Annual Report 2018

Save the Date:
SCCER HaE Conference
November 5, 2019, Empa, Dübendorf, Switzerland
# Table of Contents

## Editorial

3  SCCER Networked Research – From the Lab to the Market

## Heat – Thermal Energy Storage

5  Sensible Thermal-Energy Storage Systems Optimized for AA-CAES Plant Operation
7  AA-CAES Plant Modelling Improvements and Layout Definition
10 Numerical Phase Change Study and Optimization of High-Temperature Encapsulated Metal Phase Change Materials for Energy Storage
15 Direct Contact Latent Heat Storage Using Esters as New Phase Change Materials
18 Closed Sorption Seasonal Thermal Energy Storage with Liquid Sorbent Solutions
20 Closed Liquid Sorption Seasonal Heat Storage Using Aqueous Sodium Hydroxide
22  Thermal Insulation Materials for Thermal Energy Storage

## Batteries – Advanced Batteries and Battery Materials

26 Strategies to Improve Na-Ion Batteries
28 Development of Ionic Liquids as Electrolyte Additives and a Cathode Material for Lithium Ion Batteries
30 Stabilizing NMC811 in Full Cells with High Areal Capacity
32 Pilot Line Modules for Lithium-Ion Battery Cell Assembly and Advantages of Laser Processing
34 Ultra-High Mass Loading Graphite Anodes for Li-Ion Batteries

## Hydrogen – Production and Storage

38  Hydrogen Storage in Hydrides
40  Performance and Stability of Iron-Cobalt-Nickel Alloys for Water Oxidation
42  Titanium-Manganese-Vanadium Electrolytes, Redox Solid Boosters and Copper Contamination of an All-Vanadium Redox Flow Battery
45 Hydrogen storage and delivery in CO₂ – formic acid – methanol systems

## Synthetic Fuels – Development of Advanced Catalysts

48  Catalyst Development for the Transformation of CO₂ into Fuels and Value-Added Chemicals
50 Development of Selective Catalysts for the Conversion of CO₂ to Fuels via Surface Organometallic Chemistry
53  Synthesis and Characterization of Degradation Resistant Cu@CuPd Nanowire Catalysts for the Efficient Production of Formate and CO from CO₂
55  (Co)-Electrolysis at Paul Scherrer Institut
Assessment – Interactions of Storage Systems

60  Investigation of AA-CAES Plant Configurations and Grid Integration
64  Calculation of Heat Demand for the Assessment of Storage Potential on System Level
66  Assessment of Energy Storage at the Technology and Energy System Level
69  Technology Assessment of Energy Storage
72  Assessment of Energy Storage at the Socio-Economic Level
74  Increasing the Efficiency of the Power-To-Methane Technology
76  ESI – Energy System Integration Platform

Appendix

81  Conferences
82  Presentations
91  Publications
96  Patents
97  Organized Events
SCCER Networked Research –  From the Lab to the Market

The Swiss Competence Center for Energy Research (SCCER) Heat and Electricity Storage is now in the middle of its second phase. As expected at this stage, the collaboration within the SCCER HaE and the other SCCERs reached maturity. The successful operation of the various Joint Activities, like the generation of the White Paper on Power to Gas, where groups from 5 different SCCER collaborate, or the joint Project SwissStore with groups of SCCER HaE and CREST, on the potential of energy storage on the system level for Switzerland (see page 64) are outstanding examples.

On the international level, the SCCER HaE is well connected. The Competence Center has cooperations with institutions in Germany, Austria, Spain, France, UK, the Netherlands, Greece, Poland, USA, Canada, South Korea, Japan and Abu Dhabi.

With respect of the given scope on energy storage on large scale and on seasonal timeframes, the international collaboration is a valuable asset since changing the current energy system towards a climate friendly and sustainable system is a tremendous task which needs to be addressed on a global scale. National challenges might differ in details, every region has its individual settings, like mountains in Switzerland or salt caverns in Northern Germany, but the fundamentals in each climate zone are similar. Thanks to the SCCER Program, the collaboration among different research institutions and groups reached a new quality and synergetic effects become obvious.

Following the lines of our technical roadmap, our progress reached new and highest standards. One of our most important goals is to bring the findings from the lab to the market in order to have technologies ready for the Energy System 2050. Along these lines, within the framework of the SCCER HaE a prototype of auxiliary power supply unit based on formic acid as a hydrogen storage was developed at EPFL together with an industrial partner. Due to its large hydrogen content, and its simple structure, formic acid can be catalytically decomposed into water and $\text{CO}_2$. During the past years this process was optimized and finally an industrial prototype was developed.

The Energy System Integration Platform reached a major milestone. The Platform not only became fully operational in 2018, but its electrolyzer system also passed the qualification test for the primary and secondary reserve market.

The focus of the assessment of energy storage was set on batteries this year. The aspects of various battery technologies on life cycle aspects, like metal criticality and greenhouse gas emissions were investigated. Giving one example, it was found that Na-ion based batteries at the moment are less ecologic compared to current Li technology. It also became clear that critical metals like Co or Ni need to be substituted from battery systems in future developments.

Those are just a few selected examples of the progress the SCCER HaE made this year, and I hope you got curious to explore also the other achievements of the 25 groups of the SCCER presented on the next pages.

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

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 going 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. Some information has been gathered over the past year as part of the preparation of the Fact Sheet Heat by the Working Group «Thermal Storage» of the Forum for Energy Storage Switzerland.

Storage of high-temperature heat in industrial applications

An overarching effort on TES at high temperatures concerns our investigations of advanced adiabatic compressed air energy storage (AA-CAES). This effort is rooted in the collaboration with ALACAES during SCCER Phase I and an SNF NRP 70 project, as part of which experiments were carried out with the world’s first pilot-scale AA-CAES plant with a hard-rock cavern and a combined sensible/latent TES at temperatures of up to 575°C. To reuse existing turbomachinery, we are now considering plant layouts with maximum temperatures of about 320°C.

We have investigated in more detail the economics of an AA-CAES plant in Switzerland using a simple plant model integrated into a model of the Swiss electricity grid. The grid-plant simulations indicate that arbitrage by itself is not profitable and we are therefore investigating other use cases in collaboration with BKW. In these simulations, we have assumed that we do not reuse decommissioned military caverns based on a closer examination of such caverns in conjunction with Amberg Engineering. The simple plant model employed in the grid simulations is based on an assumed constant plant efficiency of 70%. Realistic values of the plant efficiencies for specific plant configurations are provided by detailed plant simulations in which the transient behavior of the turbomachinery, TES, and cavern are included. These simulations consider irregular charging/discharging cycles and have benefited from actual turbomachinery performance data provided by MAN Energy Solutions AG. The TES model in the detailed plant model in turn has been used to study multi-tank storage configurations, which are of interest because they may be better suited to irregular charging/discharging cycles because they allow for thermocline control. The simulations of the multi-tank configurations have shown better performance than a single-tank configuration even under non-adiabatic conditions for drops of the outflow temperature during discharging of less than 9%, and are therefore expected to enable more efficient operation of the turbine in an AA-CAES plant.

The high-temperature TES activities include also investigations of the performance of latent TES in which 44Mg-56Si is used as phase-change material (PCM), encapsulated in SiSiC tubes. To enhance the heat transfer between the PCM and the air that is used as heat-transfer fluid, the space between the tubes is filled with a reticulated porous ceramic. Simulations showed that effectivenesses of more than 92% and energy densities of more than 220 MJ/m² can be achieved. In a parallel effort, detailed simulations of the melting behaviour of PCMs are used to improve the understanding of the fundamental unsteady heat-transfer processes and random macroporous percolating structures are being investigated as encapsulations for PCM. These efforts are expected to be useful for the development of improved combined sensible/latent TES units in an AA-CAES plant.

Seasonal storage of low-temperature heat for space heating and hot water

Parallel research projects investigate closed sorption storage for seasonal storage using tube-bundle and spiral-finned tube heat/mass exchangers (HMX) and have focused on understanding and improving the limited discharge power. To increase the wetting of the tube-bundle surfaces, various hydrophilic coatings developed by CSEM were assessed using water. Judging by the maximum wetted width, structured coatings were up to 5 times better than uncoated surfaces. To improve the understanding of the mass transfer during absorption and desorption, Raman spectroscopy experiments were performed. Preliminary results confirm reduced mass transfer rates during absorption compared to desorption. The mass transfer was also studied using neutron imaging in the SINQ facility at PSI. More detailed analyses of both experiments are in progress. An upscaled HMX based on the spiral-finned tube concept with a nominal discharge power of 5 kW was designed and will be manufactured in 2019.
Sensible Thermal-Energy Storage Systems Optimized for AA-CAES Plant Operation

Scope of project

The optimization of thermal-energy storage (TES) systems for advanced adiabatic compressed air energy storage (AA-CAES) plants requires that the operational characteristics of such plants are determined first. As described in last year’s annual activity report [1] and conclusions drawn from results of grid simulations performed in the SCCER AA-CAES project [2], the operating profiles of AA-CAES plants are predicted to be very dynamic. Ultimately, the plant and therefore also the TES system have to be capable of dealing with off-design conditions without large decreases in their efficiencies. Thermocline TES systems can require up to 50 cycles to return to their nominal quasi-steady-state behaviour following a disturbance [3]. TES systems that consist of multiple smaller storage units that can be used in combination appear to be better suited to off-design operation [4–6]. The ultimate objective of our work is to assess the performance of multi-tank TES systems relative to single-tank systems under conditions that are representative of AA-CAES plants. In this report, we summarize the results of an ongoing numerical study where TES systems composed of up to four tanks are assessed for nominal, steady-state operating conditions that are representative of a 100 MW/500 MWh AA-CAES plant. The assessment of TES systems for dynamic operating conditions is the subject of future work.

The operating conditions used in this study are taken from the SCCER AA-CAES plant design shown in Figure 1. The plant contains two caverns to simplify the integration of two-stage turbomachinery. The nominal plant design contains a single-tank TES in each cavern. The objective of the work described here is to assess multi-tank TES systems of up to four tanks for the operating conditions of the low-pressure (LP) cavern. The corresponding nominal mass flow rates, air inflow temperatures during charging and discharging, and charging and discharging durations are indicated in Figure 1. To simulate daily storage operation, two idle phases of seven hours were added after the charging and discharging phases. Including the idle phases is important because the simulations included the thermal losses from the TES to take into account the larger surface area of multi-tank systems. The surface area grows as the number of tanks increases because the assessment is based on keeping the total tank volume constant. The assessment assumes that the total volume is divided equally among the tanks and that the aspect ratios of the tanks are identical. For simplicity, the structure and insulation thicknesses are identical for all tanks.

The simulations were performed with a previously developed and validated quasi-one-dimensional heat-transfer model [7] that was coupled with an external Matlab routine. This routine called the heat-transfer model for each tank and divided the flows through the tanks according to the mode of operation. There are two basic modes of operation that can be considered for multi-tank systems. The first is parallel operation, where all tanks are charged simultaneously by dividing the total mass flow. In the simplest case, considered here, the mass flow is divided equally between the TES units. The second mode is serial operation, where the tanks are being charged sequentially with the same total mass flow. For serial operation, the operation of multi-tank TES systems is equivalent...
Heat to thermocline-control (TCC) methods [8, 9]. In this report, the focus lies on the extraction TCC method, which was found to be promising in prior work.

An example of the working principle of the extraction TCC method with a four-tank storage during charging is shown in Figure 2. At the start of the charging phase, the chain of TES units is checked from top to bottom to determine the active inlet and outlet. The active inlet is chosen to be the inlet of the first tank that is not fully charged. The active outlet is chosen to be the outlet of the first tank where the temperature at the bottom is below the pre-defined switching temperature, which was chosen as 50 °C (corresponding to a dimensionless temperature of 0.1 in Figure 2). At time $t_1$, when the switching temperature of TES 2 is reached, TES 3 is also starting to be charged. At time $t_2$, when the switching temperature at the outlet of TES 3 is reached, TES 4 is starting to be charged and the active inlet is moved from TES 1 to TES 2 to decrease pressure losses and increase the efficiency. For comparison, the single-tank storage of the same volume is also shown in Figure 2. With a single-tank system, the outflow temperatures are significantly higher at the end of the charging phase. The same strategy is applied during the discharging phase with the difference that the switching temperature is 290 °C (corresponding to a dimensionless temperature of 0.9) at the outlet.

The sample results shown here indicate that with multiple tanks, the thermocline is significantly steeper than for a single tank, leading to lower maximum outflow temperatures during charging, and higher minimum outflow temperatures during discharging. Ultimately, this allows smaller total volumes to be used with multi-tank systems compared to a single-tank system for the same performance. It is important to note that despite the increased surface area and therefore increased thermal losses for multi-tank TES systems, the results showed that they are cost-competitive when low temperature drops during discharging ($\Delta T_{d,max} \leq 9\%$) are required. For all the TES systems that were analysed, the total material costs were lower than 15 CHF/kWhth. These results justify further efforts to analyse multi-tank TES systems, especially for more realistic dynamic AA-CAES plant operation.

References

Figure 2:
Top: Simulated outflow temperatures for a TES system consisting of one and four tanks (diabatic conditions, constant $V_{tot} = 4300 \text{m}^3$) with the switching times $t_1$ to $t_3$. Bottom left: Thermoclines in the four TES system at times $t_1$ to $t_3$. The TES units in use are indicated by the colored frames. Bottom right: Thermoclines in the one-tank TES system at the start and end of the charging phase.

Sensible Thermal-Energy Storage Systems Optimized for AA-CAES Plant Operation
AA-CAES Plant Modelling Improvements and Layout Definition

Scope of project

The research efforts were focused to further develop and apply the dynamic numerical model for AA-CAES plants, developed at SUPSI in the Matlab-Simscape environment. Among its features, to accurately describe the thermocline evolution within packed bed thermal energy storage (TES) systems, this model embeds a 1D Fortran code developed by ETHZ [1].

Status of project and main scientific results of workgroups

The plant layout labelled P1, and reported in Figure 1 top left, is a first example of model application [2]. In this configuration, the TES is contained in a chamber that is physically separated from the cavern where the cold air is stored. These two volumes have different pressures (LP and HP respectively) and, before the plant discharging phase, they have to be balanced at the same pressure value. The pressure equilibrium between the cavern and the TES chamber was modelled computing the unsteady inviscid flow through a converging nozzle placed between them. Furthermore, this plant layout implies that, after a discharge phase, the TES chamber has a residual high pressure that has to be discharged to allow the next charge from the LP compressor (LPC). In order to not waste the pressurized air left in the TES chamber and part of the thermal energy stored there, the depressurization is performed through an auxiliary turbine.

A second layout, labelled P2 [2] and showed at the top right of Figure 1, was conceived in order to avoid the pressure balancing actions. This was obtained by keeping constant the pressure in the TES chamber and exploiting the thermal energy at the outlet of the HP compressor (HPC). Therefore, an additional TES was placed inside the cavern and a HP-LP turbine train was added. So, the thermal energy obtained after the HPC is exploited by the HP turbine, that is placed between the cavern and the LP TES chamber.

The two layouts were compared under a regular cycling schedule composed by 5 hours of charging followed by 5 hours of discharging, both at a constant mass flow rate of 200 kg/s (232 kg/s for the LP compressor in P1 layout to compensate the air expelled through the auxiliary turbine). In the P1 layout additional idle time intervals were added between these main phases in

List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP</td>
<td>High Pressure</td>
</tr>
<tr>
<td>HPC</td>
<td>High Pressure Compres sor</td>
</tr>
<tr>
<td>HPT</td>
<td>High Pressure Turbine</td>
</tr>
<tr>
<td>LP</td>
<td>Low Pressure</td>
</tr>
<tr>
<td>LPC</td>
<td>Low Pressure Compressor</td>
</tr>
<tr>
<td>LPT</td>
<td>Low Pressure Turbine</td>
</tr>
<tr>
<td>TES</td>
<td>Thermal Energy Storage</td>
</tr>
</tbody>
</table>

Figure 1: AA-CAES plant layouts, P1 on the top-left and P2 on the top-right. Blue lines show the charging flow paths while red lines are the discharging ones. On the bottom, temperature and pressure variations within the TES chambers are reported accordingly.

Authors

Jonathan Roncolato¹
Filippo Contestabile¹
Simone Zavattoni¹
Viola Becattini¹
Giw Zanganeh³
Andreas Haselbacher²
Davide Montorfano¹
Luca Cornolti¹
Maurizio C. Barbato¹

¹ SUPSI
² ETHZ
³ ALACAES SA
AA-CAES Plant Modelling Improvements and Layout Definition

**Figure 2:**
Load profiles over one week used to simulate irregular cycles with the P2 layout. Positive/negative loads correspond to charging/discharging of the plant.

**Figure 3:**
Turbomachinery power levels resulted from simulations (top); daily and average efficiencies of the AA-CAES P2 plant for the simulated week (bottom).

Order to allow the pressure adjustments in the TES chamber. A constant isentropic efficiency of 0.85 was set for all the turbomachinery; volumes of cavern and TES chamber were set to 177'000 m$^3$ and 18'500 m$^3$ respectively.

The results reported at the bottom of Figure 1 show the TES chamber temperature and pressure evolution during the first 10 cycles. In the P1 layout, issues related to the dynamics of the TES chamber were detected, namely large temperature variations and time lags required for the pressure adjustments. The former would likely affect the components life (e.g., probes and electronics) while the additional time lags due to pressurization and depressurization of the TES chamber would be detrimental for the plant responsiveness to the grid power demand.

In the P2 layout instead, both temperature and pressure variations in the TES chamber were smaller. This result can be achieved if an adequate regulation of the mass flow rate of compressors and turbines is actuated. After the comparison of these results and considering the drawbacks caused by the pressure swings within the TES chamber, the P2 layout was preferred to test a realistic weekly schedule based on electric power exchanged with the grid (see Figure 2). This schedule was designed by PSI starting from an economic optimization of the AA-CAES plant operation. For this case, turbomachinery efficiencies were switched from isentropic to polytropic ones: namely LPC was set to 0.85, HPC to 0.88, HPT to 0.86 and LPT to 0.90. The two TESs were pre-charged for 10 hours with a 200 kg/s flow rate and at the beginning of the week simulation, the cavern was initialized at 85 bar. Feedback controls were activated to keep the cavern pressure within the 80–100 bar range. The HPC was operated in sliding pressure mode, assuming the component to be flexible enough to follow the cavern pressure increase. On the other hand, considering the limited flexibility of turbo-expanders, the pressure at the turbine inlet was throttled to 80 bar.

Top of Figure 3 shows the actual power of all turbomachinery, from which it is possible to notice that the useful power for the LPC decreases during charges to balance the increasing power request by the HPC. During discharges instead, the adoption of a throttling pressure helped in having hourly constant power output for both expanders. The effects of higher temperatures at the outlet of HPT caused by the throttling was mitigated by the presence of the LP TES, without influences on the LPT operation. The daily and weekly efficiencies calculated are plotted at the bottom of Figure 3.

The simulation of a realistic connection to the grid showed that transients of turbomachinery and their characteristics, especially turbomachines’ flexibility, are particularly significant for the AA-CAES operation. Therefore, exploiting data provided by MAN ES AG, realistic turbomachinery characteristics were included in the numerical model and tested on a new plant layout called P3.
For the P3 layout, based on the P2 plant topology, the compression ratio was evenly split between LP and HP components in order to consider «off-the-shelf» turbomachinery as suggested by MAN ES AG. This technical choice, with respect to P1 and P2, forced a lowering of the maximum temperatures at the LPC outlet.

Furthermore, driven by economic reasons, constant speed turbomachinery was considered (in fact, this avoids the need for Variable Frequency Drivers). The flexibility of turbomachinery performance, whenever possible, was guaranteed by systems that include variable guide vanes. Furthermore, compressors/turbines polytropic efficiencies as function of compression ratio and mass flow rate/«reduced mass flow rate» were included into the numerical model (i.e., turbomachinery performance maps).

Moreover, different approaches were discussed to properly model the transients of turbomachinery, starting from a very accurate physical procedure up to a more simplified approach. The former is based on specifically developed sub-models that mimic real turbomachinery start-ups accordingly to the characteristics provided by MAN ES AG. The latter consists in just accounting for parasitic energies and start-up times based on reliable data gathered from the same manufacturer [3].

References
Numerical Phase Change Study and Optimization of High-Temperature Encapsulated Metal Phase Change Materials for Energy Storage

Scope of project

Highly conductive, high melting point (above 400 °C) metal alloys can be used as phase change materials (PCMs) for high energy and power density latent heat storage applications, as an alternative to the widely used molten salts. The computational phase change model implemented last year was used to compare high- and low-temperature PCMs during melting (i.e. discharging) and solidification (i.e. charging). A parametric study was conducted with cylindrical stainless steel encapsulations of different sizes and orientations. For the optimization of the encapsulations, we focused on machine learning techniques. Random percolating macro-porous structures – used to increase the convective heat transfer between the heat transfer fluid (HTF) and PCM – were created and meshed in 2D and 3D to serve as encapsulations for the PCMs. In another design, randomly generated porous structures that resemble fins inside a pair of concentric pipes were generated to increase the heat transfer inside the encapsulation. A de-convolutional neural network was developed to predict the temperature, velocity and heat transfer values in the simulation domain of the porous structures. Once trained with enough simulations, this network will be used to optimize the porous structures depending on the specifications required for the application.

