Battery
Heat
H2
CH4
Assessment
Synthetic Fuels
Hydrogen

Annual Report 2017
Table of Contents

Editorial
3 SCCER Networked Research – The Whole Is More Than The Sum Of Its Parts

Heat – Thermal Energy Storage
5 Tubular Designing, 3D Printing and Testing of SiSiC Porous Structures
6 Numerical Optimization of High-Temperature Energy Storage Units Made of Encapsulated Metal Phase Change Materials
8 AA-CAES Plant Modelling and CFD Analysis of the TES System
10 Sensible Thermal Energy Storage Systems Optimized for AA-CAES Plant Operation
12 Closed Sorption Seasonal Thermal Energy Storage with Aqueous Sodium Hydroxide
14 Sorption-Based Seasonal Heat Storage
16 Seasonal Sensible Thermal Energy Storage Systems
18 High Power Latent Seasonal Heat Storage

Batteries – Advanced Batteries and Battery Materials
22 Development of Anode and Cathode Materials for Li- and Na-Ion Batteries
24 Development of Efficient and Inexpensive Batteries for Large-Scale Stationary Storage of Electricity
25 Nanostructured Anode Materials for High-Energy Alkali Metal Ion Batteries
26 Nanostructured Cathode Materials for High-Power Lithium Ion Batteries
28 Investigations for a Full Cell NMC Benchmark
31 Investigation of the Promising P2-Na_{0.67}Mn_{0.6}Fe_{0.25}Al_{0.15}O_2 Cathode Material
34 Electrolytes for Safe and High-Performance Alkali Metal Ion Batteries
35 Modeling a Multi-Product Battery Production Line

Hydrogen – Production and Storage
40 Hydrogen – Solid Interaction for Storage
42 Hydrogen/Energy Production and Storage with the Carbon Dioxide/Formic Acid Systems
44 Demonstration of a Redox Flow Battery to Generate Hydrogen from Surplus Renewable Energy
46 Investigations on the Active Layer Formation on Stainless Steel Electrodes in Water Oxidation Conditions
48 Ag Nanoparticles Loaded on TiO2 Nanocapsules and Nanospheres as Photocatalysts for Photoelectrochemical Water Splitting

Synthetic Fuels – Development of Advanced Catalysts
51 Catalytic and Electrocatalytic CO2 Transformation into Feedstocks and Fuels
53 Progress in the Development of Tailored Catalysts for the Hydrogenation and Electrocatalytic Reduction of CO2
57 Beyond Copper: Novel Silver Foam Catalysts for Selective Hydrocarbon and CO Formation from CO2
60 Progress in Co-Electrolysis Cells and the Development of Efficient Oxygen Evolution Catalysts
Table of Contents

Assessment – Interactions of Storage Systems

65  Investigation of AA-CAES Plant Configurations and Grid Integration
68  Assessment of Energy Storage at the Energy System Level
70  Assessment of Energy Storage at the Technology and Energy System Level
72  Assessment of Energy Storage at the Technology and Socio-Economic Level
74  Assessment of Energy Storage Demonstrators
77  ESI – Energy Systems Integration Platform

Appendix

81  Conferences
82  Presentations
88  Publications
92  Organized Events
96  Co-organized Events
The Swiss Competence Center for Energy Research (SCCER) *Heat and Electricity Storage* enjoys its operation already in the fifth year since its launch in 2013. In this report, a detailed summary of our activities and achievements from 2017 can be found, giving our interested readers from academia, industry, and politics an overview of our successful operation.

Besides following our scientific and technical goals as defined by our Innovation Roadmap, one of the important objectives of the SCCERs is the formation of a network of academic and industrial researchers with close interactions. Specifically within Energy Research with its huge complexity at the intersection of technical, economic, political and societal questions, only a cooperative and networked R&D approach can lead to answers to the grand challenges of Energy System Transitions we are facing. Cooperative research is one of the priorities within the SCCER, bringing together different expertise from 23 academic groups and 29 industrial partners. Freely referring to Aristoteles – *The Whole Is More Than The Sum Of Its Parts* –, this idea clearly holds true for our efforts where cooperative and joint R&D have been proven to be the key to our successful activities. Our SCCER network fosters the collaboration of scientists and engineers from different stakeholders in academia and industries not only clearly visible in the planning, construction and operation of the four demonstrators brought together under the roof of SCCER *Heat & Electricity Storage*, but also in numerous other multi-disciplinary cooperative R&D projects where different groups are sharing the same vision using complementary rather than redundant approaches in order to reach a common goal. Without exaggeration, over the last 4 years SCCER *Heat & Electricity Storage* and the seven sister Competence Centers developed a very successful R&D network not only within their own but within all SCCERs. As a result, we are extremely well recognized in Switzerland as well as on the international scale for our cutting edge Energy R&D.

Another important aspect of this network is often overlooked: The SCCERs are fulfilling an important task in educating young researchers not only through newly developed classes and lectures at the involved Universities, but also by designing specific summer/winter schools on the various aspects of Energy Research attracting students and Post-Docs from all European countries providing them with fundamentals and knowledge to make them ready to address the future challenges in Energy Research.

Clearly, SCCER developed into a synonym for cooperative networked R&D over the last years. As you will see in this annual report summarizing our technical results, we already achieved a lot, but at the same time we set the scene to harvest even more over the next years. By reading through the following pages, you may clearly see that *The Whole Is More Than The Sum Of Its Parts*.

Prof. Dr. Thomas J. Schmidt  
*Head SCCER Heat and Electricity Storage*
Thermal Energy Storage

Work Package «Heat Storage» at a Glance

Thermal-energy storage (TES) is expected to play an important role in Switzerland’s future energy system because the generation of heat is responsible for about 50% of primary energy consumption. The main contribution of TES in Switzerland is anticipated to be for seasonal storage of low-temperature heat for space heating and hot water. Seasonal storage is expected to be essential to achieving the objectives of the Energy Strategy 2050 (ES 2050). The storage of high-temperature heat in industrial applications has the potential to play an important role also because process heat accounts for about 50% of the total energy use in Swiss industry. At present, the potential cannot be quantified in detail yet because little information is available on the amounts and temperature levels of the required thermal energies. Efforts to gather additional information have been initiated.

Our efforts on TES at high temperatures relevant to industrial applications are focusing in improving heat-transfer rates for both sensible and latent TES. These efforts comprise the design, manufacturing, and testing of porous SiSiC structures for temperatures of up to 1600°C. One unique feature of these structures is that they are manufactured through 3D printing, allowing their topologies to be tailored to deliver both high heat-transfer rates and low pressure drops. The relevance to industrial applications is reflected in the collaboration with EngiCer SA. In addition, we are using genetic algorithms to optimize latent TES units containing metallic phase-change materials (PCMs) in cylindrical encapsulations. Future work will tackle the optimization of macroporous structures that represent a promising avenue to improve heat-transfer rate limitations arising from the encapsulation.

In addition to industrial applications of TES for process heat, an application of great interest is advanced adiabatic compression air energy storage (AA-CAES). Our current work on AA-CAES is part of a longer-term effort dating back to Phase I in which we studied AA-CAES not just theoretically, but also experimentally using the world’s first pilot-scale plant with a hard-rock cavern and a combined sensible/latent TES at temperatures of up to 575°C. The sensible TES used rocks and had a capacity of 12 MWhth. The latent TES contained an AlCuSi alloy encapsulated in steel tubes and had a capacity of 172 kWhth. The experiments proved the technical feasibility of AA-CAES in hard-rock caverns with estimated efficiencies of 63–74%. Building on this effort, in Phase II the focus has shifted toward techno-economic analyses. The overarching goal is to determine whether an AA-CAES plant could be operated profitably in Switzerland under future electricity market conditions. To this end, we have started investigating plant configurations in greater detail and analyzing possible plant sites in collaboration with industrial partners ALACAES, Amberg Engineering, BKW, MAN Diesel & Turbo AG, and Swissgrid. First analyses of possible plant sites were carried out using data on decommissioned military caverns provided by Armasuisse and models of the electricity grids of Switzerland and neighboring countries. Our AA-CAES efforts are supported by interactions with the EU project RICAS2020, an SNF NRP 70 project, and an SFOE project and are accompanied by research on thermocline control for sensible TES, sensible multi-tank TES, and the design and numerical optimization of both sensible and sensible/latent single-tank TES.

The primary focus of our efforts at low temperatures continues to be sorption-based seasonal storage using NaOH and water because of the potential for high energy densities. One challenge facing sorption-based storage are limited exchange rates in the heat/mass exchanger (HMX) that limit the discharge power. To tackle this challenge, two complementary strategies are being pursued. The first attempts to improve the wetting and residence behavior of the existing falling-film tube-bundle HMX concept using porous SiC foams and investigates alternative sorbent pairs such as LiBr-water and LiCl-water. Initial results are promising but more extensive experiments are required to fully characterize the impact of the foams. The second strategy evaluates an alternative HMX concept based on a vertically oriented tube with a spiral fin in a new lab-scale setup. Initial results are also promising, particularly when the spiral fin was modified to include cutouts that substantially increased the absorption rates of the water vapor. Future work will include the use of Raman spectroscopy to improve the understanding of the phenomena in the HMX.

An additional activity at low temperatures focuses on latent TES and in particular on overcoming low heat-transfer rates. The goal is to investigate and test novel technologies that provide high-power latent TES at temperatures up to about 120°C. Several avenues are being explored using experiments and simulations, including novel materials such as unbranched, saturated carboxylic esters, optimized finned-tube heat exchangers, PCM slurries, and direct contact between PCM and heat-transfer fluids. The research is supported by SFOE and an SNF Ambizione Energy Grant and benefits from the collaboration with industrial partner Sunamp.
Tubular Designing, 3D Printing and Testing of SiSiC Porous Structures

Scope of project

Open-cell cellular ceramics are attractive structures for high temperature applications such as heat exchangers and heat storage systems. They offer low pressure-drop due to their high porosities (typically about 75-95%) and exhibit very high heat transfer due to their large surface area per unit volume. Nowadays these structures can be designed and finely manufactured via direct or indirect rapid prototyping. In the first part of our work, we proposed two new approaches to design porous parts with various unit-cell topologies. The first approach creates lattices by mapping a selected periodic unit cell into a mesh. The second method generates the lattice inside cylindrical enclosure and crops the cells on the boundary surfaces. In the second part, the effect of morphology on the pressure drop and heat transfer behaviour of the porous structures was evaluated. To do that, lattices with four different unit cells (cube, rotate-cube, tetrakaidecahedron and Weaire-Phelan) were designed using an in-house developed CAD tool based on the second approach. The polymeric forms of the lattices were printed and used to obtain final pieces via the replica technique (figure 1). In addition, random foams (5 PPI) were manufactured by replication of commercial polyurethane foams. The final lattices had a cell size of 4.75 mm and porosity of about 0.80. The random foam also had a porosity of about 0.84.

Status of project and main scientific results of workgroups

The heat transfer experiments were performed by fixing the furnace temperature to 100°C and passing the cold air at the desired volumetric flow rate at the inlet of the tube. The air passes through the heated porous media inside the tube and the sensors’ values are recorded after the steady state condition is reached. The pressure drop measurements were also performed on the SiSiC structures by forcing air through the porous medium at different velocities. The results show that the developed numerical tools are faster and more versatile than the current CAD softwares. The produced samples revealed some of the limitations and drawbacks of the manufacturing method, which can be considered for the future designs. Pressure drop tests have been successfully performed and permeability and DuPuit–Forchheimer coefficients were obtained for all the samples and compared with the random foam. Figure 2 shows the experimental heat transfer results for different velocities, which were obtained using inverse 3D simulations. Tetra-kaidecahedron and Weaire-Phelan lattices had slightly higher volumetric heat transfer rates (about 20%), which are likely due to the higher distribution of clogged pores in their structure, formed in the manufacturing process. These clogged pores were also the main reason of the higher pressure-drops in these two structures. The results of this study will be used in the future work in which these porous architectures are used to enhance the heat transfer in a high temperature latent heat storage system.

Figure 1:
From left to right: cube, rotated cube, tetrakaidecahedron, Weaire-Phelan, and random SiSiC architectures. Dimensions of the samples: Diameter = 20 mm, Length = 100 mm.

Figure 2:
The predicted Nusselt numbers for the samples in range 60 < Re < 250.

Authors
Ehsan Rezaei1,2
Maurizio C. Barbato1
Sandro Gianella3
Sophia Haussener2
Alberto Ortona3
1 SUPSI
2 EPFL
3 EngiCer SA, Balerna, Switzerland

List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCM</td>
<td>Phase Change Material</td>
</tr>
<tr>
<td>HTF</td>
<td>Heat Transfer Fluid</td>
</tr>
<tr>
<td>LHS</td>
<td>Latent Heat Storage</td>
</tr>
<tr>
<td>OPEX</td>
<td>Operational Expenditure</td>
</tr>
<tr>
<td>SHS</td>
<td>Sensible Heat Storage</td>
</tr>
<tr>
<td>SiSiC</td>
<td>Silicon Infiltrated Silicon Carbide</td>
</tr>
</tbody>
</table>
Heat

Numerical Optimization of High-Temperature Energy Storage Units Made of Encapsulated Metal Phase Change Materials

Scope of project

Highly conductive, high melting point (above 400°C) metal alloys can be used for high energy and power density latent heat storage. We implemented a computational model accounting for the phase change process and multi-mode heat transfer within and around the encapsulated PCM structures. The model suggested that during conduction-driven charging/discharging, the Rayleigh-Benard natural convection within the PCM encapsulation significantly contributes to the heat transfer, causing 10% faster melting. The model also confirmed that during charging/discharging with a heat transfer fluid (HTF), the convective heat transfer from the HTF to the encapsulations is limiting. Structural topology optimization of the encapsulations is proposed to overcome this limitation. A genetic algorithm (GA) was tested as a proof of concept for optimizing ordered structures and optimizations for macroporous encapsulations are currently being explored. The developed models provide a design tool to build tailored high-temperature heat storage units made of encapsulated metal PCMs.

Status of project and main scientific results of workgroups

Modelling phase change is an integral part of designing latent heat storage systems. The models should allow to track the melt interface, predict the convection in the melt, capture phase change over a temperature range, account for volumetric expansion and contraction, and close contact melting. We developed a transient axisymmetric model of a cylindrical Al-12Si PCM storage unit (Figure 1a) modelled in ANSYS Fluent with an air gap to allow for thermal expansion of the metal. The air gap-PCM interface is obtained using the enthalpy-porosity method [1]. The outer walls are maintained at 900 K and 300 K during melting and solidification, respectively. A mushy constant value of $10^4$ kg/m$^3$/s was chosen to have good resemblance to model and the solid metal–molten metal mushy interface is obtained using the enthalpy-porosity method [1].

Figure 1:
(a) Conduction-driven charging/discharging simulation setup consisting of an encapsulated cylindrical PCM storage. Blue part of mesh represents the PCM, and red part the thermal expansion gap, surrounded by a constant temperature outer wall. Change in melt fraction contours and natural convection velocity plots during (b) melting and (c) solidification. The black line is the lagging melt interface for conduction-only case.

References


Authors

Nithin Mallya¹
Sophia Haussener¹

¹ EPFL
melt interface movements in experiments performed with low temperature PCMs [2, 3]. During melting (Figure 1b), Kelvin-Helmholtz instability convection cells speed up the melting process (10% faster compared to the conduction only case). During solidification (Figure 1c), natural convection has no influence but modelling the vertical motion of the solidifying PCM is imperative for replicating void formations.

With the use of metal alloys as PCMs, the convective heat transfer from the HTF becomes the limiting factor. This requires topology optimization of high-temperature latent heat storage units as a major path to overcome this limitation. Genetic algorithms are a robust optimization tool for problems with a limited number of parameters and is well suited for optimizing regularly structured heat storage systems.

**Topology Optimization: Genetic Algorithms**

A single objective binary GA problem for optimizing a structured latent heat storage unit was defined as a proof of concept. The unit consisted of ten cylinders of constant radii of 0.02 m (constant energy density) located in random positions within a 0.2 × 0.2 m² area.

The binary coded GA aimed at increasing power density measured as heat transferred into the cylinders. 20% of the individuals with the highest heat transfer in the population were also preserved for the next population. ANSYS APDL automatically created and meshed the geometry, and ANSYS Fluent performed the flow simulations.

A random population of 100 was used and 250 iterations were performed – 25,000 simulations in total. The optimum arrangements at different iterations are shown in Figure 2. The cylinders showed an increasing tendency to get arranged along a line, using most of the incoming heat and decreasing average outlet temperature.

GAs are suitable for optimizing such structured heat storage devices as they can find the global optimum, and are currently being further developed to find the optima ten times faster.

Currently the computations take in the order of minutes for one iteration without melting and several hours with melting.

**Topology Optimization: Macroporous Encapsulations**

GAs are limited by the number of parameters and are not suitable for random microporous structures that cannot be explicitly parametrized (Figure 3).

Adjoint optimization methods and neural networks, are currently being investigated. The combination of these optimization approaches and latent heat storage modelling shows to be a promising area of research for obtaining tailored latent heat storage systems.

**Acknowledgement**

The financial support of Innosuisse Swiss Competence Centers for Energy Research (SCCER Heat and Electricity Storage) is kindly acknowledged.

Figure 2: Results of optimizing positions of cylindrical PCM storage tubes: tube positions, temperature distribution in the fluid, outlet temperature distribution, and outlet average temperature for the setup all shown at: (a) iteration 0, (b) 50, (c) 100, (d) 150, (e) 200, and (f) 250.

Figure 3: A sample of a percolating, macro-porous encapsulated PCM latent heat storage structure.
**AA-CAES Plant Modelling and CFD Analysis of the TES System**

**Scope of project**

Compressed Air Energy Storage (CAES) plants are Brayton cycles in which the compression and expansion are decoupled and whose aim is to store energy, pressurizing air in underground caverns. Advanced Adiabatic Compressed Air Energy Storages (AA-CAESs) foresee to compress air adiabatically in order to store also the thermal energy content of the hot air, exiting the compressor, in a thermal energy storage (TES). The pressurized air recovers the stored thermal energy before entering the turbine, overcoming the need of fuels.

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

A physical model of an AA-CAES plant was developed in Matlab-Simscape taking into account temperature dependent properties of air, efficiency (isentropic and polytropic) maps for turbomachinery and the dynamics of the underground cavern wherein the pressurized air is stored. The detailed description of the TES and its thermocline evolution are taken into account exploiting an embedded 1D Fortran code developed by ETHZ. A power scheduling can be set to characterize the power exchanges with the electrical grid as a series of cycles, with different amplitudes and durations, or as a hourly defined week. The model is completed with optional feedback controls which turn off the turbomachinery whereas any property exceeds its limits, for instance the cavern pressure range, which might be limited by structural reasons.

The physical model was validated against the Huntorf CAES plant experimental data available from literature [1]. A typical sequence of charge (60 MW), hold and discharge (290 MW) lasting 8 h, 5 h and 2 h, respectively, was considered. Figure 1 (from [2]) depicts the p-T diagram of the air within the cavern during the cycle, showing a good agreement between the experimental and numerical data. The mass flow rates during charge (108 kg/s) and discharge (416.7 kg/s) match those reported in [1], namely 108 kg/s and 417 kg/s.

The experimental data measured in the pilot plant built by ALACAES in Pollegio (TI) were exploited to evaluate the accuracy of the model. A TES based on a packed bed of natural rocks was placed within an existing tunnel, which was sealed by means of two concrete plugs for a length of 120 m. The reference test comprehends a 42 h precharge, followed by five charges and discharges up to 71 hours. The pilot plant test was affected by some air leakages, and this unwanted effect was also considered in the model. The agreement between simulation results and experiments was quite good. Figure 2 shows the air temperature at the top of the packed

**List of abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA-CAES</td>
<td>Advanced Adiabatic Compressed Air Energy Storage</td>
</tr>
<tr>
<td>CAES</td>
<td>Compressed Air Energy Storage</td>
</tr>
<tr>
<td>CFD</td>
<td>Computational Fluid Dynamics</td>
</tr>
<tr>
<td>EES</td>
<td>Electric Energy Storage</td>
</tr>
<tr>
<td>HTF</td>
<td>Heat Transfer Fluid</td>
</tr>
<tr>
<td>PHS</td>
<td>Pumped Hydro Storage</td>
</tr>
<tr>
<td>TES</td>
<td>Thermal Energy Storage</td>
</tr>
</tbody>
</table>

**Authors**

Jonathan Roncolato¹
Simone A. Zavattoni¹
Viola Becattini²
Giw Zanganeh³
Andreas Haselbacher²
Maurizio C. Barbato¹

¹ SUPSI
² ETHZ
³ ALACAES SA, Lugano
AA-CAES Plant Modelling and CFD Analysis of the TES System

Concerning the TES system modelling and simulation, the performed activities were focused on further analysis and characterization of the selected rock-bed TES solution suitable to be implemented into the aforementioned AA-CAES plant. For this part of the work, a 100 MWhn single-tank TES unit was selected as reference for the analysis. It was constituted by a 381 m$^3$ packed bed of natural rocks, 4 m high and 12 m and 10 m the upper and the lower diameters respectively, arranged into a well-insulated concrete tank.

A previously validated computational fluid dynamics (CFD) approach [3] was followed to evaluate the thermofluid dynamics behavior of this TES system subjected to a total of 5 precharging cycles, to reduce the initial transients of the system, followed by 60 consecutive cycles. The nominal charging and discharging temperatures were 570°C and 270°C respectively.

From a graphical standpoint, a comparison between the resulting temperature contours of the TES unit during the 1$^{st}$ cycle (l.h.s of the figures) and the 60$^{th}$ cycle (r.h.s. of the figures) is reported in figure 3. An important result of the simulation is that a relatively weak thermal stratification into the packed bed characterizes the behavior of the TES unit under investigation. In terms of heat transfer fluid (HTF) outflow temperature during discharging, a monotonic decrease was observed throughout the whole phase with a more pronounced reduction at the very beginning of the process indicating that the TES unit cannot provide a stable HTF outflow temperature. Conversely, an HTF outflow temperature increase during charging, up to 35°C at most above the nominal discharging temperature, was obtained. Furthermore, as reported in figure 4, the transient performance of the TES unit showed a similar evolution increasing monotonically up to a stable value of about 90% and 88% for the energy and exergy efficiency, respectively.

Once the performance of the reference TES unit was evaluated, a parametric analysis was also carried out with the aim of assessing the effect of some parameters, such as

- HTF mass flow rate during discharging and
- particle size distribution into the packed bed.

This parametric analysis allowed to observe that the variation of both aforementioned parameters had a minor influence on the TES cyclic performance.

**Figure 3:** Comparison between the TES unit temperature contours at the end of the 1$^{st}$ (l.h.s) and the 60$^{th}$ (r.h.s.) charge (a), discharge (b) and idle (c) processes. Temperature values [°C].

**Figure 4:** Transient performance of the reference TES unit under investigation: Energy (blue dots) and exergy (red squares) efficiencies.

**References**


Sensible Thermal Energy Storage Systems Optimized for AA-CAES Plant Operation

Scope of project

For any system with an integrated thermal energy storage (TES), it is often considered to be important to have high exergy efficiency and low costs. This translates to the objectives of minimizing the storage volume to save costs and maximizing the thermocline steepness while minimizing losses to the environment to maximize the exergy efficiency. However, when dealing with thermocline TES, the steepness of any temperature profile will decrease over the number of charging-discharging cycles, leading to decreases in the exergy efficiency and utilization factor [1]. One approach to overcoming these limitations, in particular to increase the cycle efficiency as well as to stabilize the outflow temperatures during charging and discharging, is to add latent TES sections at the top and/or at the bottom of the TES [2]. A different possibility was proposed by [3, 4], using multiple ports along the height of the TES tank to inject or extract parts of the thermocline to keep a steep temperature gradient along the tank height, thereby increasing the utilization factor.

Status of project and main scientific results of workgroups

All of the above methods have in common that the system was designed for constant charge and discharge conditions. In contrast to this stands the case of a TES system integrated into an AA-CAES plant for which the electricity market defines the operating conditions. To demonstrate this observation, the preliminary results from grid simulations including an AA-CAES plant were analysed with respect to the energy and power flows requested from the plant during one year of operation [5].

Figure 1 shows the incidence histograms for average requested power and corresponding phase duration, and Figure 2 shows the energy flow incidence histogram. The red dots in Figure 1 indicate the nominal operating point for which the efficiencies and designed layouts have been analysed so far. Although these plots only show preliminary results from the grid model, it is already clear that the approach of designing an AA-CAES plant and analysing its performance under nominal charge and discharge cycles oversimplifies the problem. The plotted data shows that more than 20% of the cycles lie in the 100 MWh energy range, for which a single TES would lead to very low utilization factors and unnecessary pressure losses.

