFL) and formic acid derivatives (collaboration with P. von Rohr) has been developed. These results pave the way to develop catalysts for the efficient conversion of CO₂ to fuels and chemicals using thermal and electrochemical processes.

At EPFL efforts to develop so-called ‘soft’ two-step catalytic approaches to convert CO₂ into methanol have progressed. In the first step CO₂ is incorporated into energy-rich nucleophilic molecules such as amines to afford formamides, which can then be converted into methanol in a second step by hydrogenolysis of the newly formed N-C bond. Several catalysts were developed that can reductively functionalize amines with CO₂ to obtain formamides under mild conditions, including two new classes of catalysts for this reaction, one based on naturally occurring organic compounds and the other on palladium NPs. Investigation of ionic liquid catalysts revealed a strong anion dependency on the reaction rate in the order I⁻ < Br⁻ < Cl⁻ < F⁻ < OH⁻, and based on these data together with spectroscopic and computational studies, a molecular-level understanding of the reaction mechanism was obtained and a new catalytic system operating at ambient conditions was subsequently developed.

In another two-step approach, CO₂ can be reacted with epoxides or diols to afford cyclic carbonates and the subsequent hydrogenolysis of these compounds affords methanol. A number of new ionic polymer catalysts for the synthesis of cyclic carbonates from CO₂ and epoxides were developed and the importance of functional groups as well as cross-linking for catalytic activity and for product separation were demonstrated. Carbenes were found to be highly active catalysts for the reaction of CO₂ with diols. Notably, a cheap thiazolium carbene was used as the catalyst allowing the carbonate to be obtained in excellent yield. Moreover, it was found that air could be used as the CO₂ source in the reaction involving epoxides. Hence, the resulting catalytic process can be used to scrub CO₂ directly from air as it passes through the ionic liquid catalyst containing the epoxide substrate. A pilot-scale prototype reactor for this process is under construction.
Catalytic approaches to convert CO₂ into fuels

Scope of project

We have continued our research on the development of new catalytic strategies for the transformation of CO₂ into fuels. Various classes of catalysts are under investigation, including ionic liquid and polymer organocatalysts, homogeneous and heterogeneous metal-based catalysts and electrocatalysts. In collaboration, we have also studied the electrocatalytic water oxidation reaction to generate hydrogen. A summary of the main results from 2016 is provided below.

Status of project and main scientific results of workgroups

The direct reduction of CO₂ into methanol is an energy intensive process, owing to the high thermodynamic stability of CO₂. In principle, the transformation could be facilitated by initially incorporating CO₂ into energy-rich nucleophilic molecules such as amines, as formamides, which can then be converted into methanol in a second step (Scheme 1).

In the last year, we have discovered a plethora of catalysts that can reductively functionnalize amines with CO₂ to obtain formamides under mild conditions (Scheme 1). In 2016 we reported two new classes of catalysts for this reaction, one based on naturally occurring organic compounds and the other on palladium nanoparticles. [1, 2] Investigation of ionic liquid (IL) catalysts revealed a strong anion dependency on the reaction rate in the order \( I^- < Br^- < Cl^- < F^- \sim OH^- \) (Table 1). Based on the data, novel understanding of the reaction mechanism and a new catalytic system operating at ambient conditions was developed. [3]

We also found out that several crystalline and amorphous variants of earth-abundant metal salts in nanoscale or bulk form based on Co, Zr, Mo, Mn, Ti, Y, Bi, Fe, Ni, Cu and Ce, could selectively catalyze the N-formylation reaction using CO₂ at ambient conditions with very low catalytic loadings.

In the future, our studies will focus on the second step of the cycle shown in Scheme 1, i.e. developing catalysts for the hydrogenolysis of the formamide to release MeOH and regenerate the amine starting material.

Incorporating CO₂ to produce cyclic carbonates from epoxides or diols and the subsequent hydrogenolysis of these compounds to afford methanol is another alternative to the direct reduction of CO₂ to MeOH that we are also working on. We have developed a number of new ionic polymer catalysts for the synthesis of cyclic carbonates from CO₂ and epoxides (CCE reaction) and demonstrated the importance of functional groups as well as cross-linking for catalytic activity and for product separation. [4, 5] When diols are used as starting materials a catalytic cyclic may be imagined where the diol product is recycled (Scheme 2), and methanol may be produced via the hydrogenolysis of the carbonate product. This approach is similar to that proposed in Scheme 1. For this reaction, ILs were not suitable catalysts,

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### Table 1 (bottom):

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>T* [h]</th>
<th>Yield [%]</th>
</tr>
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<td>2</td>
</tr>
<tr>
<td>2</td>
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<td>[TBA]Cl</td>
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<tr>
<td>6</td>
<td>[TBA]F·3H₂O</td>
<td>6</td>
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</table>

Scheme 1 (top):

Two step reduction of CO₂ into methanol via formamides.

Table 1 (bottom):

N-formylation reaction yields with tetrabutylammonium ionic liquid catalyst demonstrating the halide trend.

(*) duration of experiment
but carbenes were highly active when combined with suitable additives. A cheap thiazolium carbene was employed and the carbonate could be obtained in moderate to good yields starting from the diol product.[6]

In the electrochemical reduction of CO₂ to CO (generation of CO from CO₂ and H₂ from water is viewed as an alternative way to make synthetic fuels, i.e. CO/H₂ is syngas used in Fischer-Tropsch chemistry), we recently deciphered the mechanism by which imidazolium salts lower the overpotential in the electrochemical reduction of CO₂ to CO.[7] Following on from these studies, we have developed a series of new ILs based on triazolium and pyrazolium cations, which show superior properties to the imidazolium variants. Triazolium ILs possess an unusual quasi-reversible current-potential curve, which probably can explain the IL activity by its participation in the CO₂ reduction as a redox mediator. Catalysis proceeds with excellent Faradaic efficiencies, which was confirmed by gas chromatography measurements (Figure 1).

In collaboration with Prof. Sivula, we demonstrated the potential of naturally occurring minerals, i.e. an iron-nickel containing Gibeon meteorite, as state-of-the-art electrocatalyst for water oxidation reaction to produce hydrogen.[8]
From Electro to Thermocatalytic CO2 Conversion Processes via Material and Surface Chemistry

Status of project and main scientific results of workgroups

Electrocatalyst

Complementary to CO2 electroreduction (vide infra), efficient OER materials based on high surface IrO2 were prepared via a simple and scalable modified Adams fusion method. This method yielded highly OER active iridium oxide nanoparticles of various size and shape, allowing the effects of particle size, morphology, and the nature of the surface species on the OER activity of IrO2 to be investigated. Iridium oxide synthesized at 350°C from Ir(acac)3, consisting of 1.7 ± 0.4 nm particles with a specific surface area of 150 m2g⁻¹, shows the highest OER activity (E = 1.499 ± 0.003 V at 10 A g⁻¹; Figure 1). Operando X-ray absorption spectroscopy and X-ray photoelectron spectroscopy studies indicate the presence of iridium hydroxo (Ir–OH) surface species, which are strongly linked to the OER activity. Preparation of larger IrO2 particles with higher temperatures results in a change of the particle morphology from spherical to rod-shaped particles. A decrease of the intrinsic OER activity was associated with the predominant termination of the rod-shape particles by highly ordered (110) facets in addition to limited diffusion within mesoporous features.[1]

Furthermore, in order to decrease the amount of IrO2, IrO2 was combined with a TiO2 support. Using the Adams method described above, it was possible to generate high surface area IrO2–TiO2 mixed oxides. While anatase is formed in the absence of Ir, both anatase and rutile phases of TiO2 were identified by XRD for 40% IrO2–60% TiO2. Analysis of the material via HAADF-STEM microscopy shows the formation of small IrO2 particles of ca. 1 nm in diameter, in all compositions of IrO2–TiO2. The materials display sufficient electrical conductivity, which can be described using a simple equation derived from percolation theory (Figure 1e).

This allows for electrochemical applications for materials containing only 40 mol% IrO2.[2] In parallel, we have been developing Cu-based electrocatalyst for the CO2 electroreduction.