Status of project and main scientific results of workgroups

Parametric Phase Change Study

The phase change model 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 simulation using the enthalpy-porosity method [1] for phase change inside a cylindrical PCM storage unit (Figure 1a and Figure 1b) with an air gap to allow for thermal expansion of the metal. Simulations were performed for low-temperature (Rubitherm RT-27) and high-temperature (Al-12Si) PCMs in vertical and horizontal cylinders with inner diameters of 1–10 cm, with wall temperatures set so that they have the same Stefan numbers. Time-dependent temperature contours and velocity vectors for one specific case of melting in a vertical cylinder for Al-12Si are shown in Figure 1c.
The corresponding quantification of multiple modes of heat transfer is shown in the heat transfer variation plot Figure 1d. Initially, conduction is dominating [2] due to the thin layer of melt next to the wall. A sudden drop is observed in the heat transfer rate due to the lower conductivity of the liquid metal where the dominant heat transfer mode changes to convection. Kelvin-Helmholtz instability convection cells form in the molten PCM due to shearing flows of hot rising and cold sinking molten fluid that speed up the melting process compared to the conduction only case.

In order to guide the design of an actual unit, a non-dimensional analysis was performed using Fourier, Stefan, and Grashof numbers as shown in Figure 1e. Faster melting was achieved with larger Stefan numbers (larger temperature differences) and smaller Grashof numbers (small diameters). A comparison with the low temperature PCM is currently performed to obtain a generalized relation.

**Topography Optimization: Porous Encapsulations**

Last year, we investigated genetic algorithms for optimizing latent heat storage units. But they are limited by the number of parameters and are not suitable for random macro-porous structures that cannot be explicitly parametrized (such as shown in Figure 2a).

Deep learning neural networks with multiple processing levels are well known in learning data representations of varying degree of complexity and are the state-of-the-art techniques used for recognizing objects, images, and speech, and have been used in drug discovery and genomics. Artificial neural networks require a large amount of training data to replicate flows accurately, which makes them suitable for modelling flows specific to the trained geometries and models.

While porous media can be characterized with respect to their morphology with images obtained using tomography data, a parametric description cannot be given. Deep learning optimization is currently applied to such structures, requiring two steps: training and optimization. Encapsulated macro-porous structures are currently generated with specific morphologies (poros-
Numerical Phase Change Study and Optimization of High-Temperature Encapsulated Metal Phase Change Materials for Energy Storage

For these structures, the flow, phase change and heat transfer are modelled (Figure 2c and Figure 3) to train a de-convolutional neural network – an image recognition specific feed forward deep neural network (Figure 2b) that has been previously successfully used in image recognition and recently been used to optimize aerofoils [3]. The optimization step will then follow using gradient-based methods to conceivably generate application specific macro-porous heat storage systems. While training of neural networks is typically in the order of tens of hours, optimization can be performed in the matter of a few minutes or hours in non-parametrized porous structures and even to obtain results with boundary conditions and porous characteristics beyond the training images.

The combination of these optimization approaches with latent heat storage modelling shows to be promising for providing guidance of tailored latent heat storage units.

References

Scope of project

The design of a thermal energy storage unit (TESU) with a high-temperature silicon-based phase change material (PCM) is presented. The PCM is encapsulated in a SiSiC tube and air is used as the heat transfer fluid (HTF), which passes along the encapsulation. The flow passage is filled with reticulated porous ceramics (RPC) to enhance the heat transfer between the encapsulated PCM and the HTF. A key benefit of such a configuration is its scalability by the in-series or in-parallel addition of multiple units. In our work, we propose a design strategy based on well-defined performance metrics (i.e., exergy efficiency, energy density, and effectiveness).

Status of project and main scientific results of workgroups

Mg-Si (wt% 44/56) was considered as the PCM, which has a high melting temperature (1219 K) and heat of fusion (757 kJ/kg) [1]. Only the discharging procedure is considered in this work. The TESU is assumed to be at an initial temperature of 1229 K and it is discharged with HTF entering at the inlet at 1119 K.

The design procedure starts with preliminary calculations: knowing the desired discharging time (set to 1 hour) and the discharged exergy efficiency (set to 0.95) of the system, the mass flow rate and the flow passage area were calculated for a certain porous medium and encapsulation size. The exergy efficiency ($\eta_{ex}$) was defined as follows:

$$\eta_{ex} = \frac{A - B}{C}$$

A: Net discharged exergy output by HTF
B: Equivalent thermal exergy for pumping
C: Exergy released by TESU

An axisymmetric model (Figure 1) was developed based on the preliminary calculations to analyze the performance of the storage unit with various RPC morphologies. The multi-physics model was based on the continuity and Brinkman equations (with Forchheimer corrections for the fluid flow), and on the local thermal non-equilibrium formulations of the energy equation for the porous medium. The P1 approximation was used to consider the radiation in the porous medium and the apparent heat capacity method was employed for the energy equation in the phase changing domain. Radiative and transport properties of the porous medium were obtained from the literature [2–4]. The equations were solved using Comsol Multiphysics package® (v5.3) interlinked with Matlab.

A parametric analysis was performed for all combinations of 5 different encapsulation diameters, $D_{enc}$ (2, 4, 6, 8, 10 cm), 5 different encapsulation lengths, $L_{enc}$ (20, 40, 60, 80, 100 cm) and 3 different porous foam morphologies with pore sizes, $d_{pore}$ (1.25, 2.5, 5 mm) and constant porosity ($\Phi = 0.9$). For comparison, simulations on empty channels (without porous medium) were also performed. The simulations stopped as soon as the HTF average temperature at the outlet fell bellow 1210 K.

As a measure of the storage system performance, the storage effectiveness ($\varepsilon$) was defined:

$$\varepsilon = \frac{D}{E}$$

D: Net discharged energy by HTF
E: Total possible thermal energy that can be discharged

$\varepsilon$ is indicating how effective the storage system is extracting the maximum possible energy from the storage unit. It would be equal to unity if the temperature of the system at the discharged time is equal to the HTF inlet temperature.

Figure 2 shows the effectiveness of the storage system for different unit designs. For the system with empty channels, the effectiveness increases with decreasing encapsulation diameter. However, manufacturing such small scale TESU

References


Authors

Ehsan Rezaei1,2
Maurizio Barbato1
Alberto Ortona1
Sophia Haussener1

1 SUPSI
2 EPFL
is difficult and expensive. Adding the porous medium for larger encapsulation diameters increases the specific surface area for the heat exchange between the storage unit and the HTF. As a result, higher effectiveness can be achieved. For \( d_p = 5 \text{ mm} \), a maximum effectiveness of \( \approx 0.92 \) is reached at \( D_{enc} = 2 \text{ cm} \) and \( L_{enc} = 100 \text{ cm} \). For the model with \( d_{pore} = 1.25 \text{ mm} \), the maximum effectiveness was \( \approx 0.93 \) at \( D_{enc} = 20 \text{ mm} \) and \( L_{enc} = 400 \text{ mm} \).

The volumetric energy densities of all configurations are shown in Figure 3. Systems with larger encapsulation length generally require larger mass flow rates and larger flow passage areas to discharge the system in the desired time with the desired exergy efficiency. As a result, the energy density of the storage unit decreases when increasing the encapsulation length.

**Conclusions and future studies**

For small encapsulation diameters, the specific surface area of the TESUs increased and as a result the system effectiveness increased. However the performance of the system decreased at larger diameters \( (D_{enc} \geq 20 \text{ mm}) \). For larger diameters, the use of porous media enhanced the performance of the storage unit. The energy densities of these systems were within 30–650 MJ/m\(^3\). The best performance of the TESUs showed effectiveness \( \geq 0.92 \) and energy density \( \geq 220 \text{ MJ/m}^3 \).

For future studies, a storage system with variable pore size will be considered with the aim of increasing the performance of the storage unit at larger encapsulation diameters.
Direct Contact Latent Heat Storage Using Esters as New Phase Change Materials

Scope of project

The Direct Contact Energy Storage (abbreviated as DENSE) project started in mid-January 2018 and proposes to investigate the suitability of Esters as a new class of bio-based phase change materials (PCM) to be used in direct-contact latent heat storages setups. At first, a comprehensive investigation of esters’ thermal properties and behaviour has been planned. The esters have been studied based on several «classes» such as fatty esters (deriving from fatty carboxylic acids), lactones (cyclic esters), diesters (esters deriving from dicarboxylic acids), triglycerides (esters of glycerol with carboxylic fatty acids), aromatics (esters of aromatic compounds). In parallel, first experimental and numerical investigations have been conducted aiming at the optimization of the direct contact latent heat storage technology when used with esters or other phase change materials.

Status of project and main scientific results of workgroups

The first class analysed was that of fatty esters. With this purpose, esters of five different linear saturated fatty carboxylic acids (myristic C14, palmitic C16, stearic C18, arachidic C20 and behenic C22) coupled with alcohols of different chain length (methanol C1, 1-pentanol C5 and 1-decanol C10) have been synthesized, purified and studied. The results obtained show that fatty esters are promising candidates as bio-based PCM for low-mid temperatures applications. In addition, interesting trends correlating the chemical structures to the thermal properties have been found (Figure 1) [1, 2].

The results obtained from fatty esters have been presented at the International Sustainable Energy Conference (ISEC), Graz.

The second class investigated was that of lactones. Here, two commercial lactones (ε-caprolactone and γ-valerolactone) and three synthesized ones (dibenzo-cromen-6-one, 1,2-campholide and oxa-adamantane) have been synthesized, purified and studied. In general, the lactones showed a wide range of phase change temperatures. However, they were also characterized by poor thermal stability, low enthalpies of fusion and a high degree of supercooling, which mark them as unsuitable PCM. No clear correlation between the chemical structures and the thermal properties could be observed in this case. A publication on lactones is currently being reviewed [3].

Natural and biodegradable triglycerides have been investigated through commercial samples (glyceryl triacetate from coconut oil, glyceryl trilinoleate from lignin, and glyceryl trioleate from olive oil). All commercial samples tested showed a strong tendency to form different crystalline states through polymorphism, hence triglycerides have been marked as unsuitable compounds for latent heat storage, and investigations on this class have been interrupted.

Nevertheless, a review article on triglycerides as PCM with additional data from the tri-

Authors

Anastasia Stamatiou1
Rebecca Ravotti1
Stefan Krimmel1
Jörg Worlitschek1

1 HSLU

List of abbreviations

DENSE Direct contact Energy Storage
HTF Heat Transfer Fluid
ISEC International Sustainable Energy Conference
MEPA Methyl Palmitate
PCM Phase Change Material

Figure 1:
Left: Strategy for the investigation of esters as new PCM through classes to obtain a final database of their thermal properties.
Right: First results of the phase change transition (Tm equals temperature of melting, Tc temperature of crystallization) obtained for the class of linear fatty esters (accepted for publishing from [2])
The last class of esters under investigation is that of aromatic esters. At present, nine commercial aromatic esters have been characterized, while pentyl and phenyl esters of terephthalic acid are being synthesized from methyl terephthalate via transesterification. So far, aromatic esters seem to possess a wide range of phase change temperatures, while the enthalpies of fusion vary greatly. The research on aromatic esters will continue, resulting to a publication.

The experimental and numerical investigation of the Direct Contact Latent Heat Storage Concept started as well. The first experimental screening tests in a 12 l test rig (Figure 2) have been performed in the laboratory of the HSLU and the numerical investigation with ANSYS FLUENT at the partner university, the Technical University of Vienna. The experiments show, a linear decrease of the power output until a drop of the power occurs for all experiments with different Re numbers (Figure 3c). These results have been presented at the 12th International Conference on Energy and Development, Environment and Biomedicine, Corfu. One peer-reviewed paper concerning the experimental investigation has
Direct Contact Latent Heat Storage Using Esters as New Phase Change Materials

already been published [4] and one additional paper on the numerical investigation is under review.

For the upcoming investigations, two new test-rigs are planned. A new 55 l setup will include improvements out of the experience with the 12 l test-rig. A new geometry of the test volume, optical access from four sides and a completely automatic control system are the main improvements. A new 2.5 l test-rig will be built to investigate the interface interactions between different phase change materials and heat transfer fluids.

Additionally, the models of multi-phase flow and phase change in ANSYS FLUENT will be connected, and validated with experimental observations.

References

18

Heat

Closed Sorption Seasonal Thermal Energy Storage with Liquid Sorbent Solutions

Scope of project

A closed sorption Thermal Energy Storage (TES) prototype based on water vapour absorption/desorption in a high-energy density sorbent like aqueous sodium hydroxide (NaOH-H₂O, LiBr-H₂O or LiCl-H₂O was setup at HSR-SPF (Figure 1). The two processes charging (desorption, D) and discharging (absorption, A) occur under reduced pressure i.e. at sorbate vapour pressure and the exclusion of non-condensable air [1, 2]. During the charging process in summer, the thermal energy produced by solar collectors is used to partially vaporize/desorb (in the A/D unit) the water contained in the diluted solution. While this process is running, the resulting concentrated solution (A/D unit) and the water (E/C unit) are stored at room temperature in separate tanks (high concentration (HC) Sorbent tank and H₂O Sorbate tank) until the discharging process. In this storing period, no thermal energy is lost as it is in the case of sensible thermal energy storages. During discharging in winter, ground heat is used to evaporate the stored water at its vapour pressure in the evaporator (E: E/C unit). Thus, in the A/D unit, heat is released during the exothermic process of water vapour absorption into the concentrated solution. The released heat is transferred to a heat transfer fluid that can be used, for example, in floor heating applications whereas the diluted solution is stored in the low concentration (LC) tank until the next regeneration phase.

Status of project and main scientific results of workgroups

The applied storage concept (Figure 1) allows and benefits of the liquid sorbent phase, which can be pumped. The 1 kW prototype unit is using the falling film principle implemented in a tube bundle heat and mass exchanger technology with a manifold distributing the sorbent and sorbate over the tubes. Sorbent surface wetting and residence time of the sorbent in the water vapour is influencing the efficiency of the tube bundle heat and mass exchangers from the reaction zone. These parameters were investigated by performing small scale surface wetting experiments. The modular design for the absorber/desorber unit allows the replacement of the tube bundle and implementation of the improvements from previous small-scale experiments. Thus, testing of several types of tubes and liquid sorbent modifications is possible [3].

A series of evaporation/condensation tests was carried out in order to test the facility in conditions close to the real process conditions. Figure 2 shows temperature and power curves of the first measurements. About 1 kW of power is exchanged on both A/D and E/C units.
Closed Sorption Seasonal Thermal Energy Storage with Liquid Sorbent Solutions

E/C units for a heat transfer fluid (HTF) inlet temperatures of 13 °C for the A/D and 39 °C for the E/C tube bundle. The E/C unit was run without any fluid pre-heating. This explains the first (negative) power peak. With the increase of the recirculated water temperature in the E/C loop, this power gradually reaches the designed value of 1 kW. The fluctuations of the HTF temperature at the inlet of the E/C unit are explaining the small fluctuations of the power curve of this unit.

Process improvement

To increase the wetting of the tube bundle surfaces – compared to the previous COMTES system – a feasibility study regarding the effect of a hydrophilic coating on structured tube samples was carried out. The OptoPEG coating was developed by CSEM. The wetting experiments were performed in the SPF laboratory with water and the results are shown in Figure 3. The sample code includes the short name of the coating and whether it is textured or not (OPTO_f – OptoPEG coated flat tube, OPTO_t1 to OPTO_t3 – OptoPEG coated tube with different texturing types). The maximum wetted width is the graph from Figure 3 as well as in the inset. In comparison with the non-coated tube (OPTO_f0), all the samples with hydrophilic coating show a better wetting behaviour expressed as the maximum wetted width. The structured samples may present a better wetting behaviour than the non-structured [9].

Sorbent materials

Theoretical investigations performed showed that the two sorbents NaOH-H2O and LiCl-H2O have the same absorption potential and this is higher compared with LiBr-H2O (Figure 4). These considerations include both liquid and solid phases of sorbents. Although our storage concept follows the application of liquid sorbents and because of cost reasons NaOH-H2O is preferred, these results give a hint for the selection of the second (best) sorbent material.

References

Closed Liquid Sorption Seasonal Heat Storage Using Aqueous Sodium Hydroxide

Scope of project

Empa is working on different ends to improve heat and mass transfer characteristics in the liquid sorption process using aqueous sodium hydroxide for the purpose of seasonal heat storage. Major challenges are found in the mass transfer of water within the sorbent solution and rate limitations determined by molecular diffusion. Detailed analysis of mass transfer phenomena was performed in 2018 using Raman spectroscopy and neutron imaging.

It is the goal to use results from mass transfer studies to improve the core heat and mass exchanger component and to increase its volumetric power density prior to upscaling towards larger thermal discharge power.

Status of project and main scientific results of workgroups

Mass transfer analysis

In the absence of significant turbulent mixing, mass transfer of water from its gaseous phase to its liquid phase in the liquid sorbent film is governed by molecular diffusion. The diffusion rate is proportional to the concentration gradient in the liquid film, whereby the proportionality factor is the diffusion coefficient. The diffusion coefficient again is dependent on the concentration of the liquid sorbent as well as on its temperature.

Absorption and desorption processes are characterized by mass transfer of water in opposite directions. During absorption water vapour is driven into the liquid sorbent while during desorption water is being evaporated from the liquid sorbent. As previous experiments suggested the two processes behave differently, even under similar pressure differences between the sorbent solution and the absorbate atmosphere. The desorption process was found to be less critical and could be operated at higher thermal power [1–3]. In desorption mode the transport of water in the film is thermally driven. Minimum sorbent concentrations are encountered at the heat exchanger surface, increasing towards the liquid-gas interface, inversely following the thermal gradient in the liquid film. In absorption mode an additional barrier to mass transport is assumed at the liquid surface interface. Due to quick initial absorption at the interface a so called equilibrium layer is being formed, acting as a diffusion barrier by reducing the local driving force for mass transfer, i.e. the concentration gradient.

Raman spectroscopy experiments were performed to study the mass transfer kinetics during absorption and desorption under different operating conditions (Figure 1). Raman spectroscopy proved to be appropriate to detect various sodium hydroxide concentrations. Using measured calibration curves, sodium concentrations could be calculated from Raman signals received for water molecules and OH ions, respectively. Preliminary results confirm the reduction of mass transfer rates in absorption mode compared to desorption mode. More detailed analysis of the measurement campaigns performed is ongoing and will be published in a scientific journal.

Figure 1:

a) Raman spectroscope at Empa with test cell for NaOH sample holding, pressure sensor and valve for vapor control.

b) Intensity signals recorded in initial measurements for different concentrations allowing for separating peaks generated from water molecules or NaOH.

Authors

L. Baldini1, B. Fumey1, R. Weber1

1 Empa
Another experiment campaign with reference to mass transfer in the heat and mass exchanger (HMX) was performed using neutron imaging technique available at the SINQ facility at Paul Scherrer Institute (PSI). In an aluminium test cell NaOD solution is brought in contact with water vapour during the course of droplet impingement onto the liquid film. The goal was to observe the effect of surface to bulk mixing during the experiment by monitoring the concentration of hydrogen atoms in the solution. For better image contrast deuterium was used instead of normal water in the sorbent solution. Figure 2 highlights the possibility of visualizing different sorbent concentrations in the liquid film. At the gas liquid interface where water vapour is being absorbed neutrons are more strongly attenuated resulting in a darker image. A detailed analysis of the results of this measurement campaign is ongoing and will be made available through publishing activities once consolidated.

**Experimental equipment: Lab-scale bulk reactor and upscaled heat and mass exchanger**

Another experimental setup used to study mass transfer kinetics at a bulk scale was further advanced in 2018 and will be available for first measurements in 2019 (Figure 3). This lab-scale bulk reactor can be used to determine mass transfer kinetics in liquid films under different turbulence scenarios. It can help to quantify possible absorption rates under either undisturbed or well mixed conditions and therefore give an indication of what transfer rates are possible or theoretically achievable.

The design of an upscaled HMX with nominal thermal output power of 5 kW was further advanced such that manufacturing can be initiated in 2019. The design features a transparent housing allowing for visual inspection during operation. An appropriate spiral finned tube heat exchanger candidate with maximum volumetric power density remains to be identified for upsampling.

**References**


Thermal Insulation Materials for Thermal Energy Storage

Scope of project

In combination with thermal energy storage, renewable energy technologies offer a vast potential for the supply of residential space heating and the production of domestic hot water (DHW). The problem of reaching an increased market diffusion of seasonal thermal energy storage is not attributed to a lack of knowledge of these technologies, but rather to their high cost [1]. Particularly in the case of hot-water seasonal thermal energy storage (STES), it becomes of paramount importance to minimize the annual heat losses while ensuring the economic feasibility of the storage system. These conflicting objectives lead to an optimization problem in which the costs of the insulation and the storage container 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 hot-water STES systems for multifamily houses. The simulation-based optimization includes:

- the design of the storage system,
- optimization of the control strategy, and
- optimization of the entire system including peripheral components.

In this article, we present a summary of the first phase of this project: the evaluation of thermal insulation materials suitable for STES. The outcome of this work has recently been published in Renewable and Suitable Energy Reviews [2].

Status of project and main scientific results of workgroups

In the framework of SCCER HaE, three goals have been defined for the STES task:

A. Development and construction of a seasonal water storage pilot plant with costs below 60 CHF/m³.

B. Identification of a thermal insulation method that combines vapor barrier with high thermal resistance.

C. The increase of the storage density by combining sensible and latent storage modes.

This article summarizes the ongoing work aiming to achieve goal A through economic optimization of hot-water TES systems. Alternative hot-water storage, we are investigating – in the framework of an Innosuisse project – the techno-economic potential of near-surface horizontal borehole thermal energy storage. Goal B is actively pursued in another ongoing Innosuisse project directly related to the work presented here. In terms of goal C, a parametric study is being conducted to assess the economic potential of combining sensible and latent heat storage for STES systems integrated in residential buildings.