This led to the idea of using multiple TES tanks in a system [6]. The benefit over single TES systems lies in the possibility of designing tank geometries for specific temperature levels, with different insulation...
Sensible Thermal Energy Storage Systems Optimized for AA-CAES Plant Operation

Figure 3: Thermoclines in quasi-steady state for the three systems (left) and true to scale drawings of the three TES systems (right). The dotted lines in the left plot indicate the boundaries of the different tanks. The charging order for the multi-tank systems is from left to right as indicated by the numbering.

References


Closed Sorption Seasonal Thermal Energy Storage with Aqueous Sodium Hydroxide

Scope of project

A closed sorption thermal energy storage (TES) prototype based on water absorption/desorption in a high-energy density sorbent like sodium hydroxide (NaOH) is developed at HSR-SPF (Figure 1). The two main processes (charging and discharging) occur under reduced pressure. During the charging process (Figure 1 a), the thermal energy produced by the solar collectors in summer is used to partially vaporize the water contained in a diluted sodium hydroxide solution. Then, the concentrated aqueous sodium hydroxide solution and the water are stored at room temperature in separate tanks until the discharging process. During discharging (Figure 1 b), ground heat is used as a heat source to evaporate the stored water under sub-atmospheric pressure in the evaporator. In a separate chamber, heat is produced during the exothermic process of water vapor absorption into the concentrated NaOH solution. The heat is then transferred to a working fluid that can be used, for example, in floor heating applications.

Status of project and main scientific results of workgroups

Investigations performed by HSR and Empa researchers in the EU funded project COMTES (Combined Development of Compact Thermal Energy Storage Technologies) have shown that during the absorption phase (storage discharging), a lower power compared to the theoretical value was obtained. Thus, a 1 kW prototype to optimize the reaction zone unit is developed. Different sorbent pairs with high energy density (NaOH-H₂O, LiBr-H₂O and LiCl-H₂O) are considered, and for each a numerical model is developed.

The 1 kW prototype unit is using the falling film principle and it is working under sub-atmospheric pressure, in a closed system to avoid losses and contamination of sorbent (e.g. NaOH)/sorbate (H₂O). Compared to the previous COMTES system, a decreased number of dry spots and thus a larger area for the heat and mass transfer is expected.

Sorbent surface wetting and residence time of the sorbent in the water vapour is influencing the efficiency of the heat and mass exchangers from the reaction zone. Porous silicon carbide foams (SiC), with porosity from 10 to 30 PPI (PPI = pores per inch), wrapped around tubes (Figure 2 – left) were investigated to increase the residence time. The experiments have shown that the tested ceramic foams have a highly hydrophilic behaviour with concentrated NaOH (50 %wt) and LiBr (54 %wt), thus an excellent surface wetting with the sorbent. Although the ceramic with small pores size (30 PPI) has theoretically a bigger surface area and a better residence time (expressed as a high mass uptake, Figure 2), due to clogging of the void spaces, the gas-liquid interface is reduced. This may reduce the mass exchange. However, a complete characterisation of the porous ceramic’s influence on the heat and mass transfer can be performed only after its implementation in the 1 kW prototype.

Authors
Mihaela Dudita¹
Xavier Daguenet-Frick¹
Lukas Omlin¹
Paul Gantenbein¹
¹ HSR (University of Applied Sciences Rapperswil)
A modular design was chosen for the absorber/desorber (A/D) unit from the 1 kW prototype. This will facilitate the replacement of the tube bundle and implementation of the improvements from the small-scale experiments. Thus, testing of several types of tubes and liquid sorbent modifications can be performed. The CAD design of the heat and mass transfer zone (the power unit), and the sorbent and sorbate tanks (the capacity unit) of the storage system was adapted after component selection due to the restrictions required by several sensors. Also, the parametric description of the power unit for scaling was made.

Important steps in the construction of the 1 kW prototype (Figure 3) were done in the reported period:

- production of heat and mass exchangers (HEX) for the A/D chamber with reference (plane) and textured tubes, and the evaporator/condenser (E/C) unit,
- pumps and sensors testing,
- calibration, e.g. mass flow and concentration sensors.
Sorption-Based Seasonal Heat Storage

Scope of project

In SCCER HaE, Empa and HSR work together to develop a long-term heat storage system based on sodium hydroxide (NaOH) and water (H₂O). Different strategies in heat and mass exchanger design are followed, with Empa working on a spiral-finned vertical tube design and HSR-SPF following the horizontal tube-bundle falling film approach.

Status of project and main scientific results of workgroups

**IEA SHC Task 58 participation**

Since January 2017 Empa is an official participant in IEA SHC Task 58 / ECES Annex 33 «Material and Component Development for Thermal Energy Storage» and leader of the Subtask «Component Design for Innovative TES Materials». Preceding IEA SHC tasks (32 and 42) showed a need for better and more consistent characterization of storage materials, as there is a severe mismatch in energy density between measured material samples and scaled-up systems. Further, a clear need for tailored development of components dedicated to the storage application was identified [1]. Contributions to this IEA task are funded through a pilot and demonstration project by the Swiss Federal Office of Energy (SFOE). This funding further supports the SCCER HaE activities with the goal of advancing liquid sorption storage towards higher technology readiness levels.

**Lab-scale bulk reactor (LSBR)**

In order to study the performance degradation from the material scale to the component scale a LSBR has been designed (Figure 1). The setup enables both atmospherically open and closed absorption processes to be studied, including aspects such as temperature based sorption kinetics, influence of contact resistance between a sorbent and a heat exchanger surface or effects of turbulence level in liquids on the absorption rate. For our own research the LSBR will mainly serve to study absorption rates and kinetics for different mixing scenarios (bulk vs. surface turbulence) and for the comparison of aqueous sodium hydroxide (NaOH) with other absorbents such as lithium bromide (LiBr).

The LSBR will be assembled and used for material testing in 2018.

**Lab-scale heat and mass exchanger (LSHMX)**

The design of a new spiral finned tube heat and mass exchanger (Figure 2) was tested and analyzed in 2016 and a proof of concept was reached with a concentration spread from 50%wt down to 30%wt [2]. Absorption and desorption tests were carried out for different parameter settings including variable absorbent mass flow, temperature difference between the absorber and evaporator and desorber and condenser respectively. As shown in Figure 3 an increase

List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSBR</td>
<td>Lab-Scale Bulk Reactor</td>
</tr>
<tr>
<td>LSHMX</td>
<td>Lab-Scale Heat and Mass Exchanger</td>
</tr>
</tbody>
</table>

References


Authors

Luca Baldini
Benjamin Fumey
Robert Weber

Empa
of absorbent mass flow moves the operation points away from the dashed equilibrium line highlighting absorption rate limitations. An increase in temperature difference brings it closer to the equilibrium due to higher absorption terminal concentration and hence larger time-frame per unit of absorbate transferred. Low terminal concentrations are sought in order to reach high energy density of the storage. Mass transfer rate limitations directly impose power density restrictions.

Ongoing research focuses on increased absorption rate while remaining close to the concentration vs. temperature equilibrium for maximum temperature output.

Following the initial results, performance with modified heat and mass exchangers for increased power density was tested in 2017. Cutouts were made in the spiral fins for increased mixing through droplet formation and impingement (Figure 4).

It was found that sorbent mixing from the cutouts substantially increased the water vapor absorption rate. As a consequence, a systematic analysis is needed to get a better understanding of the absorption and mass diffusion process in the liquid film and its kinetics. In collaboration with the Empa Laboratory of Advanced Analytical Technologies, Raman spectroscopy will be employed for the study. A preliminary design of a Raman-cell to allow for testing of liquid absorbents such as NaOH has been designed in 2017 and will be available for testing in 2018.

A design for a transparent HMX housing was also done in 2017. This will allow all round visual inspection of the flow and consequent studying of different flow regimes and wetting behavior on the fins of the heat exchanger.

**Cycling test with existing heat and mass exchanger setup**

A first cycling test of 7 cycles was performed with the existing LSHMX [3]. The average concentration of sodium hydroxide in the solution is 48 %wt after desorption and 27 %wt after absorption. A comparison of the thermal performance among different cycles in respect to the equilibrium condition as displayed in the temperature difference/mass fraction plane in Figure 5 shows no trend away or toward the equilibrium line among the different cycles.
Seasonal Sensible Thermal Energy Storage Systems

Scope of project

The challenge of reaching an increased market diffusion of seasonal thermal energy storage is not associated to a lack of knowledge of this technology, but rather to its high cost [1]. Particularly in the case of seasonal sensible thermal energy storage (SSTES), it becomes of paramount importance to minimize the annual heat losses while minimizing the cost of the storage system. These conflicting requirements lead to an optimization problem in which the costs of the insulation system and the storage need to be balanced against the penalty costs associated to the annual heat losses and the space occupied by the storage. The latter is particularly important when the storage is placed inside a residential building.

The focus of this project is the economic optimization of SSTES systems suitable for multifamily houses in Switzerland. The underlying objective of this SCCER Task is to achieve a specific investment cost of 60 CHF/m² for the thermal energy storage (TES) system. The optimization includes the design and control of a hot water storage and its peripheral components. The focus of the first stage of this task is the selection and evaluation of suitable thermal insulation methods and materials. The selection of the most promising thermal insulation methods will be used for detailed modeling and optimization of the TES system.

Status of project and main scientific results of workgroups

Three goals have been set for this task in the framework of SCCER HaE:

1. Development and construction of a seasonal water storage pilot plant with costs below 60 CHF/m².
2. Identification of a thermal insulation method that combines vapor barrier with high thermal resistance.
3. Increase of the storage density by combining sensible and latent storage modes.

This report summarizes the ongoing work aiming to achieve goal 1 through the economic optimization of hot-water TES systems. Alternatively, an ongoing Innosuisse project with Schenck AG aims at evaluating the techno-economic potential of a near-surface ground SSTES system. Goal 2 is also actively pursued in the framework of another Innosuisse project with swisspor AG. Modeling activities are planned to investigate the potential of combining sensible and latent heat storage toward achieving goal 3.

Current state-of-the-art SSTES systems incorporated in residential buildings require between 200 and 250 liters of hot water per m² of living space. Goal of this work is to achieve a significant reduction of this volume requirement. It is estimated that the storage volume might need to be reduced by as much as 50% in order to achieve the goal of 60 CHF/m² for the specific cost of the SSTES system.

Scenarios and boundary conditions

In the context of this report, the focus of our work is on SSTES systems for the supply of space heating and the production of domestic hot water in individual buildings.

The same concepts can nevertheless be applied also to larger SSTES systems for clusters of buildings or district heating. In larger systems, however, the energetic and economic relevance of the thermal insulation is usually not as important as in smaller storage systems. This follows from the smaller surface-to-volume ratio of larger systems and consequently the fundamentally different thermal behavior and economic characteristics of the larger system.

The scenarios considered in this work are shown in Table 1 and illustrated schematically in Figure 1. Here, the SSTES system consists of a water reservoir with a maximum tempera-

Table 1: Scenarios considered for the incorporation of SSTES systems in residential buildings.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Storage type</th>
<th>Storage location</th>
<th>Insulation arrangement</th>
<th>Suitable buildings</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Integrated tank</td>
<td>Aboveground or partially buried</td>
<td>Double-wall vacuum</td>
<td>New buildings</td>
</tr>
<tr>
<td>B</td>
<td>Room retrofitted</td>
<td>Underground</td>
<td>Inside wall</td>
<td>Existing buildings with an unused underground room</td>
</tr>
<tr>
<td>C</td>
<td>Buried tank</td>
<td>Underground</td>
<td>Outside wall</td>
<td>New or existing buildings with available/accessible space in the building vicinity</td>
</tr>
<tr>
<td>D</td>
<td>Water pit</td>
<td>Underground</td>
<td>Inside wall</td>
<td></td>
</tr>
</tbody>
</table>
ture in the range of 60–90°C. The main advantages of limiting the storage temperature to this level are that:

- the SSTES system can be realized with a non-pressurized water tank made of low-cost materials such as fiberglass or reinforced plastics, and
- the use of a non-pressurized water tank can allow the incorporation of thermal insulation materials on the inside wall of the tank.

In this context, we propose the retrofit of an unused underground room enclosure as a cost-effective method to integrate a SSTES system in an existing building. The retrofit consists of applying appropriate vapor barrier and thermal insulation materials to the walls, floor, and ceiling of the room to allow the entire space to be transformed in a hot water reservoir.

The main advantage of this concept is that the construction costs of the storage are significantly reduced by virtue of the existing structure, which can directly be used as water enclosure.

The challenges of incorporating the insulation material on the inside of the storage are similar to those faced in the construction of hot water pit storages. The first challenge is the development of an effective, robust, and cost-effective vapor barrier capable of protecting the thermal insulation against moisture. The second challenge is to predict and limit the long-term creep deformation that results from the simultaneous effect of temperature and hydrostatic pressure.

**Thermal insulation methods and materials**

Ongoing work aims at compiling the thermophysical properties (thermal conductivity, density, compressive creep strength, etc.) and cost of promising thermal insulation methods and materials. These include:

- Traditional thermal insulation materials: glass wool, EPS, XPS, and PUR/PIR, etc. These are widely available and well-proven materials. Their thermal conductivity range between 0.02 and 0.06 W m⁻¹ K⁻¹.
- Novel thermal insulation materials (VIP and aerogels):
  - VIP: commercially available, thermal conductivity as low as 0.5 W m⁻¹ K⁻¹, but cost is still relatively high. Thermal conductivity is known to increase due to continuous loss of vacuum.
  - Commercially available silica aerogels have thermal conductivities as low as 4 mW m⁻¹ K⁻¹, but their production costs are still very high. Aerogels have a relatively high compression strength, but are very fragile.
- Double-wall vacuum insulation: ZAE Bayern has developed a double-wall storage tank loaded with water at 87°C. In this layout, a 20 cm air gap between two cylindrical steel tanks is filled with perlite under a pressure of 0.08 mbar [2]. The authors calculated an effective thermal conductivity of 9.2 mW m⁻¹ K⁻¹ and estimated that it could be reduced to 7.3 mW m⁻¹ K⁻¹ through optimization.

In addition, the combination of thermal insulation material plus vapor barrier as a composite layer will be investigated as an alternative to allow the incorporation of the thermal insulation on the inside wall of the thermal storage. The final selection of the most promising thermal insulation methods and materials will be made based on a compromise between cost and thermal performance.

**Figure 1:** Scenarios considered for the incorporation of SSTES systems in buildings. The letters in brackets denote the scenarios listed in Table 1. Scenario (A) is distinguished between a tank above ground (A-1) and a tank partially buried (A-2).

**Acknowledgement**

The authors gratefully acknowledge Innosuisse (Swiss Innovation Agency) and the Swiss Federal Office of Energy for financial contributions to this work. We also extend our acknowledgement to our industrial partners for their technical support and collaboration.
High Power Latent Heat Storage

Scope of project

Latent heat storage with phase change materials is a promising technique to store thermal energy. The high latent heat of these materials and their near-steady charging/discharging temperature offer a unique energy density compared to conventional sensible-only heat storage and allow for more compact and efficient systems. However, the low heat transfer rate inherent to such units, presents a significant barrier for their widespread application in processes which require fast-response, high-thermal-power outputs and steady operational conditions. The aim of task 1.3 (low temperature high power heat storage) is to investigate and test novel latent heat storage technologies that enable high power outputs at temperatures up to 120°C. This paper presents the activities of the Thermal Energy Storage (TES) group on the topic of the development and modelling of novel high-power latent heat storage technologies in the year 2017.

Status of project and main scientific results of workgroups

Material research

An interesting example of Phase Change Material (PCM) research at HSLU is presented in [1]. In this study unbranched, saturated, carboxylic esters were evaluated as promising PCM, as they can be bio-based and in many cases have good thermo-physical properties. In the study, a selection of eleven unbranched, saturated, carboxylic esters was examined. Melting points in the range of -75°C up to 55°C were determined as well as enthalpies of fusion in the range of 99 and 219 J/g. Thermal conductivities determined at room temperatures varied between 0.142 and 0.181 W/m·K. Further investigations will be conducted in the years 2018–2021 within the framework of a SNF Ambizione Energy Grant.

Optimization of finned-tube heat exchangers

The design of cost-effective heat exchangers which provide a high thermal output with a minimal material utilization is a topic of high interest in the field of latent storage. Mathematical models which are able to accurately predict the overall heat flow from the PCM to the Heat Transfer Fluid (HTF) during solidification can provide an effective method to optimize the geometry of the heat exchanger in terms of heat transfer rate and production cost. The TES group has developed a model able to act as an optimization tool for finned-tube heat exchangers in cooperation with the company Sunamp [2]. In order to achieve low computational effort, the symmetric nature of the heat exchanger was exploited. Hence, the heat flow rate from the phase change material to the HTF was calculated only for a small segment of the HEX geometry. The enthalpy method was used to describe the phase change during discharging of the storage. The method was implemented in the commercial Computational Fluid Dynamics (CFD) software Ansys Fluent. A Matlab algorithm was used to expand the model results from the small segment to the entire storage. The model was also able to describe the effect of supercooling on the heat transfer performance of the storage.

Validation experiments were performed in a commercial latent heat storage from Sunamp (T_{in} = 58°C) with a capacity of approximately 2.5 kWh. The discharging process was experimentally investigated for HTF inlet temperatures varying from 15 to 50°C. Results from the experiments are presented in Figure 1 in terms of...
High Power Latent Heat Storage

HTF outlet temperatures and are compared with the results of the model including or neglecting kinetic (supercooling) effects. The ability of the heat exchanger to keep a stable outlet temperature for a big part of the discharging process is demonstrated for both THTF,in. For THTF,in = 15 °C the discharging time is only 15 min, revealing the high thermal power capability of the specific latent heat storage.

Both models show a very good agreement with the experimental results. For THTF,in = 50 °C where the effect of supercooling is more dominant, the model accounting for the nucleation kinetics is more precise.

Phase Change Material Slurries

The TES group investigates the concept of Phase Change Slurries (PCS) for heating and cooling applications. PCS systems promise higher energy densities both as heat transfer fluids and as storage media in comparison to sensible systems. At the same time they remain pumpable and therefore can achieve better heat transfer characteristics than conventional latent heat storage technologies. In the TES group, two PCS technologies are investigated:

- phase change dispersions for cooling applications and
- homogeneous slurries for heating applications.

Homogeneous PCS were investigated for their ability to act as heat transfer fluids and storage media in industrial applications in the range of 50–90 °C with the support of SFOE. A combination of aluminium ammonium sulfate dodecahydrate (AAH) (NH₄Al(SO₄)₂·12H₂O) and water was chosen as the most promising PCM. Key criteria for this choice were its high phase change enthalpy and the adaptability of its liquidus temperature via the addition of water to cover the whole temperature range of interest. Experimental campaigns were conducted using AAH with a concentration of 35%wt of AAH in water (liquidus point of 52 °C) and 45%wt AAH (liquidus temperature of 63 °C).

A functional, modular, proof of concept test-rig based on standard industrial components and a modular stainless steel piping system was developed and successfully commissioned (see Figure 2). The feasibility of very fast crystallization and melting of the PCS could be demonstrated in the test-rig [3]. The ability of both PCS technologies to absorb/release a significant amount of heat within a narrow temperature range has been demonstrated.

Direct contact latent heat storage

Direct contact latent heat storage has also been reported as a promising technology for the achievement of high power to capacity ratios [4]. The TES group has initiated a combination of experimental and theoretical analyses to evaluate the potential of direct contact TES in terms of its high-power performance. A preliminary setup has been built and tested with mixtures of Tetra-n-butyl-ammonium bromide (TBAB) and water as PCM and thermal oil as HTF (see Figure 3). At the same time CFD simulations have been performed in Ansys Fluent to evaluate the heat transfer coefficients between an ascending oil droplet and the PCM as they present one of the major uncertainties when designing a direct contact storage system. The first results were in accordance with experimental observations. The calculated temperature profile of an ascending oil droplet and the surrounding PCM can be seen in Figure 3.

In the next steps the simulations will be extended to include the flow of multiple droplets out of nozzles and the presence of solid PCM in the computational domain. The simulations will be used to determine the effect of the nozzle plate geometry and material properties on the heat transfer rate and the ascending velocity of the HTF. The results will serve as input for the design of an optimized experimental setup.

References

Work Package «Batteries and Battery Materials» at a Glance

One of the options for decentralized storage of electrical energy is the use of batteries. This direction was investigated within WP 2 of this SCCER. After the rather exploratory phase I, the main efforts in phase II are now focused on the advancement of two selected prospective battery systems, the high-end lithium-ion battery and the potentially cost-effective sodium-ion battery.

These two main directions were pursued with focus on material-related activities, and all partners were involved in the different topics. The core group here comprised the teams of Maksym V. Kovalenko from ETH Zürich and Empa, Katharina M. Fromm from University of Fribourg, Claire Villevieille from PSI, and Corsin Battaglia from Empa. The production processes for the new materials as well as the electrodes thereof needed to be understood as well. These activities were pursued under the lead of Axel Fuerst from Bern University of Applied Sciences (BFH) Biel. Needless to stress that all groups provided their core expertise wherever needed and demonstrated close collaboration. The guiding principles were

- to show solutions for future cost-effective energy storage, especially for the grid and mobility;
- to maintain and further develop the know-how in the field of batteries and battery materials, to support both Swiss industry and Swiss authorities to master the energy transition;
- to educate students and experts in the field of energy storage in batteries;
- to select, develop, and demonstrate materials and systems for future batteries, in favor of the Swiss industry, and
- to keep jobs in Switzerland.

Battery materials

The research activities were guided by the perspective of both electromobility and stationary storage. In the field of Li-ion batteries the focus was on high energy systems and we have pushed to increase the mass loading of both electrodes. The ETHZ/Empa group (Kovalenko) has been focusing on practical goals relevant to and supported by the Swiss industry (Belenos Clean Power Holding) aiming to develop high areal capacity anodes for Li-ion and Na-ion batteries for large-scale stationary energy storage, this research group targeted to develop a cathode for both Li- and Na-ion batteries comprising highly earth-abundant chemical elements. In this context, the NaFeF₃ fluoroperovskite cathode has been studied because of a virtually unlimited natural supply of the constituting elements, an intrinsically high oxidative stability, and a high theoretical specific charge of 197 mAh/g.

At Empa (Battaglia), an automated co-precipitation process for the shape-controlled synthesis of hydroxide precursors for cathode powders was developed and validated through the synthesis of standard NMC111 powders consisting of 3–5 μm quasi-spherical secondary particles composed of 300–500 nm primary particles. Experiments for synthesizing NMC811 and high-voltage spinels with reduced or zero cobalt content are ongoing. The co-precipitation process was also successfully transferred to and validated for the synthesis of sodium layered oxides. A NMC111 slurry preparation and coating process was developed with the aim of achieving electrode coatings with high mass loading (up to 29 mg/cm²) and high active material content (96%) while maintaining good rate capability resulting in demonstration of 3.8 mAh/cm² at 1C-rate. Validation via NMC111/graphite full cell tests was conducted at slightly lower mass loadings investigating the impact of standard electrolyte additives such as vinylene carbonate on anode passivation and cycling stability, including also the fabrication of first small prototype pouch cells. Also, a spreadsheet was developed listing all relevant parameters with the aim of defining the prototype cell design delivering in a preparatory step 220 Wh/kg (state-of-the-art reference case) and subsequently targeting >300 Wh/kg on cell level.

At the University of Fribourg research on a more fundamental level was performed. Carbon-encapsulated Sn nano-containers (Sn@C nanorattles) were synthesized with the goal to mitigate pulverization of Sn alloys and to avoid cracks in the electrode. The achieved specific charge was 600 mAh/g at C/10 rate. Also, nano-LiMnPO₄, was investigated as an alternative high-voltage cathode material, and 140 mAh/g was achieved at C/20 rate. The volumetric capacities were improved to 260 and 180 mAh/cm³ at C/20
The research activities focusing solely on Na-ion batteries targeted grid storage applications, with the goal to lower todays cost by ca. 20%. Because of the greater size/mass of Na relative to Li and the more positive standard electrode potential of Na, Na-ion batteries were hardly considered as a possible solution for mass storage applications. However, these facts are not especially relevant if Na is considered in its ionic and not in its metallic form. In commercial full cells where both anode and cathode are based on Na host materials, the energy density gap between Na and Li systems is considerably reduced to only 30% instead of a factor of 3 (if judged on metal mass). For instance, NaCoO₂ has a theoretical specific charge of 235 mAh/g with a cell voltage of around 3.5 V, whereas the theoretical specific charge of LiCoO₂ is 274 mAh/g with a cell voltage of 4 V. Additionally, Na is one of the most abundant and low-cost elements on earth and Al, which does not alloy with Na, can be used as an inexpensive current collector in Na systems, leading to cost and mass reductions for the entire battery.