Dry reforming catalyst

When considering only the metal (Ni), the CO2 adsorption strength and reactivity increases in the order Ni(111) < Ni(211) < Ni55 < Ni13 where the edges of nanoparticles, especially of subnanometric ones, are the most reactive. However, when considering the support, here γ-Al2O3, the binding energy is significantly higher than on the bare nanoparticles, which is attributed to an increased electron transfer from both the nanoparticle and the support to the CO2 molecule. The most active site toward CO2 activation is present at the interface between the Ni55 particle and the 110 surface of γ-Al2O3; it is associated with the lowest activation energy (32 kJ mol⁻¹).
and the most favored thermodynamics for the CO₂ dissociation ($E_{\text{a,b}} = -262 \text{kJ mol}^{-1}$; Figure 2). This work shows how support–metal interactions can provide more favorable activation pathways, thus opening the path for the design of more active metal/oxide interfaces toward CO₂ activation. [3]

Introducing Fe in Ni dry reforming catalysts increases catalytic performance, in particular the stability. Using Ni–Fe nanoparticles supported on Mg₃Al₂O₅ as prototypical DRM catalysts, we have shown that the best catalysts correspond to a Ni/(Ni+Fe) ratio of 0.8 (Figure 2c). Using operando X-ray synchrotron-based studies complemented by ex situ characterization techniques and DFT calculations has shown that under DRM conditions:

1. Ni remains at oxidation state 0 whether it is alloyed with Fe or not;
2. the deactivation of monometallic Ni is due to the formation of graphitic coke and whiskers;
3. the role of Fe, which is inactive for DRM, is to improve the stability of Ni-based catalysts and the optimal catalyst composition is Ni₄Fe₁;
4. Fe in NiFe alloys is partially oxidized to FeO, which induces a partial de-alloying and the formation of a Ni-richer Ni–Fe alloy;
5. FeO, located preferentially at the surface as small domains of a few atom layer thickness covering a fraction of the Ni-rich particles, reacts with carbon deposits and reduces coke formation.

These findings explain the increased catalytic stability of bimetallic NiFe catalysts via a Fe²⁺O/FeO redox cycle. This study also illustrates how important dynamic phenomena are, even for such supported bimetallic nanoparticle catalysts. [4]

### CO₂ hydrogenation

Cu is well known for its catalytic activity regarding CO₂ hydrogenation, but the nature of its active sites is highly debated. First, by combining experimental and theoretical approaches, it was possible to rationalize the number of exposed/reactive copper atoms in supported small copper nanoparticles: the reaction of H₂ and N₂O allows the selective titration of surface Cu atoms, with defined but different stoichiometry of 1O/2Cu₁ and 1H₂/2.2Cu₅. This study has also shown that determining surface sites from simple spherical model and particle size distribution from TEM leads to an overestimation of surface sites (Figure 3).

Conversely, determining particle size from chemisorption is not possible for Cu, although it provides relevant information regarding the number of active sites and sintering for instance. This study clearly supports the need to use complementary methods to understand surface sites and describe catalyst behavior. [5]

By the same approach, we have also been able to understand the support effect in CO₂ hydrogenation, and in particular the increase production rate in methanol upon addition of ZrO₂. Using computational chemistry combined with in situ IR and ex situ NMR spectroscopy, it was possible to show that the formate species formed under a broad
range of pressure readily convert to methoxy species under high pressure (>5 bars) via an acetal intermediate. Detailed labelling studies have shown that only the formate and the methoxy species can be observed by spectroscopic methods, while the acetal is only an unstable reaction intermediate. The proposed mechanism (Figure 3c) is reminiscent of what has been recently proposed for a ruthenium molecular catalyst, bridging the gap between molecular and heterogeneous catalysis. [6] These results clearly point to the crucial molecular role of the interface between the copper particles and zirconia, [7, 8] and is an important guide for a rational development of efficient heterogeneous CO₂ hydrogenation catalysts. [9]

Other discoveries

Following the development of Cu-based catalysts for CO₂ reduction, it was also possible to identify selective semihydrogenation of alkynes via High-Throughput Experimental (HTE) approach. The high-throughput ligand screening approach applied to a heterogeneous catalyst allowed identifying tricyclohexylphosphine as a potent ligand to increase the chemoselectivity of alkyne semihydrogenation (Figure 4a). The optimal catalyst Cy₃P–Cu/SiO₂–700 is thus an efficient, practical, sustainable, and cheap alternative to the Lindlar catalyst. [10]

The reaction mechanisms of the selective semihydrogenation of alkynes with silica-supported Cu nanoparticles and parahydrogen were further investigated. Parahydrogen-induced polarization (PHIP) effects were observed for the hydrogenation of 1-butyne on Cu/SiO₂–700 and were very minor for the hydrogenation of 1-butene and not observed for 2-butyne hydrogenation, indicating that different mechanistic manifolds operate with these substrates. Modification of the Cu/SiO₂–700 catalyst with PCy₃ leads to an increase in the selectivity of 1-butyne hydrogenation to nearly 100% (with by-products below the detection limit of NMR), although it was found to make this catalyst significantly less active. The remarkable selectivity of Cy₃P–Cu/SiO₂–700 also manifested in no activity in the hydrogenation of 1-bu-
From Electro to Thermocatalytic CO₂ Conversion Processes via Material and Surface Chemistry

tene, and no formation of butane from 2-butyne. Cy₃P–Cu/SiO₂-700 provided no less than 2.7% pairwise hydrogen addition to 1-butyne, with the actual value likely to be higher due to polarization losses via relaxation (Figure 4b). Our results demonstrate that copper-based catalysts are promising inexpensive alternatives to heterogeneous noble metal catalysts for the semi-hydrogenation of alkenes in the flow and the production of hyperpolarized gases.[11]

Collaboration network

In situ IR characterization of reaction intermediates for the hydrogenation of CO₂ with supported catalysts (collaboration with A. Urukawa, ICIQ) and approach to supported Cu nanoparticles on carbon with high loading was developed. This is currently being evaluated in the electroreduction of CO₂ to methanol (collaboration with T.J. Schmidt and P. Broeckmann). In addition, hybrid material for the conversion of CO₂ to organic compounds (collaboration with P. Dyson) and formic acid derivatives (collaboration with P. von Rohr) was developed. These results pave the way to develop catalysts for the efficient conversion of CO₂ to fuels and chemicals using thermal and electrochemical processes.

Part of this work was carried out in collaboration with Profs. P. Broeckmann (University of Bern), P. Dyson (EPFL), C. Müller (ETHZ – D-MATV), F. Ribeiro (Purdue University, USA), P. von Rohr (ETHZ – D-MATV), T.J. Schmidt (PSI), A. Urukawa (ICIQ, Spain).

References


Figure 4:

a) Evolution of concentration with time for the hydrogenation of 1-phenyl-1-propyne with Cu/SiO₂-700 (0.375 mol %, top) and Cy₃P–Cu/SiO₂-700 (0.18 mol %, bottom) with dotted lines added to guide an eye.

b) Non-pairwise and pairwise routes of hydrogen addition to 1-butyne over Cu/SiO₂-700 and Cy₃P–Cu/SiO₂-700 catalysts.
Metal Hydrides for Electrochemical CO₂ Reduction

Scope of project

Carbon dioxide concentration in the atmosphere is continuously increasing and corresponds to $750 \times 10^{12}$ kg C. However, most of the CO₂ on the Earth is stored in the ocean ($41'031 \times 10^{12}$ kg C). At the same time, the contribution of renewable energy (e.g. solar, wind and hydropower) is growing worldwide and substitute energy from fossil fuels potentially decreasing the CO₂ emission. The storage of renewable energy requires the conversion of electricity into an energy carrier, for example hydrogen. Moreover, the reduction of CO₂ with hydrogen to hydrocarbons (synthetic fuels) allows storing renewable energy with the same energy density as fossil fuels. Therefore, electrochemical CO₂ reduction to specific hydrocarbons after its extraction from the air is of great importance for the future energy economy based on renewable energy. The direct electrochemical CO₂ reduction from seawater would be an even more attractive and efficient process. In order to reach this goal it is necessary to use a catalyst, which is active for the CO₂ reaction on the surface and provides H for the formation of hydrocarbons. Metal hydrides allow to split water and adsorb atomic hydrogen at the surface.