Scenarios and boundary conditions

In this work, the focus is on STES systems for direct supply of space heating and production of DHW in single buildings. Storage volumes between 10 and 1’000 m³ are regarded for this application. The learnings from this work can nevertheless be applied also to larger STES systems suitable for clusters of buildings or district heating. In larger systems, however, the energetic and economic relevance of the thermal insulation is not as important as in smaller systems. This follows from the smaller surface-to-volume ratio of larger systems and consequently their fundamentally different thermal behavior and economic characteristics.

List of abbreviations

- DHW: Domestic Hot Water
- PUR-PIR: Polyurethane-Polyisocyanurate Rigid Foam
- STES: Seasonal Thermal energy Storage
- VIP: Vacuum Insulated Panels

References


Authors

Willy Villasmil1
Marcel Troxler1
Ludger Fischer1
Jörg Worlitschek1

1 Lucerne University of Applied Sciences & Arts
The storage concepts considered here are shown in Figure 1. In these scenarios, the STES system consists of a thermally stratified water tank with a maximum temperature in the range of 60–90°C [3]. Lower storage temperatures may allow a reduction of heat losses, however at the expense of a larger storage volume and the cost of incorporating supporting equipment (e.g. a heat pump) to increase the temperature to a useful level [4].

One method to be explored to allow the integration of a STES system in an existing building is the retrofit of an unused underground room enclosure (Figure 1, concept 3). The retrofit would consist of applying suitable vapor barrier and thermal insulation materials to the walls, floor, and ceiling of the room to allow the entire space to be transformed into a hot water reservoir for STES.

The challenges of incorporating the insulation material on the inside wall of the storage are similar to those faced in the construction of hot water pit storages. Identifying suitable materials for this application is the subject of an ongoing Innosuisse project.

### Thermal insulation methods and materials

A selection of thermal insulation materials that can be applied on the storage outside wall is presented in Table 1, along with their most relevant thermophysical properties. The selection was made on the basis of commercially available materials with maximum service temperatures adequate for thermal energy storage in the range of 60–90°C. From the perspective of energy efficiency, the thermal conductivity is typically the most important property to be considered in the evaluation of insulating materials. The thermal conductivity, \( \lambda \), largely depends on the density, internal structure (pore fraction and pore size), temperature, and moisture content of the insulation material. [5–9] For the sake of providing a concise overview, thermal conductivity values reported here correspond to dry materials at 20°C.

The thermal performance of insulation materials can be evaluated by comparing either the thermal conductivity (\( \lambda \)) or the material thickness (\( L \)) required to provide a given thermal resistance (\( R\)-value = \( L/\lambda \)). Here, a reference \( R\)-value of 10 m²·K/W (deemed suitable for STES) is used to allow a direct cost comparison of the various insulation materials. This comparison is presented in Figure 2, in which the required material thicknesses (\( L \)) were computed using mean thermal conductivities values of those listed in Table 1.

The work conducted in this project has allowed identifying thermal insulation materials suitable for STES. Our economic analysis [2] shows that the use of novel thermal insulation materials (such as VIP or PUR-PIR) can be favorable when the economic value of saving living space outweighs the extra cost of the thermal insulation itself. Alternatively, the method of evacuated powders (widely used in cryogenics) can offer significant advantages for STES. First, it can allow the storage to be buried underground (Figure 1, concept 2), thereby eliminating the need for valuable living space inside residential buildings. In contrast to VIP, the use of evacuated powders in a double-wall tank construction can allow maintaining the low thermal conductivity of the insulating jacket through a periodic re-evacuation of the vacuum chamber.

### Table 1:

<table>
<thead>
<tr>
<th>Insulation material</th>
<th>Type of insulation</th>
<th>( \lambda ) [mW·m⁻¹·K⁻¹]</th>
<th>( \rho ) [kg·m⁻³]</th>
<th>( T_{\text{max}} ) [°C]</th>
<th>( \sigma_{\text{CC}} ) [kPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>VIP</td>
<td>Superinsulation</td>
<td>4–8</td>
<td>65–300</td>
<td>90</td>
<td>45–120</td>
</tr>
<tr>
<td>Silica aerogels</td>
<td>Superinsulation</td>
<td>4–20</td>
<td>3–360</td>
<td>750</td>
<td>–0–5000</td>
</tr>
<tr>
<td>PUR-PIR</td>
<td>Organic, foamy</td>
<td>19–30</td>
<td>25–30</td>
<td>120</td>
<td>100–600</td>
</tr>
<tr>
<td>XPS</td>
<td>Organic, foamy</td>
<td>25–35</td>
<td>10–60</td>
<td>75</td>
<td>150–703</td>
</tr>
<tr>
<td>EPS</td>
<td>Organic, foamy</td>
<td>28–41</td>
<td>10–60</td>
<td>60</td>
<td>60–260</td>
</tr>
<tr>
<td>Glass wool</td>
<td>Inorganic, fibrous</td>
<td>30–46</td>
<td>8–165</td>
<td>500</td>
<td>15–80</td>
</tr>
<tr>
<td>Foam glass</td>
<td>Inorganic, foamy</td>
<td>38–61</td>
<td>100–200</td>
<td>&gt;400</td>
<td>400–1600</td>
</tr>
</tbody>
</table>

### Figure 2:

Material cost (top) and insulation thickness (bottom) required to achieve an \( R\)-value of 10 m²·K/W with various thermal insulation materials. Solid dots represent average cost values, while the bars indicate the range found in the literature.
The guiding principles of the work 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;
• to keep jobs in Switzerland.

The following picture shows the roadmap of the activities.

Battery materials and electrodes

At ETHZ and Empa the activities in the field of battery materials and electrodes were focused mainly on the development of high area capacity electrodes for Li-ion batteries and their demonstration in full cells. A negative graphite electrode was developed jointly with Belenos Clean Power Holding, our industrial partner. It exhibits high areal capacity of 5.4 mAh/cm², high coulombic efficiency of 99.8%, and shows low average charge voltage of 0.2 V vs. Li⁺/Li at C/2 rate. The initial coulombic efficiency of the graphite electrode was 93.7%. A capacity retention of 75% after 200 cycles was demonstrated at C/5 rate in an NMC111/graphite full cell with high mass loading electrodes (areal capacity of 4.3 mAh/cm²). Based on the measured data we projected to enable > 220 Wh/kg in a pouch cell with a stack of 11 anodes and 10 cathodes according to an xls calculation sheet developed at Empa. Further, the shape-controlled synthesis of cathode powders on multi-gram scale was extended to Co-poor and Ni-rich NMC811 using the coprecipitation system built in 2017. Finally, a selection of the best electrolyte to stabilize NMC811 in full cells against graphite anodes is underway. To this point, capacity retention of 91% after 200 cycles at C/3 rate was demonstrated in a NMC811/graphite full cell with intermediate mass loading (i.e., lower areal capacity).

At the University of Fribourg research on a more fundamental level was performed. Electrolyte additives based on ionic liquids (IL) with different sizes of crown ethers are promising showing enhancement in the cationic transference number. For instance, by adding 1 wt% of IL-crown-5 into a commercial aprotic electrolyte LP71 (1M LiPF₆ in EC/DEC/DMC) a transference number of 0.62 was obtained while that of pure LP71 was only 0.44. The electrochemical stability window is up to 4.9 V, while the ionic conductivity is about...
5.3 mS/cm. Also, some alternative cathode materials were tested. Efforts were made to increase the rate capability of LiMnPO₄ (LMP) by Fe doping; the Li-ion diffusion coefficient of Fe-doped LMP electrodes increased to ~ 5 x 10⁻⁹ cm²/s compared to that of pure LiMnPO₄ (10⁻¹¹ ~ 10⁻¹² cm²/s).

Na-ion batteries are the targeted system for stationary applications since their cost is expected to be lower than that of Li-ion batteries whereas their energy density could be only 20–30% less. Still, novel materials and electrolytes need to be developed keeping in mind the cost criteria. On the materials side, we successfully developed some carbonaceous materials using biowaste sources. Those negative electrodes for Na-ion batteries delivered up to 280 mAh/g at a cycling rate of C/3 for more than 100 cycles with a loading close to the one used in an industrial application. For the positive electrode, the challenges are bigger. We opted for the investigation of the phases Na₂/₃Mn₀.₆Fe₀.₂₅Co₀.₁₅O₂ and Na₂/₃Mn₀.₆Fe₀.₂₅Al₀.₁₅O₂ since both of them are reported to be good for Na diffusion (allowing thus fast cycling rates). We found out that it is possible to increase the Na content of the P2 phase by using sacrificial template/Na reservoir composed of the organic material Na₂C₆O₆. On the engineering side, several home-made cylindrical cells were assembled with high loaded positive electrodes (> 15 mg/cm², ratio of active materials > 90 wt%) and our carbonaceous negative electrodes as a proof-of-concept. The fading is more pronounced with such loadings however. On the electrolyte side, activities related to water-in-salt electrolytes were started to assess the viability of such a system promising both higher safety and a cost reduction.

**Battery cell production research**

The team at the BFH focuses on battery cell production research, and potential implementation partners were involved right from the start. We are aware of challenges of significant operating expenses associated with a complete manufacturing line and the challenges defining a business model for such a line. For this reason, the hardware based part of the project limits itself to specific steps in the process (mainly laser cutting, Z-folding, and quality control) where the highest potential for cost reduction is seen. The main activity of the project is, however, not the hardware but the holistic (computer) model based analysis of manufacturing. In the end, a complete cost model of the manufacturing process is built and optimization is done. This approach showed a potential of 60% cost reduction for pouch cells and 25% cost reduction for cylindrical cells, based on current material sets used in industry.

In more detail, a complete holistic model of the pre-production pilot line at an industrial partner including the electrode production was already developed. As novelty, it is dynamic and includes simultaneously product flow, product quality, process flow with production parameters, worker model, machine level with consumption and all cost (CAPEX and OPEX) in contrast to the today’s static product flow models. The main research objective is to optimize the production with new technique and «Industrie 4.0» approaches.

The combination of focusing on critical parts of the manufacturing process in hardware and the cost modeling approach is well suited to educate students to become specialists in this critical field on one hand. On the other hand, it serves well to answer urgent questions from the implementation partners. As an additional benefit academia and others can now be provided with application sized cells produced of this pilot line with today’s and new chemistries for testing. First functional cells were already built from commercial electrodes (NCA and NMC111).
Strategies to Improve Na-Ion Batteries

Scope of project

Due to the abundance of Na, Na-ion batteries (NaB) are considered as a serious alternative to the dominant Li-ion technology for stationary applications. All along this project, new electrode materials were investigated and two were selected: a carbonaceous material produced from biowaste [1] and the layered oxide P2-Na$_{0.67}$Mn$_{0.6}$Fe$_{0.25}$Al$_{0.15}$O$_2$ [2]. The combination of these materials allowed to reach a specific charge of ca. 100 mAh g$^{-1}$ at C/10 resulting in an energy density of 170 Wh kg$^{-1}$ (after 5 cycles). This report exposes the strategies employed to improve the electrochemical performance, the cost and the safety of NaB.

Status of project and main scientific results of workgroups

The P2-Na$_{0.67}$Mn$_{0.6}$Fe$_{0.25}$Al$_{0.15}$O$_2$ phase, used as cathode material, provides a high specific charge of 160 mAh g$^{-1}$ in half cell. It might be due to the higher sodiation level of the material during the discharge at 0.8 instead of the initial 0.67. In half cell configuration, the excess of Na comes from the Na metal counter electrode whereas no additional Na is present in full cell.

The use of an organic compound, the disodium rhodizonate (called thereafter SR), anionic redox activity, is described during the 1st charge. After 10 cycles, the reduction of SR coincided with a negative shift of the P2-NaMFC peak at ca. 36° whereas a positive shift was expected suggesting that the SR decomposed during the 1st charge. Interestingly, the decomposition of SR coincided with a negative shift of the P2-NaMFC peak at ca. 36° whereas a positive shift was expected during the desodiation. It indicates that a sodiation of the P2-NaMFC material occurred due to the decomposition of SR, showing that the organic molecule is playing the role of Na reservoir. Unfortunately, the formation of water during its decomposition is detrimental for long-term cycle, meaning that the organic molecule needs to be further optimized.

03-phase with a layered oxide structure material possesses a Na content allowing high specific charge in full cell system but the material suffers from a faster fading. Therefore, the reason of this fading requires deeper investigation. The O3-Na$_{0.67}$Mn$_{0.6}$Sn$_{0.25}$Ti$_{0.15}$O$_2$ phase (O3-NNMST) loses 25% of its initial specific charge after 15 cycles whereas a better stability is reached for the next cycles. The evolution of the 01s core level spectra obtained from the X-ray photo-electron spectroscopy analysis (Figure 2) showed that a peak at 530 eV, assigned to the anionic redox activity, is detected during the charge and vanished at the end of the discharge. After 10 cycles, the re-

List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMC</td>
<td>Carboxymethylcellulose</td>
</tr>
<tr>
<td>NaB</td>
<td>Na-Ion Batteries</td>
</tr>
<tr>
<td>NaMFC</td>
<td>Na$<em>{0.67}$Mn$</em>{0.6}$Fe$<em>{0.25}$Co$</em>{0.15}$O$_2$</td>
</tr>
<tr>
<td>NMP</td>
<td>N-Methyl-2-Pyrrolidone</td>
</tr>
<tr>
<td>NMPC</td>
<td>Na$_2$MnCO$_3$PO$_4$</td>
</tr>
<tr>
<td>NNMST</td>
<td>NaNi$<em>0.5$Mn$</em>{5/16}$Sn$<em>{1/16}$Ti$</em>{1/8}$O$_2$</td>
</tr>
<tr>
<td>NTP</td>
<td>NaN$_3$(PO$_4$)$_2$</td>
</tr>
<tr>
<td>SR</td>
<td>Disodium Rhodizonate</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction Spectroscopy</td>
</tr>
</tbody>
</table>

References


Authors

Cyril Marino¹
Elena Marelli¹
Maximilian Schuster¹
Claire Villevieille¹

¹ PSI
versatility of the anionic redox is not present anymore since the peak at 530 eV is seen both in the charge and the discharge spectra. Combined with on-line electrochemical mass spectroscopy and XRD, it was confirmed that the anionic redox failure is responsible of the capacity fading.

The electrode processing is an important part in the overall cell cost. In a standard procedure, electrodes of layered oxide materials are prepared in the toxic solvent, N-methylpyrrolidone (NMP), which is a drawback for industrial processing. Water-based electrodes of P2-NaMFC using carboxymethylcellulose (CMC) binder were tested and limited electrochemical performances at 90 mAh·g⁻¹ were obtained compared to a specific charge of 145 mAh·g⁻¹ for the NMP-based electrode (Figure 3a). [3] This difference can be explained by the protons exchange in the structure, occurring when the material is mixed into water, which disrupts the Na ions extraction during the charge. This finding indicates that water cannot be used as solvent in the preparation of such electrodes if a high energy density battery is targeted.

In order to improve the safety of the NaB, a new research line was opened in the laboratory using aqueous-based electrolyte. The use of water-in-salt electrolyte (highly concentrated electrolyte) instead of conventional aqueous electrolyte widens the stability window of water (from 1.23 V to > 2 V) and enables the usage of electrode materials adapted to this new potential limit in aqueous system. [4]

The material NaTi₅(PO₄)₃ (NTP), widely used as negative electrode material in aqueous NaB, was selected to be the counter electrode. On the cathode side, the first focus was on the carbonophosphonate material Na₃MnCO₃PO₄ (NMPC), successfully tested in organic-based electrolytes. [5] NMPC was tested in full cell with NTP as anode and an aqueous 15 m NaFSI electrolyte with a voltage window between 1.8 V to 0 V at C/15 rate (Figure 3b). A specific charge of 100 mAh·g⁻¹ was reached for the first discharge and, for the following cycles, a continuous decrease in specific charge from 140 mAh·g⁻¹ to 50 mAh·g⁻¹ can be observed. The evolution of the coulombic efficiency reached a maximum of 95% after the 5th cycle indicating that a good passivation is formed preventing the water decomposition.
Development of Ionic Liquids as Electrolyte Additives and a Cathode Material for Lithium Ion Batteries

Scope of project

Electrolyte additives: Crown-ether based ionic liquids (IL) have been developed as additives for electrolytes to enhance the battery properties. As critical parameters, the cation transference number, ionic conductivity, electrochemical voltage window, cycleability, and rate capability have been investigated.

Cathodes: A nanostructured composite of LiMnPO$_4$/C had shown promising electrochemical properties as a cathode material in 2017 [1]. In order to increase the rate capability, we now tested Fe-doped LiMnPO$_4$ (LMP), whose stoichiometry was determined by ICP analysis.

Status of project and main scientific results of workgroups

Electrolyte additives

The cation transference number ($T_{Li^+}$) increased from 0.44 for the pure commercial electrolyte to 0.62 upon addition of 1 wt% of a specific ionic liquid (Figure 1a). The crown-ether based ionic liquid decomposed at ca. 4.3 V vs. Li$^+$/Li and suppressed the decomposition of the solvent. Furthermore, stripping/plating of lithium is significantly reduced at low potential when the ionic liquid is present. The ionic conductivity of the electrolyte with 1 wt% IL provided 5.7 mS/cm at 25°C (Figure 1b). No degradation occurred during 100 cycles at a constant current of ±20 and ±50 μA per cm² of electrodes holding for 1 h at each ± current (Figure 1c).

The electrolytes with IL have been tested on cathodes (NMC111 and NMC811) of Li-ion batteries in collaboration with Empa. The capacity retention of NMC111 with IL additive was >65% upon 200 cycles at C/3, while it dropped rapidly after 140 cycles without IL additive in the electrolyte (Figure 2a). On the other hand, the capacity retention of the Ni-rich cathode NMC811 was slightly lower with an IL additive than that without an IL additive upon 160 cycles. The rate capability of NMC111 with an IL additive was superior to that without the additive at low C-rates between C/10 and 1C but then it decreased at 5C compared to that without the additive.

The new electrolyte additives have also been tested on carbon anodes and NaMFC cathodes of Na-ion batteries in collaboration with PSI. The

References


Authors

Jihane Hankache¹
Nam Hee Kwon¹
Katharina M. Fromm¹

¹ University of Fribourg
anodes showed no change in performance with and without IL (Figure 2b), while the capacities of NaMFC cathodes were 110 and 107 mAh/g at C/10 and C/5, respectively, with the IL additive, and 135 and 130 mAh/g at the same rates as above without an IL additive as shown in Figure 2c.

**Cathodes**

The Li-ion diffusion coefficient of Fe-doped LMP electrodes increased significantly from $10^{-11} \sim 10^{-12}$ cm$^2$/s (pure LMP) to $4.4 \sim 7.3 \times 10^{-9}$ cm$^2$/s. The rate capability of Fe-doped LMP provided 157 and 142 mAh/g at C/10 and 1C, respectively, while pure LMP gave 123 and 90 mAh/g at the same C-rates, respectively. This corresponds to a 30–60% increase in specific capacities (Figure 3a).

Good cycling stability until ~20 cycles was observed with ca. 120 mAh/g at C/5 of C-rate in Figure 3b.

Figure 3:
(a) The rate capability of LiMnP4 and Fe-doped LiMnP4 cathodes of Li-ion batteries at various C-rates.
(b) The cycleability of Fe-doped LiMnP4 electrode at the C-rate of C/5.
Stabilizing NMC811 in Full Cells with High Areal Capacity

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. In the first year of phase II, we established an automated co-precipitation setup for the shape-controlled synthesis of LiNi_{0.33}Mn_{0.33}Co_{0.33}O_{2} (NMC111) cathode materials and 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. In the second year of phase II, we extended this work towards full cells coupling high-mass-loading NMC111 cathodes with 4.3 mAh/cm² areal charge capacity with balanced high-mass-loading graphite anodes with 4.8 mAh/cm², provided by SCCER partner Prof. Kovalenko’s group at ETH/Empa, demonstrating a capacity retention of 63% after 300 cycles at C/5. This lab cell is projected to reach state-of-the-art 220 Wh/kg, when scaled to pouch cells developed by SCCER partner Prof. Fürst’s group at BFH.

Status of project and main scientific results of workgroups

To go beyond the state-of-the-art, we extended our co-precipitation capabilities to the synthesis of Ni-rich LiNi_{0.8}Mn_{0.1}Co_{0.1}O_{2} (NMC811) cathode materials. NMC811 offers almost 30% higher gravimetric capacity than NMC111 and reduces the amount of critical and expensive cobalt. Nevertheless, NMC811 still poses multiple fundamental challenges, such as irreversible structural rearrangements, transition metal dissolution, high surface reactivity, and parasitic oxidation of the organic electrolyte at the surface when delithiated, severely limiting its long-term cycling stability. Exploring electrolyte additives, we were able to stabilize NMC811 electrodes with a high areal capacity of 4.3 mAh/cm² against balanced graphite electrodes with 5.2 mAh/cm² in a full cell demonstrating a capacity retention of 74% after 300 cycles at C/5. This cell is projected to reach 245 Wh/kg when scaled to pouch cell format. Future work needs to focus on improving the Coulombic efficiency during the first cycles and reduce cell impedance growth during long-term cycling.