Current research at PSI demonstrated that it is possible to develop low cost carbonaceous, biowaste based materials with reversible specific charge > 270 mAh/g. On the cathode side, we targeted also low-coast elements to ensure that the Na-ion batteries are developed at lower costs than the Li-ion counterpart. A new Co-free cathode P2-Na₀.₆₇Mn₀.₆Fe₀.₂₅Al₀.₁₅O₂ was successfully synthesized and characterized. The rate capability tests showed higher specific charge and a better cycling stability than the analogous P2-Na₀.₆₇Mn₀.₆Fe₀.₂₅Co₀.₁₅O₂ cathode demonstrating that tuning the cathode chemistry is important not only to improve the electrochemical performance but also the cost. Finally, high reactivity of Na metal with the electrolyte and its fast degradation raised a doubt about reliability of Na metal as a reference electrode. By using electrochemical impedance spectroscopy on symmetric Na/Na cells we demonstrated how the different parameters influence the ageing of the Na metal and emphasized the importance of the Na foil preparation for electrochemical measurements. Non-uniform thickness and/or presence of the native oxide layer on the surface of Na metal leads to a substantial increase of interfacial resistance of this alkali metal by a factor of 10. In addition, the presence of water and/or air in the cell increases it by a factor of 100, thereby questioning the reliability of all published measurements performed on Na-ion half-cells. We developed a simple methodology to minimize the influence of these parameters on the performance of the Na metal.

**Battery production**

The battery cell production group is working on the implementation of battery materials in battery cells of technical size (up to A4). This work has two parts, the development of know-how on building cells for the selected chemistries, and the main research objective is to optimize the production by applying future technologies coming from the «Industry 4.0» approach. The closer contact to the battery chemistry experts helps for a faster and deeper understanding of the chemical requirements. Together with Empa a contact to an industry partner was established and a large battery pack was reengineered. In fact, for each production step one potential industrial partner was identified. Also, a joint project with SCCER Mobility is running on further optimizations.

For the process simulation the first virtual image of the real production line at the industrial partner’s premises could be built covering the span from slurry preparation to building the pouch cells. This model includes the material flow of the full production line. The pilot line at BFH is getting increasingly important to understand the process simulation and as a base for discussions with industry. Tests for the laser cutting of electrodes are ongoing with an industry partner. Further, in 2017 the Z-folding unit was built and put into operation and a design improvement is in implementation for the laser cutting and handling units, to work faster and to stack anodes and cathodes with higher precision in parallel lines still using one low cost laser.
Development of Anode and Cathode Materials for Li- and Na-Ion Batteries

Scope of project

Lithium-ion batteries (LIBs) have become the battery technology of choice for applications demanding high energy and power densities, such as portable electronics and electric vehicles, and also show great promise for the large-scale grid storage of electricity. Conceptually identical sodium(Na)-ion batteries (SIBs) have recently also received a revived interest as a viable alternative due to much greater natural abundance and more even distribution of Na reserves as compared to Li. Further energy density improvements and decreasing capital costs for both LIBs and SIBs will require the development of anode and cathode materials with higher areal capacities (≥ 3.5 mAh cm⁻²) and long cycling life.

Status of project and main scientific results of workgroups

Graphite/silicon-carbon anode materials with high areal capacities for lithium-ion batteries

Commercial graphite anodes for rechargeable Li-ion batteries offer a maximum capacity per unit area between 3 and 3.5 mAh cm⁻² which correspond to 8.5–10 mg of graphite per cm² and its capacity of 350 mAh g⁻¹.

The higher graphite loadings drastically decrease the capacity of graphite and bending properties of graphite based electrodes (ability to be rolled for industrial battery production). Therefore, the integration of active materials with higher specific capacity or increase of thickness and loads of the anodes without compromising the mechanical stability is required to further boost areal capacity of lithium anodes.

Herein, we develop graphite-based anodes comprising silicon-carbon composite as a high-capacity additive material. Silicon was homogeneously covered with carbon (inactive buffer layer) forming silicon-carbon composite, with the purpose to decrease the negative impact of large volume expansion of silicon during its intercalation with Li on its electrochemical properties. The synthesis of carbon-coated Si particles was conducted using a proprietary method. We demonstrate that graphite/silicon-carbon anodes exhibit high areal capacity of above 4 mAh cm⁻², low average charge voltage of 0.25 V vs. Li⁺/Li at C/2 rate with 89.4% of the initial coulombic efficiency.
Development of Anode and Cathode Materials for Li- and Na-Ion Batteries

**NaFeF$_3$ as low-cost sodium and lithium cathode material for stationary energy storage**

For ensuring the economic feasibility of applying Na and Li ion batteries for large-scale stationary energy storage, new cost-effective cathode materials composed of highly earth-abundant chemical elements are desired.

The NaFeF$_3$ fluoroperovskite cathode, inter alia, is appealing because of a virtually unlimited natural supply of the constituting elements, an intrinsically high oxidative stability and a high theoretical capacity of 197 mAh g$^{-1}$. Due to the low electronic conductivity of this compound in its bulk form, this work is aimed at an inexpensive synthesis method for NaFeF$_3$ in a nanocrystalline state. Herein, we present a new and simple synthetic route for creating crystalline NaFeF$_3$ nanoplates (NPLs) by thermal decomposition of heterometallic fluorinated β-diketonate NaFe(hfac)$_3$ in benzyl ether or 1-octadecene [1].

Cathodes comprising NaFeF$_3$ NPLs exhibit a high cyclic stability for both sodium and lithium ion storage, delivering high initial electrode capacities of 153 mAh g$^{-1}$ and 183 mAh g$^{-1}$, respectively. Half of these capacities were retained after prolonged operation over 200 cycles at a current density of 0.2 A g$^{-1}$ (~1 C).

**Figure 2:**

(a) Schematic of the one-pot synthesis of NaFeF$_3$ NPLs; (b, c) electrochemical performance of NaFeF$_3$ NPLs cycled with sodium and lithium electrolytes in a half-cell configuration using metallic sodium and lithium as the counter and reference electrodes, respectively; (b) galvanostatic charge-discharge curves during the 20th cycle at a current density of 0.2 A g$^{-1}$; (c) cyclic stability measured at a current density of 0.2 A g$^{-1}$ using 1.5–2 V and 2–4.2 V voltage intervals for Na and Li ion cells, respectively.

**References**

Development of Efficient and Inexpensive Batteries for Large-Scale Stationary Storage of Electricity

Scope of project

The future success of renewable but intermittent energy sources such as solar and wind will largely depend on the availability of low-cost, TWh-level stationary storage systems. Furthermore, there is a pressing need to locally and globally stabilize and diversify the electric grid. Efficient and inexpensive stationary installed batteries are expected to play the major role in this regard, in addition to conventional storage means such as pumped hydro.

Status of project and main scientific results of workgroups

The basic architecture of this battery consists of a metallic aluminum anode, AlCl$_3$-based ionic liquid and a graphite cathode (see Figure 1a). As depicted in Figure 1a, the following half-reactions occur during charging at the cathode (1) and anode (2):

$$xC + AlCl_4^- → C_x[AlCl_4]^- + e^- \quad (1)$$

$$4AlCl_4^- + 3e^- → Al + 7AlCl_4^- \quad (2)$$

Reaction (1) simply represents intercalation of AlCl$_4^-$ species into graphite while its oxidation. Reaction (2) shows plating of aluminium on the aluminium side. In the search for an ultimate cost-effectiveness, the group of Prof. Maksym Kovalenko has developed an efficient and low cost aluminium-graphite battery consisting of natural or synthetic graphite flakes of ca. 50 µm in lateral size. These flakes can be easily manufactured from kish graphite (available at the multi-ton scale as a byproduct of steel-manufacturing) or typical natural graphite flakes using sonication or ball-milling processing [1, 2]. Herein, we demonstrate that the developed graphite flakes can be used as a cathode in AlCl$_3$-GBs and exhibit high capacities of up to 142 mAh g$^{-1}$ (as compared to 60–100 mAh g$^{-1}$ in previous reports). On the contrary, round-ed («potato-shaped») graphite particles used in Li ion batteries exhibit twice lower capacities for AlCl$_4^-$ ions.

In addition, we have developed oxidatively stable, inexpensive current collectors that can operate in chloroaluminate ionic liquids and are composed of earth-abundant elements; importantly, they are also highly suited for high-voltage Li- and Na-ion batteries. In particular, titanium nitride (TiN), a conductive and stable material composed of abundant elements, is highly suited for use as an AlCl$_3$-GB current collector due to its high oxidative stability in the ionic liquid AlCl$_3$-[EMIM]Cl at potentials of up to at least 2.5 V vs. Al$^{3+}$/Al [3]. TiN films can be deposited on stainless steel and flexible polyimide substrates for use in coin and pouch cell batteries, respectively (Figure 1b, c). The superior stability of TiN toward electrochemical oxidation enables a higher coulombic efficiency of ~99.5% to be achieved at currents of 1–10 Ag$^{-1}$. The AlCl$_3$-GBs with TiN current collectors also exhibit a high power density of 4500 Wkg$^{-1}$ at a high graphite loading (10 mgcm$^{-2}$) and are stable for at least 500 cycles (Figure 1d, e). Tests are underway to demonstrate high-voltage Li-batteries with TiN current collectors.

References


Figure 1: Aluminum chloride-graphite battery with a TiN current collector.

a) Schematic of the charging process.
b, c) Photographs of the TiN-coated (500 nm film thickness) polyimide (b) and stainless-steel (c) substrates.

electrochemical performance of kish graphite flakes in a coin cell with a TiN current collector:
d) Galvanostatic charge-discharge voltage curves measured at various current densities (0.03–10 Ag$^{-1}$) in AlCl$_3$-[EMIM]Cl ionic liquid.
e) Cyclability of kish graphite flakes measured at current density of 10 Ag$^{-1}$.

Efficient aluminium chloride-graphite battery

In particular, recently, much attention has been paid to the development of aluminium chloride-graphite batteries (AlCl$_3$-GB) due to high natural abundances of their primary constituents, facile manufacturing and high energy densities.

The quest for low-cost and large-scale stationary storage of electricity has led to a surge of reports on novel batteries exclusively comprising highly abundant chemical elements.

In this context, various chemistries are being explored based on non-toxic and earth-abundant elements such as Na, K, Ca, Mg, and Al.

Author

Maksym V. Kovalenko$^{1,2}$

$^1$ ETHZ $^2$ Empa
Batteries

Nanostructured Anode Materials for High-Energy Alkali Metal Ion Batteries

Scope of project

Alloy based anodes are eligible candidates in terms of high energy density and safety. However, the main hurdle faced in commercializing these alloy anodes is the huge non-uniform volume variation (up to 300%) during lithium insertion and extraction [1]. This phenomenon leads to the rupture of the active alloy particles, resulting in poor cycling and capacity fade. Among other alloy based anode materials, Sn and SnO₂ place in remarkable top positions due to their high specific gravimetric capacity (600 to 993 mAh/kg) and specific volumetric capacity (840 to 2200 mAh/cm³) with an average potential of 0.6 and 0.43 V vs. Li/Li⁺, respectively [2, 3]. In addition, they are non-toxic and not very expensive in terms of commercialization.

Status of project and main scientific results of workgroups

Most recently, a nanocomposite approach with an «active element/inactive matrix» setup with carbon being the inactive matrix is reported [4]. The carbon-based matrix serves as cushion to survive the volume change and prevents the consequential pulverization. Herein, we report the formation of a nano-rattle composite setup of Sn@C and SnO₂@C achieved by melt diffusion method as shown in Figure 1 to accommodate the volume change.

A soft template method is applied via reverse micelle microemulsion and subsequently, thermal treatment is followed for the formation of carbon on the template. After chemical etching of the template, hollow carbon spheres are obtained as shown in Figure 2 a. Sn and SnO₂ nanoparticles were impregnated into the carbon hollow spheres to form the desired Sn@C and SnO₂@C nano-rattle composites in a controlled atmosphere. Here we show an example of Sn@C. Figure 2 b shows a SEM image of Sn@C composite which shows bright smaller particles inside the large particles. Energy dispersive X-ray analysis of this image proved that the smaller particles we obtained are tin based material and the other large particles are carbon (Figure 2 c).

The electrode properties of carbon-encapsulated Sn nano-containers were investigated. Figure 3 a shows the specific capacities of 600, 300 and 150 mAh/g at C/10, C/5 and 1C, respectively. The cyclic voltammogram of this electrode showed a reversible redox electrochemical reaction shown in Figure 3 b.

References


Authors

Sivarajakumar Maharajan¹ Nam Hee Kwon¹ Katharina M. Fromm¹

¹ University of Fribourg
Nanostructured Cathode Materials for High-Power Lithium Ion Batteries

Scope of project

Commercial LiFePO₄ has a relatively low cell-voltage of 3.6 V vs Li⁺/Li, resulting in low energy density of lithium ion batteries [1]. On the other hand, LiMnPO₄ (which has the same structure as LiFePO₄ replacing Fe with Mn) provides a higher cell voltage of 4.1 V vs. Li⁺/Li, resulting in 20% higher energy density than that of LiFePO₄[2]. In addition, olivine structured LiMnPO₄ material is reported to have high thermal stability compared to layered transition metal oxide materials [3]. Therefore, LiMnPO₄ can be an alternative high-energy cathode material for lithium ion batteries. To apply LiMnPO₄ as a cathode, it needs to improve the kinetics with lithium ion and electronic conductivity.

Status of project and main scientific results of workgroups

During the project, we discovered two points:

• Controlling the shape and the size of LiMnPO₄ is extremely critical for obtaining fast kinetics with lithium ions.

• Carbon coating on the surface of LiMnPO₄ particles is essential before making electrodes to obtain high-rate capacities [4].

It is also reported that carbon coating on LiMnPO₄ prevents Mn dissolution [5]. Our study showed the specific capacities of nanorod shaped LiMnPO₄ particles provide 140, 120 and 100–90 mAh/g at C/20, C/10 and 1C, respectively [6]. We also improved the volumetric capacities to 260 and 180 mAh/cm³ at C/20 and 1C, respectively, by creating dense and homogeneous composite structures of nano-LiMnPO₄/C shown in Figure 1 left. These values are ca. 4 times higher than for nano-LiMnPO₄ cathodes prepared by a conventional method. The rate capabilities were compared with other published literature concerning LiMnPO₄. At high C-rates, (>1C), we have >2 times higher capacity than the highest reported LiMnPO₄ electrode (Figure 2 right).

Another low-cost cathode material of nano-LiCoO₂ is developed in our group. Commercial LiCoO₂ is prepared by mixing two precursors and subsequently heating two times at 600 and 850°C for >12 hours in order to obtain a highly ordered structure of LiCoO₂[7, 8]. This commercial synthetic method requires long time and electrical energy. In...
our group, we synthesized a single precursor containing both lithium and transition metal. This single precursor reduced a calcination temperature of 400°C and formed a highly ordered layered structure of LiCoO₂ [9]. Finally, we obtained dark brown nano-LiCoO₂ with rhombohedral shape of particles.

The electrode of nano-LiCoO₂ improved the relative amount of accessible/useable Li⁺ to more than 70% of the theoretical capacity (Figure 2). For comparison, commercial micron-sized LiCoO₂ exhibits about 50% of Li⁺ available. In our study, the Li⁺ diffusion coefficient of nano-LiCoO₂ is >10–100 times higher than that of micron-LiCoO₂ due to the shortened diffusion path length in the lattice structure of nano-LiCoO₂ (Table 1).

When we compare the thermal stability of electrochemically delithiated cathode materials using EC: DMC or EC: DEC with 1–1.2 M LiPF₆ [10–17]
1. LiNiO₂ < LiMn₂O₄
2. Liₓ(Ni₁₋ₓMnₓ)O₂ < LiₓCoO₂
3. MgPO₄ < Mn₂O₄ < Co₃O₄ < FePO₄.

<table>
<thead>
<tr>
<th>LiCoO₂</th>
<th>Size</th>
<th>D_Li [cm² s⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial</td>
<td>11 μm</td>
<td>2 × 10⁻⁷</td>
</tr>
<tr>
<td>Nano-LiCoO₂</td>
<td>45 nm</td>
<td>2.6 × 10⁻⁵</td>
</tr>
<tr>
<td>Nano-LiCoO₂</td>
<td>20 nm</td>
<td>4.5 × 10⁻⁶</td>
</tr>
</tbody>
</table>

Table 1. The comparison of Li⁺ diffusion coefficients (D_Li) of commercial micron and nano-sized LiCoO₂ materials.

Table 2: Comparison of nano-LMP, nano-LCO and other cathodes.

Batteries

References

Investigations for a Full Cell NMC Benchmark

Scope of project

Lithium-ion batteries enabled the success of portable electronics and are recognized as a promising technology for electric mobility and stationary energy storage. Developing high energy density cathodes is crucial for both applications. In particular, higher energy density on materials and electrode level contributes to reduce the levelized cost of electricity stored, a key metric for the large-scale adoption of batteries for stationary electricity storage. As a preparation to go beyond state-of-the-art, the focus during the first year of SCCER HaE phase II was on building competences on materials and electrode level enabling a SCCER cell with state-of-the-art performance. In particular, LiNi,Mn,Co1-x-yO2 (NMC) materials have proven to be attractive cathodes exhibiting relatively high capacity and good cycling performance and are currently produced industrially at large scale.[1]

We established an automated co-precipitation setup for the shape-controlled synthesis of NMC-type cathode materials on a multi-gram scale. Moreover, we focused on the development of slurry and electrode processing enabling high mass loading and high active material content. Finally, the cycling performance of NMC materials in NMC/graphite full cells with and without vinylene carbonate (VC) as electrolyte additive has been investigated.

Status of project and main scientific results of workgroups

Layered NMC-type cathode materials were synthesized by a co-precipitation process of Ni,Mn,Co1-x-y(OH)2 hydroxide precursors involving transition metal sulfate precursors, NaOH, and NH4OH solutions followed by a high temperature solid-state sintering process at 800–1000°C to form the layered oxides LiNi,Mn,Co1-x-yO2.[2]. Alternatively, hydroxide precursors were also synthesized by irradiating the same reaction mixture with microwaves to accelerate the reaction and reduce the energy input during synthesis. As a test bed, NMC111 materials were synthesized and compared to commercial reference powders. Experiments on Ni-rich NMC with lower Co-content, such as NMC811, as well as application of the co-precipitation method to sodium layered oxides for sodium-ion batteries will be presented in the next report.

Powder X-ray diffraction (XRD) analysis confirms the phase purity of the NMC111 materials synthesized by the co-precipitation and microwave method, showing a layered structure belonging to the R-3mH space group (Figure 1a). Moreover, scanning electron microscopy (SEM) reveals that the NMC111 powders synthesized by co-precipitation consist of ~3–5 µm quasi-spherical secondary particles composed of 300–500 nm primary particles (Figure 1b). Microwave-synthesized NMC111 powders exhibit the same layered structure, but the formation of secondary spherical particles did not take place (Figure 1c). Instead, non-uniform aggregates of smaller primary particles of around 150–200 nm

References


Authors

Josefa Vidal Laveda¹
Evelyn Stilp¹
Jia En Low¹
Stefan Dilger¹
Corsin Battaglia¹

¹ Empa
are observed. Cycling tests of the NMC111 materials synthesized by co-precipitation demonstrate a rate performance comparable to commercial reference powder (Figure 2a), but slightly lower capacity retention (80% vs 94% capacity retention after 100 cycles at C/3) (Figure 2b), possibly due to the lower sphericity and consequently higher surface area of the particles synthesized in-house. Microwave-processed NMC111 displays a weaker rate capability already at lower mass loading (Figure 2a) and relatively poor long-term performance due to its high surface area (not shown).

A well-ordered layer structure results in favorable lithium ion diffusivity in the two-dimensional space during the lithium (de)intercalation process, leading to a good cycling performance. However, due to the similar ionic radius of Li+ and Ni2+, layered NMC cathode materials often possess a certain degree of cation disorder (Li/Ni exchange) during the synthetic process. The introduction of Ni2+ into the Li+ layers can disrupt the Li+ migration path and impede the diffusion of Li+ in the Li slab space. On the other hand, the strong Ni-O bond in Li layers may weaken the electrostatic repulsion between the MO2 sheets, and thus limit the opening of the Li slab space during cycling. Consequently, the existence of Li/Ni disorder can directly restrict the Li+ mobility and electrochemical performance on NMC-type cathodes. [3]

To better understand and overcome the Li/Ni disorder in NMC materials, a detailed structural analysis of these compounds is required in order to further improve the synthetic process. In particular, neutron diffraction is a very valuable characterization technique for the study of the Li/Ni exchange in these materials because, unlike X-ray diffraction, it can easily detect light atoms such as Li. Also, neighboring elements in the periodic table generally have different scattering cross sections and can be distinguished more readily than in X-ray diffraction. Powder neutron diffraction measurements on commercial NMC powders and NMC synthesized by co-precipitation have been conducted in collaboration with Heinz Maier-Leibnitz Zentrum in Munich, revealing that our NMC materials synthesized by co-precipitation display a slightly higher degree of Li/Ni disorder compared to commercial reference powders (3.1% vs 2.1% Li/Ni exchange), which could contribute, besides the increased surface area, to the lower capacity retention of our co-precipitated NMC in the long-term cycling tests (Figure 3).

Furthermore, we developed a NMC slurry preparation and coating process enabling high mass loadings (up to 29 mg/cm²) and high active material contents (96%) in the electrodes, displaying a high areal capacity that reaches 3.8 mAh·cm⁻² at a charge/discharge rate of 1 C (Figure 4a). A high areal charge capacity is key to reach high energy density on cell and pack level, as it reduces the amount and weight of inactive materials needed to reach a specified capacity. Due to a higher active material content, our electrodes reach higher areal capacity than commercial NMC111 reference electrodes at comparable mass loading. The areal capacity of our NMC111 electrodes is also higher than...
Investigations for a Full Cell NMC Benchmark

that of a commercial NMC811 reference electrode, which possesses higher gravimetric capacity on active material basis (NMC811 200 mAh/g vs NMC111 160 mAh/g at C/10), but is more difficult to process into electrodes with high areal capacity. SEM analysis of the electrodes evidences a more homogeneous distribution of the NMC particles, carbon, and binder in the in-house prepared NMC electrodes (Figure 4b) in comparison to the commercial reference electrode (Figure 4c).

Finally, we also investigated the effect of electrolyte additives in full cells. Full cells NMC111/graphite were tested at slightly lower mass loadings and their performance optimized using VC as an electrolyte additive (5%vol). Discharge capacities of ~155 mAh·g⁻¹_NMC and ~140 mAh·g⁻¹_NMC were displayed at C/10 and C/2 rates, respectively (Figure 5). The VC additive can form a passivation layer of decomposed VC molecules on the electrodes surface, which plays a key role in the reduction of side reactions in the electrode/electrolyte interface and in the suppression of transition metal dissolution. VC can lower the charge transfer resistance, improve Coulombic efficiency, and hence promote prolonged cycling life. [4, 5]

Conclusions

In this work, we presented results on the synthesis of NMC-type materials by co-precipitation and microwave methods. We established a slurry processing and coating process for the preparation of electrodes with high areal capacity maintaining good rate performance. Finally, full cell NMC/graphite tests demonstrated an enhanced cycling performance when using VC as an electrolyte additive, delivering ~140 mAh·g⁻¹_NMC at C/2.