We have designed and prepared new catalytic copper-containing electrode materials, which form a hydride and offer highly active surface sites for the adsorption and reduction of CO₂ with atomic hydrogen.

Status of project and main scientific results of workgroups

The advantage of the simultaneous electrochemical reduction of CO₂ and H₂O allows the direct synthesis of hydrocarbons from electricity. The reaction is more efficient since no hydrogen gas phase is formed and therefore the entropy change is minimal.

Furthermore, the co-electrolysis may allow the production of hydrocarbons directly from seawater, subject of a large research program in the US [1].

The electrochemical CO₂ reduction in acidic electrolyte involves the dissociation of water and the reduction of H⁺ to atomic hydrogen at the cathode:

$$\text{H}^+ + \text{H}^+ \rightarrow \text{H}_2 \uparrow$$

The CO₃²⁻ ion in the electrolyte moves to the anode, where oxygen is evolved.

$$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$$

Therefore, only the neutral CO₂ molecules dissolved in the electrolyte are available on the cathode for reduction. The CO₂ bound to the surface is electronically connected to the potential of the electrode, i.e. the chemical potential of the bound CO₂ follows the electrode potential. The reduction reaction of CO₂ with H requires the carbon atom bound to the surface and atomic hydrogen close to the oxygen atoms. Metal hydrides (MH) are substrates that can bind CO₂ and provide atomic hydrogen at the surface. In the reduction reaction there is a competition between O-H, C-H and C-C bond formation. While O-H and C-H bond formation requires large activity of hydrogen, the C-C bond formation requires the absence of oxygen and surface bound carbon close to each other.

The mechanism of C-C coupling on the surface and further formation of *CO and *CHO was described by the group of Norskov on a copper electrode. They show that the kinetics of C-C coupling during electrochemical CO₂ reduction...
Metal Hydrides for Electrochemical CO₂ Reduction

strongly depends on the applied potential [2] (Figure 1 left). Therefore, the control of the potential allows to tune the reduction process towards the desired product.

The product distribution in CO₂ reduction varies widely, depending primarily on the electrode metals and the electrolyte used for the process. The key factor in determining the product distribution in CO₂ reduction is the cathode material. Among the other metals copper is a unique metal on which hydrocarbons can be obtained according to the one of the early work of Hori [3]. At the same time hydrides of metals [4] and alloys [5] according to the literature have ability to adsorb CO₂ and may be ideal catalysts for the reaction as well as a source of atomic reactive hydrogen at the surface. Ohkawa et al. [4] studied the electrochemical behavior of CO₂ on hydrided Pd electrodes and showed that the activity for CO₂ reduction increases with higher hydro-
Metal Hydrides for Electrochemical CO₂ Reduction

Gen content in Pd. Moreover, it is declared by authors that the hydrogen absorbed on the Cu-modified Pd electrodes participates in the electrochemical reduction of CO₂ via surface adsorption or reacts with the intermediates directly [6].

A series of LaNi₈-xCuₓ type alloys with partially substituted nickel by copper were synthesized by arc melting under Ar atmosphere and single phase was detected by means of XRD. All obtained alloys have a hexagonal CaCu₅ structure (space group P6/mmm) and show random distribution of Cu on Ni sites. The crystal structure of alloys is presented on the example of LaNi₄Cu alloy unit cell and is shown in Figure 1. The La and Ni atoms, which form the interstitial sites hosting hydrogen atoms, are the source of atomic hydrogen on the electrode surface while copper atoms represent active sites for CO₂ binding. This unique combination forms a new type of highly active catalytic sites.

The cold pressed pellet electrodes from the grinded copper-containing alloys were fully activated during 30 charge/discharge cycles in 6 M KOH electrolyte in standard electrochemical cell (Ni plate as a counter electrode, Hg/HgO as reference electrode). Afterwards, the equilibrium potentials of electrodes were measured with pulsed cycle method at different temperatures (20°C, 30°C, 40°C). The equilibrium charge (absorption)/discharge (desorption) curves obtained at 20°C and corresponding density of states (DoS) for hydrogen in LaNi₄Cu alloy are presented in Figure 2 left. Maximum of the DoS corresponds to the equilibrium pressure of plateau (3.129 bar for absorption, 1.406 bar for desorption). Based on the obtained (electrochemically at different temperatures) absorption/desorption curves the Van’t Hoff plot was evaluated and enthalpies together with entropies for both absorption and desorption processes were calculated (Figure 2 right).

According to [5] the atomic hydrogen flux from the metal hydride is crucial for the reduction of carbon dioxide and surface oxides, especially at grain boundaries or adlayer sites, while at the initial stage, the dissociation of hydrogen molecules from the gas phase is hindered by the high activation barrier on the oxidized 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. This indicates that the activity of the surface for the CO₂ reduction strongly depends on the hydrogen concentration in the metal hydride (between 2 and 4 H/f.u., Figure 2 left).

The electrochemical CO₂ reduction was carried out in the standard three electrode electrochemical cell (WE – MH alloy electrode, CE – Pt mesh, RE – Ag/AgCl in 3 M KCl solution) using 0.1 M KHCO₃ electrolyte (Carl Roth, 99.9%) with continuous CO₂ bubbling through it in order to saturate the electrolyte by supplying neutral CO₂ to the working electrode and homogenization by a magnetic stirrer at the bottom of the cell to avoid locally increasing pH close to the electrode during the reduction process (Figure 3 left). After saturation of the electrolyte for 30 minutes the pH of the electrolyte was slightly acidic (6.65–6.8). On the cyclic voltammograms (Figure 3 right) obtained without and with CO₂ on LaNi₄Cu electrode the potential region at which electrochemical conversion of CO₂ with hydrogen results in HCOOH, CO, C₂H₄, CH₄ (listed in sequence of reaction potential decreasing) is indicated.

Since all the products listed above are formed under potentials lower than hydrogen evolution reaction (HER) (starts at ~0.414 V vs. SHE at 25°C and pH 7 according to Pourbaix diagram) the main byproduct of CO₂ reduction on copper-containing MH electrodes, as well as on pure Cu, is hydrogen. Suppressing the HER and therefore, increasing the faradaic efficiency of the formation of hydrocarbons is challenging and a crucial task, which is of our interest for further investigation of these materials.

References
Towards *in operando* Characterization of High Surface Area Catalysts for Electrochemical CO₂ Conversion

### Scope of project

In the focus of the SCCER project were two types of catalyst materials for CO₂ electroconversion:
- carbon-supported oxidic nanoparticles (SnO₂-NPs@rGO)
- metal foam catalysts (oxide-derived Cu foams).

Synthesis strategies for both were further improved during the last project year. In addition, catalyst degradation pathways were studied under *in operando* conditions by means of Raman spectroscopy.

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

In the focus of this SCCER project is the conversion of the environmentally unfriendly green house gas CO₂ into high value products (e.g. ethylene, methanol, formic acid etc.) by means of electrochemical processing. The particular technological challenge is related to the extraordinary stability of the CO₂ molecule thus requiring extremely high over potentials for its electrochemical reduction. Only by the use of proper catalysts the CO₂ reduction can be accelerated so that the process might become feasible from an economic point of view. Up to now, only copper based catalysts show a promising activity towards the CO₂ conversion into hydrocarbons whereas tin based catalysts are the most promising candidates for formate production.[1,2]

A number of catalyst specific issues, however, still need to be addressed which are related to a lack of selectivity in the case of Cu and a lack of stability in case of carbon-supported SnO₂-NPs. For a more tailored design of catalysts it is important to know which surface sites and which particular chemical states of the catalyst are the most active ones towards CO₂ electroreduction. In particular, oxidic catalysts might undergo changes of their chemical state, their composition and morphology under those harsh experimental conditions which are relevant for the CO₂ conversion. Therefore *in operando* approaches are important to characterize the catalyst under reactive conditions.