Layered (NMC811) cathode powders were synthesized by co-precipitation of Ni_{0.8}Mn_{0.1}Co_{0.1}(OH)_{2} hydroxide precursor followed by high temperature solid-state calcination with LiOH.H₂O at 800°C under O₂ flow. Powder X-ray diffraction (XRD) analysis confirms the phase purity of the NMC811 powder, showing a layered structure belonging to the R-3mH space group (Figure 1a). Moreover, no presence of impurity phases is detected. Scanning electron microscopy (SEM) imaging reveals that the NMC811 powders consist of ~3–7 µm quasi-spherical secondary particles composed of 150–300 nm primary particles (Figure 1b). NMC811 powders display a tap density of around 2.2 g/cm³ with a BET surface area of approximately 2.1 m²/g.

Galvanostatic cycling in half cells of the NMC811 vs. Li metal at room temperature demonstrates initial discharge capacities of 203 mAh/g, 197 mAh/g and 190 mAh/g at rates of C/10, C/5 and C/3, respectively. Long-term cycling reveals a discharge capacity retention of 86% and 51% after 100 and 240 cycles at C/3, respectively (data not shown here). A high areal charge capacity is key to reach high energy density on cell and pack level, as it reduces the weight and volume fraction of inactive materials in the cell. Therefore, 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, reaching a high areal capacity of ~5.2 mAh·cm⁻² at a rate of C/10 in NMC811 vs. Li metal half cells (Figure 2a). Due to a high active material content and the high mass loading, our electrodes can reach significantly higher areal capacity than commercial NMC111 and NMC811 reference electrodes.

List of abbreviations

- NMC111 LiNi_{0.33}Mn_{0.33}Co_{0.33}O_{2}
- NMC811 LiNi_{0.8}Mn_{0.1}Co_{0.1}O_{2}
- SEM Scanning Electron Microscopy
- XRD Powder X-Ray Diffraction

References


Authors

Josefa Vidal Laveda¹
Jia En Low¹
Corsin Battaglia¹

¹ Empa

Figure 1: a) Powder XRD pattern and b) SEM image of NMC811 powders.
Stabilizing NMC811 in Full Cells with High Areal Capacity

(Also shown for comparison in Figure 2a). High-mass-loading NMC811 delivers initial discharge areal capacities of up to 5.2 mAh/cm² at a rate of C/10, but at such a high mass loading of almost 30 mg/cm² stable cycling is limited to rates up to C/5. At lower, but still high, mass loadings near 20 mg/cm², the performance of our NMC811 electrodes is comparable to commercial reference electrodes. Extended cycling in half cells with high mass loading NMC811 electrodes at C/5 shows 4.7 and 2.6 mAh/cm² after 50 and 100 cycles at C/5, respectively (Figure 2b).

Next, high-mass-loading NMC111 (~29 mg/cm²) and NMC811 (~24 mg/cm²) electrodes were cycled in balanced full cells against a high-mass-loading graphite electrode (~15 mg/cm²) provided by SCCER project partner Prof. Kovalenko’s group [2] employing an electrolyte formulation developed by us specifically to stabilize NMC811 [1]. Galvanostatic cycling of the NMC111/graphite and NMC811/graphite full cells at a rate of C/5 demonstrates initial gravimetric discharge capacities of approximately 145 mAh/g and 175 mAh/g, respectively. These cells exhibit similar areal discharge capacities of 4.3–4.5 mAh/cm², but NMC811 displays more rapid fading during the first cycles compared to NMC111. However, NMC811 demonstrates better capacity retention probably due to the lower mass loading required with NMC811 in order to balance graphite electrode with an equal mass loading of 15 mg/cm² (practical capacities at low rates are 200 mAh/g vs. 160 mAh/g for NMC811 vs. NMC111). The NMC811/graphite cell delivers a discharge capacity retention of 74% after 300 cycles at C/5 corresponding to 3 mAh/cm² after 300 cycles (Figure 3). Cell energy density projections for a stacked pouch cell based on our high areal capacity NMC111/graphite and NMC811/graphite cells result in estimated 220 Wh/kg and 245 Wh/kg, respectively, when using 11 anode sheets and 10 cathode sheets. Our projections also indicate that when increasing the NMC811 electrode mass loading to 29 mg/cm² and the gravimetric capacity to 200 mAh/g, and cycling it against 18 mg/cm² graphite electrode, ~275 Wh/kg could be attained (Figure 4), which corresponds to the energy density target for the SCCER project.

Conclusions

We presented results on the synthesis and characterization of high capacity NMC811 cathodes in half and full cells. We established a slurry processing and coating process for the preparation of electrodes with high areal capacity reaching ~5.2 mAh·cm⁻² in half cells vs. Li metal. NMC811/graphite full cells delivered a discharge capacity retention of 74% after 300 cycles at C/5 reaching 3 mAh/cm² employing an electrolyte formulation developed specifically to stabilize NMC811. Cell energy density projections for a stacked pouch cell based on the presented NMC111/graphite and NMC811/graphite lab cells estimate that energy densities of 220 Wh/kg and 245 Wh/kg, respectively, could be reached when using 11 anode and 10 cathode sheets. To reach the project target of 275 Wh/kg, Coulombic efficiency during the first cycles needs to be improved and impedance growth during long-term cycling needs to be mitigated.
Pilot Line Modules for Lithium-Ion Battery Cell Assembly and Advantages of Laser Processing

Scope of project

The main goal of the «Batteries and Battery Materials» work package at the SCCER program is to produce battery cells with a gravimetric energy density of 275 Wh/kg, whereas current state-of-the-art cells exhibit energy densities of around 220–240 Wh/kg. The goal shall be reached by improving material synthesis and slurry formulation, thicker electrodes and cell assembly with optimized inactive materials.[1] The team at BFH has established a virtual pilot line and hardware modules for pouch cell assembly, which are used to build test cells for research and industry and investigate current challenges in battery cell production.[2] In particular, the application of laser processing for cutting, ablation and electrode conditioning are in focus.

Status of project and main scientific results of workgroups

Figure 1 shows performance results of a stacked test battery for formation and for cycling at different C-rates. In each cycle the cell is charged to 4.2 V at constant current followed by a constant voltage phase and discharged to 2.75 V at constant current. One can see that the design capacity is reached. Further reduced capacity at higher c-rates is in the expected range. Additionally, a life cycle test at 1C was executed with the same potential window: The battery reached 80% of initial capacity at about 200 cycles, which is in line with current state-of-the-art for NMC-based lithium-ion materials.

The test of the cell with 6 anode sheets and 5 cathode sheets each sized 65 x 85 mm indicated that the design capacity of 1100 mAh was reached (Figure 2). The cell weighs 19.2 grams and has a measured capacity of 1054 mAh which equals to a discharge energy of 3846 mWh at C/5. This is close to the current state-of-the-art even without further design optimizations.

Above results show that the BFH team is capable to assemble application-sized pouch cells with required quality.

References

Authors
Michael Stalder1
Aysegül Haktanir1
Axel Fuerst1

1 BFH (Bern University of Applied Sciences)
Further, practical knowledge gained from building test batteries is used to continuously optimize the construction of the pilot line modules. Besides the technical optimization studies, the team continuously improves the production quality.

Advantages of laser processing

Lasers have the potential to be used in various steps in lithium-ion battery cell production such as cutting of electrodes, structuring and modification of electrodes, cutting and welding of tabs and cutting of pouch cell laminate. [3]

At BFH the laser unit is used to cut electrodes and for ablation of active materials.

Laser foil cutting provides several advantages over mechanical foil punching: Laser cutting has minimal tool wear which makes it more cost-effective in terms of operational costs because there are no replacement tooling and outage times. Due to tool wear in mechanical punching the edge quality degrades over time, an issue which is not present in laser cutting. Further Laser cutting is highly flexible in geometrical shapes, such that different electrode sizes can be cut on the same equipment with much shorter setup times and no additional tooling compared to mechanical punching.

At BFH the functionality of the laser has been extended to ablation of active materials where the same equipment as for cutting is used. In ablation of active material, the material is removed from the current collector with the goal of removing all the active material in a defined area without affecting the current collector (alumina or copper foil).

This process can be used to manufacture electrode sheets from foils of coated material where the coating profile is not constant towards the edge or edge quality is poor. By using ablation, a coated foil without well defined boundaries can be used to produce a usable electrode sheet by removing active material in the tab area, see Figure 3.

In the future, further application of laser ablation of active material shall be investigated, e.g., for correcting the thickness of electrodes if qualitatively insufficient sections are detected or perforating electrodes to create electrode channels for improved ion transport in thick coatings.
Ultra-High Mass Loading Graphite Anodes for Li-Ion Batteries

Scope of project

At present, rechargeable Li-ion batteries (LIBs) became a key energy storage technology, which served mankind for the past two decades in a variety of applications, e.g. portable electronic devices and electric vehicles, owing to its high energy density, long cycling lifetime, and high power performance [1-5]. The practical energy density of present-day LIBs composed of electrodes with areal capacities of 3.5 mAh cm⁻², however, is approaching its limit of 220–250 Wh kg⁻¹. In this context, the development of anodes and cathodes with higher areal capacities has been considered as the main objective within this SCCER project, enabling to increase the energy density of LiBs by up to 5–15%.

Status of project and main scientific results of workgroups

Since the commercialization of LIBs in 1991 by Sony Corporation, graphite remains the most prominent anode material for LIBs. When comparing it with other anode materials such as Si, Sb, Sn or Li₄Ti₅O₁₂ (LTO), most important advantages of graphite are its low cost, non-toxicity, safety, low de-lithiation potential of 0.2 V vs. Li⁺/Li, high coulombic/energy efficiencies, as well as long operation life span over hundreds to thousands charge/discharge cycles.

In the context of further improvement of graphite anodes for LIBs, great research efforts are presently focused on the development of high areal capacity graphite electrodes of >3.5 mAh cm⁻² with high rate capability (maintaining the gravimetric capacity of >350 mAh g⁻¹ at C/2 rates or higher).

We have developed a graphite anode (jointly with an industrial partner) with an ultra-high areal capacity of 5.4 mAh cm⁻², the high initial coulombic efficiency of 93.7% and the low average charge voltage of 0.2 V vs. Li⁺/Li at C/2 rate (Figure 1). The developed graphite anode delivers a capacity of ~350 mAh g⁻¹ for 35 cycles at a C/2 rate and shows high coulombic efficiency of 99.8%.

The galvanostatic measurements of full cells in combination with LiNiₓMnᵧCo₁₋ₓ₋ᵧO₂ (NMC) cathodes are in progress.

Figure 1:
a) Galvanostatic charge/discharge curves and b) cyclic stability of a graphite anode (cells were cycled at different C rates (1C rate is 372 mAh g⁻¹) in the potential range of 0.01–1.5 V using constant current-constant voltage (CCCV) protocol at 5 mV; Specific capacities and currents correspond to the mass of graphite active material.

List of abbreviations

LIB Lithium-Ion Battery
LTO Li₄Ti₅O₁₂

References


Author
Romain Dubey¹,²
Kostiantyn Kravchyk¹,²
Maksym V. Kovalenko¹,²

¹ ETHZ
² Empa
Hydrogen Production and Storage

Work Package «Hydrogen Production and Storage» at a Glance

The energy economy based on renewable energy is developing very quickly and produces a large demand for energy storage. Seasonal storage requires storing approximately half of the annual energy demand and is, therefore, a challenging materials science and technology task. In Switzerland the average annual electricity demand is approx. 10 MWh/capita and the energy demand slightly less than 60 MWh/capita incl. nuclear, jet fuel, and embedded energy. A seasonal storage if the energy is produced from renewable is in the range of 5–30 MWh/capita (corresponds to 500–3000 l of oil). In WP 3 new materials for energy storage with hydrogen are investigated. The carbon free hydrogen cycle is based on purely technical means and is a closed materials cycle, because the water released into the atmosphere precipitates spontaneously. The energy is stored by splitting of water into hydrogen and oxygen and the hydrogen is stored. The combustion of the hydrogen with air releases the energy in the form of heat and electricity. In this work package the research concentrates on two methods to produce hydrogen, i.e. the alkaline electrolysis and the hydrogen evolution from the electrolyte of a redox-flow-battery, and two methods to store hydrogen in hydrides and in formic-acid.

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 electrolyzers 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 emerges, with stable overpotentials as low as 270 mV (for 10 mA·cm⁻²) and Tafel slopes of 37 mV decade⁻¹. The Faradaic efficiency for the OER was unity and no deterioration in performance 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 Co₀.₁₁Fe₀.₃₃Ni₀.₅₅, 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

Alternatively, electricity is stored in a redox-flow battery with a high flexibility in charge and discharge power. The electrolyte containing the storage material reacts on a catalyst and splits water, i.e. chemical discharge of the battery into hydrogen. This method allows to split water without the need of electrodes nor gas separator and has the potential to reach very high power densities. In the particular case of a RFB dual circuit, 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. Hydrogen was generated from V(II) using an abundant and low cost Mo₂C catalyst and achieved a production yield of 96 ± 4%. Water oxidation was achieved over IrO₂ and RuO₂ nanoparticles from positive electrolytes comprising Ce(IV) in various acid solutions. A 78 ± 8% O₂ yield was obtained in 1 M H₂SO₄ and a partially hydrated RuO₂ 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.

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. 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 reac-
tions 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 optimizing the catholyte dis-
charge and to further characterize the catalytic reactions
are in progress. For instance, the use of Mn(II) electrolyte
to replace Ce(IV) in the positive electrolyte is under prog-
ress.

**Hydrogen storage in complex hydrides**

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.

These materials have been combined with ionic liquids in or-
der to destabilize the borohydride. The hydrogen desorption
temperature was lowered significantly. A new 3D structure
of carbon based on graphene oxide and carbon nanotubes
linked together exhibits a large hydrogen storage capacity.
The material absorbs more than 5 mass% of hydrogen at
room temperature and desorbs the hydrogen with almost
no hysteresis. Metal hydrides can be used to compress hy-
drogen. The increase of the temperature to 200 °C allows to
compress hydrogen to 200 bar without any moving parts.

Large scale hydrogen storage has been developed and
built with a capacity of 2 kg of hydrogen (80 kWh of en-
ergy). The hydrogen is stored in an intermetallic compound
((La₀.₇₄Ce₀.₂₄)Ni₄.₂₁Co₀.₆₈Mn₀.₁₀) with an equilibrium hydro-
gen pressure of 3 bar at 20 °C. The storage is installed in
the small scale demonstrator for Sion and filled by a PEM
electrolyzer. The modular design of the storage allows up-
scalling and a several storage system for 1 MWh (25 kg of
hydrogen) to 3 MWh is currently built.

**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 work sum-
marizes the recent progress of research on the develop-
ment of homogeneous catalysts mainly focusing on formic
acid and CH₃OH and the reports on the catalysts 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 elec-
tricity using a proton exchange membrane (PEM) fuel cell.
Although various catalysts have been reported to be very
selective towards formic acid dehydrogenation (resulting in
H₂ and CO₂), a side-production of CO and H₂O (formic acid
dehydration) should also be considered, because most PEM
hydrogen fuel cells are poisoned by CO.

In this research, a highly active aqueous catalytic sys-
tem containing Ru(III) chloride and meta-trisulfonated
triphenylphosphine (mTPPTS) as a ligand was applied
for formic acid 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 formic acid feed. It was concluded that
unwanted CO concentration in the H₂ + CO₂ gas stream was
dependent on the current formic acid 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).

An industrial prototype has been built and presented on
19.03.2018, the world’s first formic acid-based power sup-
ply unit, using PEM fuel cell for electricity production.
Hydrogen Storage in Hydrides

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, reversible and compact. 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. Some of the new carbon materials, e.g. graphene oxide, exhibit unique gas sorption properties. These materials can be functionalized, e.g. Boron and Nitrogen, are low cost and easy to produce in large quantities. The start-up company GRZ Technologies SA has developed large scale solid hydrogen storage systems with a capacity of > 1 MWh and sold several hydrogen compressors (HyCo) based on metal hydrides as well as the advanced gas analysing system (AGAS).

Status of project and main scientific results of workgroups

Study of borohydride ionic liquids as hydrogen storage materials

Sodium borohydride (NaBH₄) is a complex hydride containing 10.5% of its mass as hydrogen; however, it is too stable to desorb hydrogen at room temperature. A ionic liquid (IL), vinylbenzyl trimethylammonium chloride, was applied to modify the charge distribution in BH₄ and promote the dehydrogenation of NaBH₄ (Figure 1).

The effect of IL concentration as well as particle size on the amount of desorbed hydrogen was investigated. The dehydrogenation reaction of the ILeNaBH₄ complex was exothermic (negative enthalpy), which is in contrast to the endothermic hydrogen desorption reaction for pure NaBH₄ (positive enthalpy). The enthalpy of the ILeNaBH₄ complex for dehydrogenation was lower than NaBH₄ due to the interactions of the cation, the IL, and the borohydride. Dehydrogenation of the mixture (mass ratio of NaBH₄ : IL 1 : 4 and 1 : 2) started below 160 °C, with a maximum hydrogen desorption capacity of 2.1 wt% (Figure 2). The strong amine cation in the IL led to destabilization of the borohydride by polarization, thus resulting in improved dehydrogenation of the complex hydride. The enthalpy of the dehydrogenation reaction is 4.8 kJ mol⁻¹ of hydrogen. The exothermic nature of the reaction was caused by deformation of the lattice and destabilization from the IL.
First hydrogen storage beyond physisorption in carbon nanostructures

Hydrogen storage in carbon materials has been intensively investigated, adsorption of hydrogen on the surface of carbon due to Van der Waals interaction is only observed at low temperatures. As a consequence, the equilibrium pressure is low and limits the application of the hydrogen storage material. A new 3D structure of carbon based on graphene oxide (GO) and carbon nanotubes linked together (Figure 3) exhibits a large hydrogen storage capacity. The material absorbs more than 5 wt% of hydrogen at room temperature (Figure 4) and desorbs the hydrogen with almost no hysteresis. The 3D carbon material shows a stronger interaction with Hydrogen as compared to physisorption on carbon nanotubes. The 3D carbon material was investigated for the adsorption of various gases H₂, Ar, N₂, He. International Patent application was filed.

Metal hydrides for hydrogen compression (HyCo)

The thermodynamic properties of metal hydrides can be used to compress hydrogen. According to the Van’t Hoff equation \(-R \cdot \ln(p/p₀) = ΔH/ΔT + ΔS\), the hydrogen pressure depends on the temperature (Figures 5, 6).

The intermetallic compound \((La₀.₇₄Ce₀.₂₆)Ni₄.₂₁Co₀.₆₈Mn₀.₁₀\) from Baotou Santoku Battery Materials Co., Ltd. absorbs hydrogen at 20 °C and 3 bar and releases hydrogen at 100 °C and 25 bar and at 225 °C and 200 bar.
Hydrogen, foreseen to replace fossil fuels as energy carrier in the future, can be produced electrochemically from water and renewable and 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-cobalt alloys have evidenced state-of-the-art catalytic activity for the OER, with overpotentials below 0.3 V. Electrodes made from these relatively inexpensive and abundant metals (compared to Ir or Pt) 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] Indeed, the composition of stainless steel is not tuned for such application and the overpotential and stability is not ideal. In our recent efforts to understand the performance and stability of iron-based anodes for water oxidation we have prepared alloys of Iron, Cobalt and Nickel of different compositions. The procedure used to prepare the electrodes was using an arc melting system at EPFL Sion. Photographs showing the electrode preparation procedure are shown in Figure 1.

The compositions of Nickel-iron-cobalt alloy electrodes prepared are shown in Figure 2 (left) and their performance and stability for OER in alkaline conditions were investigated using standard electrochemical techniques (1 M NaOH at 0.5 A/cm$^2$ current density for 200 hours). The samples of this experiments showed promising performances. The samples FeCoNi-33-33-33-H and FeCoNi-55-22.5-22.5-H of the first batch displayed the best overall overpotentials, with 246 and 248 [mV at 10 mA/cm$^2$] respectively.

The second batch of samples, used to qualitatively compare the performance of the electrodes, showed that FeNi-50-50 displayed the best overpotential among the compositions tested, with an overpotential of 284 [mV at 10 mA/cm$^2$]. As it was the case for the first batch, the best trimetallic samples were FeCoNi-33-33-33 and FeCoNi-55-22.5-22.5 with 314 and 318 [mV at 10 mA/cm$^2$] respectively (see Figure 2 right).
Performance and Stability of Iron-Cobalt-Nickel Alloys for Water Oxidation

The Tafel slopes calculated for the samples of the second batch were homogeneous, with values around 40 [mV/dec]. These values are promising for the performance of the electrodes and they might also give a hint about the active site of the catalyst, as cobalt-based catalysts usually display Tafel slopes in this range.

The density of nickel active site was found to increase with the nickel content in the sample, as expected. More interestingly, no correlation was found between the active site density and the overpotential of the samples, which might prove that cobalt playing an important role in the OER catalysis.

Inductively coupled plasma mass spectrometry (ICP-MS), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) measurement all pointed to a reduction in iron content on the surface of the electrode during the oxidation process. However, it was found that the overpotential was lower for samples with higher iron concentration on their surface after oxidation.

Two hypothesis were made to explain this behavior. The first is that iron promotes the catalytic activity of the samples, but is etched out of the sample. The samples with better performance would continue to etch iron and progressively lose their activity as their composition rejoins the one from the less active samples. The second hypothesis is that the samples displaying a better overpotential are the ones that initially had a higher iron content. During the etching, they therefore release more material, making them more porous and thus more active for OER.