These results, together with insights gained from reverse-engineering and analysis of a state-of-the-art industrial NMC111/graphite cell, serve to define a state-of-the-art NMC111/graphite benchmark cell for the cell manufacturing activities within SCCER, which in turn represents the basis for further performance improvements incorporating the new materials developed within SCCER.
Investigation of the Promising P2-Na₀.⁶⁷Mn₀.⁶Fe₀.₂⁵Al₀.₁⁵O₂ Cathode Material

Scope of project

Na-ion batteries (SiBs) are considered the most promising complementary storage system due to their low-cost compared to Li-ion batteries. The electrochemical performance of the first prototype illustrates a good example of the ability of SiBs [1]. Among the possible cathode materials, layered oxides proved to deliver large specific charges [2]. P2-phases in particular, present higher voltage stability and better Na diffusion than the O3 equivalent phases. Cobalt is often used to stabilise layered structures upon cycling [3], despite being expensive and toxic. Recently we investigated Na₀.₆₇Mn₀.₆Fe₀.₂₅Co₀.₁₅O₂ and demonstrated that we can lower the Co content (P2-Na₀.₆₇Mn₀.₆Fe₀.₂₅Co₀.₁₅O₂ (NaMFC) [4]) and keep remarkable electrochemical performance. Based on this approach, we developed and studied the less expensive and toxic Co-free analogue Na₀.₆₇Mn₀.₆Fe₀.₂₅Al₀.₁₅O₂ (NaMFA).

Status of project and main scientific results of workgroups

Experimental

NaMFA was prepared through solid state synthesis from stoichiometric quantities of aluminium and manganese acetate, iron acetylacetonate and an excess of sodium acetate dissolved in ETOH/H₂O (1:3). The mixture was then calcined at 400°C for 3 h and annealed at 900°C for 12 h. The obtained powder was stored in an Ar filled glovebox.

The electrodes were prepared by casting a mixture of 80/10/10 (NaMFA / Carbon black / polyvinylidene fluoride (PVDF)) dispersed in N-methyl-2-pyrrolidone (NMP), onto an aluminium foil. Electrodes were dried, calendared, punched and further dried at 120°C. Electrochemical tests were performed in half-cell configuration using Na as counter electrode, glass fibre as separator and 1 M NaPF₆ in ethylene carbonate (EC):diethyl carbonate (DEC) mixture as electrolyte. The cells were cycled galvanostatically at 25°C between 2.1 V and 4.5 V (versus Na+/Na) with rate capability measurements consisting of series of three cycles at C/10, C/5, C/2.5, C/1.25 and C/0.625, followed by a constant C/5 rate.

Operando X-ray diffraction spectroscopy (XRD) patterns were collected on a PANalytical Empyrean diffractometer using Cu Ka radiation and an operando XRD cell. Synchrotron data were acquired at the MS-X04SA beamline at the SLS using a 0.563315 Å wavelength.

X-ray absorption spectroscopy (XAS) measurements were performed at the SuperXAS beamline at the SLS using the quick EXAFS monochromator on ex situ samples.[5]

Results

The XRD refinement of the pristine NaMFA confirms the formation of the desired P2-phase (P63/mmc space group with a = 2.89366(4) Å and c = 11.1781(3) Å) with minor impurities identified as O3-NaMFA and NaFe₀.₃₅Al₀.₃₅O₂ (Figure 1). The SEM image shows micron sized hexagonal-platelet particles, ascribed to the P2-phase, and smaller spherical particles due to the impurities.

The electrochemical performance of P2-NaMFA is compared with that of the parent NaMFC in Figure 2. At the end of the 1st cycle, the specific charge of NaMFA is higher than that of NaMFC, with 163 and 141 mAh·g⁻¹, respectively. Despite the absence of Co, a similar trend is observed at C/0.625 with values higher than 130 mAh·g⁻¹ for

Authors

Elena Marelli¹
Cyril Marino¹
Claire Villevieille¹

¹ PSI
Investigation of the Promising P2-Na_{0.67}Mn_{0.6}Fe_{0.25}Al_{0.15}O_2 Cathode Material

NaMFA and only 110 mAh·g⁻¹ for NaMFC. Once the current is back to C/5 rate, the Coulombic efficiency for NaMFA is restored and a value close to 100% is obtained 10 cycles later. In comparison, the Coulombic efficiency for NaMFC does not exceed 95%. After 80 cycles, the specific charge of NaMFA is 91% of the capacity obtained with the current restored at C/5 rate (22nd cycle), while only 72% of the specific charge is maintained for NaMFC.

The galvanostatic curves obtained upon first cycle present three different features, labelled on Figure 3 as i, ii and iii. The initial plateau from 2.75 V to 3.0 V counting for ca. 10% of the total specific charge is followed by ascending curves till ca. 4.15 V ascribed to a solid-solution mechanism. Between 4.15 and 4.5 V the coincident voltage profiles of NaMFA and NaMFC flatten indicating the Fe(III)/Fe(IV) oxidation [6]. On discharge both galvanostatic curves present a potential plateau centred at 3.65 V for NaMFA and 3.8 V for NaMFC, difference probably due to the presence of the electrochemical activity of Co in the material. Both curves slope then down to reach 2.1 V, contributing for 60% and 45% of the specific charge for NaMFA and NaMFC respectively.

Figure 4 shows the Mn K-edge of pristine, charged and discharged samples. Due to presence of Al instead of Co, the charges are compensated by a higher average oxidation state of Mn in the pristine NaMFA. The half-height of the Mn K-edge moves to higher energies as the desodiation proceeds and the oxidation state of the Mn in the two samples increases, respectively. On sodiation, the Mn K-edge moves to lower energies than in the pristine samples, indicating a lower Mn oxidation state. The discrepancy between the two samples spectra is however reduced, which could indicate a higher amount of sodium being involved in NaMFA and thus could explain the better electrochemical performance shown in Figure 2.

In Figure 5, the reaction mechanism is also investigated by mean of operando XRD. On charge, the a lattice parameter shrinks (e.g. (100) reflection in Figure 5) as a consequence of the reduced metals–metals distances. The interlayer distance instead barely moves on charge (e.g. (002) reflection) but a clear decrease of the intensity is observed at the end of charge coupled to the formation of new peaks (e.g. at ~17°). This high-potential phase possibly corresponds to the O2-phase [7] in which the metals slabs glide to a more stable octahedral geometry around the Na atoms. The P2-phase is restored on discharge with, however, an orthorhombic distortion (P"2-phase [8, 9]) at the end of discharge caused by a Jahn-Teller distortion.
Investigation of the Promising P2-Na$_{0.67}$Mn$_{0.6}$Fe$_{0.25}$Al$_{0.15}$O$_2$ Cathode Material

**Figure 4:**
XANES Mn K-edge spectra of NaMFA (blue) and NaMFC (magenta). Reference Mn(III) and Mn(IV) spectra are shown for comparison.

**Figure 5:**
Operando XRD patterns of NaMFA vs. Na and the corresponding first cycle galvanostatic cycle.

**References**


**Conclusion**

The Co-free P2-Na$_{0.67}$Mn$_{0.6}$Fe$_{0.25}$Al$_{0.15}$O$_2$ was successfully synthesised and characterised. The rate capability test showed higher specific charge and a better cycling stability than the analogous P2-Na$_{0.67}$Mn$_{0.6}$Fe$_{0.25}$Co$_{0.15}$O$_2$ cathode.

The better electrochemical performance of NaMFA could be associated with the deeper Mn reduction on discharge and thus the higher number of Na intercalated. The reduced phase transition on charge (P2→O2), instead, insures a better structural stability upon cycling.

The next stage for this material will be to scale it up to 100–500 g while reducing the production costs (lower temperature treatment, shorter thermal treatment, lowering the costs of the chemical etc.).

Once the cathode will be obtained with a sufficient quality (controlled of the morphology, porosity and purity), it will be tested in cylindrical cell 18650 toward a carbonaceous negative electrode material.

**Acknowledgement**

The Swiss Competence Centre for Energy Research (SCCER) and the PSI Career Return Program are kindly acknowledged for the financial support.

The authors are thankful to Dr. O. Safonova and Dr. M. Nachtengaal (SuperXAS beamline, SLS, PSI, proposal number 20161347) and, Dr. N. Casati (MS beamline, SLS, PSI, Mesquick proposal number 20170006).
Electrolytes for Safe and High-Performance Alkali Metal Ion Batteries

Scope of project

Ionic liquids are considered to be used as a safe electrolyte in alkali metal ion batteries because of their non-flammability [1]. However, they have high viscosity, which reduces ionic conductivity and mobility. Therefore, we targeted to develop novel ionic liquids to increase ionic conductivity, stability and safety for Li⁺ and Na⁺ ion battery systems.

Status of project and main scientific results of workgroups

We designed and synthesized various molecular structured ionic liquids based on crown-ether. After synthesis, several series of ionic liquid were characterized to evaluate their properties.

Cation transference numbers of the synthesized ionic liquids were in the range of between 0.5 and 0.8 while that of commercial aprotic electrolyte (EC: DMC: DEC with 1 M LiPF₆) was in the range of 0.3 to 0.4.

The ionic conductivity of 15-crown-5 was $5.28 \times 10^{-5}$ S/cm while that of the commercial organic electrolyte was lower with $4.2 \times 10^{-5}$ S/cm.

The thermal stability of synthesized ionic liquid was also superior to that of the commercial electrolyte. They are stable until about 380°C shown in Figure 1 left. The commercial carbonate electrolytes with 1 M LiPF₆ show an exothermic reaction at 200–230°C [2].

The electrochemical stability test revealed that the voltage retention is almost 80% after 200 cycles in the cell configuration of Li/ionic liquid/Li shown in Figure 1 right. We also observed that these ionic liquids are chemically stable with lithium metal, which is different from other unstable imidazolium-based ionic liquids which react with lithium metal.

Nowadays, an electrolyte additive plays a critical role to achieve higher performance of batteries. Even a small amount of electrolyte additive (3–10%) enhances the performance dramatically. Therefore, many battery manufacturers do not open their additive used in their commercial batteries.

Our developed ionic liquids have a high potential of using as a safe and high-performance electrolyte additive. So far, we tested the own properties of ionic liquids such as ionic conductivity, chemical and electrochemical stability, durability etc. On the other hand, the entire battery performance is strongly related to the relationship among all the battery components such as cathode and anode. Therefore, to apply the developed ionic liquids in a real battery and to make the commercialization, they need to verify battery properties with commercial cathodes and anodes in entire cells.

References


Authors

Hervé Yao¹
Nam Hee Kwon¹
Katharina M. Fromm¹
University of Fribourg¹

Figure 1: The characterization of thermal stability (left) and electrochemical stability (right) tests of synthesized ionic liquids.
Modeling a Multi-Product Battery Production Line

Scope of project

The research team «Manufacturing technologies for battery production» at Bern University of Applied Sciences (BFH) is leading research activities on battery manufacturing. The work of the team supports battery production industry, its equipment manufacturers and material suppliers in Switzerland. Machinery and process knowledge is combined in a holistic approach in cooperation with industry. The setup of this activity, not only allows for bilateral, mostly confidential industry projects, but also for research studies for mutual know-how transfer.

Status of project and main scientific results of workgroups

Building a new battery line requires significant investments. In order to be profitable, large quantities of cells need to be produced and sold.

Traditionally, the cell design is fixed for a given production line which makes it expensive to produce cells with customized design. Producing several battery types on one production line could be a strategy to increase the utilization of production lines and reduce cost. However different batteries require different processing parameters, different quality conditions and different raw materials. These distinctive properties of processing stages create a challenging environment to find most cost-effective combinations of process flow and product mix.

The aim of the team at BFH is to build simulation models for battery production optimization towards flexibility. Such a model must cover battery production from the raw material delivery dock to the final product packing. The product mix imposes complexity on the materials storage and logistics. The suggested model accounts for the related flows of material, resources and information and assesses the costs between the different production steps. The output parameters are captured with a graphical method proposed in [1]. Holistic modelling of manufacturing systems is described in [2], and a detailed structure for battery production is proposed in [3].

Following these proposals combined with our findings and simulation requirements the following model structure has been defined:

- The process step model describes a single process step such as slurry mixing or electrode stacking (see Figure 1).

![Figure 1: Lithium-ion battery production steps.](image)

Authors

Michael Stalder¹
Aysegül Haktanir¹
Axel Fuerst¹

¹ BFH (Bern University of Applied Sciences)
functions are described in terms of different operation states like «idle», «setup», «processing», «tear-down» and «failure», whereas the process model describes characteristics such as operation time, resources and materials required to process the workpiece correctly on the given station.

- The **product model** describes the material, process and quality requirements for a product.
- The **worker model** describes cost, skill and work schedule of a pool of workers and captures different worker states.
- The **process flow model** is the main model which combines process step, product, worker and transport models to a holistic model of the battery production line.

Further it describes rules how to break down product orders into manufacturing jobs, describes the routing of materials and manufacturing jobs, defines mode and distance of transport between stations, manages allocation of workers and represents physical location of machinery.

Compared to the approach presented in [3], the chosen modelling approach focuses more on rigorous modelling of production logistics and production costs.

At this point, a detailed dynamic model of interaction between machine/process and technical building services is not considered. Simpler static models are deemed to be sufficient for simulation studies in consideration.

Based on the goals and required model structure, a DES (discrete event simulation) has been created to simulate time dependend production flows including the named submodels. This allows a holistic study in contrary to the static models used in production planning today.

A first model of a full production line was implemented (see Figure 2), covering process steps from slurry mixing to cell formation. Models of individual process steps have been verified according to the information captured during the system analysis.

The model can run a product mix, where different products can have different manufacturing routings, e.g. one or the other production step may not be required, depending on the product requirements. Further the model can cluster product orders over a given period and convert these into manufacturing jobs for slurry mixing with ideal batch sizes. The manufacturing orders can also be arranged in order to reduce change-over times between products within the model and this within a single simulation run.

As next steps, more details on resource costs will be added to the model. Thereafter the model shall be verified on real production lines and used to perform simulation and optimization studies.
Water splitting by electrolysis is limited to a few MW in power, which is 3 orders of magnitude less than current power stations are operating. The goal is to significantly increase the efficiency and the power (current) density in electrolysers in order to increase the hydrogen production rate.

Examining the electrocatalytic performance of naturally-occurring metallic minerals is of interest for energy conversion applications given their unique atomic composition and formation history. Herein, we report the electrocatalytic function of an iron-based Gibeon meteorite for the oxygen evolution reaction (OER). After ageing under operational conditions in an alkaline electrolyte, an activity matching or possibly slightly superior to the best performing OER catalysts was detected during 1000 hours of OER operation at 500 mA cm\(^{-2}\).

Mechanistic studies suggest an operando surface modification involving the formation 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. The unique composition and structure of the Gibeon meteorite suggest that further investigation of Ir–Co–Ni–Fe systems or other alloys inspired by natural materials for water oxidation are of interest.

Hydrogen production by alkaline electrolysis

Water splitting by electrolysis is limited to a few MW in power, which is 3 orders of magnitude less than current power stations are operating. The goal is to significantly increase the efficiency and the power (current) density in electrolysers in order to increase the hydrogen production rate.

Examining the electrocatalytic performance of naturally-occurring metallic minerals is of interest for energy conversion applications given their unique atomic composition and formation history. Herein, we report the electrocatalytic function of an iron-based Gibeon meteorite for the oxygen evolution reaction (OER). After ageing under operational conditions in an alkaline electrolyte, an activity matching or possibly slightly superior to the best performing OER catalysts was detected during 1000 hours of OER operation at 500 mA cm\(^{-2}\).

Mechanistic studies suggest an operando surface modification involving the formation 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. The unique composition and structure of the Gibeon meteorite suggest that further investigation of Ir–Co–Ni–Fe systems or other alloys inspired by natural materials for water oxidation are of interest.

**Hydrogen production by Dual Circle Redox Flow Battery**

Redox flow batteries (RFBs) are well suited for storing the intermittent excess supply of renewable electricity. Conventional RFBs are charged and discharged electrochemically, with electricity stored as chemical energy in the electrolytes. In the RFB system, the electrolytes are conventionally charged but are then chemically discharged over catalytic beds in separate external circuits. The catalytic reaction generates hydrogen gas as secondary energy carrier. For demonstration, indirect water electrolysis was performed generating hydrogen and oxygen in separate catalytic reactions. The electrolyte containing V(II) was chemically discharged through proton reduction to hydrogen on a molybdenum carbide catalyst, whereas the electrolyte comprising Ce(IV) was similarly discharged in the oxidation of water to oxygen on a ruthenium dioxide catalyst. This approach is designed to complement electrochemical energy storage and may circumvent the low energy density of RFBs especially as hydrogen can be produced continuously whilst the RFB is charging.

For an all sulfuric acid battery, the coulombic charging efficiency of the battery is 94% (at 60 mA cm\(^{-2}\)). Hydrogen was generated from V(II) using an abundant and low cost Mo\(_2\)C catalyst and achieved a production yield of 96 ± 4%. Water oxidation was achieved over IrO\(_2\), and RuO\(_2\) nanoparticles from positive electrolytes comprising Ce(IV) in various acid solutions. A 78 ± 8% O\(_2\) yield was obtained in 1 M H\(_2\)SO\(_4\) and a partially hydrated RuO\(_2\) catalyst. This system is unique in the field of energy storage, merging two highly pursued technologies: renewable electrochemical energy storage and renewable power-to-gas. The novel technique allows surplus electricity to be stored as hydrogen beyond the limited energy density of the RFB electrolytes, with rapid discharge of the electrolytes also possible to provide an immediate sink for excess electricity. As water oxidation is not of commercial interest, alternative discharge reactions for
the anolyte must be investigated. With commercial all-vanadium RFBs the chemical discharge of the positive (V(IV)) species may also be envisaged, such as reduction by hydrazine to produce protons and N₂, SO₂ oxidation to produce H₂SO₄, or the oxidation of wastewater pollutants. Further investigation into optimising the anolyte discharge and to further characterise the catalytic reactions are in progress.

Hydrogen storage in complex hydrides

The storage of hydrogen is a critical issue because hydrogen cannot be liquefied at room temperature by compression (for physical reasons). Therefore, large quantities of hydrogen are either stored in liquid form (density 70.8 kg/m³) at low temperature (<-253 °C) or by reaction of hydrogen with a host material. Hydrogen reacts in aqueous solutions with CO₂ and forms formic acid, a product easy to handle, low cost and abundant. Hydrogen is released by applying a catalyst and then separated from the CO₂. The research focus is on the control of the hydrogen absorption and desorption reaction by the appropriate catalyst and the suppression of side reactions. Physisorption of hydrogen on carbon nanostructures allows to store several mass% of hydrogen, however, requires low temperatures (-196 °C). The highest known volumetric and gravimetric hydrogen densities are found in complex hydrides. These are chemical compounds that only exist with the hydrogen and decompose into several phases upon hydrogen desorption, which makes the reabsorption technically challenging.

Among the potential hydrogen storage materials, the borohydrides exhibit a high gravimetric and volumetric hydrogen storage capacity, up to 20 % mass of hydrogen with 150 kg H₂/m³. However, the challenge for borohydrides is the high enthalpy for hydrogen desorption and the kinetic barrier for re-hydrogenation. This materials have been investigated in the form of nanoparticles and the size effects, e.g. destabilization with decreasing size, where described. The nanoparticles of borohydrides show a faster sorption rate at low temperatures than that of bulk material due to the large specific surface area and the short diffusion path length. Sodium borohydride (NaBH₄) nanoparticles were successfully formed on the carbon support by the metathesis reaction of LiBH₄ with NaCl. Various carbon supports such as graphite, graphene oxide (GO) and carbon nanotubes (CNT) were used. The effect of nanoparticle size and dispersion on the hydrogen storage capacity was investigated. The nanoparticle size of NaBH₄ deposited on carbon support was in the range of 3–6 nm through mutual intercalation and shows the hydrogen desorption at a temperature of 120 °C. Also, NaBH₄ particles evenly distributed on the carbon supports desorb up to 12.3 % mass of hydrogen.

Large scale hydrogen storage has been developed and built with a capacity of 2 kg of hydrogen (80 kWh of energy). The hydrogen is stored in an intermetallic compound ((La0.74Ce0.24)Ni4.21Co0.68Mn0.10) with an equilibrium hydrogen pressure of 3 bar at 20 °C. The storage is installed in the small scale demonstrator in Sion and operated between a PEM electrolyzer and a methanation reactor. The modular design of the storage allows scaling up, a new storage system for 1 MWh (25 kg of hydrogen) is planned.

Hydrogen storage in formic acid

Formic acid (FA) and methanol (CH₃OH) are considered as effective liquid chemicals for hydrogen storage as being easier to handle than solid or gas materials. This review summarizes the recent progress of research on the development of homogeneous catalysts mainly focusing on FA and CH₃OH and the reports on the complexes based on both precious and non-precious metals which are rapidly increasing in the past few years.

Formic acid (FA) contains ~4.4 % wt of hydrogen (or 53 g/L) which can be catalytically released and converted to electricity using a proton exchange membrane (PEM) fuel cell. Although various catalysts have been reported to be very selective towards FA dehydrogenation (resulting in H₂ and CO₂), a side-production of CO and H₂O (FA dehydration) should also be considered, because most PEM hydrogen fuel cells are poisoned by CO. In this research, a highly active aqueous catalytic system containing Ru(III) chloride and meta-trisulfonated triphenylphosphine (mTPTPS) as a ligand was applied for FA dehydrogenation in a continuous mode. CO concentration (8–70 ppm) in the resulting H₂ + CO₂ gas stream was measured using a wide range of reactor operating conditions. The CO concentration was found to be independent on the reactor temperature but increased with increasing FA feed. It was concluded that unwanted CO concentration in the H₂ + CO₂ gas stream was dependent on the current FA concentration in the reactor which was in turn dependent on the reaction design. Next, preferential oxidation (PROX) on a Pt/Al₂O₃ catalyst was applied to remove CO traces from the H₂ + CO₂ stream. It was demonstrated that CO concentration in the stream could be reduced to a level tolerable for PEM fuel cells (~3 ppm).
Hydrogen – Solid Interaction for Storage

Scope of project

The storage of hydrogen in hydrides offers many advantages over the conventional compressed or liquid hydrogen storage. The density of the hydrogen in the solid material can reach twice the density of liquid hydrogen at room temperature in the equilibrium with the gas phase. The equilibrium pressure is moderate and, therefore, the storage, is safe. Beside the well-known interactions of hydrogen with solids, i.e. physisorption, chemisorption and ionic compounds, new interactions like the pore condensation in nanomaterials and the Kubas interaction are of great interest for the development of new storage materials. Furthermore, some hydrides, e.g. the high temperature phase of LiBH₄, show super ionic conductivity, a property that enables the manufacturing of all solid state Li-ion batteries. Some of the new carbon materials, e.g. graphene oxide, exhibit unique gas sorption properties. These materials can be functionalized, e.g. Boron, are low cost and easy to produce in large quantities. The start up company GRZ Technologies SA focuses on the development of large scale solid hydrogen storage systems. The current systems exhibit an energy storage density of >1kWh/kg and can be further optimized.

Status of project and main scientific results of workgroups

Functionalised metal–organic frameworks: A novel approach to stabilising single metal atoms [1]

The potential of metal–organic frameworks for immobilising single atoms of transition metals was investigated using a model system of Pd supported on NH₂-MIL-101(Cr).

Our transmission electron microscopy and in situ Raman spectroscopy results give evidence for the first time that functionalised metal–organic frameworks may support, isolate and stabilise single atoms of palladium. Using thermal desorption spectroscopy we were able to evaluate the proportion of single Pd atoms.

Furthermore, in a combined theoretical-experimental approach, we show that the H–H bonds in a H₂ molecule elongate by over 15% through the formation of a complex with single atoms of Pd. Such deformation would affect any hydrogenation reaction and thus the single atoms supported on metal–organic frameworks may become promising single atom catalysts in future.
Effect of boron doping on graphene oxide for ammonia adsorption [2]

Boron doped graphene oxide (B-GO) is a highly effective adsorbent for ammonia due to the high density of strong Lewis acid sites arising from the boron. Graphene oxide (GO) was doped by various amounts of boron described as xB-GO (x = 1.0, 3.0, and 5.0). B-GO was successfully synthesized and the boron doping was confirmed by X-ray diffraction, Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy. The adsorption characteristics of B-GO were investigated by adsorption isotherm and thermal desorption spectroscopy. The adsorption isotherm shows an increase of ammonia adsorption with increasing concentration of boron such as 12.03 mol kg\(^{-1}\), 16.30 mol kg\(^{-1}\) and 15.58 mol kg\(^{-1}\). It is confirmed that the amount of ammonia adsorbed on the boron sites is limited to a certain amount due to the reduction of Lewis acid sites by B–O bonds. Boron doped into GO significantly enhances the adsorption capacity for ammonia.

Hydrogen storage properties of NaBH\(_4\) with various carbon supports

Among the potential hydrogen storage materials, the borohydrides exhibit a high gravimetric hydrogen storage capacity. However, the challenge for borohydrides is the high enthalpy for hydrogen desorption and the kinetic barrier for re-hydrogenation.