**SnO₂-NPs@rGO catalysts for CO₂ conversion**

The potential dependent stability of SnO₂-NPs was monitored by *in operando* Raman spectroscopy and correlated to the resulting Faradaic efficiency towards formate production \(\text{FE}_{\text{formate}}\).[3,4] It turned out that the SnO₂-NPs undergo first a partial electrochemical reduction to transient SnO in the potential regime where the highest \(\text{FE}_{\text{formate}}\) is observed. From this study it can therefore be concluded that the most active catalyst contains both Sn(IV) and Sn(II) species at its interface to the working electrolyte. At most negative potentials the SnO₂ catalyst undergoes a full reduction to metallic tin which goes along with a drastic drop of \(\text{FE}_{\text{formate}}\) from 75% (Sn(IV)/Sn(II) composite) down to 25% at pH 8.5.[3,4]

This complete reduction process to metallic tin also involves a structural degradation of the NPs which has to be considered as irreversible.

Attempts to recover the SnO₂ catalysts by switching back the potential into the thermodynamic stability regime of SnO₂ indeed leads to the reappearance of SnO₂-NPs which, however, show a changed size distribution as compared to the as synthesized NPs. The appearance of sub-4 nm SnO₂-NPs during the recovery process can be monitored by the *in operando* Raman spectroscopy through appearance of a characteristic broad Raman feature in the range between 400 and 800 cm⁻¹ (Figure 2). Unfortunately, these smaller SnO₂-NPs show a higher FE towards HER on the expense of \(\text{FE}_{\text{formate}}\).

Further stability measurements of the SnO₂-NPs demonstrate that their partial reduction to the transient SnO is, by contrast, fully reversible over number of potential cycles.

These *in operando* degradation studies allow confining the optimum potential window for operating this type of oxidic NP catalysts with regard to both catalyst stability and Faradaic efficiency.

**Oxide-derived Cu foam catalysts for CO₂ conversion**

High surface area Cu foams obtained by an additive controlled electrodeposition pro-

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**List of abbreviations**

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<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>FE</td>
<td>Faradaic Efficiency</td>
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<tr>
<td>HER</td>
<td>Hydrogen Evolution Reaction</td>
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**References**


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Towards *in operando* Characterization of High Surface Area Catalysts for Electro-chemical CO$_2$ Conversion

Figure 1:

a) Three-dimensional surface plot of Raman intensities created by a continuous acquisition of Raman spectra as the electrode potential was slowly stepped from less (~0.25 V) to more negative values (~1.55 V vs. Ag | AgCl).

b) The intensities of SnO$_2$ and SnO related peaks as a function of electrode potential; the lines here correspond to those shown on the surface plot in (a).

c) Potential-dependent Raman spectra recorded on the course of stepping the potential back from ~1.55 V to ~0.25 V vs. Ag | AgCl.

d) The intensity of the SnO$_2$ related wave as a function of electrode potential; the line here corresponds to the one shown on the surface plot in (c).

Conclusions and next steps

*In operando* Raman spectroscopy will be applied to study the role of oxide species on Cu foam catalysts. In addition the Cu-foam on Cu-mesh catalyst needs to be tested with respect to their FE$_{C_2}$.
Electrochemical Cell Configuration for CO₂ Reduction in Gas Phase at Low Temperature

Scope of project

The electrochemical production of chemical products like syngas, format, methane, ethylene, methanol or other transportation fuels starting from CO₂ reactant appears like a suitable technology to recycle and reduce this greenhouse gas. However, a suitable process using only CO₂, water and renewable energy is currently not available. Only few models of co-electrolysis cells exist but they are limited by factors like energetic efficiency, reaction products selectivity and cost [1, 2]. So far only carbon monoxide and formate products appear to be economically interesting when produced by electrochemical CO₂ reduction compared to other well established chemical processes [3]. As the catalyst used for CO₂ reduction reaction (CO₂RR) is crucial for selectivity but also for the energetic efficiency of the whole process (i.e. kinetic overpotentials), a majority of the studies aim towards high-performance catalyst development [4, 5]. Product selectivity as a function of electrode material was established by Hori [6] and this is generally accepted by the scientific community. For example Au, Ag, Zn are widely known to be efficient for CO formation. However, the overall efficiency of the process is not entirely dependent on the catalyst nature; mass transport phenomena and pH conditions are equally crucial parameters for an optimal CO₂ conversion process.

The direction of this work package was oriented on the production of CO starting from CO₂ in the gas phase using typical membrane electrolyzer cells. Au electrodes were chosen for their selectivity against CO but also for their chemical stability in a broad pH range. Various cell configurations using solid polymer electrolyte are discussed.

Status of project and main scientific results of workgroups

The process from CO₂ to syngas (H₂ + CO) in gas phase takes place in an electrochemical reactor / electrolysis cell. The electrochemical cell consists of two metallic gold coated flow fields, two electrodes and different solid electrolytes / membranes. To efficiently design such a system we first focused on finding the appropriate solid electrolytes.

With this respect, various cell configurations, electrolyte’s pH and operation conditions (temperature, pressure and current densities) were studied in order to achieve efficient CO₂ conversion to CO.

Since the starting of the project, many activities have successfully been started with a wide variety of results:

- development of analytical tools for online and operando detection of reaction products in the electrochemical reduction of CO₂;
- design of electrocatalyst systems with high selectivity in the CO₂ reduction;
- development of polymer electrolyte based electrochemical cell.

For comparison, a cell configuration containing a buffer layer between the cathode and the proton exchange membrane was tested [6]. The buffer layer was a Watman® paper impregnated in 0.5 M KHCO₃ solution in order to mimic a bipolar membrane architecture.

CO₂ was fed to the cathode side at 10 mL/min, whilst the anode side was fed with pure H₂ at 50 mL/min. Gas humidification was achieved by passing through a water-bubbling system; their temperature was set to yield 100% humidification values. The cells were operated at 40°C and ambient pressure. Polarization curves were measured galvanostatically. For each data point, the cell current was stabilized for 5 minutes and the data were averaged from the last 3 minutes. The gas product from cathode was analyzed by mass spectroscopy (MS Prisma).

References


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Electrochemical Cell Configuration for CO₂ Reduction in Gas Phase at Low Temperature

Results

Standard cell configurations – acidic vs alkaline system

When CO₂RR takes place at the gold cathode the principal electrochemical reactions are:

in alkaline environment

\[ \text{CO}_2 + \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{CO} + 2\text{OH}^- \quad E = -0.932 \text{ V/RHE} \quad [1] \]

\[ 2\text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad E = -0.828 \text{ V/RHE} \quad [2] \]

or in acidic environment

\[ \text{CO}_2 + 2\text{H}^+ + 2 \text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O} \quad E = -0.104 \text{ V/RHE} \quad [3] \]

\[ 2\text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2 \quad E = 0 \text{ V/RHE} \quad [4] \]

Cation exchange membrane (CEM) and anion exchange membrane (AEM) were used for CO₂ reduction from the gas phase. The polarization curves obtained under N₂ and CO₂ are shown in Figure 1. In the case of CEM configuration high current densities were obtained under CO₂ at low overpotential (~400 mA/cm² at ~0.4V/RHE). Despite the good electrochemical performances achieved using a CEM cell configuration, H₂ was the majority reaction product obtained as shown by the MS results (Figure 2). In view of this result, it is likely that the acidity of the membrane shifts the cathode selectivity toward hydrogen evolution. Contrary, in the case of AEM configuration low current densities are obtained at high reaction overpotential. Moreover, an increase in membrane high frequency resistance (up to 15 Ωcm²) and losses of membrane stability were observed. A product analysis was not possible under these conditions by MS.

However, the use of AEM configuration can be interesting for CO₂ reduction from gas phase due to the pH increase, but membranes with improved stability, lower resistance and better affinities for carbonate and bicarbonate species must be found. Another possible limitation of this kind of system can be the anode reaction when a complete co-electrolyser is used (i.e. oxygen evolution reaction at the anode side). In this case, HCO₃⁻, CO₃²⁻ and OH⁻ are possible charge carriers and CO₂ can be produced at the anode side according to reactions 5 and 6.