The overall score, combining the overpotential and the metal etching density of the electrode to rank the samples on both performance and stability, showed that the two best samples were FeCoNi-55-22.5-22.5 and FeCoNi-33-33-33. Additional experiments were performed on these two compositions, to assess the two hypothesis arising from the previous measurements. The performance after 200 hours of oxidation showed no significant drop in performance for both samples, which tends to disprove the first hypothesis. However, the measurement of the capacitance density of the samples did not prove the second hypothesis either, as FeCoNi-55-22.5-22.5 displayed a lower capacitance, and therefore lower porosity, despite its superior performance.

These hypotheses could be further assessed by thoroughly analyzing the change in performance of the samples of all the different compositions, as well as their capacitance density in order to obtain a trend on a more significant number of sample. Other techniques could also be used to try to determine the porosity of the samples, and XPS at different depths could be performed on the samples, in order to try to identify the depth of the active layer. This work could also be repeated for other trimetallic compositions, with metals such as chromium, manganese or molybdenum, which are found in the catalytically active stainless steel samples, or copper, which is known to promote the activity of cobalt.

These concepts will be considered in future work.
Scope of project

Redox flow batteries (RFBs) are suffering from low energy density compared to other energy storage devices.[1–5] To overcome this weakness, a new concept was developed by Amstutz and co-workers which includes a second pathway to discharge chemically the RFB. This pathway allows the system to generate hydrogen and oxygen using catalytic beds as heterogeneous catalyst, without affecting the functioning of the RFB. It was found that the positive half-cell of V-Ce RFB suffered from degradation due to the high oxidizing properties of cerium electrolyte. As an alternative, we investigated the use of another positive electrolyte composed of titanium, manganese and vanadium.

Another way to increase the energy density of the RFB is to add solid phase materials with high energy storage capacity in the electrolyte tanks in order to increase the whole capacity of the RFB. Polyaniline was the first material studied as proof-of-concept in acidic media.[1] We went further by screening a variety of solid phase storage materials working at neutral pH, such as potassium and sodium intercalation compounds or redox conducting polymers.

In the framework of the Martigny demonstrator, a commercial vanadium redox flow battery (VRFB) operates for 3 years now. Stack leakage was observed, advanced corrosion of the carbon electrodes and cracks of the bipolar plates on several stacks were discovered. The cracks enabled the electrolyte to leach the copper current collectors and contaminated the entire electrolyte solution with copper ions. Here we present a method to purify the contaminated electrolyte.

Status of project and main scientific results of workgroup

Investigation of titanium-manganese-vanadium electrolytes as catholyte for dual-circuit redox flow batteries

To overcome the low energy density of RFB,[1–5] a new concept was developed by Amstutz and co-workers which includes a second pathway to discharge chemically the RFB. This pathway allows the system to generate hydrogen and oxygen using catalytic beds as heterogeneous catalyst, without affecting the functioning of the RFB. The concept of dual-circuit redox flow battery was studied for a V-Ce RFB, using Ce(IV)/Ce(III) and V(III)/V(II) as positive and negative redox couples, respectively. Ce(IV) is chemically discharged through the oxidation of water to oxygen on RuO₂ catalyst and V(II) is chemically discharged through proton reduction to hydrogen on Mo₂C catalyst. [6]

The positive half-cell of V-Ce RFB suffered from degradation due to the high oxidizing properties of cerium electrolyte. As an alternative, we investigated a V-Mn RFB. The main redox reactions are described below:

- At the Cathode: \[ \text{VO}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{VO}^{2+} + 2\text{H}^+ + 2\text{e}^- \quad E^\circ = +0.991 \text{V vs. SHE} \]
  \[ \text{Mn}^{3+} + \text{e}^- \rightleftharpoons \text{Mn}^{2+} \quad E^\circ = +1.51 \text{V vs. SHE} \]

- At the Anode: \[ \text{V}^{3+} + \text{e}^- \rightleftharpoons \text{V}^{2+} \quad E^\circ = -0.225 \text{V vs. SHE} \]

- Disproportionation reaction at high potential: \[ 2\text{Mn}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Mn}^{2+} + \text{MnO}_2 + 4\text{H}^+ \]
Mn(III) is known for its disproportionation at 1.5 V vs SHE, leading to the formation of MnO₂ solid particles and Mn²⁺. It was previously reported that Mn(III) can be stabilized by increasing the concentration of acid. However, this method was not significant as the energy density of Mn(III) redox species was still low. Dong et al reported a novel Ti-Mn RFB wherein they realized that upon mixing TiO⁺ ions with Mn(II) in H₂SO₄ solution, they prevent the oxidation of Mn(III) to MnO₂. In order to understand the exact redox mechanism behind the inhibition of MnO₂ formation by addition of TiO⁺ in the electrolyte, electrochemical and surface characterizations were intensively investigated. It was shown that 1:1:1 of Ti/V/Mn in 5 M H₂SO₄ was the best compromise to reduce the formation of MnO₂ and maintains the reversibility of Mn(III) to Mn(II) reduction. As a perspective, a dual V-Ti-Mn RFB will be studied.

Redox solid boosters for aqueous redox flow batteries

In order to increase the energy density of the RFB, one possibility is to add solid phase materials with high energy storage capacity in the electrolyte tanks in order to increase the whole capacity of the RFB. Starting in 2017, with our work on polyaniline [11], we went further by screening a variety of solid phase storage materials, i.e. boosters, and near neutral pH aqueous electrolytes i.e redox mediators. One important challenge is to match the fermi level of the boosters with the standard potential of the redox mediators in order to drive the interfacial charge-transfer.

The positive electrolyte consists of the use of a K⁺ intercalation compound, CuHCNFe as booster, and TEMPTMA, a tempo derivative, as soluble redox mediator (+0.9 V vs SHE). At the negative side, polyimide derivatives and amino ethylvisogen (EV) have been evaluated as booster and redox mediator (−0.7 and 0.9 V vs SHE) respectively (Figure 1). From our previous work, we demonstrated that a high electronic conductivity of the booster was necessary in order to prevent insulating path upon cycling. To that purpose, carbon nanotubes (CNT) were investigated as electronic supporting material for both CuHCNFe and polyimide. Galvanostatic cycling of both carbon nanotubes based boosters (ratio 30% of CNT and 70% of booster) have been investigated in 1M KCl solution leading to specific capacities of 150 and 300 mAh·g⁻¹ for polyimide and CuHCNFe, respectively. As a perspective, a near neutral pH booster-based RFB will be designed. As expected from the standard redox potential of the redox mediators, an open circuit voltage of 1 V should be reached at pH 5 and room temperature.
After 3 years of operation, stack leakage was observed on the 10 kW/40 kWh commercial vanadium redox flow batteries (VRFB) installed in the framework of the Martigny demonstrator. Advanced corrosion of the carbon electrodes and bipolar plates on several stacks were discovered. It led to the failure of the VRFB. Moreover, cracks through bipolar plates enabled the electrolyte to leach the copper current collectors and contaminated the entire electrolyte solution with copper ions. The deleterious effects of copper contaminants were first highlighted on the operation of a VRFB. It was observed that metallic copper improved the parasitic hydrogen evolution reaction (HER) on the negative side. To tackle the problems related to copper pollution, a simple, eco-friendly and cost-effective procedure to identify copper contamination on-site and to purify the electrolyte was developed.

A classical VRFB stack was used to plate out the copper removing from the solution. The optimal cathode potential for copper deposition onto carbon felt electrode was determined to be $-100 \text{ mV vs SHE}$. Moreover, the stack can be regenerated after the purification. The process described here was successfully used to purify 6000 L of vanadium electrolyte ($V^{3+}/V^{4+}$ mixture). At the end of the purification, the stack was regenerated by flashing 20–30 L of electrolyte. That represents only a fraction of what would have been necessary to dispose the contaminated electrolyte. This work has been accepted as a full paper in ChemSusChem. [13]
Hydrogen storage and delivery in CO₂–formic acid–methanol systems

Scope of project

Formic acid (HCOOH) and methanol (CH₃OH) are considered as effective liquid chemicals for hydrogen storage as being easier to handle than solid or gas materials (Figure 1). This work summarizes the recent progress of research on the development of homogeneous catalysts mainly focusing on formic acid and CH₃OH and the reports on the catalysts based on both precious and non-precious metals which are rapidly increasing in the past few years.

Status of project and main scientific results of workgroup

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 formic acid dehydrogenation (resulting in H₂ and CO₂), a side-production of CO and H₂O (formic acid 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 (mTPPTS) as a ligand was applied for formic acid 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 formic acid feed. It was concluded that unwanted CO concentration in the H₂ + CO₂ gas stream was dependent on the current formic acid 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).

An industrial prototype has been built and presented on 19.03.2018, the world’s first formic acid-based power supply unit, using PEM fuel cell for electricity production (Figure 2).

List of abbreviations

CH₃OH Methanol
HCOOH Formic Acid (FA)
mTPPTS meta-Trisulfonated Triphenylphosphine
PEM Proton Exchange Membrane

Figure 1:
Reversible hydrogen storage and delivery.

Figure 2:
Article in 24 heures about the presentation of the world’s first formic acid-based power supply unit, using PEM fuel cell (industrial prototype).

Authors
Gábor Laurenzy¹
Nordahl Autissier²
¹ EPFL
² GRT GROUP SA, Orbe
**Synthetic Fuels**

Development of Advanced Catalysts

**Work Package «Synthetic Fuels» at a Glance**

The work package «Synthetic Fuels» is devoted to 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 in two main parts, addressing catalytic (Part 1) and electrocatalytic (Part 2) processes. A short summary of the 2018 highlights is provided below.

**Part 1: Catalytic conversion of CO₂**

The hydrogenation of CO₂ to methanol is investigated at ETHZ, where selective supported Cu catalysts are being developed. ETHZ has shown that introducing Lewis acid dopants at the periphery of supported copper nanoparticles using Surface Organometallic Chemistry dramatically improved the methanol activity of Cu-based catalysts with selectivity above 80%. This approach has shown to be general and providing guidelines to improve CO₂ hydrogenation catalysts — that includes converting poor catalysts such as Cu/TiO₂ into highly efficient systems by dispersing Ti(IV) sites on silica. In addition, silica-supported Ag-based catalysts have been developed to convert CO₂ in the presence of methanol into methyl formate with high selectivity. Detailed operando spectroscopic studies have shown that interfacial sites are essential for the efficiency of that transformation. All these findings are currently being used to develop more robust catalysts amiable to scale-up.

EPFL has investigated alternative approaches, where CO₂ from biogas (gas produced from organic wastes, typically 35:65 CO₂:CH₄) is separated and catalytically incorporated into cyclic carbonates using ionic liquids (ILs) as the catalyst. The process is being scaled-up and discussions to implement a reactor at a biogas plant are underway. The resulting cycling carbonate can be used in pure form in many applications or converted into glycols and methane/methanol using a heterogeneous Ru catalyst.

Furthermore, EPFL has also uncovered another promising way of CO₂ conversion using frustrated Lewis pairs (FLPs) by designing, for instance, a water stable and heterogeneous MOF catalyst — SION-105 — that converts CO₂ to value-added benzimidazoles.

**Part 2: Electrocatalytic conversion of CO₂**

Regarding CO₂-reduction, the electrocatalytic conversion of CO₂ to alcohols is an intense research area, where Cu-based catalysts are particularly appealing. Detailed studies at PSI on thin films prepared via DC magnetron sputtering have shown that Cu²⁺ is the active species causing the enhanced alcohol selectivity of (reduced) copper oxides.

In parallel, ETHZ has shown that highly dispersed Cu particles supported on carbon are formed under electroreduction conditions yielding high Cu-normalized CH₄ currents and UniBern has successfully transferred their work on Cu foam to technical substrates such as 2D meshes and 3D skeleton supports that show superior performances for C2 and C3 alcohol formation reaching total alcohol efficiencies of 25%. UniBern has also shown that high Faradaic efficiencies for alcohol production can be maintained for more than 8 hours. Besides Cu, UniBern has shown that Ag-foams are also efficient electro-catalysts for the reduction of CO₂ to CH₄ with Faradaic yields reaching 55%. This unexpectedly high hydrocarbon production has been shown to be due to the high bond strength of CO on Ag foam which prevents the parasitic hydrogen evolution reaction. The loss of Faradic efficiency over time in these catalysts has been related to a significant poisoning through carbon species deposition.

In parallel, EPFL has investigated novel approaches for the reduction of overpotential in CO₂ electro-conversion by tuning the electrolyte. Using choline chloride (ChCl) and its derivatives in combination with the concept of deep eutectic solvents (DES) provided active media for the CO₂ electro-reduction to CO with low onset potentials and good selectivities (Faradaic efficiencies). A very versatile approach has been devised that combines DES...
and IL approaches that allows high-throughput screening of co-catalysts that should accelerate the discovery of new, more efficient systems.

The CO₂-to-CO electro-reduction process in co-electrolysers, best carried out in alkaline solution, is also being investigated at PSI. While the state-of-the-art anodic electrodes in alkaline water electrolyser (AWEs) have been based on NiO for several decades, PSI has shown that the stabilization by the incorporation of Fe is due to the inhibition of the transformation of the compact and crystalline rock salt structure of Ni₁₋ₓFeₓO into more layered and disordered polymorphs. Furthermore, alternative transition metal oxides catalysts based on perovskite-related structures have been investigated because of the immense compositional possibilities. Detailed structure-activity relationships have been found using a combined experimental and computational approach based on OER/multi-descriptor relationships that will help the design of highly active oxygen evolution catalysts for efficient anodes for AWEs. In parallel, highly efficient OER Ir-based catalysts for acid media have been developed at ETHZ following earlier studies with PSI, showing that only few (down to one) Ir atoms are enough to obtain highly active OER catalyst.

Moving to co-electrolysis studies, a process mostly limited by the low solubility of CO₂ in aqueous solutions and associated CO₂ transport-limited current densities, PSI has developed a bipolar-like membrane assembly to facilitate this process. Using Au black as cathode catalyst shows that this novel configuration successfully suppressed the formation of CO₂ on the anode side, while maintaining similar Faradaic efficiency as the alkaline electrolyte system.
Catalyst Development for the Transformation of CO₂ into Fuels and Value-Added Chemicals

Scope of project

CO₂ can be reduced and incorporated into organic scaffolds by catalysis and/or electrocatalysis. Effective catalysts include ionic liquids (ILs), organic salts and frustrated Lewis pairs (FLPs). Here, we present a status overview of our main results related to catalytic CO₂ conversion.

Status and main scientific results of workgroups

Electrochemical reduction of carbon dioxide

Electrochemical reduction of carbon dioxide (ERC) provides a sustainable alternative to transform CO₂ into valuable products. However, electro-reduction occurs through high-energy intermediates, resulting in large overpotentials, which can be reduced by employing ionic liquids (ILs). It was also found that presence of hydroxyl groups in the proximity of reaction centres further promotes the ERC.

Combining these two ideas, we decided to employ choline chloride (ChCl) and its derivatives as promoters and media for the ERC (Figure 1) in the form of deep eutectic solvents (DESs) in order to obtain homogeneous systems, suitable for application as electrolytes. The novel systems are active media for the reduction, providing low onset potentials and good selectivities (Faradaic efficiencies) for the production of CO (Table 1). Moreover, this concept of employing DESs instead of ILs can be broadened to the cations other than choline, for example, imidazolium chlorides, which are precursors to conventional ILs. This approach avoids additional synthetic steps and affords cheap co-catalytic systems of high purity and enables high-throughput experimentation (currently ongoing) that should accelerate the discovery of superior electrolytes for this important reaction.

Heterogeneous catalysis

Another promising way of converting CO₂ harnesses frustrated Lewis pairs (FLPs), comprising Lewis acids and bases sterically hindered in such a way that the acid-base adduct is not formed as in classical Lewis pairs, and exhibit outstanding ability to activate CO₂. Progress in FLP-chemistry includes efforts to improve the moisture stability of FLPs and transfer this concept from homogeneous to biphasic IL and heterogeneous environments.

Following this latter strategy, we have designed a water stable heterogeneous MOF catalyst – SION-105 – for the metal-free and FLP-mediated conversion of CO₂ to value-added benzimidazoles. The introduction of Lewis acidic B centers within the MOF structure provides steric protection, suppressing irreversible binding and deactivation with bases and water. The high stability of SION-105, CO₂-responsiveness, recyclability, tolerance against a wide variety of functional groups, and catalytic activity, achieved through the in situ formation of FLPs with o-diamine aromatic substrates as complementary bases, highlight the utilization of MOF catalysts for CO₂ conversion. Our findings open the way for the next generation of heterogeneous catalysts, which are intricately designed via direct

Table 1:

<table>
<thead>
<tr>
<th>Catholyte</th>
<th>FE_{CO}</th>
<th>FE_{H2}</th>
<th>E_{Ag/AgCl}</th>
</tr>
</thead>
<tbody>
<tr>
<td>ChCl-Urea (1:2)</td>
<td>15.8</td>
<td>17.0</td>
<td>-1.40</td>
</tr>
<tr>
<td>ChCl-Urea (1:2): H₂O (15% vol)</td>
<td>59.0</td>
<td>26.3</td>
<td>-1.38</td>
</tr>
<tr>
<td>ChCl-EG (1:2)</td>
<td>78.0</td>
<td>9.9</td>
<td>-1.43</td>
</tr>
<tr>
<td>BMImCl-EG (1:2)</td>
<td>95.8</td>
<td>6.8</td>
<td>-1.44</td>
</tr>
<tr>
<td>1M ChCl + 2M EG in H₂O</td>
<td>23.3</td>
<td>75.6</td>
<td>N/A*</td>
</tr>
<tr>
<td>1M ChCl + 2M EG in MeCN</td>
<td>98.8</td>
<td>4.7</td>
<td>-1.52</td>
</tr>
<tr>
<td>1M ChCl + 2M EG in 3EOH</td>
<td>92.3</td>
<td>8.4</td>
<td>-1.4</td>
</tr>
<tr>
<td>1M ChCl + 2M EG in PC</td>
<td>101.5**</td>
<td>0.5</td>
<td>-1.5</td>
</tr>
<tr>
<td>1M ChCl in EG</td>
<td>71.1</td>
<td>28.2</td>
<td>-1.42</td>
</tr>
<tr>
<td>1M ChCl in PEG-200</td>
<td>83.2</td>
<td>7.9</td>
<td>-1.40</td>
</tr>
<tr>
<td>1M BMImCl in PEG-200</td>
<td>85.9</td>
<td>3.7</td>
<td>-1.41</td>
</tr>
<tr>
<td>1M BMImOHCl + 2M EG in PC</td>
<td>101.8**</td>
<td>1.6</td>
<td>-1.45</td>
</tr>
<tr>
<td>1M EMImOHCl + 2M EG in MeCN</td>
<td>98.9</td>
<td>0.8</td>
<td>-1.45</td>
</tr>
</tbody>
</table>

* Cannot be determined due to concomitant HER.
** The experimental error is in the order of +/- 5% (GC)

Experimental conditions: U-type divided cell, Ag polished disc cathode, Pt wire anode, Ag/AgCl reference, analyte – H₂SO₄ (aq, 0.5 M), catholyte – depicted in the Table, Nafion 117 membrane separator.

Author
Paul J. Dyson¹

¹ EPFL
assembly and functionalization for the activation of small molecules. We are also working towards the direct synthesis of methane from CO$_2$ and H$_2$ using FLP-chemistry.

We have identified biogas (gas produced from organic wastes, typically 35:65 CO$_2$:CH$_4$) as a CO$_2$ source for our catalytic CO$_2$ extractor from gas streams, in which the CO$_2$ is removed and catalytically incorporated into cyclic carbonates. To this end, we have revealed the intricacies of the reaction catalyzed by homogeneous ILs, which in turn will lead to the development of very robust catalysts. This novel scrubbing approach is relevant since biogas upgrading methods into biomethane are expensive, and are only suitable for large scale biogas plants. The resulting cyclic carbonates can be used in pure form (solvent, electrolyte in batteries, etc.) or processed into a variety of different chemicals, including polymers and glycols. In this context, we have reported two simple approaches to convert cyclic carbonates into glycols and methane/methanol, using a heterogeneous Ru catalyst/H$_2$ combination and a metal-free F-salt/hydrosilane combination, respectively.\[3,4\]

With respect to a two-step reduction of CO$_2$ to methanol via formamides, the mechanism of amine N-formylation with CO$_2$ and hydrosilane reducing agents was investigated in detail.\[5\] Formation of a carbamate was identified as the rate-determining step of the reaction. Catalyst pKa-activity relationship (Figure 4) confirms the role of salt catalysts as bases required for carbamate stabilization similarly to the related quinazoline-2,4-dione formation investigated previously.

Figure 2: Reaction of aromatic o-diamines with CO$_2$ as a C1-source. Atom color code: Eu—green; C—grey; O—red; B—magenta; H—white.

Figure 3: Indirect CO$_2$ reduction to fuels via catalytic biogas upgrader.

References


Figure 4: Reaction yield dependency on the pKa of the catalyst.
Development of Selective Catalysts for the Conversion of CO₂ to Fuels via Surface Organometallic Chemistry

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 possesses 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

Towards the selective hydrogenation of CO₂ to CO₃OH

In the recent years, we have worked on developing selective CO₂ hydrogenation catalysts to methanol. In particular, we have investigated the effects of ZrO₂ as a Lewis acidic support for Cu nanoparticles to promote CH₃OH synthesis. This finding resulted in the development of active catalysts prepared by flame-spray pyrolysis, with similar activity and higher selectivity than the state-of-the art Cu/ZnO/Al₂O₃ catalysts.[1] In addition, we generated a library of supports consisting of isolated surface metal sites (Zr, Ti, Ga, Zn etc.) on SiO₂ (denoted as M@SiO₂) via a surface organometallic chemistry (SOMC) approach (summarized in Scheme 1).