These materials have been investigated in the form of nanoparticles and the size effects, e.g. destabilization with decreasing size, where described. The nanoparticles of borohydrides show a faster sorption rate at low temperatures than that of bulk material due to the large specific surface area and the short diffusion path length.

Sodium-borohydride (NaBH\(_4\)) nanoparticles were successfully formed on the carbon support by the metathesis reaction of LiBH\(_4\) with NaCl (Figure 3). Various carbon supports such as graphite, graphene oxide and carbon nanotubes (CNT) were used. The effect of nanoparticle size and dispersion on the hydrogen storage capacity was investigated. The nanoparticle size of NaBH\(_4\) deposited on carbon support was in the range of 3–6 nm through mutual intercalation and shows hydrogen desorption at a temperature of 120°C. Also, NaBH\(_4\) particles evenly distributed on the carbon supports desorb up to 12.3% mass of hydrogen.

References
Scope of project

The reversible catalytic reduction of CO$_2$ with hydrogen to formic acid (FA, HCOOH) under mild conditions offers a convenient solution to store H$_2$ with a comparably high volumetric energy density. Formic acid is a moderately toxic liquid at room temperature and used as feedstock chemical for industries. Finally, formic acid can be decomposed to H$_2$, releasing only CO$_2$ as the by-product on demand. If the CO$_2$ is recycled a carbon-neutral hydrogen storage cycle is established.

Status of project and main scientific results of workgroups

Dehydrogenation of formic acid over a homogeneous Ru-mTPPTS catalyst: Successful removal of the CO trace impurities for the direct use of the H$_2$–CO$_2$ gas mixture in PEM fuel cells.

Formic acid (FA) is considered as a potential durable energy carrier. It contains ~4.4 %wt of hydrogen (or 53 g/L) which can be catalytically released and converted to electricity using a proton exchange membrane (PEM) fuel cell. Although various catalysts have been reported to be very selective towards FA dehydrogenation (resulting in H$_2$ and CO$_2$), a side-production of CO and H$_2$O (FA dehydration) should also be considered, because most PEM hydrogen fuel cells are poisoned by CO. Here, a highly active aqueous catalytic system containing Ru(III) chloride and meta-trisulfonated triphenylphosphine (mTPPTS) as a ligand was applied for FA dehydrogenation in a continuous mode. CO concentration (8–70 ppm) in the resulting H$_2$+CO$_2$ gas stream was measured using a wide range of reactor operating conditions. The CO concentration was found to be independent on the reactor temperature but increased with increasing FA feed. It was concluded that unwanted CO concentration in the H$_2$+CO$_2$ gas stream was dependent on the current FA concentration in the reactor which was in turn dependent on the reaction design. Next, preferential oxidation (PROX) on a Pt/Al$_2$O$_3$ catalyst was applied to remove CO traces from the H$_2$+CO$_2$ stream. It was demonstrated that CO concentration in the stream could be reduced to a level necessary for PEM fuel cells (~3 ppm).
Hydrogen / Energy Production and Storage with the Carbon Dioxide / Formic Acid Systems

Base and additive free direct carbon dioxide hydrogenation into formic acid, in aqueous solutions using iron (II) phosphine complexes as catalysts

The valorization of CO₂ and its transformation into useful chemicals, as formic acid or methanol, become essential as we consume more and more fossil fuels and thus are producing equivalently carbon dioxide waste.

Here the unprecedented direct CO₂ hydrogenation has been developed using an iron (II) phosphine complex as catalyst. In water, with meta-trisulfonated-tris[2-(diphenylphosphino)ethyl]phosphine sodium salt (PP₃TS) as ligand, at room temperatures and with the gas pressures of hydrogen and carbon dioxide, up to 1.5 M of formic acid were produced, without any additives or base.

The same catalyst is also active to release hydrogen on demand from formic acid by decreasing the pressure and increasing the temperature.

This dehydrogenation of formic acid and CO₂ reduction cycle can be repeated several times without the loss of activity and catalyst/system does not suffer from air/oxygen sensitivity.

Hydrogen being a future energy carrier, using this catalyst could result in a battery-like system with a charge/discharge of hydrogen, safely providing gaseous H₂ to PEM fuel cells and storing energy in formic acid.

Carbon dioxide to methanol:
The aqueous catalytic way at room temperature

Carbon dioxide may constitute a source of chemicals and fuels if efficient and renewable processes are developed that directly utilize it as feedstock. Two of its reduction products are formic acid and methanol, which have also been proposed as liquid organic chemical carriers in sustainable hydrogen storage. Both the hydrogenation of carbon dioxide to formic acid and the disproportionation of formic acid into methanol can be realized at ambient temperatures and in aqueous, acidic solution, with an iridium catalyst. The formic acid yield is maximized in water without additives, while acidification results in complete (98%) and selective (96%) formic acid disproportionation into methanol. These promising features in combination with the low reaction temperatures and the absence of organic solvents and additives are relevant for a sustainable hydrogen/methanol economy.
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 independency 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) 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.

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, compressed hydrogen exhibits a much higher energy density than a RFB. Indirectly, this system therefore allows to increase the energy density of the RFB.

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 made of two catalytic beds enables an external chemical discharge of both electrolytes.

On the negative side (right circuit in Figure 1), the catalytic chemical discharge reaction is the reduction of protons by the V(II) species present in the electrolyte, generating hydrogen and regenerating the discharged V(III) species. The catalyst used for this reaction was 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, 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 power of the negative electrolyte was equivalent to 2.4 kW. Concerning the chemical discharge of the positive electrolyte, as water oxidation could not be performed using the V(V) electrolyte, the oxidation reactions of N₂H₄, SO₂ and H₂S were investigated [3].

As a follow-up of the successful demonstration of the system, an alternative discharge method for the positive V(V) electrolyte was demonstrated in 2017. In this approach, the V(V) electrolyte is reduced in a separate electrochemical flow cell, while O₂ is evolved at the opposite electrode (Figure 1). Some energy input to the cell is required to overcome the
Demonstration of a Redox Flow Battery to Generate Hydrogen from Surplus Renewable Energy

thermodynamic and kinetic limitations imposed by the O₂ evolution reaction. To maximize the efficiency of the system, the energy input was reduced by using a dimensionally stable anode (DSA), consisting of a Ti mesh coated with mixed metal oxides (predominantly IrO₂). DSA is very stable in oxidizing conditions, and relatively active for O₂ evolution.

The behavior of the V-O₂ cell was studied in detail, and some optimization of the cell was performed. Later, this regeneration cell was directly coupled with a vanadium redox flow battery (Figure 1) to create a true dual-circuit system. In our laboratory-scale system, the V-O₂ cell required ca. 120 mW cm⁻² at 110 mA cm⁻² and the complete dual circuit system exhibited an overall efficiency between 42–63%.

Although the lab-scale system was not highly optimized, the efficiency is already comparable to a conventional alkaline electrolyzer coupled with a vanadium redox flow battery (VRFB).

In parallel, another research direction focused on the increase of the energy density of the RFB through the addition of solid particles in the electrolyte tanks. Polyaniline (PANI) has been used as a successful test-case to demonstrate the complete concept of a redox mediated flow battery. PANI was paired with Fe³⁺/Fe²⁺ as a redox mediator on the positive side of the battery, and VO²⁺/V³⁺ on the negative side. The energy density of the system increased by a factor of 3 compared with the liquid electrolytes alone. Interestingly, the system also exhibited improved energy efficiency during cycling. This positive outcome has encouraged our search for new solid charge storage materials and redox mediators.

Screening of a variety of solid charge storage materials began in 2016, and continued in 2017. Several lithium intercalation compounds have been evaluated, however these materials present unique challenges in aqueous conditions due to problems of stability and decomposition of the electrolyte. For lithium intercalation materials which are stable in neutral or basic environments, work is underway to identify suitable redox mediators. A particular class of metal-organic frameworks is also being explored. These materials have demonstrated promising performance in acidic conditions (up to 36.4 mAh/g), and will be disclosed in an upcoming publication. Various redox mediators are also being considered, including V, Fe, viologens, ferroin, and others.

A wide range of research on redox flow battery is being conducted with the financial help of SCCER HaE, 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.

References
Investigations on the Active Layer Formation on Stainless Steel Electrodes in Water Oxidation Conditions

Scope of project

Hydrogen, foreseen to replace fossil fuels as energy carrier in the future, can be produced electrochemically from water and renewable abundant energy sources through water electrolysis. The water oxidation half reaction is considered as a bottleneck due to larger required overpotentials (>0.35 V) as compared to water reduction (~0.1 V). [1] Our efforts have been consequently focused towards understanding and improving the oxidation half reaction (OER). Nickel-iron alloys have evidenced state-of-the-art catalytic activity for OER, with overpotentials below 0.3 V. Electrodes made from these two inexpensive and abundant metals can be prepared synthetically or as we have recently shown, can also be derived from naturally occurring minerals, such as the Gibeon Meteorite. [2, 3] This active catalyst can also be formed in situ during OER operation on mass-produced inexpensive materials, such as Ni-containing stainless steel but the stability both in terms of performance and composition remains unclear. [4] Our efforts in the last year have been dedicated to gaining more insight into these points, which are critical for the industrial deployment of this technology.

Status of project and main scientific results of workgroups

To investigate stability, three different grades of stainless steel were selected for experimental testing due to their different nickel content: AISI 1.4307, AISI 1.4404 and AISI 1.4435 (8, 10 and 12% Ni, respectively, see sample preparation in Figure 1a). The establishment of a highly active catalytic layer on the surface of the electrode during the first hours of water oxidation operation (0.5 or 1 A cm⁻² in 1 M NaOH) was evidenced by the cathodic shift of the current-voltage characterization of the electrodes, as shown for one type of steel on Figure 1b. After an induction time of 5–10 hours, only overpotentials of ca. 0.2–0.25 V were required to reach 10 mA cm⁻² of water-oxidizing current. This improvement in performance has been associated to the formation of a nickel-iron mixed oxy-hydroxide layer. The nickel iron compound herein produced can be detected electrochemically in cyclic voltammograms (redox wave for Ni²⁺/³⁺ couple at around 1.4 V vs. RHE) and characterized by typical features measured on such materials with various spectroscopic techniques (Raman, X-ray photoelectron, not shown here). All stainless-steel samples have also shown good long-term stability, both in terms of performance and density of active species (assumed to be equivalent to the area under the Ni²⁺/³⁺ reduction wave) for time exceeding 1000 hours (as shown for AISI 1.4307 on Figure 1c).

References

Despite a constant density of active species with respect to the operation time at steady state, the long-term stability of the active layer was cast into doubt due to the observed coloration of the electrolyte after experiments and the periodic detachment of the active layer. Several tests were conducted including renewal of the electrolyte during OER operation and texturing of the electrode with abrasive blasting. The outcome of these investigations suggests that the anodization of the electrode does not stop during long term operation. Thus a remaining challenge has been clearly identified: to mechanochemically stabilize the catalyst formed in situ.

X-ray photoelectron spectroscopy has been conducted on the different grades of stainless steel tested, before and after OER operation, to investigate the modification of the metal composition in the active layer (see Figure 1d, e and f). Analyses suggest significant surface enrichment in nickel and manganese (or cobalt for the Gibeon meteorite) [3] to similar proportions and presumably induced by a dissolution mechanism of iron and chromium atoms in solution. The surprisingly comparable end-composition of the active layer, approximately one third in iron, nickel and manganese, has suggested that the optimal composition for a stable and efficient OER catalyst emerges despite the initial composition. To test this hypothesis, and in order to understand the composition effect on the activity and final composition of the catalyst, ternary transition metal alloy electrodes with defined composition have been synthesized via an arc melting technique in collaboration with the group of Prof. Züttel (Figure 2a). These pellets have been prepared last year and are currently under analysis.

In addition, with respect to the development of our SCCER testing platform, a new medium-scale electrochemical cell based on a polymethyl methacrylate (PMMA) enclosure has been designed to further our electrochemical test conditions closer to industrial application (see Figure 2b). Our experimental cell now includes a hydroxide anion exchange membrane (Zirfon® from Agfa, Belgium) and allows control over the cell temperature and volume of electrolyte.

Figure 2:
a) Ternary metal electrode compositions (in blue) selected for next stability tests under OER conditions (pellets synthesized by arc-melting in collaboration with the group of Prof. Züttel).
b) New electrochemical test cell design to incorporate a hydroxide anion exchange membrane (Zirfon, from Agfa).
Hydrogen

Ag Nanoparticles Loaded on TiO₂ Nanocapsules and Nanospheres as Photocatalysts for Photoelectrochemical Water Splitting

Scope of project

The photoelectrochemical water splitting using the TiO₂-based materials could be a great option for hydrogen production to obtain clean and renewable energy sources. For this process, titanium dioxide-based materials with various structures are commonly used as photocatalysts [1, 2].

In collaboration with the group of P. Broekmann at the University of Bern (WP 4), we developed in this project TiO₂ nanocapsules and nanospheres with different crystalline structures. We investigated further the photocatalytic properties of different morphologies of TiO₂ by changing the crystalline phase, the size and the shape of TiO₂. Moreover, the embedment of silver nanoparticles (AgNP) into the TiO₂ material is explored. Indeed, the presence of silver islands may enhance its photoactivity [3].

Status of project and main scientific results of workgroups

Figure 1:
Representative scheme of new synthetic routes for making Ag/TiO₂ nanocapsules.

References

Figure 2:
SEM images of the electrodes of (A) AgNP/TiO₂ nanocapsules and (B) AgNP/TiO₂ nanospheres from method 2.

Authors
Nelly Hérault¹
Katharina M. Fromm²
¹ University of Fribourg

List of abbreviations
NP Nanoparticles
SEM Scanning Electron Microscopy

New strategies of synthesis

Based on our new synthetic method 1 (Figure 1), AgNPs were formed on the crystalline TiO₂ nanocapsules rather than on the surface of template. On the other hand, the method 2 in Figure 1 provided that silver nanoparticles were impregnated into the layer of TiO₂ nanocapsules and nanospheres. The loading of Ag was 3%wt. The electrodes with TiO₂ nanocapsules and nanospheres were prepared.

Scanning electron microscopy (SEM) images showed the capsules of TiO₂ are destroyed in Figure 2 (A) but the nanospheres of TiO₂ kept the desired structure with AgNP shown in Figure 2 (B).

Therefore, the method 2 is encouraging to control the AgNP size and the deposition on the surface of TiO₂ capsules and spheres.

The process of making electrodes requires optimization in order to obtain high-photocatalytic properties.
Work Package «Synthetic Fuels» at a Glance

The work package «Synthetic Fuels» is devoted to the conversion of CO\(_2\) to fuels and focuses on exploring and developing efficient processes to convert carbon dioxide – using excess energy obtained from renewable intermittent energy sources – into fuels, with a specific focus on methanol and hydrocarbons. This work package is sub-divided into two main parts, addressing catalytic (Part 1) and electrocatalytic (Part 2) processes. A short summary of the 2017 highlights is provided below.

Part 1: Catalytic conversion of CO\(_2\).

The direct hydrogenation of CO\(_2\) to methanol is investigated by ETHZ, where supported Cu catalysts are being developed. Following the discovery in 2016 that interfacial sites in Cu/ZrO\(_2\) are essential for the increased activity and high methanol selectivity, scalable catalysts using flame spray pyrolysis have been developed; they show higher catalytic performances (activity and selectivity) than commercial catalysts. In addition, an alternative approach, which is currently being patented, has been developed that consists in tailoring the interface of Cu nanoparticles supported on high surface area oxides through selective doping. This approach allows an increase of activity and methanol selectivity of the Cu-catalysts. Discussion with industrial partners on development of more efficient industrial catalysts based on this approach is currently ongoing.

With homogeneous catalysts, indirect conversion of CO\(_2\) to methanol and hydrocarbons are being pursued by EPFL. Through the development of efficient trapping of CO\(_2\) using ionic liquids, the concentrated CO\(_2\) can be converted first to cyclic carbonate and then to methane, using a complementary Ru-based heterogeneous hydrolysis catalyst. CO\(_2\) can also be converted to methanol using N-formylation of amines as a key step followed by hydrogenation. Discov-ered with homogeneous catalysts, this process is currently being investigated using heterogeneous catalysts based on both precious metal and earth abundant metals.

Part 2: Electrocatalytic conversion of CO\(_2\).

The CO\(_2\)–to–CO electro-reduction process in a co-electrolyser is best carried out in alkaline solution in order to minimize the competitive hydrogen evolution reaction (HER), but this process suffers from diffusion to the anode of carbonates, which reduces the efficiency of the process. Through a rational approach, PSI has thus developed a membrane-electrode-assembly to improve the efficiency of the electro-catalytic process by using tailored bipolar ionomer/membrane configurations that avoids CO\(_2\) percolation. In order to optimize the process, a large effort has also been devoted to the development of the complementary anodic catalytic reaction, namely oxygen evolution reaction (OER). Tailored metal oxides have been developed by PSI and ETHZ, for the OER reaction run under alkaline and acid conditions; they display higher activity and stability by comparison to state of the art catalysts.

In parallel, Cu foam catalysts were successfully transferred into technical substrates such as 2D meshes and 3D skeleton supports by UoB; they show superior performance for C2 and C3 alcohol formation reaching total alcohol efficiencies of 25%. Moreover, deactivation pathways related to methane production were identified and suppressed, allowing stable alcohol production for >8 h. In parallel, a new methodology to prepare carbon-supported nanometric Cu nanoparticles was developed by ETHZ; their catalytic performances in CO\(_2\) electro-reduction are severely hindered by the competing HER. Finally, a novel foam-type of Ag catalyst has been developed by UoB, showing good activity towards CH\(_4\) formation with Faradaic yields of 55%. These catalysts also show remarkable stability under ec-CO\(_2\)RR conditions, but poisoning through carbon deposition is observed leading to deactivation when the C1 hydrocarbon pathway is active.

In addition to catalysts, new electrolytes have been developed at EPFL; they are based on pyrazolium (Pz) cation. This system shows significantly higher current densities at similar onset proposal in CO\(_2\) reduction, making Pz ionic liquid attractive for further investigation, in particular when combined with porous copper electrodes.

Illustration: BeholdingEye / iStock
Catalytic and Electrocatalytic CO₂ Transformation into Feedstocks and Fuels

Scope of project

Ionic liquids (ILs) act as catalysts and co-catalysts in a number of CO₂ related transformations including direct electrocatalytic reduction of CO₂, conversion of cyclic carbonates to epoxides, N-formylation of amines, etc. In order to understand the underlying mechanism of ILs in these reactions, to improve their catalytic function, we systematically investigated the active role ILs play in these reactions.

Status of project and main scientific results of workgroups

Continuing the development of IL catalysts for electrochemical reduction of carbon dioxide, we investigated activity and performance of a new class of ILs based on the pyrazolium (Pz) cation (Figure 1).

These ILs, employed as additives in anhydrous acetonitrile-based electrolytes and using a silver electrode, are efficient promoters for CO₂ reduction to carbon monoxide (superior to any other class of cation reported in the literature). Compared to conventional imidazolium ILs, for example, the Pzs possess similar reduction onset potentials, but current densities and stable working range for the Pz co-catalysts are significantly higher, which makes the Pz ILs attractive for further investigation, e.g. in combination with porous copper electrodes.

We have developed a catalytic system based on a simple, cheap IL ([BMIm]Cl) that can extract 100% of CO₂ from gas streams (containing a few hundred ppm CO₂ through to pure CO₂) under continuous flow conditions, and a patent has been filed based upon this discovery.[1] The CO₂ is extracted and incorporated into an epoxide compound to generate a cyclic carbonate product. In this approach, we rely on large molecular weight bis(epoxides) that will lead to bis(carbonates) that can be subsequently reduced to afford methane (see below) to ultimately form a cyclic process to generate fuels (or potentially other products). We are in the process of securing further funding to scale-up and commercialize this process.

The cyclic carbonate products are useful (valuable) products, but they can be converted further and our goal is to generate methane and/or methanol from the cyclic carbonates and to regenerate the epoxide. For this purpose, we have developed a novel ruthenium hydrolysis catalyst supported on zeolites that is capable to quantitatively convert propylene carbonate into propylene glycol and methane (Scheme 1). The method is advantageous because it enables easy separation of the products because methane is a gas, propylene glycol is a liquid than can be filtered, and the catalyst is a heterogeneous solid that can be easily recycled.

The two-step conversion of CO₂ to methanol via formamides by N-formylation of amines (Figure 2) is being studied in detail using heterogeneous catalysts based on both precious metal and earth abundant metal and metal oxide catalysts under ambient conditions.

We have developed a novel nano-catalytic system based on rhodium that could be

List of abbreviations

IL Ionic Liquid
Pz Pyrazolium

Figure 1:
Comparison of cyclic voltammetry data for imidazolium (BMIM)- and pyrazolium-based ILs against Ferrocene (Fc) (left) and structures of the IL cations developed for the project (right).

Scheme 1:
Hydrogenolysis of propylene carbonate catalyzed by supported Ru nanoparticles. Reaction conditions: Ru-NH₄Cl/MS-10Å (0.2 mmol of Ru loading, 200 mg of the catalyst).

References

(b) F.D. Bobbink, P.J. Dyson, Patent Application No. 17 164 326.5.

Author
Paul J. Dyson¹

¹ EPFL
used to hydrogenate the formamides to methanol thereby recovering the parent amine as well as converting the CO₂ to a fuel. This procedure is advantageous because it offers good selectivity, good recyclability, cost-effectiveness and good yield. Moreover, the combined system was found suitable for the conversion of formic acid (another CO₂ and H₂ carrier) to methanol. We investigated a related reaction of 2-aminobenzonitriles to quinazoline-2,4-dione. The discovered catalyst pKa dependency (Figure 2) not only demonstrates the limit of IL catalysts in quinazoline-2,4-dione formation but also a novel mechanism for this reaction,[2] potentially applicable to many other CO₂ related transformations.

Figure 2:
Left: General scheme showing the formation of methanol from CO₂ via N-formylation of amines. Right: Reaction yield dependency on the pKa of the catalyst in DMSO. Linear dependency is observed in the range 9.2–14.4; \( R = 0.99 \).
Progress in the Development of Tailored Catalysts for the Hydrogenation and Electrocatalytic Reduction of CO₂

Scope of project

The conversion of CO₂ to fuels, such as methanol, using hydrogen produced from alternative energies or directly via electroreduction is a dynamic research area, in view of the constant increase of CO₂ emission and the abundant excess of unused intermittent and renewable energy sources available today due to the increase availability of wind and solar power sources. This research area posses several technical challenges and in particular the development of stable and selective thermo- and electrocatalysts.

This work package focuses on the development of improved catalytic materials via rational design for the selective

- hydrogenation (Part 1) and
- electroreduction of CO₂ coupled with the oxygen evolution reaction (OER) (Part 2).

Status of project and main scientific results of workgroups

CO₂ hydrogenation

In CO₂ reduction to methanol (methanol synthesis), the role of supports/promoters for supported copper nanoparticles in the improvement of catalysts performances was shown in the 2016 period to be related to the existence of interfacial sites between the copper and a support with specific properties, in particular Lewis acidity in the case of ZrO₂ as support or promoter as reported last year by our group. [1] Therefore, several actions have been undertaken at the level of the catalyst preparation in order to optimize the creation of these interfacial sites, and ultimately improve the activity/selectivity of the catalysts. We present below the two most promising research developments of 2017.

Our related work on dry reforming and water gas shift has mostly focused on catalyst development, understanding of deactivation and kinetic aspects. These works have been published [2] and will not be discussed here. However, some of the concepts derived from the aforementioned work will be used to develop the selective CO₂ hydrogenation catalysts discussed below.

Preparation of mixed metal oxides via flame spray pyrolysis

Several Cu/ZrO₂ supported catalysts were prepared using a two-nozzle Flame Spray Pyrolysis technique (FSP) in collaboration with the group of Prof. Pratsinis (D-MATV – ETHZ). The parameters of the 2 flames could be adjusted independently to tune the catalysts properties (e.g. O₂ flow in the flame, see Figure 1a).

![Figure 1](image_url)

(a) Scheme of the two-nozzle Flame Spray Pyrolysis technique, with the associated STEM-EDX micrographs associated for two catalysts prepared with different O₂ flow in the flame (in green: copper).
(b) CO₂ to methanol catalytic results (230°C, 25 bar, CO₂:H₂ ratio 1:3) for selected catalysts. Left: Methanol formation rate per gCu. Right: methanol selectivity vs. CO₂ conversion.