A considerable production of CO₂ at the anode side will obviously lead to an inefficiency of the system.

\[ 2\text{HCO}_3^- \rightarrow \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2 \text{e}^- + 2\text{CO}_2 \quad E = -0.765 \text{ V/RHE} \quad [5] \]

\[ \text{CO}_3^{2-} \rightarrow \frac{1}{2}\text{O}_2 + 2 \text{e}^- + \text{CO}_2 \quad E = -0.692 \text{ V/RHE} \quad [6] \]
Alternative cell configurations

A buffer layer cell configuration was also used for CO₂ reduction in gas phase [6]. The polarization curves are shown in Figure 3 and the results are comparable with the available literature data [6]. With this cell configuration current densities > 200 mA/cm² were achieved with reasonable overpotentials. The consumption of CO₂ (m/z 44) was observed by MS (Figure 4). CO and H₂ were the only products obtained in this configuration using Au mesh electrodes. The CO selectivity calculated from the mass spectrometer signal was ca. 35% at ~400 mA/cm².

Currently, the buffer layer cell configuration is only a proof of concept, the cell stability being a major issue in this case. Therefore new stable layered cell configurations are needed.

With this in mind, bipolar membranes were tested. The alkaline side was used at the cathode. The polarisation curves are compared against the buffer layer cell configuration in Figure 3. Using this type of membrane high current densities were achieved, but with higher overpotentials (most probably due to the high membrane resistance, ca. 5 Ωcm²). The CO selectivity was 23% at ~400 mA/cm².

Outlook

Various cell configurations for reduction of CO₂ in gas phase have been presented and their performances compared. For convenience, only Au mesh was used as cathode catalyst for CO₂ reduction to CO.

A membrane electrolyzer like configuration using CEM was shown to be unfavorable for CO₂ reduction, leading to H₂ evolution only. The same configuration using a commercially available AEM (Fumasep® AA 130) was not successful due to high membrane resistance and a loss of membrane stability. That said, we believe that this configuration can be improved by using different alkaline membranes.

Alternative cell configurations were also tested and it was proved that by using a bipolar membrane system (alkaline side used at the cathode) high current densities are achieved and the cathode selectivity to CO is enhanced. This first promising result shows the feasibility of using such a system for electrochemical CO₂ conversion from gas phase. However at this point the energetic efficiency is low and optimisation work must be carried out in order to reduce the high cathode overpotentials.

Figure 3: Performances of alternative cell configurations: buffer-layer cell vs bipolar membrane cell. The raw data (full symbols) are compared with the iR corrected data (empty symbols). Same conditions for anode and cathode as in Figure 1.

Figure 4: Ion current recorded by MS for m/z 44 and m/z 28 recorded in an electrochemical cell using a bipolar membrane (Fumasep® FBM) at different current densities and under cell operation at ~400 mA/cm² proving the formation of CO.
Work Package Assessment of Storage Systems at a Glance

This work package 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.

Within the work package a combined techno-economic and environmental assessment method for energy storage was developed and applied. Based on this method different energy storage technologies and applications were assessed. While energy storage is being proposed in the context of climate change mitigation, typically linked with renewable energy, past evaluations have mainly focused on the techno-economic aspects, and rarely differentiated the implications of the various applications and storage technologies. The results found within this work package thus help to inform the current storage debate about the integrated impacts of different technologies and applications from both, techno-economic and environmental perspectives. The work contributes to a better informed decision analysis of the role of energy storage technologies towards the energy transition in Switzerland.

Stationary storage technologies including pumped hydro storage (PHS), advanced adiabatic and isothermal compressed air energy storage (AA- and I-CAES), power-to-gas-to-power (P2G2P) and Li-ion battery (nickel cobalt aluminium/lithium titanate (NCA/LTO)) are compared in terms of levelised cost and life cycle greenhouse gas emissions (GHG). The scenarios include three applications representing frequency control, arbitrage and seasonal storage, as well as two system scales (1 and 100 MW).

We have also focused on particular storage technologies such as power-to-gas, power-to-heat, and residential batteries for various scenarios under the Swiss context. The role of energy storage for communities from a techno-economic, environmental and social perspective was also reviewed.

With the commissioning of Switzerland’s first power-to-methane plant, Hochschule IET-HSR established itself as a competence centre for the practical application of power-to-gas on a system level. In the last two years, tests were performed on the plant and experience with practical aspects of power-to-gas was collected. Different sources of CO₂ were investigated and the product gas was used for mobility applications as well as for grid injection.
A Uniform Techno-Economic and Environmental Assessment for Electrical and Thermal Storage in Switzerland

Scope of project

A comprehensive methodology combining techno-economic analysis and life cycle assessment for storage technology assessment is demonstrated. While energy storage solutions are being proposed in the context of climate change mitigation, typically linked with renewable energy technologies, energy storage evaluations have mainly focused on the techno-economic implications of energy storage technologies. Therefore, the current debate has neglected so far the environmental impacts of the potential penetration of various energy storage technologies. The results created in the context of this work package help to inform the current storage debate about the integrated impacts of various technologies and therefore contribute to a more comprehensive decision analysis of the role of energy storage technologies towards the energy transition in Switzerland.

This report describes the work undertaken at the University of Geneva, at Paul Scherrer Institut and at Hochschule Luzern in 2016. 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

**Integrated economic and environmental assessment of energy storage technologies for different time scales**

This ongoing study compares pumped hydroelectric energy storage (PHS), advanced adiabatic and isothermal compressed air energy storage (CAES), power-to-gas-to-power (P2G2P) and lithium-ion batteries for three different storage scenarios characterized by storage discharge time scale (TS) and for two different storage system scales. In particular, short-term (<1 min), medium-term (4.5 hr) and long-term (seasonal) storage time scales are compared for systems with a power rating of 1 MW and 100 MW corresponding to distributed and bulk ES respectively.

The preliminary results (Figure 1) of the analysis show that (with the Swiss electricity consumption mix with an assumed price of 0.10 EUR/kWh) for the short time scale battery

Figure 1:

Preliminary results: Integrated economic and environmental evaluation of electricity storage for different system sizes (1 MW, left, and 100 MW, right) and time scales (TS) considering technical factors including lifetime, efficiency, and cost (above), and technical factors as well as electricity price range and types (Swiss wind electricity and Swiss grid supply based on consumption mix) (below). GHG emissions are based on Life Cycle Assessment (LCA).
A Uniform Techno-Economic and Environmental Assessment for Electrical and Thermal Storage in Switzerland

Technology is the most attractive option, whereas for medium time scale both PHS and CAES are more attractive due to comparable cost but lower emissions. The long time scale results show that PHS is more attractive than P2G2P due to significantly lower emissions in large scale systems, and the preference between these two technologies for small scale systems is rather unclear, and depends on the relative weighting factor between LCOE and life cycle GHG emissions of the decision making. In the case of storing 100% renewable electricity with low or zero marginal cost and low emissions associated with the electricity being stored, P2G2P gains significant attractiveness and may even be competitive with other technologies for medium and long time scales.

Integrated techno-economic and environmental assessment of power-to-gas systems

Interest in power-to-gas (P2G) as an energy storage (and energy conversion) technology is increasing, since it allows to utilize the existing natural gas infrastructure as storage medium, which is supposed to reduce capital investments and facilitate its deployment. P2G systems using renewable electricity can also substitute fossil fuels used for heating and transport. In this study, both techno-economic and life cycle assessment (LCA) are applied to determine key performance indicators for P2G systems generating hydrogen or methane (synthetic natural gas – SNG) as main products. The proposed scenarios assume that P2G systems participate in the Swiss wholesale electricity market and include several value-adding services in addition to the generation of low fossil-carbon gas.

We find that none of the systems can compete economically with conventional gas production systems when only selling hydrogen and SNG. For P2G systems producing hydrogen, four other services such as heat and oxygen supply are needed to ensure the economic viability of a 1 MW power-to-hydrogen (P2H) system, while for SNG with CO₂ captured from the atmosphere there is no economic case yet. The CAPEX and OPEX contribute 28% and 72% of the levelised cost for the P2H system, while the CAPEX share increases to 48% for P2M with CO₂ from the atmosphere (see Figure 2).

As for environmental performance, only the input of «clean» renewable electricity to electrolysis results in environmental benefits for P2G compared to conventional gas production. In particular, the electricity supply to electrolysis for hydrogen production, and the source of CO₂ in case of SNG dominate the environmental performance of P2G (see Figure 3).