Levis acidic coordination sites. These findings confirmed our conclusions as to the nature and role of Zr in our previous work on Cu/ZrO₂; furthermore, the understanding garnered from this work enables the rational design of more efficient catalysts by increasing the dispersion of Zr.[2, 3]

By using electron paramagnetic resonance (EPR) and ultraviolet-visible (UV-Vis) spectroscopy, the structure silica behaves quite differently from Ti sites on the surface of titania; it opens new avenues in (re)exploring previously discarded promoters for CH₃OH synthesis.[4]

In parallel, we have investigated the role of interfaces in alternative CO₂ conversion processes such as the hydrogengation of CO₂ in the presence of methanol that provides methyl formate and showed that the Ag-supported on silica...
Development of Selective Catalysts for the Conversion of CO$_2$ to Fuels via Surface Organometallic Chemistry

is one of the most efficient catalysts for that transformation and that the interface plays an essential role for the selectivity of that transformation. [5]

In relation to these studies, we are currently exploring the effects of different promoters as well as further understanding different oxide supports to obtain a structure-activity relationship by using ex situ and in situ spectroscopic studies.

**CO$_2$ reduction and water oxidation electrocatalysts**

Copper is of major interest for CO$_2$ electroreduction, since it has a unique ability to electrocatalyze the formation of highly reduced, energetically dense fuels. Achieving high dispersion of copper on an electrode substrate thus constitutes a possible route to access highly active copper-based electrocatalysts. Here, we used a surface organometallic chemistry approach to generate small copper nanoparticles (4.0 ± 1.4 nm) well dispersed onto an activated carbon black support (4.2 Cu wt%). [6] After air oxidation, the material was filtered on a gas diffusion layer to obtain CuO$_x$/CB/GDL electrodes. Cyclic voltammetry at this electrode confirmed the presence of electroactive Cu species in a density of 1.6·10$^{-8}$ mol·cm$^{-2}$. Electrocatalytic performance of the electrode was then assessed under aqueous conditions (KHCO$_3$ 0.5 M) with constant CO$_2$ stream (20 mL·min$^{-1}$).

The on-line analysis of volatile products by a gas chromatograph-mass spectrometer (GC-MS) demonstrated the evolution of CO$_2$-reduction products (Figure 1), namely CO at lower overpotentials (starting from −0.6 V vs. RHE) with Faradaic efficiency (FE) up to 5% at −1.1 V vs. RHE. When potentials are scanned downward, C$_2$H$_4$ and CH$_4$ are also detected with CH$_4$ FE reaching 13% at −1.6 V vs. RHE. Besides, the major gas phase product evolved is H$_2$, which we identified as arising from catalysis at the carbon black support itself.

We further analysed the CuO$_x$/CB material after a 4-hour electrolysis at −1.0 V vs. RHE. TEM images do not show the presence of well-dispersed Cu NPs in the range 1–10 nm, as compared to the starting material. Instead, Energy Dispersive X-Ray Spectroscopy (EDX) elemental mapping reveals that Cu is present on the post-electrolysis material with some Cu-rich regions together with discrete Cu species (single sites or small clusters) dispersed all over the carbon support, pointing to Cu NPs reconstruction under electrocatalytic conditions. Interestingly, under these conditions large Cu particles (several tens of nanometers) are not formed upon turnover as reported typically for other catalysts. Here, the presence of highly dispersed Cu species also corroborates with the high Cu mass-activity observed for CH$_4$ evolution. We are now investigating the origin for the reconstruction of Cu nanoparticles under electrocatalytic conditions and the precise nature of the active sites formed.

Water electrolysis is complementary to CO$_2$ electroreduction and the most direct way for generating hydrogen – a green alternative to fossil fuels. While in acidic media the cathodic process (hydrogen evolution reaction, HER) proceeds with small overpotentials, the concomitant anodic process (oxygen evolution reaction, OER) requires high overpotentials, which translates into significant energy loss [7]. Moreover, the harsh reaction conditions limit the pool of possible anodic catalysts to the expensive and scarce noble metals, namely Ru and Ir. Therefore, decreasing the noble metal content while maintaining high catalytic activity is a critical requirement for the anodic water oxidation catalysts.

Decreasing the noble metal loading can be achieved via synthesis of high surface area noble metal oxides [8] or by dispersing the noble metal active species on the surface of a support [9] as we have shown earlier. In the present work, we prepared indium tin oxide (ITO) supported Ir species and Figure 1: Total current density (squares, left scale) and potential dependence for Faradaic efficiencies of CO$_2$-reduction gas-phase products (dots, right scale) for CO (blue), C$_2$H$_4$ (purple) and CH$_4$ (green) at CuO$_x$/CB/GDL. Conditions: CO$_2$-saturated 0.5 M KHCO$_3$ aqueous electrolyte (pH = 7).
Development of Selective Catalysts for the Conversion of CO₂ to Fuels via Surface Organometallic Chemistry

metallic, while the surface becomes oxidized into the form of an oxo-hydroxide layer, which is likely responsible for the high catalytic activity. The Ir single sites show significantly higher activity as compared to the supported nanoparticles because all the Ir atoms participate in catalysis, while only a portion of Ir is accessible for the particles (<60% of Ir is on the surface of 1.5 nm particles).

Taking advantage of our electrode design we were able to couple electrochemical studies with spectroscopy to probe reaction intermediates and evaluate possible reaction mechanisms for the Ir single site catalyst. XPS and in situ XAS show that the catalyst originally existing as Ir(III) oxidizes to Ir(IV) (0.89 V vs. RHE) and Ir(V) (1.35 V vs. RHE) with increasing anodic potential. The in situ XAS studies suggest that Ir(V) is a resting state of the catalyst under OER conditions and that the O-O bond formation takes place upon water nucleophilic attack on the high valent Ir-O intermediate.

References
Synthesis and Characterization of Degradation Resistant Cu@CuPd Nanowire Catalysts for the Efficient Production of Formate and CO from CO₂

Scope of project

In the focus of this part of the SCCER is the conversion of the environmentally unfriendly greenhouse gas CO₂ into high value products (e.g. ethylene, ethanol, propanol, carbon monoxide, 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 at acceptable reaction rates. 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, Sn and Ag based materials have been mainly used as catalysts for the production of formate and CO at high and medium overpotentials, respectively.

In this study, we introduce a new synthesis approach towards Pd-based bimetallic CO₂RR catalysts which show not only excellent activity and selectivity towards formate at particularly low overpotentials and towards CO at medium overpotentials but demonstrate at the same time superior resistance to chemical and mechanical degradation.

Status of project and main scientific results of workgroups

Bimetallic Pd₄₅Cu₅₅ catalysts were synthesized by a controlled galvanic displacement reaction in the presence of a Pd(II) source starting from Cu nanowire (Cu-NW) templates (Figure 1).[1] Such formed Pd-modified nanowires (denoted as Cu@CuPd-NWs) demonstrate a high Faradaic efficiency (FE) towards formate at particularly low overpotentials (e.g., FE_formate ~80% at -0.3 V vs. RHE) close to the thermodynamic potential of formate formation (Figure 2). This is rationalized by an anomalous CO₂ reduction pathway which involves an initial CO₂ hydrogination reaction step from the formed metal hydride, a catalytic effect that is so far known only from pure Pd nanoparticles (Pd-NPs).[2] Our electrolysis results clearly indicate that the binary Pd₄₅Cu₅₅ alloy also forms metal hydrides as crucial prerequisite for the CO₂ hydrogenation pathway. In contrast to the pure Pd-NPs the novel Cu@CuPd-NW catalysts demonstrate in addition a high resistance against irreversible CO poisoning which forms as a minor by-product of the formate at low overpotentials thereby degrading the catalyst.

The product distribution of the CO₂ electrolysis switches at medium overpotentials (from -0.6 V to -1.0 V vs. RHE) from predominant formate formation to selective CO production with Faradic efficiencies never falling below FE_CO = 86% (Figure 2). Long-term electro-

List of abbreviations

Cu-NW Copper Nanowire
FE Faradaic Efficiency
IL-HAADF-STEM Identical Location High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy
IL-SEM Identical Location Scanning Electron Microscopy
Pd-NP Palladium Nanoparticle

Figure 1:
Identical location high-angle annular dark-field scanning transmission electron microscopy (IL-HAADF-STEM) and spatially resolved EDX analysis of a single Cu@CuPd-NW prior to (a–e) and after (f–j) 1 h CO₂RR at -0.8 V vs. RHE. Panels (d) and (i) show the 2D-EDX mapping (Pd: red and Cu: green) of the Cu@CuPd-NW. 1D-EDX cross-sections shown in panels (e) and (j) are indicated by the cyan lines in panels (d) and (i), respectively.

Figure 2:
Product distribution of the CO₂RR on Cu@CuPd-NWs catalyst at different applied potentials.

Author
Yuhui Hou¹
Aline Bornet¹
Abhijit Dutta¹
Motiar Rahaman¹
Roland Widmer²
Rolf Erni²
Peter Broekmann¹

¹ University of Bern
² Empa
lysis experiments demonstrate CO efficiencies which remain at a high level of 85% ± 5% for up to 20 h electrolysis time (Figure 3). The bimetallic Cu@CuPd catalyst remains active even under massive CO production conditions.

This excellent electrochemical catalyst stability could be further confirmed by identical location high-angle annular dark-field scanning transmission electron microscopy (IL-HAADF-STEM), energy-dispersive X-ray spectrometry and identical location scanning electron microscopy (IL-SEM) applied to the catalyst before and after the CO2 electrolysis (Figure 1). The HAADF-STEM and SEM inspection did not reveal severe structural and compositional changes of the catalyst after the CO2 electrolysis.

Conclusions and next steps

This study clearly demonstrates that Pd-based binary alloy nanomaterials are promising candidates in particular for the production of formate at exceptionally low overpotentials. Co-alloying of Cu to the Pd leads to an increase in the resistance of the catalyst against irreversible CO poisoning.

References

(Co)-Electrolysis at Paul Scherrer Institut

Scope of project

The development of clean energy storage and conversion systems and efficient methods of CO₂ capture are absolutely necessary to reduce the steadily increasing levels of atmospheric greenhouse gases, which are the primary contributors to destructive climate change. Within this scenario, water electrolysis technologies have been at the center of the spotlight owing to their abilities to efficiently convert renewable energy surplus into hydrogen, which can then be reconverted into electricity via fuel cell or converted into other useful fuels. Therefore, water electrolyzers appear to be central to the development of a clean, reliable and emissions-free hydrogen economy. Additionally, the electrochemical reduction of CO₂ gas via co-electrolysis is a rather attractive option for minimizing the atmospheric carbon dioxide levels. By efficient electrochemical reduction, CO₂ can be converted into fuels and other useful chemicals. In the following, the main approaches undertaken at the Paul Scherrer Institut towards the development of highly active and durable OER electrodes for electrolysis applications, the development of cathode catalyst materials for CO₂ reduction, and the rational design and engineering of the co-electrolysis device will be described.

Status of project and main scientific results of workgroups

State-of-the-art anodic electrodes in alkaline water electrolyzers (AWEs) have been based on NiO for several decades due to this material’s relatively high activity and stability for the oxygen evolution reaction (OER) in alkaline media. More recently, however, the effect of Fe doping on the OER has been the subject of many intensive investigations since the incorporation of small amounts of Fe into NiO can greatly enhance its OER activity.[1] In a recent work, we have produced highly crystalline Ni₁₋ₓFeₓOₙ nano-powders by flame-spray synthesis (see Figure 1a, b) with different Ni-to-Fe ratios to investigate how Fe incorporation influences the surface electronic properties and local coordination structures of Ni catalysts and how this impacts the electrochemical stability and OER activity.[2] Beyond the state-of-the-art NiO-based catalysts, transition metal oxides with perovskite-related structures have recently emerged as promising electrocatalysts for the OER in AWEs.[1, 3] Given the immense compositional possibilities offered by the perovskite structure and the many open questions about the mechanism at the origin of their electrocatalytic activity, the research has been mostly focused on identifying catalytic descriptors able to predict the optimal physicochemical properties for maximizing the OER activity. In our recent work[4], the correlation between ex situ electronic conductivity, oxygen vacancy content, flat-band potential (Eₜₐ₈), and the OER activity for a wide range of perovskite compositions have been investigated experimentally and theoretically. It has been found that all of these parameters can affect the OER activity; however, none of them alone plays a crucial role in determining the electrocatalytic activity. The correlation of one single physicochemical property with the OER activity always presents deviation points,[4] indicating that a limitation does exist for such 2-dimensional correlations. Nevertheless, these deviations can be explained considering other physicochemical properties and their correlation with the OER activity. The novel concept of the OER/multi-descriptor relationship that we have recently introduced in our study[4] (see Figure 1e) represents a significant advancement in the search and design of highly active oxygen evolution catalysts and in the quest for efficient anodes for AWEs.

Moving on to our activities dealing with CO₂-reduction electrocatalysis, the appealing electrochemical transformation of CO₂ into methanol or ethanol has preponderantly been carried out using catalysts based...
on copper oxides (CuOx), for which the (surface) oxidation state in the course of the reaction and its concomitant effect on the product selectivity remain controversial. To study this effect, we used DC magnetron sputtering to prepare low roughness Cu2O thin film (TFs) with a controlled oxide thickness of 100 nm, and used these as electrocatalysts for the reduction of CO2 [5]. The TFs were characterized prior to and after chronoamperometric (CA) CO2-reduction at −1.0 V vs. the reversible hydrogen electrode (RHE) using X-ray photoelectron spectroscopy (XPS) and Ar-sputtering. Chiefly, sample re-oxidation upon disassembly of the electrochemical cell and/or transfer to the XPS were avoided by performing the electrochemical measurements in a N2-filled glovebox and transferring the sample in an air-tight chamber, respectively. As illustrated in Figure 2, this resulted in clear changes in the Cu-2p and -LMM spectra specifically. Whereas in the former
no significant differences were observed when the post-CA samples were transferred in air or N₂ (see blue v. green lines, respectively), likely due to the identical Cu-2p spectra exhibited by Cu⁰ and Cu₂O, the Auger spectra were much more sensitive to the transfer means. Moreover, the excellent agreement between the spectrum of the N₂-transferred sample and reports for Cu⁰ confirmed the complete reduction of the TF upon CO₂-electroreduction, probing that Cu⁰ is the active species causing the enhanced alcohol selectivity of (reduced) copper oxides [5].

While such co-electrolysis studies in liquid electrolytes are of great fundamental interest, the process is limited by the low solubility of CO₂ in aqueous solutions, resulting in CO₂ transport-limited current densities of 30 mA/cm². In order to scale the process up to larger scales, direct use of CO₂ from gas phase in a polymer electrolyte membrane cell configuration can be used. While, generally, an alkaline environment promotes the CO₂ reduction reaction (CO₂RR) at the cathode, a secondary effect in such a system is the transport of carbonate and bicarbonate towards the anode side, where they form CO₂ via oxidation. Because of this, for each CO₂ molecule reduced at the cathode, one or two CO₂ molecules are formed at the anode, contributing to a loss in efficiency of the overall system. To solve this issue, while maintaining high selectivity for CO₂RR, we recently started working on a system using a bipolar-like membrane assembly [6,7]. However, unlike a bipolar membrane system, our system does not contain two rigid and connected ionomer layers of similar thicknesses, but rather it contains a thin film alkaline ionomer layer, which is sprayed onto the cathode catalyst layer and Nafion® XL membrane separating the cathode from the anode side (see Figure 3). By employing only a thin alkaline ionomer film, the CO₂ and H₂O molecules formed at the interface of the two layers can more easily diffuse towards the cathode and participate in the reactions once more.[6]

Our preliminary results using Au black as the cathode catalyst show that this novel configuration successfully suppressed the formation of CO₂ on the anode side, while maintaining similar Faradaic efficiency as the alkaline electrolyte system. In order to be able to detect the produced gases online during the tests, we developed a new versatile multivariate calibration method for mass spectrometers, which was employed during our experiments.[8]
Assessment

Interactions of Storage Systems

Work Package «Assessment of Storage Systems» at a Glance

The assessment of energy storage is applied at three nested levels: technology, energy system, and socio-economic impact. It is furthermore supported by a holistic assessment of demonstrators. Feedback for other work packages (WPs) of the SCCER HaE, for different SCCERs, and towards industry, society & politics is the main goal. The approaches of the work package «Assessment – Interactions of Storage Systems» include a combined methodology for life cycle analysis (LCA) and techno-economic analysis, while new pathways for socio-economic assessment are meant to aid understanding the broader societal impact. The challenges and risks of succeeding in this work package have previously been identified mainly in the direction of data acquisition and data uncertainty. When employing scenarios and assumptions, which is inevitable for providing an assessment of energy systems (containing storage technologies) to an unknown future of 2035 and 2050 (a horizon the federal «Energy Strategy» is aiming at), sensitivities of capacities, efficiencies, and prices have a strong impact on the results. Therefore, in cooperation with SCCER «Joint Activity Scenarios and Modelling» (JASM) we push forward to have a homogenized setting of scenarios, share data on load profiles and technology descriptions as well as having a common agreement on data sources.

Choices of scenarios and system boundaries for heat (technology) modelling turned out to be rather complex and difficult to deal with in comparison to electricity modelling, whereas the time dependency and resolution poses lesser constraints, due to the very high inertia of building masses and thermal systems in general. This opens new modes of sectoral coupling between electricity, heating and cooling, giving thermal storage technologies a massive potential for compensating for intermittent renewable (electrical) energy production from any source. In order to meet the challenges on the technological level, the theoretical assessments are based and validated on demonstrator systems for energy storage and expertise developed in this and other SCCERs, namely the power to gas plant HEPP, the AACAES demonstrator of WP1, but also in battery research. The groups working on the technology directly benefit from theoretical assessment since the relevant boundary conditions for the systems and systemic research questions are provided. Therefore, the team is strongly interlinked with the Joint Activities CEDA, JASM and the White Paper Power to X.

The assessment of batteries was a major focal point in this reporting period and assessed on all three nested levels:

- On the technology level, a comparison of carbon and life-cycle costs of storing electricity in battery systems for various regions was made. It turned out that the environmental characteristic of electricity generation (to be stored) is primarily influencing the result. The type of battery system is less important with the exception of lead acid and vanadium redox flow batteries which are most problematic in this sense. The study on material criticality indicated that lead acid batteries are especially problematic as well due to Zinc, Lead and Iron. All batteries containing Co also have an issue with regard to metal criticality. Additionally, the economic & environmental assessment of Lithium-Ion vs. Sodium-Ion cells came to the conclusion that at the current state of development the Sodium system lacks behind the state of the art Lithium system in terms of cost and environmental impact due to their still significant difference in energy density at the current state. These assessments were done in close collaboration with the battery work package team, which is implementing the results in their future research strategy.

- On energy system level, the long-term evaluation of flexibility options for the Swiss energy system was evaluated with the Swiss TIMES energy model by PSI and it was found that under continuation of the current policy mainly pump storage and low voltage battery are needed in 2050. In case of a policy to meet the Swiss climate targets in the Paris Agreements, the additional capacity includes also medium and high voltage batteries. At the local energy system level, an additional model has been already developed by UniGeneva to optimize a battery schedule in 24 h framework, assuming perfect day-ahead forecast of the electricity demand load and solar PV generation. The objective function is to minimize the electricity bill including energy and power components. The model considers as well four consumer applications (PV self-consumption, avoidance of PV curtailment, demand load-shifting and demand peak shaving), different technologies and locations.

- At the socioeconomic level, the inter-sectoral learning in value chains for lithium-ion batteries was assessed in order to inform innovation policy makers on useful next steps. It was found, based on expert interviews and patent search that a focus should be set on facilitating trans-
fer of tacit knowledge between chemical sector, cell manufacturers and users. At the same level, the questions on how the battery industry responded to the emergence of new markets, and what is opportunity for latecomers in the lithium-ion battery industry, could be addressed. Based on publication- and patent-analysis, as well as by expert interviews it was found that industry responded by branching the chain of innovations following the new direction, while the former line of development still progressed.

In the area of demonstrators two new units can be reported. For the power to gas system (HEPP) at HSR, the majority of 2018’s work was the specification and procurement of plant components which lead to completion and the formal start of operation was in October 2018. The specialty of this system lies in the reactor scheme which allows for regeneration operation of the catalyst (developed in the large consortium of the Pentagon and Store to go (both EU projects) with partners from ZHAW) and the installation of a high temperature, solid oxide electrolyser, also developed in the consortium. The second demonstrator, formally put into operation, is the small scale demonstrator at Sion. This demonstrator represents a combination of PV system with battery storage (different types) and hydrogen as a long term storage option, scaled to the needs of a single family home. The SCCER teams look forward to the insights the new demonstrators will give. On the level of existing demonstrators, progress was made at the Energy System Integration Platform (ESI) it was possible to demonstrate the combined operation of electrolyser, methanation and fuel cell along a day power profile, proving the dynamics and readiness. The COSYMA direct methanation passed 1'000 hours of operation at an industrial site (SCCER Biosweet). At the grid to mobility demonstrator an analysis of conversion losses in grid to mobility pathways was done and design and sizing recommendations based on renewable profiles were derived. It was investigated how stationary storage systems for local businesses can be optimized.