Authors

Erwin Lam¹
Kim Larmier¹
Quasim Imtiaz¹
Sohei Tada¹
Patrick Wolf¹
Nicolas Kaeffer¹
Jean-Daniel Compain¹
Christos Mavrokefalos¹
Dmitry Lebedev¹
Lucas Foppa¹
Aleix Comas-Vives¹
Christophe Copéret¹

¹ ETHZ
We found that using a specific set of parameters afforded catalysts exhibiting higher selectivity to methanol than a commercial benchmark catalyst (Cu/ZrO2/Al2O3) under similar reaction conditions (Figure 1b). [1] At 6% of CO2 conversion (230°C, 25 bars of CO2/H2 1:3 mixture), the selectivity to methanol is improved to around 45% (balance: CO) for our FSP-made catalyst CuO-ZrO2-R compared to the reference catalyst (30% of conversion). We assign this increased performance to the intimate mixing between Cu and ZrO2 afforded by the preparation technique. [3] Additional work is ongoing to further optimize the flame properties and catalytic performances.

**Preparation of tailored interfacial sites via surface organometallic chemistry**

In order to optimize the amount of promoter for the copper particles that can be introduced in the catalyst, a procedure based on Surface Organometallic Chemistry (SOMC) has been used to disperse the dopant atoms as single species at the surface of an inert support (silica). Grafting a suitable molecular precursor of the siloxide family M(TBOS)X – where M is the promoter of interest (Zr, Ga, Zn, In...) –, TBOS stands for tris-tertbutyloxsilane and x depends on its oxidation state – followed by a thermal decomposition under vacuum affords isolated M species at the surface of silica (M@SiO2). Copper particles are then prepared according to a reported SOMC procedure [4] to afford the Cu/M@SiO2 catalysts (copper particles on promoted silica). We show that the low amount of M introduced in this way (typically 0.5–1.5%) is in most cases sufficient to trigger a selectivity and activity enhancement of the copper nanoparticles in CO2 hydrogenation to methanol (Figure 2). The enhancement is variable depending on M, with Zn, Ga, Zr and V being so far the most promising candidates. [5] The current procedure and the associated catalysts are currently under evaluation for a patent application. In situ XAS spectroscopy is also currently being investigated to understand the fate of the catalysts under reaction conditions. In view of the above results, an Atom Layer Deposition (ALD) approach is currently being investigated in collaboration with the group of Prof. Mueller (D-MATV - ETHZ) in order to maximize the number of interfacial sites and increase the selectivity towards methanol formation.

**CO2 electroreduction and oxygen evolution reaction (OER)**

CO2 electroreduction to fuels faces several challenges – in particular the efficient production (high faradaic efficiency) of methanol or related products at the cathode, which need to be coupled with an efficient OER reaction at the anode. The work described below aims at the development of more efficient materials for each process.

**CO2 electroreduction**

In CO2 electroreduction, a major issue is the competitive formation of H2, which reduces the faradaic efficiency of the CO2 electroreduction process. Towards this goal, we have developed a methodology to prepare small, well dispersed copper nanoparticles by a surface organometallic chemistry approach, grafting an organometallic precursor onto pre-treated carbon black support. The obtained CuNPs/Cblack ma-
terial was filtered onto gas diffusion layer to obtain functionalized electrodes. Cyclic voltammograms of the prepared electrodes (20 µgIr·cm⁻²) were recorded in 0.5 M KHCO₃ aqueous electrolyte under Ar atmosphere. Redox events attributable to Cu⁴⁺ and Cu⁺ coupled were identified. The performance of these electrodes have also been further evaluated by chronopotentiometric measurements with investigation of the volatile products by a gas chromatograph-mass spectrometer (GC-MS) on-line setup and of the non-volatile products using nuclear magnetic resonance (NMR) spectroscopy and high-performance liquid chromatography (HPLC). Under electrocatalytic conditions (electrolyses between -1.1 V to -0.6 V vs RHE, Figure 3), hydrogen (H₂) was found to be the major product that we identified arising from the C吸附 support. Besides, carbon monoxide (CO), methane (CH₄) and ethylene (C₂H₄) were evolved, consistent with reports in literature. Regarding the non-volatile products, formate (HCOO⁻) was identified in overall faradic efficiency of 7%. To increase faradic efficiency towards C-products, we are now investigating alternative supports displaying limited proton reduction abilities. As well, modulating the amount of electrocatalytically active nanoparticles on the support would enable fostering the performance of the resulting electrode and improve its selectivity towards the CO₂ electroreduction.

**Oxygen evolution reaction**

Decreasing the overpotential of oxygen evolution reaction and optimizing the content of the noble metals used in the catalyst are vital steps for achieving sustainable hydrogen or CO₂ reduction processes. The present work focuses on the preparation and study of high surface area Cl-free IrO₂ nanoparticles of various size and shape via modified Adams fusion method.[6] The applied approach allows investigating the effects of particle size, morphology, and the nature of the surface species on the OER activity of IrO₂. Iridium oxide synthesized at 350°C, consisting of 1.7 ±0.4 nm particles (Figure 4) with a specific surface area of 150 m²·g⁻¹, shows the highest OER activity (45 ± 9 A g⁻¹ at 1.525 V vs RHE) surpassing activity of the industrial IrO₂–TiO₂ catalyst (14 ± 4 A g⁻¹ at 1.525 V vs RHE). Operando X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) studies indicate the presence of iridium hydroxo (Ir–OH) surface species, which are strongly linked to the OER activity. Preparation of larger IrO₂ particles using higher temperatures results in a change of the particle morphology from spherical to rod-shaped particles, which causes a decrease of the intrinsic OER activity due to the predominant termination of the rod-shape particles by highly ordered (110) facets.[7, 8]

The developed Adams Fusion method approach was further expanded for the preparation of novel OER catalysts with a decrease amount of IrO₂, based on Y–Ir, Yb–Ir, Bi–Ir and Pb–Ir pyrochlores (pyrochlore: A₂B₂O₆.₅+x, where A is Bi, Pb, Ae, Li ... and B is Ti, Sn, Nb, Ir, Ru, Os ...).[9] These materials are synthesized at moderate temperatures (500–575°C) and consist of highly crystalline iridium pyrochlore nanoparticles with surface areas up to

![Figure 3: High-angular dark field transmission electron microscopy image of the CuNPs@Cblack material (left) and faradaic efficiency for gaseous products and current densities versus applied potential for electrolyses at CuNPs/C₆₅₄₁/GDL in CO₂-saturated 0.5 M KHCO₃ aqueous electrolyte.](image)

**References II**


Progress in the Development of Tailored Catalysts for the Hydrogenation and Electrocatalytic Reduction of CO₂

40 m²·g⁻¹, which is a significant improvement compared to the traditional high temperature solid-state synthesis.

Electrochemical measurements in acidic media showed that yttrium and bismuth pyrochlore catalysts possess high OER activity approaching the activity of state-of-the-art IrO₂ nanoparticles. High intrinsic activities and stability behavior of yttrium iridium catalysts were correlated with the formation of the highly active IrOₓ surface layer due to leaching of the Y³⁺ cations into the electrolyte solution (Figure 4), revealed both experimentally and computationally using Density Functional Theory calculations. We are currently further developing materials for the more efficient use of IrOₓ for OER.

Figure 4:
Structures of IrO₂ (a) and pyrochlore (b), TEM images of 1.7±0.4 nm IrO₂ nanoparticles (c) and Y-Ir pyrochlore (d), OER activity of iridium pyrochlores, IrO₂ and industrial IrO₂-TiO₂ catalyst; scheme illustrating leaching of Y³⁺ from Y pyrochlore (f).
Beyond Copper: Novel Silver Foam Catalysts for Selective Hydrocarbon and CO Formation from CO₂

Scope of project

In the main focus of the previous project year were high-surface area metal foam catalysts suitable for the CO₂ reduction reactions (CO₂RR). Electrolysing strategies for the Cu based metal foam catalysts were further extended to permeable, carbon-free technical supports (e.g. metallic 2D meshes and 3D skeletons/sponges) which might be applicable in the future for gas-flow/liquid-flow electrolysis cells.[1]

A particular focus was on the stability and durability of these Cu catalysts under CO₂RR conditions which could significantly be improved by the selective suppression of C₁ reaction pathway (methane production). Identical location (IL) HR-SEM and HR-TEM were applied for the first time to study CO₂RR catalyst activation and degradation processes in depth.

Novel directions of catalyst design concern the electrodeposition of Ag based foam catalysts which show superior CO₂ efficiencies up to 100% at low overpotentials (-0.4 V vs RHE) and most intriguingly a high selectivity towards C₁ hydrocarbon (methane) formation at higher overpotentials (FECO = 50% at -1.5 V vs RHE). These novel foam catalysts are the first metallic CO₂RR electrocatalysts demonstrating profound activity towards hydrocarbon formation beyond Cu.

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, ethanol, propanol, 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. A number of catalyst-specific issues, however, still need to be addressed which are related to a lack of selectivity and long-term stability.

For a more tailored design of catalysts it is important to learn which surface sites and which particular chemical states of the catalyst are the most active ones towards CO₂ electroreduction. In particular, oxidative catalysts might undergo severe changes of their chemical state, their composition and morphology under those harsh experimental conditions which are relevant for the electrochemical CO₂ conversion. Therefore rational synthesis strategies need to be developed which allow for the production of highly selective and stable CO₂RR catalysts on the basis of a mechanistic understanding of the catalyst activation and degradation pathways.

Results and discussion

C₂/C₃ alcohol production on high-surface area oxide-derived (OD) Cu catalysts [2]

Potential-dependent CO₂RR were carried out on technical Cu mesh supports that were stepwise modified by

- electrodeposition of dendritic Cu catalysts under mass transfer control of Cu(II) ions followed by
- an extra 3 h thermal annealing at 300°C in air.

The initial electrodeposition of dendritic Cu activates the technical supports for highly efficient formate productions at low overpotentials (FE Formate = 49.2% at -0.7 V vs RHE) and in particular for C–C coupling reactions at higher overpotentials (FE Alcohol = 34.3% at -1.1 V vs RHE).

The subsequent thermal annealing treatment directs the CO₂RR product selectivity towards mult-carbon alcohol formation (ethanol/EtOH and n-propanol/n-PrOH) resulting into a total Faradaic yield of FE Alcohols = 24.8% at -1.0 V vs RHE (FE Alcohols = 13%). The maximum of the n-ProOH efficiency is observed at slightly less negative potentials of -0.9 V with FE n-ProOH = 13.1%.

Identical location (IL) SEM analysis was applied prior and after the annealing preparation steps and in addition prior and after CO₂RR to monitor severe morphological changes which

References


Author

Abhijit Dutta¹
Motiar Rahaman¹
Alberto Zanetti¹
Alexander Rudnev¹
Soma Veszttergomb¹
Peter Broekmann¹

¹ University of Bern
Synthetic Fuels

Beyond Copper: Novel Silver Foam Catalysts for Selective Hydrocarbon and CO Formation from CO₂

Figure 1:
Identical location (IL) HR-SEM and RH-TEM results demonstrating the morphological changes an electrodeposited nano-dendritic Cu catalyst undergoes upon thermal annealing (in air at 300 °C, 3 h) and CO₂RR at -1.0 V vs RHE.[2] The actually active catalyst is formed under reactive conditions of the CO₂RR.

go along with the formation of Cu₂O/CuO surface phases upon thermal annealing and their subsequent electroreduction under *operando* conditions of the CO₂RR. IL-SEM and HR-TEM analyses identify nano-dendritic Cu as being the active component for the desired production of multicarbon alcohols (Figure 1).

In addition, nano-dendritic Cu shows a remarkably high resistance against degradation with alcohol efficiencies that can be maintained on a high level (FE_{alcohol} = ~24% at -1.0 V) over 10 hours whereas the untreated electrodeposited catalyst suffers from a rapid and drastic drop-down in the ethylene efficiency from 33% to 15% (Figure 2).

The extraordinary stability of the annealed Cu catalyst can be assigned to a changed CO₂RR mechanism and, related to that, to the complete suppression of the coupled C1/C2 hydrocarbon pathway, thereby avoiding the accumulation of poisoning surface carbon species.

The introduced multistep approach of catalyst activation was successfully applied also to other support materials, e.g. Au and Ag meshes, resulting in similarly high yields of C2 and C3 alcohols as observed for the Cu mesh support.[2] Potential dependent product analysis (1 h electrolysis time) reveals a plateau region in the FE_{CO} in the broad potential window between -0.4 and -1.2 V vs RHE with CO efficiencies never falling below 90% (Figure 3). The drop down of the FE_{CO} at potentials below -1.1 V is anti-correlated with the rise in the FE_{H₂}. In an intermediate potential window between -1.4 V and -1.6 V there are C1 (methane) and C2 (ethylene) hydrocarbons formed with efficiencies reaching FE_{CH₄} = 50% and FE_{C₂H₄} = 5%. This is the first metallic CO₂RR catalyst beyond Cu that produces hydrocarbons in significant amounts.

Figure 2:
Long-term stability of the (a) electropolished 2D Cu mesh catalyst, (b) the electrodeposited nano-dendritic Cu catalyst on the Cu mesh and (c) the thermally annealed nano-dendritic Cu catalyst. Presented are the product distributions of the main CO₂RR products as function of electrolysis time. Alcohols formed in (c) are ETOH (C₂) and n-PROH (C₃).
Conclusions and next steps

Our study clearly demonstrates that high-surface area CO$_2$RR catalysts do not necessarily have to be based of NP/C-support systems. Metal foam deposition seems to be a valuable alternative to NP synthesis [3] yielding
- highly selective and
- stable CO$_2$RR catalysts.

So far, the reaction mechanisms of hydrocarbon formation on Ag catalysts are not well understood. Operando IR/Raman in combination with operando EXAFS/XANES techniques will be applied to shine light on this novel catalyst system. In addition, we will extend the metal foam approach to binary systems (e.g. Cu/Pd) to establish highly selective and energy efficient catalysts for formate production.

In addition, the specific impact of CO$_2$ transport on the reaction rate and the product distribution will be elaborated more systematically. [4, 5]
Synthetic Fuels

Progress in Co-Electrolysis Cells and the Development of Efficient Oxygen Evolution Catalysts

Scope of project

Carbon dioxide emissions represent one of the major environmental problems. Several strategies are considered to reduce CO₂ atmospheric concentrations and one of the most important is related to the energetic transition from a global energy scenario based on fossil fuels to one based on renewable energy sources. Wind and solar are promising energy sources and they are already implemented worldwide but their inherent intermittency often results in a mismatch between energy production and demand that renders the development of novel energy storage and conversion systems urgent [1].

A «classical» envisaged solution is the transformation of this excess electricity into storable hydrogen that can be subsequently utilized e.g. in fuel cells. But this excess energy can be also used to convert CO₂ into fuels or other useful chemicals [2]. This process will not only allow storing excess energy but also to close the CO₂ cycle, i.e. recycling of this greenhouse gas. Both of these energy storage solutions proposed are obtained by using adapted devices named electrolyzers, where H₂ is produced by water splitting and a co-electrolyser when CO₂ is transformed into fuels.

This work package focuses on the development of different aspects of (co)-electrolysis processes:

- improve the anodic reaction, oxygen evolution reaction (OER) which is critical in both processes;
- design of a co-electrolyser.

Status of project and main scientific results of workgroups

Co-electrolyser development

The efficiency of such a process depends on the cathode catalyst materials which need favourable electrokinetics towards CO₂ reduction as well as highly rational device engineering. Two novel cell configurations were investigated for CO₂ reduction from gas phase that are based on a highly rational design approach taking into account a variety of subtle, but significant details that appear to be ignored in previous cell designs [2].

The first configuration utilizes a bipolar membrane with the anion conductive (alkaline) side of the bipolar membrane facing towards the cathode. In this way, the cathode pH can be maintained at high values desirable for efficient CO₂ reduction. The cation conductive (acidic) side of the bipolar membrane, which faces the anode, prevents carbonate/bicarbonate species of the alkaline side to migrate to the anode and to be oxidized there to release CO₂. This latter process represents a major loss channel for CO₂ in an entirely alkaline membrane system. The bipolar cell configuration has been further optimized in a second cell configuration presented in this work, which enables highly improved energetic efficiency.

The CO₂ reduction reaction (CO₂RR) is pH dependent and in gas phase co-electrolysis systems, the reaction pH is defined by the type of polymer electrolyte. During co-electrolysis in the presence of gaseous CO₂, the following dominant reactions occur on an Au catalyst at the cathode side in alkaline conditions:

\[
\text{CO}_2 + \text{H}_2\text{O} + 2e^- \rightarrow \text{CO} + 2\text{OH}^- \quad \text{E} = -0.932 \text{ VRHE} \quad (1)
\]

\[
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad \text{E} = -0.828 \text{ VRHE} \quad (2)
\]

Generally, the alkaline system appears more promising for the purpose of CO₂RR, because in these conditions the parasitic hydrogen evolution reaction (HER) is disadvantageous when compared to acidic conditions.

However, if alkaline membranes are used in a co-electrolyser a severe problem occurs: the pumping of CO₂ from the cathode side to the anode side. The mobile ions inside an «alkaline» anion exchange membrane in the presence of CO₂ are expected to be rather carbonate (CO₃²⁻) and bicarbonate (HCO₃⁻) species than OH⁻ hydroxide ions.

It is evident from Reactions (1) and (2) that all cathode reactions lead to the formation of OH⁻ at the cathode in alkaline conditions. This is not only true for the actual CO₂RR, but also for the concomitant hydrogen evolution reaction. In abun-
Synthetic Fuels

Progress in Co-Electrolysis Cells and the Development of Efficient Oxygen Evolution Catalysts

dance of CO₂, these OH⁻ are transformed into (bi)carbonate anions. Due to the electrostatic field in the membrane during operation, the (bi)carbonate anions migrate to the anode side where they are oxidized into O₂ and CO₂ according to Reactions (3) and (4):

\[2 \text{HCO}_3^- \rightarrow \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- + 2\text{CO}_2\]  
\[\text{E} = -0.765 \text{V/RHE} \quad (3)\]

\[\text{CO}_3^{2-} \rightarrow \frac{1}{2} \text{O}_2 + 2\text{e}^- + \text{CO}_2\]  
\[\text{E} = -0.692 \text{V/RHE} \quad (4)\]

In other words, for each electron exchanged in the cell reactions, one-half (bi)carbonate anion must flow from the cathode side to the anode side in order to close the electric circuit. This parasitic «CO₂ pumping» from cathode to anode side provides a huge loss channel for CO₂ and therefore, makes «alkaline» AEM co-electrolyser systems intrinsically inefficient for the desired electrochemical reduction of CO₂. The formation of CO₂ at the anode side as a result of this CO₂ pumping effect was proven in the alkaline cell with results shown in Figure 1.

One possible solution to mitigate this problem of CO₂ pumping whilst maintaining alkaline conditions at the cathode is the use of a bipolar membrane instead of an entirely alkaline membrane. In such a configuration, the alkaline anion exchange side of the membrane is facing towards the cathode and the acidic cation exchange side is facing towards the anode. In principle, the acidic side of the membrane prevents the transport of (bi)carbonate species all the way to the anode. Instead, at the internal interface of the bipolar membrane between the alkaline and the acidic layers, (bi)carbonate anions react with protons from the acidic side to form water and CO₂.

The gas analysis at the anode side of a bipolar membrane cell in full co-electrolysis operation, i.e. using IrO₂-TiO₂ as anode catalyst for oxygen evolution reaction, is shown in Figure 1. It is clear that the release of CO₂ at the anode was significantly reduced, but not completely eliminated. Moreover, the bipolar membrane cell provided similar current densities as the alkaline cell, and the CO selectivity remained at the same order of magnitude as shown in Figures 2a and 2b.

Despite the significant results obtained with a bipolar membrane, the formation of water at the internal interface can result in membrane delamination and reduce the system stability.

An improved bipolar like cell configuration was proposed to solve this issue, the novel cell configuration [3]. The special design of the cathode catalyst layer in combination with an acidic Nafion membrane is expected to combine several advantages:

Figure 1: Volume flows of CO₂ produced at the anode side of full co-electrolyser cells with Au-based cathode and IrO₂-TiO₂ anode catalyst using different membrane configurations. The anode gas composition was analyzed using MS at various cell current densities in galvanostatic mode. Cells were operated at 40 °C under ambient pressure.

Figure 2:

a) Cathode polarization curves of CO₂ co-electrolysis cells with alkaline membrane, bipolar membrane, and «novel configuration» obtained from linear sweep voltammetry at 50 mV/s, 40 °C and ambient pressure. The cathode was fed with 50/50% vol. CO₂/Ar, while the anode consisted of Pt/C catalyst fed with pure H₂.

b) CO selectivities obtained in galvanostatic experiments at various fixed current densities.
Progress in Co-Electrolysis Cells and the Development of Efficient Oxygen Evolution Catalysts

- High catalytically active surface area for the CO₂RR is provided by the «alkaline» anion exchange ionomer within the cathode catalyst layer providing an optimal alkaline environment for the reduction of CO₂.
- The membrane delamination is solved by the morphology of the alkaline ionomer thin film which is adjusted to the rough surface of the cathode catalyst layer, here, H₂O and CO₂ formed at the interface can laterally escape «in plane» at the perimeter of these interface spots back to the cathode electrode pore structure.
- The cation exchange membrane guarantees that the (bi)carbonate anions from the alkaline cathode ionomer are prohibited from being transferred to the anode side, thus avoiding parasitic CO₂ pumping from cathode to anode side.
- And finally the use of a cation exchange membrane provides lower electrical resistance than anion exchange membranes or bipolar membranes enabling increased energetic efficiency of the proposed co-electrolysis cell design (Figure 2).

Oxygen evolution reaction investigation on perovskites

The field of perovskite electrocatalysts studied as thin porous electrodes is relatively new, and therefore, as a first approach, the effect of the processing conditions on the perovskite electrochemical activity has been examined, particularly the mixture of the Ba₅Sr₅Co₉Fe₃O₂₀₋ₓ (BSCF) perovskite with carbon support such as acetylene black (AB).

To gain a fundamental understanding of the nature of BSCF and AB interaction, the X-ray absorption near edge structure spectroscopy (XANES) technique has been used to study the electronic structure of BSCF as prepared and after being processed with AB to prepare composite electrodes [4]. Performing this study we have shown for the first time that electronic effects play an important role in the OER catalytic activity of BSCF/carbon composite electrodes compared to the single material electrodes in alkaline environment.

To summarize, this finding provides a novel understanding of perovskite/carbon composite electrodes, consequently opening new perspectives for the optimization of the composite electrodes or for tailoring new perovskite compositions.

In the recent publication we have revealed, for the first time, by performing operando X-ray absorption measurements (XAS) that the electronic and local structure of perovskite oxide catalysts changes during the water splitting reaction (operando conditions) [5]. Particularly, we could demonstrate that the key for highly active catalysts is a self-assembled, (oxy)hydroxide top layer. This is completely different from the message of several water electrolysis-related publications, which consider the surface of oxide catalysts as an ideal, atomically flat surface.

This new concept completely revolutionizes the currently most accepted view of design principles for highly active perovskite catalysts. It also points towards the paramount necessity of investigating other perovskite properties under operando conditions in order to develop accurate design principles for highly active perovskite catalysts.
Work Package «Assessment of Storage Systems» at a Glance

The assessment of energy storage is a crosscutting effort through various applied storage technologies and scales of investigation: on a technology level, from an energy system’s perspective, and about the socio-economic impact.

In 2017 research has been carried out in basically all domains mentioned above, led by and including all groups (including the institutions Paul Scherrer Institute, University of Applied Sciences Rapperswil, Swiss Federal Institute of Technology Lausanne, University of Geneva, Swiss Federal Institute of Technology Zurich, and Lucerne University of Applied Sciences and Arts).

Through a top-down approach, the Swiss TIMES model has been employed to analyse the impact of electricity storage options and alternative energy sources like biomass. The sensitivity to boundary conditions as well as the performance of storage technologies in conjunction with intermittent (renewable) energy sources like wind and solar photovoltaics (PV) have been studied. Potential for storage to reduce overall costs and improving reliability under certain conditions have been shown. According to the study, in particular batteries can play a major role with increasing wind and solar PV installation. A detailed investigation of the Advanced Adiabatic Compressed Air Energy Storage (AA-CAES), power-to-gas and battery as storage options provided further insights from the technology side.