Interdisciplinary review of energy storage for communities: challenges and perspectives

Given the increasing penetration of renewable energy technologies as distributed...
generation embedded in the consumption centres, there is growing interest in energy storage systems located very close to consumers (see Figure 4).

These systems allow to increase the amount of renewable energy generation consumed locally, they provide opportunities for demand-side management and help to decarbonise the electricity, heating and transport sectors.

An interdisciplinary review of community energy storage (CES) with a focus on its potential role and challenges as a key element within the wider energy system was compiled. The discussion includes:
• the whole spectrum of applications and technologies with a strong emphasis on end user applications;
• techno-economic, environmental and social assessments of CES;
• an outlook on CES from the customer, utility company and policy-maker perspectives.

Currently, in general only traditional thermal storage with water tanks is economically viable.

However, CES is expected to offer new opportunities for the energy transition since the community scale introduces several advantages for electrochemical technologies such as batteries. Technical and economic benefits over energy storage in single dwellings are driven by enhanced performance due to less spiky community demand profile and economies of scale, respectively.

In addition, CES brings new opportunities for citizen participation within communities and helps to increase awareness of energy consumption and environmental impacts.

**Life cycle assessment of power-to-gas: approaches, system variations and their environmental implications**

This recently published work provides a comprehensive environmental evaluation of P2G with insights into methodological aspects as well as various technology options. The study focuses on the following three aspects:
1) discussion of differences as consequence of the approach applied for CO2 Capture and Utilization (CCU);
2) evaluation of technology variations including supply of electricity, alternative system processes (electrolysis technologies and CO2 sources), product gases (hydrogen and methane), and comparison of these P2G systems with conventional technologies.

Currently, in general only traditional thermal storage with water tanks is economically viable.

However, CES is expected to offer new opportunities for the energy transition since the community scale introduces several advantages for electrochemical technologies such as batteries. Technical and economic benefits over energy storage in single dwellings are driven by enhanced performance due to less spiky community demand profile and economies of scale, respectively.
Table 1: Various scenarios and related implications for BESSs and curtailment strategies considered in this study regarding the location, stakeholder and control respectively.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
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<td>BESS</td>
<td>BESS</td>
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<tr>
<td>Service benefits</td>
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<td>PVts, PVCt and T&amp;D</td>
<td>PVCt and PVCt</td>
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<td>T&amp;D</td>
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<tr>
<td>Economic benefits</td>
<td>PVts and PVCt</td>
<td>PVts, PVCt and T&amp;D</td>
<td>PVts and PVCt</td>
<td>T&amp;D</td>
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3) investigation of further environmental impacts of P2G in addition to the impact of global warming potential.

We found that in case of power to methane (P2M), system expansion provides more meaningful results than subdivision for CCU, since it reflects the added value of CO₂ utilization providing electricity or cement with low GHG intensity. The results of system variations show that P2G can, depending on electricity supply and CO₂ source, reduce GHG emission compared to conventional gas production technologies, and that P2H has higher potential of emission reduction than P2M.

Concerning other impact categories, P2H can have lower impacts than conventional hydrogen production, while P2M most often has higher impacts than using conventional natural gas (see Figure 5).

Figure 6: Levelised cost, LCOES (CHF/kWh), and levelised value, LVOES (CHF/kWh), as a function of the battery capacity for:

(a) A BESS connected to the distribution transformer depending on whether the battery capacity is selected to avoid any PV curtailment (i.e. the BESS is only charged when surplus PV energy exceeds the nominal power of the transformer), or a BESS is charged whenever there is surplus PV energy. The capacity, without assuring that the PV reverse power, exceeds the nominal capacity of the transformer. For the latter, 10 battery capacities are tested, the largest having the same capacity as the first scenario.

(b) A residential BESS connected to the PV system of a dwelling. 10 battery capacities are tested up to 20 kWh. For PV curtailment, the levelised cost, LCOt (CHF/kWh), and levelised value, LVOt (CHF/kWh), are also given as straight lines. PVts means energy time shift, PVCt means avoidance of Curtailment, T&D denotes as transmission and distribution grid.
Practical Aspects of Power-to-Methane

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 commissioning 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

In the SCCER’s annual report 2015, the pilot and demonstration plant power-to-methane at IET-HSR (Figure 1) was presented together with its goals, industry partners, technical data and first results. 2016 was the second year of operation. Testing on the behaviour of the reactor under different conditions was continued and the grid injection was completed and commissioned.

A new CO₂-collector built by Climeworks and provided to IET-HSR by Audi was integrated. Fundamental considerations and the summary of learnings were published in the report of Friedl, Meier, Ruoss and Schmidlin «Thermodynamik von Power-to-Gas», published on the website of IET-HSR, 20 October 2016.

Complementary activities were continued: In addition to the 500 visitors mentioned in the annual report 2015, 230 more people visited the plant during 2016. The steering committee met in February and November. The exchange of experience continued in including further parties (Umweltarena, EPFL from Martigny) and meetings took place in April, June and September. The conference «Expertengespräche Power-to-Gas» was organised the fourth time, but unfortunately almost no participants from the French speaking part of Switzerland enrolled and the simultaneous translation into French was cancelled.

The year 2016 lead to new industry co-operations with KVA Linth, Hitachi Zosen Inova, Groupe e, Biogas Zürich and Nordur. Due to delays in commissioning and testing at the plant Hybridwerk Aar - matt built by Regio Energie Solothurn, no analysis of data could be performed nor published. A feasibility study of a large-scale power-to-methane
Assessment

Practical Aspects of Power-to-Methane

installation at the waste incineration plant KVA Linth showed that power-to-methane is very close to profitability.

To our own judgement, large-scale application of power-to-methane has reached the following status in Switzerland. A large scale power-to-gas plant can be close to profitability under the condition that:

a) the electricity used is renewable and free from fees for the usage of the electricity grid;
b) the plant can operate in full load during more than 5’000 hours per year;
c) income can be generated from selling the gas as renewable and maybe «Swiss Made» for a premium price;
d) additional income is generated from providing a service to the electricity grid e.g. in the form of secondary balance energy.

Electricity is only free from fees for the usage of the electricity grid, if the power-to-gas plant is located on the same ground as the production of renewable electricity. The requirement of less than 5’000 operating hours per year excludes PV installations as the only source of renewable electricity for a power-to-methane plant, because in Switzerland PV only reaches 1’000 full load hours.

Support of the investment e.g. by the pilot, demonstration and beacon programme of the Swiss Federal Office of Energy (SFOE) and other benefits like the recognition of the CO₂ used in the methanation when calculating the CO₂-emissions of an importer’s fleet can make a power-to-gas installation profitable. In comparison to Germany, Switzerland offers favourable conditions for large-scale power-to-gas installations and several projects are being discussed by different parties. However, the uncertainties about future regulations and about energy prices (gas, renewable gas and electricity) are a problem for launching large-scale power-to-gas projects.

Our investigations have shown, that the cost of electricity (including fees for utilisation of the electricity grid if applicable) are the dominant cost factor and determine the business case. Furthermore, the emissions for the production of the electricity used are dominant when assessing the environmental impact of the gas produced in a power-to-gas plant, e.g. in a life cycle analysis.

Hence the future development on a system level has to go towards higher efficiencies, which at the moment is at 53% (upper heating value of gas produced divided by the electricity used). The efficiency of power-to-methane can be increased in using a high temperature electrolysis (solid oxide electrolyser cell = SOEC, [1–3] and www.helmeth.eu).

IET-HSR participates in the EU-funded project «Pentagon» (www.pentagon-project.eu), part of which is building a small-scale power-to-methane installation as a co-operation of IET-HSR and EPFL, where a SOEC is integrated. IET-HSR has done extensive modelling and calculations on the thermodynamics of this plant in order to be able to define the installation’s layout early 2017.

References
ESI – Energy Systems Integration Platform

Scope of project

The Energy Systems Integration (ESI) Platform at the Paul Scherrer Institute (PSI) provides a basis for research and technology transfer activities for the SCCERs «Heat and Electricity Storage» (HaE) and «Biomass for Swiss Energy Future» (BIOSWEET). Main topics so far are power-to-gas processes and conversion of biomass.