The contribution of SCCER HaE in the Joint Activities (JA) in this reporting period was the model implementation of a new methodology for estimating building energy demand in the residential sector for heating and cooling, used in JA Simulation and Modelling (JASM). Going along the same line, in the collaboration with CEDA the residential heating load profiles from heating days were elaborated. Finally the JA White Paper Power to gas was put forward significantly by support of the assessment team and it is close to completion by now. In terms of collaborations, the application for a joint project (SwissStore) with groups from CREST was successful. This project started at end of 2017 and investigates the role of competing and/or complementary electric, thermal and chemical energy storage technologies for Switzerland and runs till October 2021.

In summary, the interlinkage between this and the other WPs has strengthened significantly. This results in feedback loops into the research strategies of the technical WPs in particular of WPs 1 and 2 based on recent findings. Regarding the full roadmap, the overall picture of the assessment is supported on the one hand by working through groups of storage technology assessments (high power electricity storage options in 2016, batteries in 2018, thermal storages 2019) and planning to publish those on a Web Platform. On the other hand by the intense work on adding storages into new and existing energy system models like SwissTimes and Energy System Models from CREST and furthermore supplying the models and data within the JASM framework.
Investigation of AA-CAES Plant Configurations and Grid Integration

Scope of project

In Phase I of this project, the focus was primarily on technical aspects, culminating in experiments with the world’s first AA-CAES pilot-scale plant, constructed and operated by ALACAES with support from the SFOE, SNF, and CTI in an unused tunnel near Pollegio, Switzerland. The plant was characterized by an unlined rock cavern and experiments were carried out with both sensible and combined sensible/latent thermal-energy storage (TES) units, attaining plant efficiencies of 63–74% [1, 2].

In Phase II, the focus has shifted to the analysis of AA-CAES plants on three levels:

- the plant layout, its siting, and costs,
- the plant performance in the electricity grid, and
- detailed plant simulations and life-cycle analyses.

The overarching goal of Phase II is to determine whether an AA-CAES plant can be operated profitably in Switzerland’s future energy system.

Status of project and main scientific results of workgroups

During the first two years of Phase II, the modelling framework for the three levels and the interfaces between the levels were defined and implemented. More specifically, the AA-CAES plant model has been improved by adding more accurate component representations including transient effects. The grid model was used to assess the impact of AA-CAES plants of different power and capacity ratings on the Swiss electricity market in one specific location and showed that there was a benefit of adding this storage capacity to the grid. This report gives a brief overview of the current state of our efforts and describes future work.

Level 1: Plant layout, siting, and costs

Compared to earlier studies of an AA-CAES plant in the SNF NRP 70 project, the plant layout considered in the SCCER project was adapted in two respects: The maximum temperatures were lowered from about 600°C to 320°C and the expansion train was extended to consist of a high-pressure and a low-pressure turbine. The main motivation for these changes was to be able to use existing turbomachinery by MAN Energy Solutions AG. Reusing existing turbomachinery is the only feasible way forward because the market for AA-CAES plants is unlikely to ever be large enough to justify the very costly development of turbomachinery that can operate at both high temperatures and high pressures. Using two turbines in turn meant that it was natural to incorporate two thermal-energy storage (TES) units and two caverns. Simulations of the SCCER plant layout will be shown below.

Regarding the siting of an AA-CAES plant in Switzerland, our original objective was to reuse decommissioned military caverns. The rationale was that depending on the volumes of military caverns, the cost of excavating a cavern could be at least reduced and perhaps even entirely eliminated. However, the investigation of a list of decommissioned military caverns provided by Armasuisse showed that none were large enough for our target cavern volume of 170'000 m³. Most of them were so small that the cost savings were not significant compared to the total plant capital costs [3]. Furthermore, several disadvantages of reusing unused military caverns became apparent.

- First, the caverns do not have the required overburden of about 1000 m to contain the maximum cavern pressures of about 100 bar.
- Second, the caverns typically have multiple entrances and exits, all of which represent potential paths for air leakages.
- Third, the caverns are typically highly branched, leading to large surface-to-volume ratios, which would increase heat losses from the air to the surrounding rock.
- Fourth, the cross-section of most of the caverns is horseshoe-shaped, which may lead to stress concentrations and consequent fracturing and air leaks.
- Finally, few caverns were located in regions with high-quality rock (such as in...
the Aare massif), and they would therefore likely have required costly measures to render them airtight.

For these reasons, the plantsiting study has shifted attention to excavating entirely new caverns, which gave us the flexibility to pick plant sites purely on the rock quality and the vicinity to nodes in the Swiss electricity grid. Based on these considerations and results from previous simulations with the grid model described in the next section, our current investigations assume that the AA-CAES plant is located in the vicinity of the grid node near Bitsch in the canton of Valais.

With the information on the plant layout and siting, it is possible to construct simple models for the capital costs [3]. Our model includes, for example, the costs of the cavern, the turbomachinery, the TES units, the electrical equipment, and the transmission line to the nearest grid node.

**Level 2: Plant performance in the Swiss electricity grid**

The objective of the simulations with the coupled grid-plant model is to evaluate the profitability of several plant power and capacity ratings for various use cases. The evaluation is based on a simple AA-CAES plant model that assumes a constant plant efficiency coupled with a model of the Swiss electricity grid [4]. Over the past year, the coupled plant-grid model was extended in two ways. First, the fidelity of the grid model was improved. It now includes the full 2025 AC grid model of Swissgrid as well as an aggregated model of the neighboring countries, see Figure 1, in which Bitsch is indicated by a blue circle. Load demand, generator costs, and production availability were projected from historical data to match the 2025 model (collaboration with the SNF NRP 70 project AFEM). The second extension is that the evaluation now makes use of the above-mentioned cost estimates, thereby allowing the profits to be estimated for various use cases.

To evaluate the use case of electricity price arbitrage, an
Investigation of AA-CAES Plant Configurations and Grid Integration

The coupled plant-grid simulations in Level 2 rely on assumed plant efficiencies. Providing realistic values of these efficiencies for specific plant configurations is one objective of the detailed plant simulations carried out in Level 3. The detailed model, implemented in Matlab-Simscape, now contains submodels for the unsteady operation of the turbomachinery, the temporal evolution of the pressure and temperature in the caverns, the behavior of the TES units, and allows for temperature-dependent air properties. The TES units are modelled using a previously developed heat-transfer model that accounts for the time-dependent temperature profiles in the storage materials as well as the structural and insulation layers [7].

The detailed model has been validated with data from the Huntorf CAES plant and the Pollegio AA-CAES pilot plant. The detailed simulations are performed with operational schedules that correspond to either regular cycles with fixed charging and discharging durations or to irregular cycles representing the anticipated operation in the electricity grid.

The detailed plant model was used to analyse the two plant layouts shown in Figure 3. Schematic plant layouts that have been simulated with the detailed plant model. Optimal power-flow model [5, 6] was used to quantify and compare the annual electricity costs with and without the AA-CAES plant with a time-coupled 48-hour rolling horizon optimal dispatch. For simplicity, we assumed a plant efficiency of 70% and that the plant construction costs were annualized over 50 years for the turbomachinery and 100 years for the cavern.

The results presented in Figure 2 indicate clearly that arbitrage alone is not a profitable use case irrespective of the power and capacity ratings. Therefore, additional use cases, e.g., reserve markets and other flexibility services, will be considered in future work. Furthermore, the plant model will be extended to better reflect the unsteady plant operation by including the power consumption and the reduced efficiencies during the start-up and shut-down transients.

Level 3: Detailed plant simulations and coupled LCA assessment

The coupled plant-grid simulations in Level 2 rely on assumed plant efficiencies. Providing realistic values of these efficiencies for specific plant configurations is one objective of the detailed plant simulations carried out in Level 3. The detailed model, implemented in Matlab-Simscape, now contains submodels for the unsteady operation of the turbomachinery, the temporal evolution of the pressure and temperature in the caverns, the behavior of the TES units, and allows for temperature-dependent air properties. The TES units are modelled using a previously developed heat-transfer model that accounts for the time-dependent temperature profiles in the storage materials as well as the structural and insulation layers [7].

The detailed model has been validated with data from the Huntorf CAES plant and the Pollegio AA-CAES pilot plant. The detailed simulations are performed with operational schedules that correspond to either regular cycles with fixed charging and discharging durations or to irregular cycles representing the anticipated operation in the electricity grid.

The detailed plant model was used to analyse the two plant layouts shown in Figure 3. Schematic plant layouts that have been simulated with the detailed plant model. Optimal power-flow model [5, 6] was used to quantify and compare the annual electricity costs with and without the AA-CAES plant with a time-coupled 48-hour rolling horizon optimal dispatch. For simplicity, we assumed a plant efficiency of 70% and that the plant construction costs were annualized over 50 years for the turbomachinery and 100 years for the cavern.

The results presented in Figure 2 indicate clearly that arbitrage alone is not a profitable use case irrespective of the power and capacity ratings. Therefore, additional use cases, e.g., reserve markets and other flexibility services, will be considered in future work. Furthermore, the plant model will be extended to better reflect the unsteady plant operation by including the power consumption and the reduced efficiencies during the start-up and shut-down transients.

Level 3: Detailed plant simulations and coupled LCA assessment

The coupled plant-grid simulations in Level 2 rely on assumed plant efficiencies. Providing realistic values of these efficiencies for specific plant configurations is one objective of the detailed plant simulations carried out in Level 3. The detailed model, implemented in Matlab-Simscape, now contains submodels for the unsteady operation of the turbomachinery, the temporal evolution of the pressure and temperature in the caverns, the behavior of the TES units, and allows for temperature-dependent air properties. The TES units are modelled using a previously developed heat-transfer model that accounts for the time-dependent temperature profiles in the storage materials as well as the structural and insulation layers [7].

The detailed model has been validated with data from the Huntorf CAES plant and the Pollegio AA-CAES pilot plant. The detailed simulations are performed with operational schedules that correspond to either regular cycles with fixed charging and discharging durations or to irregular cycles representing the anticipated operation in the electricity grid.

The detailed plant model was used to analyse the two plant layouts shown in Figure 3. Schematic plant layouts that have been simulated with the detailed plant model. Optimal power-flow model [5, 6] was used to quantify and compare the annual electricity costs with and without the AA-CAES plant with a time-coupled 48-hour rolling horizon optimal dispatch. For simplicity, we assumed a plant efficiency of 70% and that the plant construction costs were annualized over 50 years for the turbomachinery and 100 years for the cavern.

The results presented in Figure 2 indicate clearly that arbitrage alone is not a profitable use case irrespective of the power and capacity ratings. Therefore, additional use cases, e.g., reserve markets and other flexibility services, will be considered in future work. Furthermore, the plant model will be extended to better reflect the unsteady plant operation by including the power consumption and the reduced efficiencies during the start-up and shut-down transients.

Level 3: Detailed plant simulations and coupled LCA assessment

The coupled plant-grid simulations in Level 2 rely on assumed plant efficiencies. Providing realistic values of these efficiencies for specific plant configurations is one objective of the detailed plant simulations carried out in Level 3. The detailed model, implemented in Matlab-Simscape, now contains submodels for the unsteady operation of the turbomachinery, the temporal evolution of the pressure and temperature in the caverns, the behavior of the TES units, and allows for temperature-dependent air properties. The TES units are modelled using a previously developed heat-transfer model that accounts for the time-dependent temperature profiles in the storage materials as well as the structural and insulation layers [7].

The detailed model has been validated with data from the Huntorf CAES plant and the Pollegio AA-CAES pilot plant. The detailed simulations are performed with operational schedules that correspond to either regular cycles with fixed charging and discharging durations or to irregular cycles representing the anticipated operation in the electricity grid.

The detailed plant model was used to analyse the two plant layouts shown in Figure 3. Schematic plant layouts that have been simulated with the detailed plant model. Optimal power-flow model [5, 6] was used to quantify and compare the annual electricity costs with and without the AA-CAES plant with a time-coupled 48-hour rolling horizon optimal dispatch. For simplicity, we assumed a plant efficiency of 70% and that the plant construction costs were annualized over 50 years for the turbomachinery and 100 years for the cavern.

The results presented in Figure 2 indicate clearly that arbitrage alone is not a profitable use case irrespective of the power and capacity ratings. Therefore, additional use cases, e.g., reserve markets and other flexibility services, will be considered in future work. Furthermore, the plant model will be extended to better reflect the unsteady plant operation by including the power consumption and the reduced efficiencies during the start-up and shut-down transients.

Level 3: Detailed plant simulations and coupled LCA assessment

The coupled plant-grid simulations in Level 2 rely on assumed plant efficiencies. Providing realistic values of these efficiencies for specific plant configurations is one objective of the detailed plant simulations carried out in Level 3. The detailed model, implemented in Matlab-Simscape, now contains submodels for the unsteady operation of the turbomachinery, the temporal evolution of the pressure and temperature in the caverns, the behavior of the TES units, and allows for temperature-dependent air properties. The TES units are modelled using a previously developed heat-transfer model that accounts for the time-dependent temperature profiles in the storage materials as well as the structural and insulation layers [7].

The detailed model has been validated with data from the Huntorf CAES plant and the Pollegio AA-CAES pilot plant. The detailed simulations are performed with operational schedules that correspond to either regular cycles with fixed charging and discharging durations or to irregular cycles representing the anticipated operation in the electricity grid.

The detailed plant model was used to analyse the two plant layouts shown in Figure 3. Schematic plant layouts that have been simulated with the detailed plant model. Optimal power-flow model [5, 6] was used to quantify and compare the annual electricity costs with and without the AA-CAES plant with a time-coupled 48-hour rolling horizon optimal dispatch. For simplicity, we assumed a plant efficiency of 70% and that the plant construction costs were annualized over 50 years for the turbomachinery and 100 years for the cavern.

The results presented in Figure 2 indicate clearly that arbitrage alone is not a profitable use case irrespective of the power and capacity ratings. Therefore, additional use cases, e.g., reserve markets and other flexibility services, will be considered in future work. Furthermore, the plant model will be extended to better reflect the unsteady plant operation by including the power consumption and the reduced efficiencies during the start-up and shut-down transients.

Level 3: Detailed plant simulations and coupled LCA assessment

The coupled plant-grid simulations in Level 2 rely on assumed plant efficiencies. Providing realistic values of these efficiencies for specific plant configurations is one objective of the detailed plant simulations carried out in Level 3. The detailed model, implemented in Matlab-Simscape, now contains submodels for the unsteady operation of the turbomachinery, the temporal evolution of the pressure and temperature in the caverns, the behavior of the TES units, and allows for temperature-dependent air properties. The TES units are modelled using a previously developed heat-transfer model that accounts for the time-dependent temperature profiles in the storage materials as well as the structural and insulation layers [7].
Investigation of AA-CAES Plant Configurations and Grid Integration

layouts depicted in Figure 3 for regular cycles. Both plants contain low- and high-pressure compressors and two caverns. As indicated in the figure, the low-pressure compressor takes ambient air to about 33 bar and the high-pressure compressor charges the cavern up to 100 bar. The main difference between the two plants is that the first has only one TES located in the low-pressure cavern and one turbine, whereas the second has two TES and high- and low-pressure turbines.

The simulations indicated that the first layout suffers from a lack of operational flexibility arising from the pressure equilibration of the two caverns prior to discharging. The equilibration introduces a time scale that may prevent the plant from being able to react to power demands. The second plant layout does not require pressure equilibration and hence does not suffer from a lack of operational flexibility. We have therefore investigated this layout also for the irregular charging-discharging cycles covering one week of operation depicted in Figure 4. The daily and weekly plant efficiencies are plotted in Figure 5, confirming that the plant efficiency of 70% used in the plant-grid simulations in Level 2 can be regarded as realistic.

We have since progressed to the analysis of a third plant layout that is similar to the second but for which both the low- and high-pressure compressor have pressure ratios of 10, allowing the use of existing turbomachinery by MAN Energy Solutions AG as well as realistic compressor performance data.

The plan for the coming year is to use the detailed plant simulations of this third plant layout to devise a simplified plant model for the plant-grid simulations in Level 2.

References
Assessment

Calculation of Heat Demand for the Assessment of Storage Potential on System Level

Scope of project

The assessment of energy storage within WP 5 of the SCCER HaE employs a nested-level approach, where storage is studied on the level of technologies, on level of the system, and on level of the socio-economic impact. To understand the potential of energy storage on the system level, University of Basel, University of Geneva and the Lucerne University of Applied Sciences and Arts teamed up in the SNF research project SwissStore. One of HSLU’s tasks, which is a joined deliverable with SCCER, includes the development of demand curves for space heating (residential, commercial and industry sectors). Those load curves are later on used in a social planner model, which basically follows the standard approach of large scale energy system models.

Status of project and main scientific results of workgroups

As described in Figure 1, the key features of electricity modelling are a spatial aggregation (only differentiating on the grid level) and a very high temporal resolution of the diurnal electricity demand curve. Electricity grids have little inertia or intrinsic storage capacity, consequently the generation of electricity has to match the consumption exactly. More intermittent electricity sources from wind and solar power would make this endeavour more challenging. Energy storage technologies are one strategy to deal with this problem, sectoral coupling between electricity and e.g. mobility another. For Switzerland, a promising combination would be sectoral coupling with the (residential and commercial) space heating sector, as described in. [1] A high share of non-renewable heat generation for space heating could be adapted towards low or zero carbon emissions. This would be a major move towards the fulfilment of the ratified Kyoto targets for Switzerland. Another opportunity is given by the usage of thermal energy storage as a flexible sink for electricity generation regulation. Three independent storages can be identified in a house: • its thermal mass and inertia, • the storage for domestic hot water at 65–70 °C and • a new storage for space heating.

Coming back to Figure 1, the SNF project SwissStore requires load curves for heat demand. The difficulty is located at the unavailability of true data about the energy end use for space heating, the demand. What is given is data about the consumption of all kind of energy carriers (fuel oil, natural gas, wood pellets etc.) for heating. The Swiss Federal Office for Energy has a sound database on those. Data from Prognos would suggest a one-to-one translation from fuel consumption to energy end use, which in many cases is not realistic: Considering e.g. a given case of a single-family house, with given insulation and therefore given seasonal
heat losses, and finally given demand of heat to compensate these losses per day.

There are many technological options for realizing the heat production, for instance an air-water heat pump feeding a 35°C underfloor heating, compared to a state-of-the-art condensing boiler supplying radiators at 70°C. While the condensing boiler is usually operated in direct response to the occupancy and daytime (night setback, peaks in morning, evening and during weekend hours), an underfloor heating has a large time constant, it would most of the time make sense to run on constant level.

As it is clearly visible with this example, a given heat demand is not per se resulting to an universal demand curve. The scientific answer in [2] is hence based on a different methodology: the combination of maps of the distribution of population and climate, both in high spatial resolution and for the climate, in daily mean temperature levels. For modelling and simulation, this means the solver has the freedom to pick a technology and deliver the heat for the day at any time; the thermal mass of the building and assuming the increased proliferation of underfloor heating are the justification.

When looking into distant future of 2035, 2050 or 2099, the big question is how climate change would potentially alter our heating (and cooling) demand in Switzerland in the long run. For a historic benchmark period of 1981 to 2017, a trend of warming and the influence on heating demand has been proven with data from MeteoSwiss in Reference [3]. Figure 2 and Figure 3 are giving an idea of the spatial distribution and the deviation from average for Switzerland. For the future perspective, we obtained data from MeteoSwiss and C2SM for the CH2018 climate scenarios for Switzerland.

References
Assessment of Energy Storage at the Technology and Energy System Level

Scope of project

On the technological scale, the University of Geneva (UNIGE) examines which electricity storage technologies can support PV and wind technologies to meet various type of demand profiles (e.g., peak and baseload) depending on the scale of deployment, namely residential, utility and bulk, as well as how they compare with traditional power generators on a levelised cost basis. UNIGE also collaborates with PSI-LEA, ETHZ and HSLU in the assessment of storage technologies for different applications, e.g., batteries and thermal storage.

The main objective on the energy system level 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).

- At the local scale, UNIGE is, so far, focusing on individual dwellings and analysing PV-coupled battery systems and PV-coupled heat pump systems, including both thermal and electric storage and performing various applications from the consumer perspective (i.e. reducing the electricity bill). We then analyse trade-offs between consumers benefits and electricity grid impacts.
- At the national scale, we have built a dedicated optimisation model of the Swiss power sector as well as how they compare with traditional power generators on a levelised cost basis. 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

Research outputs on technological level

Energy Storage can play an enabling role to tackle the problem of intermittency associated with solar and wind generation. However, the techno-economic performance of these hybrid systems depends on a large number of parameters, including wind and solar production profiles, the widely varying performance along the two dimensions of energy and power costs, as well as type of electricity demand profile to be met. In our study, we assess the operation of hybrid systems including renewable and storage technologies supplying constant electricity to various types of electricity demand profiles at different scales, namely, residential, utility and bulk across Switzerland. In particular, we defined 5 different supply modes:

- during generation hours, referred to as «Generation»;
- during the maximum two peak period, referred to as «Bi-peak»;
- during generation and peak hours, referred to as «Generation and peak»,
- during time-of-day hours, referred as «Time-of-day»;
- during 24 hours, referred to as «Baseload».