Research on the levels of technology and system in terms of life-cycle costs and emissions have been complemented by a socio-economic perspective pursuing three approaches. A system-dynamics model has been introduced to understand competitiveness of storage options, the role of innovation and patents has been studied, and finally, in a collaboration with an external energy intelligence partner, a technology-neutral economic model was set up to search for barriers of and to technological change. It becomes more and more evident that technology is an enabler, but studies need to address the system integration and performance as well as the overall societal embedment, which is even more important to realize the «Energiewende».

Following the Swiss Energy Strategy 2050 by the Swiss Federal Office of Energy’s vision of future energy supply and demand a first step into the modelling of the Swiss energy system in conjunction with energy storage options has been made. Based on household and neighbourhood demand curves in high temporal resolution an optimization model for power distribution and storage operation has been built. This requires not only accurate data on loads/demand, but furthermore a deep understanding on technology characteristics from renewable energy sources and energy storages. For example, the joint operation of residential battery systems to store the fluctuating output of rooftop-mounted PV is of interest. The level of autonomy from the distribution grid versus the levelized cost of storage are a major concern. Data on PV production forecast depending on the geographic position and particularities of the installation (roof orientation, inclination, shading etc.) is required here and part of an investigation with external partners. It is well considered that PV together with batteries are just one scenario among a population of alternatives for the future energy landscape in Switzerland.

On the applied technology level the aim of Work Package 5 «Assessment of Storage Systems» is to compare existing demonstrators of emerging energy storage concepts. Together with other SCCERs, in particular BIOSWEET and Mobility, the properties and performance of demonstrators were studied and compared. The demonstrators under investigation include high-temperature electrolysis (solid oxide electrolysis cell, SOEC) in Rapperswil, the hydrogen lab (fuel cell and e-mobility) in Martigny, the Small-Scale Demonstrator Sion (SSDS) which converts solar energy to synthetic hydrocarbons, and PSI’s Polymer Electrolyte Membrane (PEM) based electrolyser for power-to-gas applications. Here, not the technological aspects per se were the focus of the investigation; the overall performativity integration of these storage options on the system level and with respect to higher-level societal goals (reduction of CO2 emissions, security of supply etc.) are our main concern here.

In summary, 2017 was a successful year yielding many insights in all domains. Missing links especially around data availability and interdisciplinary research have been identified. Closer collaboration within the SCCER Joint Activities are aspired, and additional side projects with external project partners launched.
Investigation of AA-CAES Plant Configurations and Grid Integration

Scope of project

Phase I of this SCCER project provided a proof of concept of the Advanced Adiabatic Compressed Air Energy Storage (AA-CAES) concept in the form of a working pilot plant with a combined sensible/latent thermal energy storage (TES). The goal of Phase II is to assess whether economic operation of an AA-CAES plant is possible in Switzerland’s (future) energy system. The methodology focuses on the system analysis of AA-CAES plants on three interconnected levels.

In the first level, the energy market is modelled, including scenarios of future energy systems as well as general economic, technical, and regulatory considerations about the plant siting and layout. The second level focuses on the electricity grid to allow assessing the performance of an AA-CAES plant operating under realistic (modelled) conditions in the grid. The third and most detailed level is concerned with the plant itself and consists of dynamic component models for the turbomachinery, the TES, the cavern, and the electrical equipment. In the third level, detailed life-cycle cost analyses and life-cycle assessment are also carried out.

By connecting the three levels, a detailed model of an AA-CAES plant within the Swiss energy system will be realized that will provide unique insights into whether and how an AA-CAES plant can be operated profitably in Switzerland’s future energy system.

Status of project and main scientific results of workgroups

The main goal of the first year was to set up a workflow between the three levels, to develop interfaces between the models used in the three levels, and to perform first analyses to determine suitable plant sites, sizes, and layouts.

Level I: Plant layout, siting, and costs

The industrial project partners ALACAES and MAN Diesel & Turbo Schweiz AG defined a new plant layout at the beginning of the project. The layout considered the availability of existing turbomachinery and experience gathered during Phase I of the project. The main characteristics of the plant are two-stage compression and expansion trains with maximum pressure ratios of 10 for each stage. The plant uses two caverns, each equipped with one TES. The first cavern operates at a constant low-pressure level of 10 bars, while the second cavern stores the high-pressure air that reaches a maximum of 100 bars. The storage capacity of the plant is 500 MWh, which requires a total high-pressure cavern volume of 170‘000 m3. The power rating was set to 100 MW for both charging and discharging. These capacity and power ratings are not fixed but will be optimized once higher-fidelity market and grid models become available.

In the first year, we have explored the possibility of converting a decommissioned military cavern into an AA-CAES plant. The idea is to decrease the necessary excavation volume to reduce construction costs. Armasuisse provided a list of suitable decommissioned military caverns. Starting from this list, potentially suitable caverns were selected using two criteria, namely the estimated cavern volume and the distance to the nearest node in the electricity grid. The objective is to reduce cavern excavation costs, costs of the transmission lines between the cavern and the nearest grid node, and the environmental impact of transmission lines.

In Figure 1, we present the estimated costs required to enlarge the existing cavern to 170‘000 m3 and to connect it to the nearest grid node, based on 175 CHF/m3 of excavation and 125 kCHF/km of grid connection. Taking into account also geological considerations, the most promising cavern

List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA-CAES</td>
<td>Advanced Adiabatic Compressed Air Energy Storage</td>
</tr>
<tr>
<td>TES</td>
<td>Thermal Energy Storage</td>
</tr>
</tbody>
</table>

References


Figure 1:
Estimated additional cavern excavation costs to enlarge existing caverns to 170‘000 m3 and transmission line construction costs based on the distance of the decommissioned military cavern site to the nearest grid node.

Authors

P. Roos1 J. Roncolato2 M. Barbato2 J. Garrison1 T. Demiray1 T. Motmans2 W. Schenler2 A. Fuchs1 A. Haselbacher1 A. Steinfeld2 G. Zanganeh4 P. Jenny5 M. Scholtysik4 E. Jacquemoud5 F. Amberg6 F. Pacher5 J. Mühlethaler7 M. Arnal8

1 ETHZ
2 SUPSI
3 PSI
4 ALACAES
5 MAN Diesel & Turbo Schweiz AG
6 Amberg Engineering
7 Swissgrid
8 BKW
Investigation of AA-CAES Plant Configurations and Grid Integration

candidates are three sites in the Aaremassif area, namely one site near Göschienen and two sites in the region of Visp. The calculated added costs for cavern excavation and grid connection of these sites lie between 28 and 30 Mio. CHF. One conclusion of this first sitting study is that reusing decommissioned military caverns may not be particularly advantageous. The primary reason is that the volumes of existing caverns are relatively small, so the cost saving of reusing existing caverns is correspondingly small also. In addition, the requirements of a minimum overburden of 1000 m to hold the maximum pressure and the availability of high-quality rock in Switzerland is likely to restrict plant sites to the Aaremassif.

**Level II: Evaluating the grid and economic impact of AA-CAES in Switzerland**

An analysis was conducted to evaluate the relative benefits of adding an AA-CAES plant at several unique positions within Switzerland’s high-voltage electricity network. The power system implemented in this model is a representation of the full high-voltage transmission network of Switzerland as well as an aggregated representation of the surrounding countries (Germany, France, Italy, and Austria). Since Switzerland is highly interconnected with its neighboring countries, it is critical to capture those countries’ generators and costs. This work assesses the transmission system and dispatch cost benefits of adding a 100 MW AA-CAES facility in eight locations of the Swiss electricity grid. The locations were chosen based on the above-mentioned cavern site selection with additional sites outside of the Aaremassif, but still within the Alps, to get a general picture of the sensitivity to the location within the grid. This assessment uses a nonlinear AC power flow model that includes multi-period dispatch optimization to simulate this interconnected electricity network. The AA-CAES plant characteristics in the model are represented by its power and capacity ratings.

Preliminary results showed that the AA-CAES plant is heavily utilized, which indicates that its operational abilities and costs are useful to the system. The addition of storage does increase the occurrences of high line loading, but this occurs because the storage system is enabling greater utilization of the grid to increase the amount of energy provided by low-cost nuclear, coal, and biomass resources. By switching to lower cost sources, the presence of a single AA-CAES plant is able to achieve an annual cost savings of up to 6.3 million Euros per year across the five countries modeled. Based on the higher cost savings of the southwestern AA-CAES locations, it appears that enhancing the transmission corridors between Switzerland and France achieved better system benefits.

It is important to note that the results so far derived from this analysis should only serve to show the potential of this modeling framework. Future additions to the assumptions in this work could significantly change the results and indicate different relative benefits of the simulated plant locations. Most notably, changing from the represented transmission network to the real physical transmission network of Switzerland could yield very different results. Additionally, adding the potential for the AA-CAES plant to participate in the reserve markets could yield very different optimal operating strategies for the storage system and require different plant layouts. Updating these aspects, as well as other minor improvements, will be the primary near-term focus.

**Level III: Plant simulation, coupled LCA and cost assessment**

**Plant simulation**

The work started from an AA-CAES plant model developed in Simscape into which a one-dimensional TES code is integrated. The cycle consists of 5-hour charging and discharging phases with mass flow rates of 200 kg/s. Assuming a constant isentropic efficiency of 0.85 for the turbomachinery, after 500 cycles an overall efficiency of approximately 74% was reached, defined as the ratio of the energy extracted from the turbines divided by the energy consumed by compressors. Further work will address the incorporation of realistic turbomachinery efficiency maps and their transient operation using data provided by MAN Diesel & Turbo Schweiz AG. The efficiency will be modelled as a function of the compression ratio and mass flow rate as depicted in Figure 2. It is anticipated that these efficiency maps as well as the precise operation during
the charging and discharging phases will play an important role in assessing the performance of alternative plant layouts.

**Coupled life-cycle and cost assessment**

An analysis that coupled life-cycle assessment with life-cycle cost analysis of an AA-CAES plant configuration was performed [1]. For the cradle-to-gate and decommissioning analysis, a parameterized life-cycle inventory was compiled based on the literature and input from project partners. For the operational phase, an in-house scheduling model based on economic optimization for energy arbitrage was coupled with hourly projections of electricity spot market prices and hourly average supply mixes from Swissmod [2]. This model was constrained by using an exogenous amount of spinning reserve to provide secondary reserve power and energy.

The results show that the environmental impact of the AA-CAES infrastructure is 2–4 times smaller than for pumped hydro storage. The results also show that the environmental impact of the combined sensible/latent TES is 3–5 times smaller than an oil-based TES from the literature [3]. The results for the operational phase show that the system charges mostly overnight when prices are low, which is related to a larger share of fossil-based technologies in the supply mix due to cheap imports. This result is not technology-specific, however, and could be complemented with further analysis based on a marginal approach.

The cost analysis shows that the capital investments are smaller per unit of power rating for AA-CAES than for any other bulk electricity storage technology. The levelized cost of electricity of AA-CAES is also low due to the long lifetime and low operation and maintenance costs of the system. Based on historical energy and secondary reserve prices, it is clear that reserve revenue dominated energy arbitrage revenue and the amount of secondary reserve should be maximized, even as this reduces energy revenue, see Figure 3.

All in all, the outcomes of this work suggest that AA-CAES is a cost-effective solution with small carbon footprint, thereby underlining its potential for bulk electricity storage.

**Figure 2:** Example of a compressor efficiency map as a function of the mass flow rate (mfr) and the compression ratio β.

**Figure 3:** Testing effect of secondary reserve power levels on scheduling pattern and revenue with 2016 EPEX prices, for winter.
Assessment of Energy Storage at the Energy System Level

Scope of project

The main objective of the work package is to define the role and the requirements of energy storage within defined Energy Systems compliant with the Swiss Energy Strategy 2050. To this end, we model energy systems and the value proposition of energy storage for those systems at high temporal resolution (≤1 hour) and at various geographical scales.

At the local scale, the University of Geneva (UNIGE) is initially focusing on individual dwellings and analysing batteries performing various applications from the consumer perspective (i.e. reducing the electricity bill).

At the national scale, we have built a dedicated optimisation model of the Swiss power sector including neighbours with a temporal resolution of 1 hour.

Finally, we are also analysing the impact of solar and wind intermittency on the cost of future supply incorporating storage. In order to get data and define scenarios, we are collaborating with utilities and other SCCERs (including joint SCCER activity on modelling and scenarios). UNIGE also collaborates with PSI-LEA, ETHZ and HSLU in the assessment of storage technologies for different applications, e.g., batteries and thermal storage.

Status of project and main scientific results of workgroups

Local scale

So far, UNIGE has focused on individual dwellings with solar photovoltaics (PV) and residential battery storage given the increasing penetration of PV in the built environment and the growing interest in energy storage systems located very close to consumers.

Since residential batteries are not economically attractive yet, we study various applications which residential batteries can perform for consumers (i.e. to reduce the energy bill, namely PV self-consumption, demand load-shifting, avoidance of PV curtailment and demand peak-shaving) in order to understand to which extent benefit stacking could contribute to create a positive economic case.

In particular, we determine the optimal battery technology and size depending on the type and number of applications combined. Six different battery technologies currently available in the market are considered (i.e. NMC, LFP, NCA, LTO, advanced lead-acid and VRLA).

Furthermore, we analyse the impact of the type of demand profile by comparing results across dwellings in Switzerland and dwellings in USA in collaboration with the Massachusetts Institute of Technology (MIT).

Our methodology includes a linear programming optimization to solve the residential energy management problem. It minimises the cost of the daily electricity bill, taking as parameters the electricity demand, PV generation, battery characteristics as well as various storage applications. The battery schedule is optimised with a temporal resolution of 15-minutes on a daily basis and we assume perfect day-ahead forecast of the electricity demand and PV generation to determine the maximum economic potential of batteries regardless of the forecast strategy used.

National scale

To analyse the potential role of energy storage in the national electricity supply of Switzerland a dedicated optimization model was devised.

It is a classic linear dispatch model obtaining a minimum cost solution for the electricity supply under fixed demand conditions. The objective function includes all variable and fixed costs. The mode variables cover both the operation (notably the hourly electricity generation from power plants) and the generator capacities. The power system operation is optimized for all hours of a single year. The neighbouring countries of Switzerland are explicitly included, in order to accurately describe cross-border power exchanges.

Using this model the role of storage capacity can be investigated from different perspectives: a prescriptive analysis makes use of the fact that the model results correspond to a social optimum. Based on this,
Assessment of Energy Storage at the Energy System Level

Research questions related to the ideal capacity and use of additional storage capacities can be addressed. For predictive analyses the optimization’s resemblance to idealized free market conditions can be exploited to answer questions centred on the impact of changes to the system, such as the installation of additional storage capacity.

Corresponding studies are work in progress, see for example Figure 1 which includes results of the model for various supply mixes depending on the PV and wind penetration in Switzerland.

Finally, UNIGE is also analysing the intermittency patterns of PV and wind generation across Switzerland using historic time-series of environmental variables over the last eight years with high temporal resolution of 10 min. We use these data as basis to calculate the energy storage needs and determine the levelised cost of various storage technologies.

Later, it will be interesting to compare hybrid systems (comprising renewable and storage technologies) with traditional technologies, nuclear and hydro, depending on various scenarios across the Swiss energy transition.

Solar irradiance and outdoor temperature have been obtained from a network of 26 automated measuring stations (one by canton) across Switzerland deployed by MeteoSwiss. For wind, we consider 36 existing wind turbine sites (with capacity >100 KW) across Switzerland as well as alternative potential locations.

Figure 1: Example of the output of the national-scale optimization model. We show the average weekday dispatch in summer (top) and winter (bottom) in Switzerland for different shares of PV and wind power as a fraction of the yearly demand (left: status quo, far right: 50%). In the high-renewable case, overproductions in summer are met with curtailments of electricity.
Assessment of Energy Storage at the Technology and Energy System Level

Scope of project

In 2017, PSI-LEA (Laboratory for Energy Systems Analysis) was involved in the assessment of energy storage (ES) technologies at the technology level and at the system level, collaborating mainly with ETHZ, University of Geneva and HSLU. The research activities included a comparative environmental and economic evaluation of different electricity storage technologies, an in-depth evaluation of Advanced Adiabatic Compressed Air Energy Storage (AA-CAES) in Switzerland, an economic and environmental assessment of different battery technologies, and the evaluation of biomass as feedstock for synthetic methane production. Furthermore, the Swiss TIMES model was used to investigate the role of electricity storage within the future Swiss energy system under various boundary conditions and scenarios.

Results show that the technology-specific competitiveness of ES technologies strongly depends on the storage period; system efficiency is the main driving factor for the environmental performance. System analysis reveals that power supply systems with large shares of intermittent renewables will profit from integration of ES in Switzerland and operate more cost-efficiently.

Status of project and main scientific results of workgroups

Assessment of energy storage at the energy system level

At the energy system level, ongoing research activities aim at a better understanding under which boundary conditions energy storage will play a role in the Swiss future energy system and at quantifying economic and environmental benefits and drawbacks of implementing various energy storage technologies. Some of the research activities were carried out in collaboration with the Research Center for Energy Networks at ETH Zurich [1] and Sherbrooke University in Canada [2].

Figure 1 shows – as an exemplary result – the requirement of electricity storage capacities within the Swiss electricity system for a large range of generation and demand scenarios in year 2050 [1]: As soon as intermittent generation from wind and solar power reaches certain levels (corresponding to installed capacities larger than 2 GWel), storage technologies need to be added to the system in order to operate in the most economic way and batteries seem to be the most cost-effective option.

List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA-CAES</td>
<td>Advanced Adiabatic Compressed Air Energy Storage</td>
</tr>
<tr>
<td>ES</td>
<td>Energy Storage</td>
</tr>
<tr>
<td>GHG</td>
<td>Greenhouse Gas</td>
</tr>
<tr>
<td>LCOES</td>
<td>Levelized Costs of Energy Stored</td>
</tr>
</tbody>
</table>

Authors

Christian Bauer
Xiaojin Zhang
Evangelos Panos

1 PSI
Assessment of energy storage at the technology level

At the technology level, the research activities focused on the following aspects:

- finalization of a first, consistent environmental and economic comparative evaluation of electricity storage technologies for different storage periods and scales [3];
- an in-depth environmental and economic assessment of AA-CAES [4];
- the completion of the technology portfolio for power-to-gas energy conversion systems [5, 6];
- an in-depth environmental and economic comparative evaluation of various current battery technologies for different stationary applications.

All these partially completed, partially ongoing activities were and are carried out in collaboration with research partners from the SCCER HaE community, namely the Chair for Energy Efficiency at the University of Geneva, the Energy Politics Group at ETH Zurich, the Energy Storage research group at Lucerne University of Applied Sciences and Arts, the Professorship of Renewable Energy Carriers at ETHZ, and others.

Figure 2 shows some exemplary results from the environmental and economic comparative evaluation of electricity storage technologies for different storage periods and scales [3]: The technology-specific competitiveness of ES technologies strongly depends on the storage period; system efficiency is the main driving factor for the environmental performance of ES technology application.

Figure 2: Levelized costs of energy stored (LCOES) vs. greenhouse gas (GHG) emissions of electricity, supplied by different storage technologies (1 MW systems); ranges represent variations in terms of technical factors (lifetime, efficiency and costs) and electricity types (upper range: Swiss grid supply mix, lower range: Swiss wind supply) and price (0–0.15 EUR/kWh); from left to right: short, medium- and long-term storage [3].
Assessment of Energy Storage at the Technology and Socio-Economic Level

Scope of project

Several members of ETH Zurich’s Energy Politics Group were conducting research for HaE’s research on the assessment of energy storage (ES). Work at the technology level, focused on the life-cycle cost aspect of different storage technologies. To this end, a database on cost and technical parameters as well as a levelized-cost of electricity storage model was developed. At the socio-economic level, we performed three activities.

- A systems dynamic model was developed to analyze the effect of different mobility scenarios (driven by different policy incentives) on the competitiveness of storage technologies in stationary applications.
- We analyzed learning patterns of different storage technologies, based on a newly built patent data base covering different storage technologies and interviews with industry experts.
- We performed an analysis of barriers for distributed flexibility offers in energy market participation together with a new industry partner.

Status of project and main scientific results of workgroups

Assessment of energy storage at the technology level

The Energy Politics Group contributed to the assessment of energy storage on the technological level in a joint initiative with PSI’s Laboratory for Energy Systems analysis and University of Geneva’s Chair for Energy Efficiency.

The common objective of this initiative is to achieve an integrated environmental and economic assessment of various battery storage technologies. Therefore, we strive to assess lifecycle CO₂ emissions (LCE) as well as lifecycle cost (LCC) based on a probabilistic and consistent assessment model. The same input parameters are used for both parts of the analysis where sensible (e.g., application definitions, technology characteristics) and a consistent analysis of uncertainty (e.g., efficiency, lifetime, end of life and depth-of-discharge influence both LCE and LCC) is ensured.

The Energy Politics Group contributed to this initiative by developing the integrated probabilistic assessment model and by conducting the LCC analysis based on a newly developed ES database of technical and cost data. The assessment model covers six different battery technologies in five distinct applications across three different geographies (Switzerland, Germany and Poland).

Preliminary results show very strong differences in the role of the use phase vis-à-vis the manufacturing phase for the two dimensions LCE and LCC.[1]

Assessment of energy storage at the socio-economic level

Three key activities were carried out by the Energy Politics Group to assess ES at the socio-economic level.

First, we developed a system-dynamic simulation model to assess competitiveness of different battery technologies over time. The model provides insights into potential future market shares of a battery technology under different scenarios of electric mobility adoption. Basis for the calculation are experience curves for the costs of the technologies investigated, which were established based on the above mentioned ES database. Based on stochastic modelling, we calculate the share of the overall investment decisions in the market, in which the investors would opt for a certain technology. First results indicate that in the reference scenario, Li-ion batteries are outcompeting other technologies over time in most applications.

Second, ongoing research is zooming in on technological learning, which is essential to make storage technologies market-ready. Thus far, very little is known about differences in patterns of innovative activity between different technologies. To address this gap, we characterize different storage technologies (fly-wheels, lead-acid batteries, super-capacitors and lithium-ion batteries) based on the type of innovation exhibited by them. We use patent analy-
Assessment of Energy Storage at the Technology and Socio-Economic Level

sis (top 100 cited patents for each technology) and in-depth interviews with research institutions, manufacturers, project developers and industry experts (13 interviews in total) to understand the relative emphasis on product and process innovation and the capabilities required for innovation in the technologies.

Figure 1 shows some exemplary results from the patent analysis for lithium-ion batteries. We find that product and process innovation both are important and closely interlinked for lithium-ion batteries.

Third, the Energy Politics Group established a cooperation with the company EnerNOC to assess barriers for distributed flexibility offers in energy market participation. This is an add-on to the original research proposal. Available flexibility options (including ES) have thus far only been rarely exploited. Our study attempts to improve our understanding of this situation by conducting an in-depth literature review of barriers, complemented by expert interviews. We also develop a technology-neutral economic model, comparing Germany, Great Britain and Texas (ERCOT).

Our results indicate that barriers have not been resolved over time. The most commonly observed barrier is that markets to value flexibility are designed based on traditional, centralized generation assets. Therefore, standards for contracting and operational requirements hardly/seldom enable distributed flexibility units and the role of aggregators remains unclear. Our model reveals, that removing barriers adds significant value and would enable activation of further distributed flexibility in all analysed geographies.[3]
Assessment of Energy Storage Demonstrators

Scope of project

Within the SCCER Hae, four technology demonstrators are currently under development. The demonstrators differ in scale and technology but provide sector coupling and power storage services. The assessment activity shall ensure that the findings and results obtained by the different systems find their way fast into the community allowing fast learning, error prevention. The demonstrators are located at various locations, like High Efficiency Power-to-Methane Pilot at HSR Rapperswil, the Grid-to-Mobility Demonstrator and the Small-Scale Demonstrator at EPFL Valais and the ESI Platform at PSI, Villigen. The overarching scope of the demonstrators are:

- to design superior power-to-gas systems using technologies developed in Switzerland;
- to bring them to technology readiness level (TRL) 6;
- to coordinate the assessment and analysis of demonstration plants within this SCCER «Heat and Electricity Storage» (HaE) and other SCCERs, particularly SCCER «Biomass for Swiss Energy Future» (BIOSWEET) and SCCER «Mobility».

The following status summary covers the High Efficiency Power-to-Methane Pilot, the Grid-to-Mobility Demonstrator and the Small-Scale Demonstrator. The status of the ESI platform is given separately.

Status of project and main scientific results of workgroups

In 2017, the academic partners designed, ordered and installed their research equipment. Several meetings were organized in order to exchange the experience and preliminary results. It is planned to compare the demonstrators with each other. Results are expected as from 2018.