Status of project and main scientific results of workgroups

Work in 2016 focussed on finishing the hardware infrastructure on the platform and on commissioning both the basic platform infrastructure (support structure for individual sub-systems, supply of media-gases, (cooling) water and electricity, safety system & controls) and the first sub-systems. In parallel, intensive interactions have started between the technology oriented sub-systems and the teams working on cross-cutting scientific topics such as catalysis research (synthesis and characterisation), process diagnostics tools (sampling, analysis, process validation) and energy system modelling (energy scenarios, technology assessment, life cycle analysis).

Electrochemical systems

The polymer electrolyte membrane (PEM) based electrolyser and the connected gas cleaning system are now fully operational and can convert electric energy to dry, pure hydrogen and oxygen in 100 kW scale. In the first series of experiments, the system is characterized with respect to system efficiencies at various load points, dynamic system response (load ramps) and operational limits.

The two gas tanks for hydrogen and oxygen are prepared to be filled the first time in early 2017. With this sub-system, storage of even highly fluctuating electricity will be realised in pilot scale which subsequently could be used for mobility purposes (fuel cell cars) or for re-electrification, especially as positive balancing power service.

The fuel cell system on the ESI platform which will allow dynamic and highly efficient re-electrification of the stored hydrogen and (pure) oxygen without significant emissions is close to mechanical completion. Four pilot scale PEM fuel cell stacks will be installed and all necessary subsystems are already in place. Commissioning will start in spring 2017.

SNG production routes

Catalytic fluidised bed reaction systems are being used to on the ESI platform to convert hydrogen and carbon oxides to methane, i.e. synthetic natural gas, SNG. This way, hydrogen can not only be stored in dedicated gas tanks or as limited addition (<2%) to natural gas in the existing gas grid, but in unlimited amount. As source for the carbon oxides, biogas from anaerobic digestion or CO₂ separated from industrial flue gas are being investigated. Additionally, the conversion of (simulated) producer gas from biomass gasification to SNG is possible as well, both with and without hydrogen addition.

For the investigation of these synthesis processes, two plants have been built in conjunction with the ESI platform. The smaller one in 10 kW scale, referred to as COSYMA, is a fully automated, mobile system in a container which was commissioned successfully on the ESI platform and then transferred to a biogas plant in Zürich (in January 2017) in order to demonstrate direct methanation of real biogas in a 1000 h operation campaign.

A 160 kW pilot scale system, referred to as GanyMeth, will be used to investigate scale-up effects in these synthesis processes and to deliver realistic data for model validation. The main parts of GanyMeth were delivered in autumn 2016. The next steps are the mechanical and electrical completion, followed by the commissioning.

Hydrothermal gasification allows converting wet or liquid biomass (such as algae, sewage sludge, manure or residuals from food production) to methane/SNG. A fully automated, mobile system in a container is in operation on the ESI platform and was already used successfully for tests with food production residues.
as well as for investigation of power-to-gas applications.

In the next phase 2017–2020, a scale-up of the technology to 100 kW scale is planned.

**Integrated operation**

Subsequently to the start-up of the individual sub-systems, integrated operation of several systems is prepared for 2017, e.g. combined electrolysis to convert electricity to hydrogen and its further conversion to SNG. The platform infrastructure has significant flexibility to accommodate additional technologies in the next phase 2017–2020.

One goal is to close the link between SNG production and storage in the gas grid on the one hand, and flexible re-electrification in combined heat and power (CHP) systems, on the other hand. For this, conversion technologies like micro gas turbines or internal combustion engines are being considered for complementation of the test infrastructure.

**Outlook**

Within joint activities of several SCCERs – coherent energy demonstrator assessment (CEDA) – intra-platform data handling procedures and data evaluation standards will be developed and applied for data generated at ESI.

Figure 1: The ESI installations at PSI.
Conferences

- 32nd PSI Electrochemistry Symposium, «Electrolytes: The Underestimated Player in Electrochemical Processes». 27.04.2016, PSI.
- Swiss Mobility Days, 07.04.2016, Martigny.
Presentations

Work Package «Heat – Thermal Energy Storage»

- S. Stroehle, A. Haselbacher, Z. Jovanovic, A. Steinfeld, «High-temperature thermochemical energy storage: Getting the most of it». AICHE Annual Meeting, 2016, San Francisco, CA, USA.

Work Package «Batteries – Advanced Batteries and Battery Materials»

- M.V. Kovalenko, 18th International Meeting on Lithium Batteries, June 19–24, 2016, Chicago, USA.
- M.V. Kovalenko, Fall Meeting of the European Materials Research Society, Sept. 19–22, 2016, Warsaw, Poland.
- M.V. Kovalenko, 1st International Symposium on Magnesium Batteries (Mag-Batt), July 21–22, 2016, Blautal/Ulm, Germany.
- H. Yao, «Ionic liquids based on crown ether as electrolyte for batteries». SCCER WP1 meeting, Jan. 21, 2016, Fribourg, Switzerland.
- S. Maharajan, «Sn/C composite anode material for high energy batteries». SCCER WP1 meeting, Jan. 21, 2016, Fribourg, Switzerland.
- N. Herault, «TiO₂ nanocontainers and nanospheres as photocatalysts for photoelectrochemical water splitting». SCCER WP1 meeting, Jan. 21, 2016, Fribourg, Switzerland.
- S. Maharajan, «Sn/C composite anode material for high energy batteries». SCCER WP1 meeting, July 7, 2016, ETHZ, Zürich, Switzerland.
- S. Maharajan, «Sn/C composite anode material for high energy batteries». SCCER WP1 meeting, Oct. 19, 2016, ETHZ, Switzerland.
Appendix

Presentations

- N.H. Kwon, «Nanomaterials and nanostructured composites of cathode for lithium ion batteries». Metrohm user meeting, Oct. 28, 2016, Zofingen, Switzerland.

- N.H. Kwon, «Rechargeable Li-air batteries». Metrohm user meeting, Oct. 28, 2016, Zofingen, Switzerland.

**Work Package «Hydrogen – Production and Storage»**


**Work Package «Synthetic Fuels – Development of Advanced Catalysts»**


- C. Copéret, «The role of the interface in supported metal catalysis: Water Gas Shift, Dry Reforming and CO2 hydrogenation, CO2 conversion». From Fundamentals towards Applications Meeting, Aug. 29 – Sept. 2, 2016, Villars, Switzerland

- P.J. Dyson, «Enhancing sustainable catalytic processes with ionic liquids». Swiss Chemical Society Spring Meeting, April 2016, University of Zürich, Zürich, Switzerland.


- P.J. Dyson, «From Swiss alpine forests to Zika control: the role of green chemistry». Oct. 2016, University of York, UK.


- F.D. Bobbink, A. Redondo, P.J. Dyson, «Synthesis and characterization of novel imidazolium-based ionic poly(styrenes) and their application as supports for Pd nanoparticles». SCS Fall Meeting, Sept. 15, 2016 University of Zurich, Zürich, Switzerland.
Appendix

Presentations

- A. Gopakumar, P.J. Dyson, «Earth-abundant metal oxide nanoparticles as recyclable catalysts for N-methylation and N-formylation reactions using CO₂ as C₁ source in mild conditions». SCS Fall Meeting, Sept. 15, 2016 University of Zurich, Zürich, Switzerland.
- D. Vasilyev, P.J. Dyson, «Triazolium ionic liquids for electrochemical reduction of CO₂». SCS Fall Meeting, Sept. 15, 2016 University of Zurich, Zürich, Switzerland.
- M. Hulla, P.J. Dyson, «CO₂ based N-formylation of amines catalyzed by Fluoride and Hydroxide ions». SCS Fall Meeting, Sept. 15, 2016, University of Zurich, Zürich, Switzerland.
- T.J. Schmidt, «Oxygen Evolution Electrocatalysis on Perovskites». University of Birmingham School of Chemistry, Dec 02, 2016, Birmingham, UK.
- T.J. Schmidt, «Technische Optionen der Energiespeicherung». Technische Gesellschaft Zürich, March 07, 2016, Zürich, Switzerland.
- T.J. Schmidt, «H₂ Production by Electrolysis». Workshop on Electrolysis, Aalborg University, Feb. 9, 2016, Copenhagen, Denmark.