As a perspective for the end of the SCCER HaE phase II the academic partners involved in this work package will jointly release their results, especially on the specific efficiencies of their Power-to-Gas technology. For this purpose, it is expected to follow a harmonized assessment protocol suggested in a forthcoming publication [1] and to combine it with scientific research of Life Cycle Assessment of Power-to-Gas technologies [2].

HSR Rapperswil—High Efficiency Power-to-Methane Pilot

Within SCCER HaE Phase I the first Power-to-Methane pilot was built up in Switzerland at the University of Applied Sciences Rapperswil (HSR).

It was found out that the degree of efficiency plays a key role for the economics and the environmental impact of Power-to-Methane plants, which is characterized by the input of the electricity used in the plants. The improvement of the efficiency reduces the cost and the environmental impact of the produced gas. The use of renewable electricity reduces the environmental impact of the produced gas [3].

In SCCER HaE Phase II the University of Applied Sciences Rapperswil is realizing a High Efficiency Power-to-Methane Pilot (HEPP). The project runs from 2017 to 2020. The aim of the project is to increase the degree of efficiency and to make the technology applicable for the industrial use.
The main achievements of HEPP are realized with the integration of a high-temperature electrolysis (solid oxide electrolysis cell SOEC) to the plant and the development of a new heat management: The waste heat from catalytic methanation is used for the supply of the SOEC. Furthermore, high performing catalysts are tested and prepared for the use in a Power-to-Methane plant [4].

In 2017 the funding is completed with the project partners and the piping and instrumentation diagram is developed. Scientific results are expected towards mid-2018.

**EPFL Valais/Wallis, Martigny – Grid-to-Mobility Demonstrator**

The demonstration site in Martigny currently hosts several demonstration projects with the aim of evaluating the performance, the technical feasibility, the advantages and limitations and defining potential applications of several energy conversion and storage technologies (Figure 2).

Within the frame of the SCCER HaE phase I, the goal was to develop a demonstration-scale dual-circuit redox flow battery which is able to produce hydrogen while being discharged chemically. The goal was achieved in the sense that the all-vanadium flow battery was characterised and that hydrogen was successfully generated [5]. However, the chemical discharge of the positive electrolyte was still to be improved and the overall system optimised.

In SCCER HaE phase II, it is planned to continue to work on the same system both at the research and the demonstration scales. In 2017, we focussed on the understanding of the reaction of hydrogen evolution at higher pressures and in particular on a specific solution for an external discharge of the positive electrolyte. The latter one consists in an electrolysis cell performing the reduction of V(V) at the negative electrode and the reaction of water oxidation at the positive electrode. The overall efficiency of the system (electricity to hydrogen) was measured to be at least 40%.

It is expected to improve this efficiency with different optimisations to be conducted in the next years. Alternative approaches will also be investigated in the next years.

Regarding the demonstrator project Grid-to-Mobility, it is planned to be fully functioning by the end of 2017. It includes a redox flow battery feeding a fast charger for electrical cars and feeding an electrolyser generating hydrogen for a refilling station for hydrogen vehicles. The first characterisation results are being obtained currently and most of the results will be obtained in 2018.

![Figure 2: Process scheme of grid-to-mobility demonstrator at EPFL in Martigny.](image-url)
The Small-Scale Demonstrator Sion (SSDS) project was launched at the beginning of 2016. The project aims at demonstrating the technical feasibility of the conversion from solar energy to synthetic hydrocarbons.

The average power of the installation is set to 2 kW, which corresponds to the global average energy consumption of a single individual.

The installation should also serve as a test bench for emerging technologies that have to be investigated under real-working conditions. Furthermore, it serves as an educational platform, e.g. for students’ semester- or master projects.

The main components of the system are solar cells (four different types installed at two different inclinations), batteries (lead acid and nickel metal hydrides), a Polymer Electrolyte Membrane (PEM) electrolyser, a metal hydride storage system, a metal hydride compressor and chemical reactors converting hydrogen and carbon dioxide into synthetic hydrocarbons (Figure 3).

In the course of the year 2016 and the first half of 2017, many of the core components (metal hydride storage, metal hydride compressor, methanation reactor) of the demonstrator were developed, built and tested in-house. The development and assembly of these devices was documented in [6]. The development of this installation was also the opportunity for two students to perform semester and master projects.

As the demonstrator will be installed in the heart of the main building at EPFL Valais/Wallis in Sion, many modifications had to be performed in order to comply with safety and technical requirements. These modifications are currently being performed and the full installation is expected to be commissioned in the late fall 2017.
**ESI – Energy System Integration Platform**

**Scope of project**

The Energy System 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 2017 focussed on commissioning both the basic platform infrastructure (support structure for individual sub-systems, supply of media – gases, cooling-water, electricity, safety system & controls) and all sub-systems including the main processes on the platform.

In parallel, the intensive interactions have been continued between the technology oriented sub-systems and the teams working on cross-cutting scientific topics such as catalysis research (synthesis and characterization), process diagnostics tools (sampling, analysis, process validation) and energy system modelling (energy scenarios, technology assessment, life cycle analysis).

The dynamic Polymer Electrolyte Membrane (PEM) based electrolyser which increases the overall process efficiency by electrochemical production of hydrogen (at up to 50 bar) and the gas cleaning system are ready to convert electric energy to dry, pure hydrogen in 100 kW scale, which in turn can be stored in the tank. In a first series of experiments, the system has been 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 have been filled the first time in early 2017. With this sub-system, storage of even highly fluctuating electricity can be realised in pilot scale. The energy stored in form of H₂ can subsequently be used for mobility purposes (fuel cell cars) or for re-electrification in PEM fuel cells, especially as positive balancing power service.

The fuel cell platform which allows dynamic and, due to the pure oxygen, highly efficient re-electrification of the...
stored hydrogen without significant emissions is now in operation with one pilot fuel cell stack. Additional fuel cell stacks (50 kW each) are currently being built and will be implemented soon. With the commissioning of the fuel cell module, the complete efficient and clean Power-to-Power-path via direct use of pure hydrogen produced from water is now operational.

An additional container module for Fuel Cell Systems is currently being realized with the target to enable the commissioning of fuel cell systems (from small scale series production) and to enable qualification tests of commercial systems in a 100 kW-Scale.

Within the ESI project framework catalytic fluidised bed reactors are being used to convert hydrogen and carbon oxides to methane, i.e. synthetic natural gas (SNG). This way, the excess energy from fluctuating renewable energy sources (converted in a first step to pure, clean and efficient hydrogen) can not only be stored in dedicated gas storage units or as limited addition (<2%) to natural gas in the existing gas grid. By the further processing to methane (CH₄) it can be stored in very large amounts with today’s infrastructure i.e. for the seasonal transfer of energy from summer to winter. As source for the carbon oxides, biogas from anaerobic digestion or CO₂ separated from industrial flue gas are investigated in the ESI project.

For the investigation of these processes, two experimental facilities have been built: The smaller one in 10 kW scale, referred to as COSYMA, is an automated, and container based, mobile system. This system has been installed temporarily at a biogas plant in Zürich within a collaboration with Energie 360° to demonstrate direct methanation of real biogas for more than 1000 h. With this field test the durability of the technology was proven.

The other experimental facility (a 160 kW pilot scale system), referred to as GanyMeth, is being used to investigate scale-up effects in these processes and to deliver realistic data for model validation. GanyMeth has been taken into operation with air and currently the fluid mechanics are being characterized. The next steps are the mechanical and electrical completion, followed by the hot commissioning.

Hydrothermal gasification allows converting wet or liquid biomass (such as algae, sewage sludge, manure or residuals from food production such as coffee dregs) to methane/SNG. A fully automated, mobile system in a container is in operation at the ESI platform and was recently successfully used to demonstrate the feasibility of the hydrothermal gasification of coffee ground. As a next step, a scale-up of the technology to 100 kW scale is planned.

Subsequently to the start-up of the individual ESI platform installations, integrated operation of several sub-systems has been performed in 2017, with the target to demonstrate the collective simultaneous operation of all sub-systems placed on the platform. This included the use of a representative electric load profile taken from an energy system scenario of the year 2050, water electrolysis to convert electricity to hydrogen, the re-electrification of hydrogen by fuel cells, and the further conversion of H₂ to SNG by methanation of carbon dioxide. Simultaneously the sub-system for hydrothermal production of biogas from wet biomass was in operation as well.

In order to close the bridge 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, the platform will be complemented in 2018 with a micro gas turbine module. Even with this expansion, the platform infrastructure still has significant flexibility and capacity to accommodate additional technologies (as e.g. battery storage systems).

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 on the ESI platform.

An overarching activity has been launched to connect on a virtual basis the demonstration platforms at Empa and PSI (and possibly ETHZ) in order to gather experience on the inter-connected operational behaviour of large and diverse energy systems including elements of the residential, industrial and mobility related energy sectors.
Conferences


• 2nd Experts Meeting IEA SHC Task 58 / ECES Annex 33 (hosted at Empa), October 4–6, 2017, Dübendorf, Switzerland.

• 21th International Conference on Solid State Ionics (C. Battaglia, Empa), June 2017, Padua Italy.
Work Package «Heat – Thermal Energy Storage»


Work Package «Batteries – Advanced Batteries and Battery Materials»

- M. Bodnarchuk, K.V. Kravchyk, M.V. Kovalenko, «Novel nanoscale electrode materials for sodium-ion batteries». PSI Electrochemistry Symposium, May 9, 2017, Villigen, Switzerland.
Appendix

Presentations


- C. Villevieille, «On the way to low cost Na-ion batteries». 68th Annual Meeting International Society of Electrochemistry (ISE), Aug. 27–Sept. 1, 2017, Providence, RH, USA.


- C. Villevieille, «Les batteries sodium, mythe ou réalité?». Mobility days. April 26, 2017, Martigny, Switzerland.

- E. Marelli, C. Marino, C. Villevieille, «Exploring the cobalt impact in the sodium-ion cathode materials P2-Na0.67MnFeCokAlzOi (i+j+k+z = 1)». European Materials Research Society Fall Meeting (E-MRS), Warsaw, Poland, Sept. 18–21, 2017.


- N.H. Kwon, «Post-Li Batteries: The study of electrolytes for Li-air batteries». 5th Symposium SCCER HaE and 33th PSI Electrochemistry Symposium, May 9–10 2017, PSI, Villigen, Switzerland.

- S. Maharajan, «Carbon coating and optimization for composite alloy anode materials». 5th Symposium SCCER HaE and 33th PSI Electrochemistry Symposium, May 9–10 2017, PSI, Villigen, Switzerland.

- H. Yao, «Ionic liquids based on crown ether as electrolyte for batteries». 5th Symposium SCCER HaE and 33th PSI Electrochemistry Symposium, May 9–10 2017, PSI, Villigen, Switzerland.


- S. Maharajan, «Sn/C composite anode material for high energy batteries». Swiss Chemical Society (SCS) fall meeting, Aug. 21–22, 2017, Berne, Switzerland.


- N.H. Kwon, «Rechargeable Li-air and Li-water batteries». 6th Symposium SCCER HaE, Oct. 25, 2017, Martigny, Switzerland.


- N.H. Kwon, «Nanomaterials meet Li-ion batteries». Doctoral program, April 20, 2017, Neuchatel, Switzerland.


Appendix

Presentations


Work Package «Hydrogen – Production and Storage»

- A. Züttel, «From renewable energy to hydrogen & synthetic fuels». Technische Universität, Bergakademie Freiberg, Jan. 25, 2017, Freiberg, Germany.
- M. Spodaryk, «Formation of a catalytic active surface layer on Cu for the CO₂ reduction». SCCER Heat & Electricity Storage 6th Symposium, October 25, 2017, Martigny, Switzerland.
Presentations


K. Sivula, «Engineering semiconductor materials and catalysts for photoelectrochemical solar fuel production». Werner prize lecture at the SCS Spring Meeting April 2017, Bern, Switzerland.

K. Sivula, «Charge transport, recombination, and defects in CuFeO₂ and WSe₂ photocathodes for solar H₂ production». Workshop on Charge Trapping Defects in Semiconductors and Insulators March 2017, York, UK.


Work Package «Synthetic Fuels – Development of Advanced Catalysts»


T.J. Schmidt, «Die Energiespeicher der Zukunft». Podiumsdiskussion, Das Energiesystem der Zukunft, Nov. 28, 2017, Zurich, Switzerland.


T.J. Schmidt, «Strategies on Oxygen Evolution Catalyst Developments for Polymer Electrolyte Water Electrolyzers». University of Cape Town and HySA/Catalysis, Nov. 02, 2017, Cape Town, South Africa.


Work Package «Assessment – Interactions of Storage Systems»

- D. Parra, «Where is Energy Innovation Heading?». Discussion organised by the University of Geneva and the MIT Energy Initiative, Nov. 9, 2017, Swissnex Boston, Cambridge, USA.
- A. Malhotra, T.S. Schmidt, J. Huenteler, «Considering different types of learning in low-carbon energy innovation policy». 5th Symposium SCCER Hae Heat and Electricity Storage, May 9, 2017, Villigen, Switzerland.
- T.S. Schmidt, «The role of policy design in inducing technological change in the energy sector». 4th Educational workshop of the Simulation Lab, SCCER CREST, March 29, 2017, Zurich, Switzerland.
Presentations

- L. Vandepaer, «Battery changes – environmental assessment of stationary batteries and their consequences in energy systems, a case study for Switzerland». LCA XVII conference, Oct. 2–5, 2017, Portsmouth, NH, USA.
- C. Bauer, «Batterien und Elektromobilität: Ökologischer Fluch oder Segen?». BET Suisse Challenges, Nov. 21, 2017, Olten, Switzerland.
Publications

Work Package «Heat – Thermal Energy Storage»


Work Package «Batteries – Advanced Batteries and Battery Materials»

- S. Wang, M. He, M. Walter, F. Krumeich, K.V. Kravchyk, M.V. Kovalenko, «Monodisperse CoSn2 and FeSn2 nanocrystals as high-performance anode materials for lithium-ion batteries». (Submitted).
- C. Marino, E. Marelli, C. Villevieille, «Impact of cobalt content in Na0.6MnFe,CoO2 (x + y + z = 1), a cathode material for sodium ion batteries». RSC Advances, 7(23), 13851–13857, 2017.
Work Package «Hydrogen – Production and Storage»


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


X. Cheng, E. Fabbri, B. Kim, M. Nachtgeaal, T.J. Schmidt, «Effect of Ball Milling on the Electrocatalytic Activity of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3} towards the Oxygen Evolution Reaction». J. Mater. Chem. A **5**, 2017, 13130–13137, doi: 10.1039/C7TA00794A.


Work Package «Assessment – Interactions of Storage Systems»

5th Annual Symposium, SCCER «Heat and Electricity Storage», May 9, 2017
«From the Lab to the Market»

The 5th Annual Symposium «SCCER Heat & Electricity Storage» was held on May 9, 2017, at Paul Scherrer Institut.

Organizers
Thomas J. Schmidt, Jörg Roth, Ursula Ludgate

Speakers
Philip Hassler, IFJ Institut für Jungunternehmen AG, CH
Dr. Jan Wurzbacher, Climeworks, CH
MSc. Guillaume Jung, PARK INNOVAARE, CH
MSc. Daniel Steitz, novoMOF, CH
Viola Becattini, IET, EHTZ, CH
Cornel Fink, LCOM, EPFL, CH
Bae-Jung Kim, ECL, PSI, CH
Jachin Gore, Institut für Energietechnik, HSR, CH
Abhishek Malhotra, Energy Politics Group, ETHZ, CH
Dipl. Ing. Peter Trawitzki, Energiedienst, D
Dr. Hilmi Buqa, Leclanché, CH
Dr. Adrian Spillmann, Bühler, CH
MSc. Guillaume Bourtourault, FAFCO SA, CH
Prof. Dr. Jörg Worlitschek, HSLU, CH

Oral Presentations

- P. Hassler, «Sensitization to Entrepreneurship».
- J. Wurzbacher, «Climeworks: From the Idea to the Market».
- G. Jung, «Switzerland Innovation PARK INNOVAARE».
- D. Steitz, «Metal-Organic Frameworks (MOF): From the Idea to the Market».
- P. Trawitzki, «Power to Hydrogen at the Wyhlen Site: Motivation and First Experiences».
- H. Buqa, «How to be Competitive in the Booming Li-Ion Market?»
- A. Spillmann, «From Coin Cell to Gigafactory – Scale-up of LiB Slurry Processing».

Posts

Battery and Materials

- E. Marelli, C. Marino, S. Park, C. Villevielle, «P2-Na$_{2/3}$Mn$_{0.8}$Fe$_{0.2}$Co$_{0.15-0.15}$Al$_2$O$_3$ (x = 0.075, 0.15) as Cathode Materials for Sodium Ion Batteries».
- M.-L. Doublet, «Conceptual vs. Computational Approaches to High-Energy-Density Materials for Li-ion Batteries».
- C.P. Guntlin, A. Tobler, M.V. Kovalenko, «Synthesis and Electrochemical Performance of Nanocrystalline Pyrochlore Iron(III) Fluoride as Cathode Material for Lithium-Ion-Battery».
- K. Kravchyk, M. Kovalenko, «Novel Nanoscale Electrode Materials for Sodium-Ion Batteries».
- S. Maharajan, N.H. Kwon, K.M. Fromm, «Carbon Coating for Nano-Rattle Sn@C Composite Anode Material for Alkali Metal Ion Batteries».
- ZHANG, Tong, «Practical Sulfolane-Based Electrolytes for Secondary Lithium-Ion Batteries».
- E. Stilp, S. Dilger, J. Vidal Laveda, C. Battaglia, «Investigations for a Full Cell NMC111 Benchmark».
- M. Held, «A Second Life for Old Batteries».
- A. Fuerst, A. Haktanir, «Pilot Production Line for Battery Cell Manufacturing».
Thermal Energy Storage
- L. Geissbühler, A. Mularczyk, A. Mathur, A. Haselbacher, A. Steinfeld, «Thermocline Control for Sensible Thermal Energy Storage».

Hydrogen Generation and Storage

Synthetic Fuels
- A. Gopakumar, F.D. Bobbink, Z. Fei, P.J. Dyson, «Production of Methanol from CO₂: Indirect Approaches via N-formylation or Carbonate Formation».
- A. Dutta, M. Rahaman, A. Zanetti, P. Broekmann, «Electrochemical CO₂ Conversion (CO₂RR) using Skeleton/ Sponge Type of Cu Catalysts».
- X. Cheng, E. Fabbr, B. Kim, M. Nachtegaal, T.J. Schmidt, «Effect of Ball Milling on the Electrocatalytic Activity of Ba₄₋₅Sr₃₋₅Co₁₋₅Fe₂₋₅O₁₆ Towards the Oxygen Evolution Reaction».

Assessment of Storage Systems
- B. Meier, F. Ruoss, M.J. Friedl, «Investigation of Carbon Flows in Switzerland with the Special Consideration of Carbon Dioxide as a Feedstock for Sustainable Energy Carriers».
6th Annual Symposium, SCCER «Heat and Electricity Storage», October 25, 2017

The 6th Annual Symposium «SCCER Heat & Electricity Storage» was held on October 25, 2017, in Martigny.

**Organizers**
Thomas J. Schmidt, Jörg Roth, Ursula Ludgate, Hubert Girault, Andreas Züttel, Patricia Byron

**Speakers**
- Prof. Dr. Andreas Züttel, EPFL, Sion, CH
- Dr. Noris Gallandat, GRZ Technologies, CH
- Prof. Dr. Peter Broekmann, Uni Bern, CH
- PhD. Joep Huijsmans, Long Range Research & New Energy Technologies, Shell, NL
- Dr. Olaf Conrad, JenaBatteries GmbH, D
- Prof. Dr. Axel Fuerst, Berner Fachhochschule, CH
- Dr. Pascal Häring, Renata, CH
- Dr. Luca Baldini, Empa, CH
- Prof. Dr. Andreas Haselbacher, ETHZ, CH
- Gilles Verdan, GazNat, CH
- Prof. Dr. Markus Friedl, HSR, CH

**Oral Presentations**
- A. Züttel, N. Gallandat, «Hydrogen and Hydrides, Storage and Compression».
- P. Broekmann, «Catalyst Design for the Electrochemical CO₂ Conversion».
- J. Huijsmans, «Powering Progress Together - Providing Energy Storage Solutions for a Changing World».
- Olaf Conrad, «The All-Organic Redox Flow Battery».
- Axel Fuerst, Pascal Häring, «Battery Production Research for Switzerland».
- Luca Baldini, «Thermal Energy Supply and Storage in Energyhub and NEST».
- Andreas Haselbacher, «Experimental and Numerical Investigation of a Pilot-Scale AA-CAES Plant».
- G. Verdan, N. Gallandat, «Energy Storage and Synthetic Methane».
- M. Friedl, «Energy Storage Demonstrators within SCCER Heat and Electricity Storage».

**Posters**
- Battery and Materials
  - E. Marelli, C. Marino, C. Villevieille, «Investigation on the Promising P2-Na₀.₆₇Mn₀.₆Fe₂₃Al₀.₁₅O₂ Cathode Material».
  - J. Conder, C. Marino, C. Villevieille, «How Reliable is the Na Metal as a Reference Electrode?»
  - J. Vidal Laveda, E. Stilp, S. Dilger, C. Battaglia, «Investigations for a Full Cell Li(Ni₁/₃Mn₁/₃Co₁/₃)O₂ (NMC) Benchmark».
  - M. Deng, M. Li, H.G. Park, «MoS₂ Lamellar Membrane for Selective Molecular Transport, HER and its Application in Li Water Battery».
  - N.H. Kwon, H. Yao, K.M. Fromm, «Rechargeable Li-Air and Li-Water Batteries».
  - S. Maye, P. Peljo, «Non-Aqueous Copper Battery for Heat-to-Power Conversion and Storage».
Thermal Energy Storage
- L. Baldini, B. Fumey, R. Weber, «Sorption-based long term thermal energy storage using sodium hydroxide».

Hydrogen Generation and Storage
- H. Yang, L. Lombardo, A. Züttel, «Synthesis and Characterization of Core-Shell Structure of NaBH4 for Hydrogen Storage».
- V. Costa Bassetto, A. Lesch, «Inkjet Printing of Electrocatalysts and Electrocatalyst Gradients in 2D and 3D for the ORR and OER».
- M. Montandon-Clerc, A.F. Dalebrook, G. Laurenczy, «Formic Acid: A Viable Option to Chemical Hydrogen Storage».
- C. Fink, G. Laurenczy, «Formic Acid on the Way to an Industrial-scale Energy Storage Vector».

Synthetic Fuels
- E. Lam, K. Larmier, P. Wolf, C. Copéret, «CO2 Hydrogenation of Copper Nanoparticles Supported on Zirconium Modified Silica».
- F.D. Bobbink, P.J. Dyson, «Indirect MeOH Production from CO2 via Cyclic Carbonates under Solvent-Free, Metal-Free Conditions».
- M. Spodaryk, A. Züttel, «Role of the Initial Amount of Hydrogen and CO2 for Successful CO2 Reduction to Hydrocarbons».

Assessment of Storage Systems
Co-Organized Events

33rd PSI Electrochemistry Symposium, May 10, 2017
«From the Lab to the Market»

The «33rd PSI Electrochemistry Symposium» was co-organized by SCCER «Heat & Electricity Storage» and Electrochemistry Laboratory at Paul Scherrer Institut.

Organizers  Thomas J. Schmidt, Cordelia Gloor
              (Electrochemistry Laboratory)
              Jörg Roth, Ursula Ludgate
              (SCCER «Heat & Electricity Storage»)

Contributions from
(in order of appearance)
Steven J. Visco,
PolyPlus Battery Company, Berkley, CA, USA

Peter Axmann,
Zentrum für Sonnenenergie und Wasserstoff-Forschung,
Baden-Württemberg, Stuttgart, Germany

Nigel Brandon,
Imperial College London, UK

Mark F. Mathias,
General Motors, Pontiac, MI, USA

Cortney Mittelsteadt,
GINER INC., Newton, MA, USA
Contact

Swiss Competence Center for Energy Research
Heat and Electricity Storage (SCCER HaE-Storage)
c/o Paul Scherrer Institut
5232 Villigen PSI, Switzerland
Phone: +41 56 310 5396
E-mail: info@sccer-hae.ch
Internet: www.sccer-hae.ch

Thomas J. Schmidt, Head
Phone: +41 56 310 5765
E-mail: thomasjustus.schmidt@psi.ch