Work Package «Assessment – Interactions of Storage Systems»

- B. Meier, «Hybridwerk Aarmatt: Die Energiezukunft wissenschaftlich begleitet». FOGA Forschungstag, June 6, 2016, Zürich, Switzerland.
Presentations

Appendix

Publications

Work Package «Heat – Thermal Energy Storage»


Work Package «Batteries – Advanced Batteries and Battery Materials»

- C. Marino, T. Block, R. Pöttgen, C. Villevieille, «CuSbS2 as negative electrode material for sodium ion batteries». *Journal of Power Sources*, 2016.

Work Package «Hydrogen – Production and Storage»

Appendix

Publications

Work Package «Synthetic Fuels – Development of Advanced Catalysts»


Appendix

Publications


Work Package «Assessment – Interactions of Storage Systems»


Organized Events

4th Annual Symposium, SCCER Heat and Electricity Storage, October 24, 2016

The 4th Annual Symposium «SCCER Heat & Electricity Storage» was held on October 24, 2016, at Hochschule Luzern – Technik und Architektur.

Organizers
Thomas J. Schmidt, Jörg Roth, Ursula Ludgate, Jörg Woriitschek, Svetlana Vangesova

Speakers
Prof. Mark O’Malley, Energy Institute and Electricity Research Centre University College Dublin, Ireland
Dipl.-Wirt.-Ing. Julia Badeda, RWTH Aachen, D
Dr. David Hart, E4tech, Lausanne, CH
Prof. Dr. Bright Scheppat, Hochschule Rhein Main, D
Prof. Dr. Sophia Haussener, EPFL, CH
Dr. Claire Villevieille, Paul Scherrer Institut, CH
Prof. Dr. Hubert Girault, EPFL, CH
Prof. Dr. Christophe Copéret, ETHZ, CH
Dr. Christian Bauer, Paul Scherrer Institut, CH
Prof. Martin Patel, University of Geneva, CH

Oral Presentations
• M. O’Malley, «The Value of Energy Storage: The Good, the Bad and the Ugly».
• J. Badeda, «Development of the PV homestorage market and the implications for local distribution grids».
• D. Hart, «Policies for energy storage? I wouldn’t start from here...».
• B. Scheppat, «Energiepark Mainz: Operational and Economical Experiences of the worldwide largest Power-to-Gas plant with PEM electrolysis».
• S. Haussener, «High Temperature Heat Storage System Performance and Design».
• C. Villevieille, «Recent development in Na-ion batteries».
• H. Girault, «Grid to Mobility».
• C. Copéret, «Strategies and Current State of the Art in CO2 Conversion processes within Hae».
• C. Bauer, M.K. Patel, «Integrated evaluation of energy storage technologies: economic and environmental aspects».

Posters

Battery and Materials
• J. Cabañero, C. Marino, C. Villevieille, «Almond Shell-Derived Carbonaceous Materials as Anodes for Sodium-Ion Batteries».
• C. Marino, S. Park, C. Villevieille, «Electrode formulation of a P2-layered oxide material for Na-ion batteries».
• C. Marino, S. Park, C. Villevieille, «P2-Nax(0.6)(Mn0.6Fe0.25Co0.15-Alx)O2 as cathode material for Na-ion batteries».
• B. Baichette, K.M. Fromm, «Heterometallic single precursor of oxides for Na-ion battery cathode materials».
• N. P. Stadie, S. Wang, K. Kravchyk, M.V. Kovalenko, «Ordered Microporous Carbons as the Cathode for High Energy and Power Density Aluminum Batteries».
• N.H. Kwon, Y. Sheima, K.M. Fromm, «Rechargeable Dual Electrolytes for Li-Air and Li-Water Batteries».
• S. Maharajan, N.H. Kwon, K.M. Fromm, «Sn/C composite anode materials for high energy batteries».
• H. Yao, K. M Fromm, «Ionic Liquids based on Crown Ethers as electrolytes for batteries».
• P. Sutton, M. Fischer, I. Gunkel, U. Steiner, «Solid polymer electrolytes for lithium batteries».
• E. Cuervo Reyes, E. Stilp, C.P. Scheller, M. Held, U. Sennhauser, «Footprint of Sub-diffusive Transport in the Impedance Spectrum of Lithium Ion Batteries».
• C. Brivio, V. Musolino, M. Merlo, P.-J. Alet, L.-E. Perret-Aebi, C. Ballif, «Battery modeling and performances evaluation».
• A. Fuerst, A. Haktanir, H. Roth, B. Löffel, M. Müller, «Pilot production line for battery cell manufacturing».
Thermal Energy Storage

- L. Geissbühler, A. Mularczyk, A. Haselbacher, A. Steinfeld, «Thermocline Control for Sensible Thermal Energy Storage».
- S. Zavattoni, M. Barbato, L. Geissbühler, A. Haselbacher, G. Zanganeh, A. Steinfeld, «CFD modeling of the Pollegio AA-CAES prototype TES system».
- M. Dudita, X. Daguenet-Frick, P. Gantenbein, «Increasing the heat and mass transfer by improving surface wetting of adsorbers in sorption storage systems».
- E. Rezaei, M. Barbato, S. Gianella, S. Haussener, A. Ortona, «High temperature tubular SiSiC structures for solar applications».
- S. Maranda, R. Waser, A. Stamatiou, L. Fischer, J. Worlitschek, «Modeling and experimental investigation on the solidification in a latent heat storage unit using a finned tube bundle heat exchanger».
- G. Seitz, R. Helmis, H. Class, «Numerical Model of a CaO/Ca(OH)2-heat storage tank».

Hydrogen Generation and Storage

- S. Kato, M. Spodaryk, A. Züttel, «Metal Hydride Catalyst for Energy Storage».
- C. Fink, G. Laurenczy, «Screening for Potential Catalysts for Selective Formic Acid Dehydrogenation of the type [Cp*Ir(N,N)Cl]».
- M. Montandon-Clerc, A.F. Dalebrook, G. Laurenczy, «Hydrogen Storage Using the Formic Acid/CO2 Couple in Aqueous Solution Catalyzed by First Row Transition Metal Complexes».

Synthetic Fuels

- M. Rahaman, A. Dutta, P. Broekmann, «Energy Efficient CO2 Conversion to Formate at Very Low Overpotential on Size Selective Pd Nanoparticles».
- M. Rahaman, C. Morstein, A. Dutta, P. Broekmann, «Electrodeposited Ag Microcrystals for CO2 Electroreduction».
- N. Kaeffer, H.-J. Liu, C. Coperet, «Surface-supported Cu-based catalysts towards CO2 conversion».
- D. Lebedev, D. Abbott, M. Povia, K. Waltar, E. Fabbri, A. Fedorov, T.J. Schmidt, C. Coperet, «Highly active and stable iridium oxide and pyrochlore materials for the oxygen evolution reaction».
- M. Spodaryk, S. Kato, A. Züttel, «Electrochemical CO2 reduction with H2 to synthetic fuels».

Organized Events

Organizers and speakers (from left to right):
Top
Søren Klein,
Sivarajakumar Maharajan,
Christophe Copéret,
Julia Badera,
Claire Villeveille
Middle
Jörg Worlitschek,
Christian Bauer,
Birgit Scheppe,
Markus Friedl,
Hubert Girault
Bottom
Mark O’Malley,
Sophia Haussener,
Thomas J. Schmidt,
Jörg Roth,
David Hart
Organized Events

- N. Hérault, V. Kaliginedi, P. Broekmann, K.M. Fromm, «TiO₂ nanocontainers and nanospheres as photocatalysts for CO₂ reduction and photoelectrochemical water splitting: Structural modification».

Assessment of Storage Systems
- D. Parra, M. K. Patel, «Assessment of energy storage technologies for further renewable energy penetration, and beyond».
- P. Schuetz, D. Gwerder, L. Gasser, B. Wellig, J. Worlitschek, «Thermal storage facilitates higher flexibility in smart grids for residential heating systems with heat pumps».
Contact

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