We develop a model with a temporal resolution of 10 minutes and run it on a daily basis to calculate the required size and schedule of the storage technology as well as the levelised cost of the hybrid system (LCOHS). This subsequently allows us to discuss the most optimal hybrid systems and compare them with conventional power generation technologies. Furthermore, we determine the sensitivity of the LCOHS to the size of the storage system in both power and energy terms. Finally, we also examine the competitiveness of these hybrid systems vis-à-vis conventional electricity generators based on future cost reduction trajectories of renewable energy and storage technologies.

We find that the optimal choice for energy storage technology in a hybrid system depends on the scale rather than the supply mode or the renewable energy technology. Our results show that Li-ion batteries prove to be the most optimal storage option at the residential scale (0.58 to 1.22 EUR/kWh with PV), I-CAES at the utility scale (0.23 to 0.50 EUR/kWh with PV), and HPL at the bulk scale (0.10 to 0.13 EUR/kWh with PV), irrespective of the type of supply mode or renewable generation supply (the ranges in brackets represent the impact of the type of supply mode on the LCOHS).
Assessment of Energy Storage at the Technology and Energy System Level

The comparison with conventional technologies in Figure 1 shows, that further cost reduction in renewable energy and storage technologies is needed for hybrid systems to supply electricity on demand at competitive cost. Sensitivity analysis shows that reduction in cost of both renewables and storage technologies as well as the energy storage size by allowing some distortion in the required supply strategy hold a key towards future cost-competitive of hybrid systems.

Research outputs
energy system related

Local scale

UNIGE focuses on individual dwellings with solar photo-voltaics (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 closely to consumers.

Since residential batteries are not economically viable yet, combining applications has been suggested as a way to increase their attractiveness, but the extent to which this can be achieved, as well as how the different applications may influence the choice of the optimal battery technology, remain unclear.

We develop an optimization framework to determine the best-suited battery technology and size depending on the applications combined, including PV self-consumption, demand load-shifting, demand peak shaving and avoidance of PV curtailment. Moreover, we evaluate the impact of the annual demand and electricity prices by applying our method to some representative dwellings in Switzerland and the U.S. in collaboration with the Massachusetts Institute of Technology (MIT). Finally we determine the break-even point for all battery technologies and compare the results when only PV self-consumption is included and when all applications are combined (see Figure 2). We conclude that residential batteries may reach profitability (without subsidies) in both countries in the next decade if all applications are combined according to the expected cost reduction trajectories for battery technologies.

Given the PV potential to simultaneously decarbonize other sectors such as heating and cooling, a second ongoing study in collaboration with HSLU focuses on PV-coupled heat pump systems delivering cooling, heating and hot water on individual dwellings, including residential storage, both thermal and electric. These systems can be used to increase PV self-consumption, but also to simultaneously provide other residential applications (i.e., demand load-shifting, avoidance of PV curtailment and demand peak-shaving), ultimately helping to reach economic viability.

We focus on different Swiss dwellings in terms of electricity and heat demand, with rooftop PV generators and compare which type of storage, namely electric and thermal, offers more benefits for the consumer and the electricity grid. In particular, we discuss trade-offs between benefits for consumers (e.g., bill minimization) and grid impacts (e.g., maximum grid relief) depending on the type of consumer, building characteristics and technologies. Additionally, we analyse the differences between floor heating and traditional radiators.

Our methodology includes an open-source mixed-integer linear programming optimisa-
Assessment of Energy Storage at the Technology and Energy System Level

Assessment

Figure 2:
Break-even point of a 7 kWh battery for all battery technologies depending on the type of combination of applications, PV self-consumption only (blue), the full combination of applications (green) and for comparison, the installed cost per kWh used in this study (red), for the U.S. (right) and Switzerland (left). The size of the PV system corresponds to the median installed capacity across both locations.

Figure 3:
Impact of bulk storage on the production of nuclear power in high-VRE scenarios. The storage power share is expressed as a fraction of average electricity demand.

Figure 3:
Impact of bulk storage on the production of nuclear power in high-VRE scenarios. The storage power share is expressed as a fraction of average electricity demand.

Assessment to solve the residential energy management problem. It minimises the cost of the daily electricity bill as a function of the electricity and heat demand, PV generation, battery, heat pump and water tank characteristics as well as various types of storage applications and their combinations. The storage 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

A national-scale dispatch model was developed to answer questions centred on the role of bulk electric storage in Switzerland and its neighbouring countries. This model optimises the power production for each hour of the year. Stylised power plants are represented by linear cost supply curves. This allows to approximate power plant fleets comprising units with varying efficiency and therefore varying specific costs of power production. The model is calibrated with respect to the electricity price profiles and the power production in the reference year 2015. Within each of the five countries, transmission constraints are neglected. Cross-border power exchange is subject to optimization within a certain capacity range.

In a first step, this model is used to assess the impact of large volumes of electric storage on the replacement of conventional dispatchable capacity. This is done by optimising the power system for future scenarios with high solar and wind power production. The cases with and without additional storage capacity are analysed separately. This allows to determine the relative impact of bulk storage on the operation and retirement of conventional power plants. Since this study relies on an optimisation framework, it represents the situation in a free market setting with rational power plant retirement decisions.

This study thus answers the question to what extent electric storage counteracts or amplifies the replacement of conventional power plants due to rising variable renewable electricity (VRE) generation. It is found that this strongly depends on both the level of VRE production and the technical properties of the storage. In the most general case, additional storage capacity increases dispatchable power production (e.g. nuclear, coal) for small VRE shares. This is due to charging from these sources for both the replacement of more expensive generators and the optimization of capacity utilization. For larger VRE shares storage decreases the produced amount of dispatchable power, for example due to charging from otherwise curtailed energy. This general pattern strongly depends on the technical storage parameters. For certain VRE shares long-term storage with low round-trip efficiency causes greater production from nuclear power plants, while the opposite holds for battery-type storage with higher efficiency (see Figure 3).
Technology Assessment of Energy Storage

Scope of project

Activities of PSI’s LEA team (Laboratory for Energy Systems Analysis) within WP5 of the SCCER Heat and Electricity Storage in 2018 focused on the environmental and techno-economic assessment of batteries, both on the technology as well as on the energy system level. Alternative energy storage technologies such as power-to-gas options were mainly investigated in the context of increasing the (seasonal) flexibility of the Swiss energy system.

Status of project and main scientific results of workgroups

On the technology level, we established a comprehensive basis for the environmental assessment of indirect («consequential») impacts of electricity storage within the energy system by integrating new and updated long-term marginal electricity mixes into the eco-invent life cycle assessment (LCA) database. [1]

Together with ETHZ and the University of Geneva, we quantified greenhouse gas (GHG) emissions and cost from storing electricity in stationary battery systems. [2] We developed a modelling framework to assess performance, costs and environmental impacts of Li-ion and Na-ion batteries. [3] We evaluated material criticality in home-based battery systems [4] and analysed optimal battery application in various local contexts. [5, 6]

On the energy system level, we quantified the environmental effects of integrating batteries in the future Swiss electricity supply system applying a consequential LCA approach [7] and contributed to the evaluation of flexibility measures for the Swiss energy supply system. [8, 9]

Our analysis of various battery technologies for various applications used in different countries – based on technology and application specific costs and life cycle inventories – shows that, for a base case assumption of social costs of carbon emissions of 70 €/ton CO2, the GHG emission related costs are much lower than the direct technology costs (Figure 1). [2]

Hence, our analysis finds that – other than in alternative low-carbon passenger vehicles – there seem to be only very few cases with major trade-offs along the two dimensions of GHG emissions costs and life cycle costs (LCC). The fact that we do not find major trade-offs between the LCC and life cycle emissions (LCE) of different technologies implies that even in the absence of a carbon price, choosing a battery technology purely based on LCC will also pick the socially optimal technology. This can inform the debate on the design of battery-support policy, which – based on our results – does not have to differentiate between technologies.

Addressing potential future battery technologies, our economic and environmental

List of abbreviations

GHG Greenhouse Gas
LCA Life Cycle Assessment
LCC Life Cycle Costs
LCE Life Cycle Emissions

Figure 1: Comparison of GHG emissions cost and lifecycle costs (LCC) of storing one kWh of electricity in battery systems under different social cost of carbon assumptions. Each dot represents one technology application combination which forms the clusters (but overlap): wholesale arbitrage (left), transmission & distribution, increase of self-consumption, demand peak shaving and area & frequency regulation (right). The sloped grey lines represent different ratios of GHG emission cost over LCC.

SCC: Social Costs of Carbon emissions [2];
VRFB: Vanadium-Redox flow battery,
VRLA: Lead-Acid battery,
NCA: Nickel-Cobalt-Aluminum,
LTO: Lithium-Titanium-Oxide,
NMC: Nickel-Manganese-Cobalt,
LFP: Lithium-Iron-Phosphate.

Authors

Christian Bauer1
Xiaojin Zhang1
Simon Schneider1
Evangelos Panos1
Laurent Vandepaepe1,2
T. Kober1
K. Ramachandran1
Tom Terlow1,3

1 University of Geneva
2 Sherbrooke University, Canada
3 Utrecht University, Netherlands
evaluation of Na-ion vs Li-ion batteries shows that – based on the current status of technology development – Li-ion batteries outperform their Na-ion counterparts both in terms of costs and production related GHG emissions (Figure 2). [3] However, fundamental battery chemistries suggest that especially for high power applications future Na-ion batteries might become competitive in terms of specific energy and therefore also in terms of production costs and associated GHG emissions.

Our evaluation of metal criticality for different batteries – based on the life cycle inventory data established in [2] – shows that vanadium-redox flow batteries as well as Li-ion batteries perform much better than lead-acid batteries and that «bulk-materials», i.e. materials used in comparatively large quantities such as copper and aluminium, primarily determine performance regarding metal criticality (Figure 3). However, also few other metals used in small quantities, but associated with large supply risks such as cobalt contribute to criticality scores. We also show that the concept of metal criticality requires further developments to become more useful. Overall, metal criticality can be reduced by improving energy density of batteries, reducing the use of rare metals (e.g., Co) and establish large-scale battery recycling industries.

Flexibility within the Swiss energy supply system will become a key factor as soon as

Figure 2: Production costs (left) and associated GHG emissions (right) of Na-ion and Li-ion batteries today. [3]

Figure 3: Metal criticality scores of the batteries throughout the system lifetime, per kWh stored, applying three different assessment methods («Graedel et al.», NSTC, EC) [4].

large quantities of intermittent renewable energy (e.g., electricity from photovoltaics and wind power) will be part of the supply system.

Our evaluation of various flexibility options for the Swiss energy system, i.e. different electricity storage technologies, but also energy conversion pathways such as power-to-gas, shows that seasonally balancing production and demand will not only require energy storage, but also conversion of electricity into other energy carriers; those can be used in other sectors, i.e. for heating and mobility purposes (see also Figure 4).[8]

Other important flexibility options are the integration of Switzerland in the European electricity grid and measures on the demand side (e.g., temporal shifts).

To which extent specific flexibility options will have to be implemented in the future will primarily depend on political issues:

Key aspects will be the level of GHG emission reduction Switzerland is aiming at and the question to which extent domestic energy supply will represent a priority for security of supply.

Figure 4: Electricity production during summer that enters into the power-to-X pathway in 2050 (PJ/yr.) in the low carbon scenario.[10]
Assessment of Energy Storage at the Socio-Economic Level

Scope of project

In 2018, the activities of ETH Zurich’s Energy Politics Group (EPG) for the SCCER HaE covered the techno-economic assessment of different battery types, the CO₂ emissions impact of operating batteries in different European grids, the dynamic competition between different storage types, and the role of new applications in triggering innovation in lithium ion batteries. These activities are described in more detail below.

In a common project with PSI and the University of Geneva, we compared the life-cycle cost and emissions of six different battery chemistries across five stationary applications and three countries (CH, DE, PL). The analysis reveals that, assuming carbon prices of up to 180 EUR/ton, no major tradeoffs between the emissions and economic cost dimensions exist – in other words, the least cost technologies are typically also the least carbon emitting technologies [1, 2]. For more details on this project, please see «Technology Assessment of Energy Storage» (page 69).

Status of project and main scientific results of workgroups

On the socio-economic level, as reported in last year’s annual report, EPG has developed a system-dynamic simulation model to assess competitiveness of different battery technologies over time. In 2018, we finalized this model and analyzed the effect of electric vehicle (EV) uptake on the competitiveness of stationary storage technologies. The model projects future market shares by technology under different scenarios of EV adoption. Results have been finalized and the study is under peer-review.[3] Model-ling projects Li-ion batteries to gain highest market shares across electricity sector applications by 2030, unexpectedly outcompeting even pumped-hydro storage plants, with the timing of this change depending on EV uptake. This development is driven by cost reductions of 60–70% in Li-ion battery packs and a reduction of about 60% in balance-of-system cost from 2017 to 2030, based on experience curves.

By focusing on technology competition, our work goes beyond individual battery storage cost projections and contributes to the policy debate on how to actively manage resilience and avoid inefficiencies in future electricity systems. Exemplary results can be viewed in Figures 1 and 2.

In a new project, EPG developed a model to assess the impact of storage operation on the CO₂ imprint of electricity systems. Our newly developed approach couples energy system modelling with storage dispatch optimization. This allows to assess the effect of battery dispatch on CO₂ emissions across electricity system contexts, storage applications and various policy scenarios. Currently, no such modelling approach exists, which is why...
past studies paint an overly negative and less nuanced picture on the abovementioned effects. First results indicate that impacts differ strongly across the analyzed dimensions and show potential of higher CO₂ prices to improve emissions footprints across applications.

Finally, ongoing research at EPG is analysing windows of opportunity for latecomers in the lithium-ion battery industry. Thus far, little is known how changing applications for lithium-ion batteries have influenced the knowledge base of the industry, and whether they provided windows of opportunity for latecomers.

To investigate this, we conducted a patent-citation network analysis to analyse the trajectory of evolution of the knowledge base of the lithium-ion battery industry. The analysis is based on 56'996 patents covering the period 1970–2018 from 140 countries, which was retrieved from the European Patent Office PATSTAT database using keyword and classification code-based searches.

Early results indicate that the increasing emphasis in focus of patenting activity on electric vehicles was accompanied by a shift in knowledge sourcing strategies. Figure 3 shows an exemplary result of the analysis.

References
Increasing the Efficiency of the Power-To-Methane Technology

Scope of project

The University of Applied Sciences Rapperswil (HSR) contributes to the SCCER HaE with a High Efficiency Power-to-Methane Pilot (HEPP). The main aim of the HEPP project is to increase the efficiency of the power-to-methane technology. This task is achieved through thermal coupling of a catalytic methanation and a solid oxide electrolysis (SOE). This coupling is realized with the development of a new heat management and a steam generator as key components. This steam generator uses the waste heat from the catalytic methanation to evaporate water and supplies the steam to the SOE.

Status of project and main scientific results of workgroups

The newly developed sensors from our research partner MEMS AG have also been characterized. During these tests in comparison with a mass spectrometry, it was found that the sensors work very well for gas mixtures consisting of three different gases. After implementing a correction factor in the evaluation software, the sensors were found to give accurate results.

Thermal coupling of SOE and methanation

The thermal coupling of a catalytic methanation and a SOE is a key element and is investigated in the new project HOTCAT4STEAM. The key component for this coupling is the steam generator making use of the waste heat from the catalytic methanation to evaporate water and supplies the SOE with steam. In contrast to similar projects in our project, the heat is directed from the methanation to the steam generator by a heat management system using thermal oil as heat transfer fluid (see Figure 4).

Extensive tests with the steam generator prototypes were done showing that generating steam in using thermal oil at the very low pressure fluctuations required by the SOE is a
Increasing the Efficiency of the Power-To-Methane Technology

challenge. In close co-operation with Dr. MER Jan Van herv-le's Group of Energy Materials GEM at EPFL Sion, who deliver the SOE, the thermal coupling is realized during 2019.

Natural Gas Filling Station

The natural gas (NG) station on the HEPP site was approved by the TISG in April 2018 and has been operating since then. The NG station supplies around 10 vehicles with biogas with a consumption between April and November 2018 of around 1'000 kg CH₄. The Directorate General of Customs (Oberzolldirektion) has granted the license for the tax-free feed-in of the SNG produced by the HEPP plant.

Events

Beside the scientific work at the demonstrator, the HSR team has hosted several events and welcomed guests:

- Expert Discussions Power-to-Gas, June 2018, with around 100 participants.
- Delegation of the full project meeting of the EU project Pentagon, September 2018, with around 30 participants.
- Inauguration of the HEPP facility, October 2018, with around 70 participants.
- Hosting the SCCER HaE Annual Conference, November 2018, with around 130 participants.
- Guided tours on the HEPP facility, September until December 2018, around 300 participants.

Publications

In 2018, the focus was to inform the public about our research activities, because scientific publications are expected after the construction of the HEPP demonstrator in the years 2019–2020. Many articles about project HEPP have been published by journalists and by ourselves in the following media:

- Aargauer Zeitung
- Aqua&Gas
- Bulletin.ch
- die Baustellen
- ee-news
- Erdgas
- ET Elektronik
- Folio
- Höfner Volksblatt
- Leader Special
- Linth-Zeitung
- NZZ am Sonntag
- Panorama – Bildung/Beratung/Arbeitsmarkt
- Punkt 4 Info
- Rundschau Ausgabe Süd
- Schweiz am Wochenende
- St.Galler Tagblatt
- Südostschweiz
- Südzgaller Zeitung
- Youtility
- Zug Kultur
- Zürichsee Zeitung

Goals for 2019 – 2020

In 2019 the electrical installations and the gas infrastructure for the HEPP demonstrator will be completed in early 2019. Afterwards the HEPP demonstrator can be run and the produced SNG can be fed into the natural gas grid unlimitedly. The measuring campaign for the high efficiency of the HEPP demonstrator will be executed in 2019 and 2020.
ESI – Energy System Integration Platform

Scope of project

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

Status of project and main scientific results of workgroups

In 2018 final details of the basic platform infrastructure (support structure for individual sub-systems, supply of media-gases, cooling-water, electricity, safety system & controls) have been completed and all sub-systems (electrolysis, fuel cells, methane synthesis, wet biomass conversion) became operational.

One of the issues resolved for the platform infrastructure was related to the purity of oxygen being fed into the storage tank. In a joint effort together with the supplier of the gas cleaning equipment for H₂ & O₂, the root cause for insufficient catalytic conversion of trace amounts of H₂ in O₂ could be identified and measures be taken to achieve low ppm-levels of impurities for the gas to be fed into the pressure tanks.

Joint activities have been continued between the technology oriented sub-systems (represented with hardware on the ESI platform) 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 PEM electrolyser (a prototype system from Siemens) has been tested intensively within a project with Swissgrid in order to prove its capabilities for primary and secondary frequency control services (Figure 2). The system turned out to be 100% fit for such network services even though some optimization still remains in terms of the control scheme (especially the stack management).

The predefined load profiles could be realized with the system within the given (narrow) deviation boundaries. Only during load ramps in the part load regime very brief/short term violations of the given boundaries could be observed in some cases (load spikes caused by the stack management). These issues can be mitigated by an optimized stack management control algorithm, and will be anyway less significant for larger scale systems (MW systems) for which the individual stack management has less influence on the overall system performance.

The fuel cell container system on the ESI platform (based on PEM technology and suited for H₂/O₂ re-electrification with high efficiency, i.e. up to 70%) has been equipped with additional fuel cell stacks. In total the system will accommodate up to four (4) fuel cell stacks (50 kWₑ each). After the commissioning of the fuel cell modules, the system will undergo similar load ramp test campaigns as for the electrolyser system (see previous paragraph).

A second container for fuel cell system testing is about 60% complete and will be commissioned in spring 2019. In this container PEM fuel cell systems (from small scale series production of industrial partners) will be exposed to qualification tests in order to support the market introduction of commercial systems at about a 100 kW scale.

The catalytic fluidised bed reactor for methane synthesis (dubbed GanyMeth; output capacity: up to 20 m³/h of SNG, i.e. an energy equivalent of up to 200 kWₑ) has been undergoing cold commissioning tests and hydraulic fluidization studies in order to confirm the design rules applied for the internal heat exchanger tube array. Advance optical techniques as well as pressure probes have been used to characterize the 2-phase (gas/solid) flow regime in between the heat exchanger tubes which are immersed in the fluidized bed zone (void fraction, bubble diameters, bubble rise velocities). The system is now being readied for pressurized operation and for heat transfer tests in order to confirm the cooling capacity of the rig required for subsequent first synthesis tests.

In a process study (supported financially by the canton Aargau) performed in the 2nd half of 2018 we were able to show that with a scale-up of some of the components available on the ESI platform (electrolyser, PEM electrolyser, PEM fuel cell system, catalytic fluidised bed reactor for methane synthesis) the overall system performance can be significantly improved.
H₂ storage, methane synthesis) one could achieve a sufficient supply of H₂ for a fleet of fuel cell trucks for transportation of goods. With system components in the single (< 3) MW scale enough electricity can be provided by photovoltaic (PV) panels on an annual basis to secure the H₂ demand of a fleet of 20 trucks for regional transport (Figure 3).

Excess H₂ produced in summer time is transformed into methane (CH₄) and injected into the natural gas grid. In winter time the same amount of CH₄ is re-processed to produce H₂ in a C-neutral fashion in order to supplement the reduced production via electrolysis. This way sufficient H₂ production can be guaranteed without additional burden imposed on the electric grid during winter time when there are frequent periods of time when Switzerland is dependent on electricity imports.

With these encouraging results in hand, it will be exploited if a first demonstration project can be realized within Switzerland based on this concept.

In order to close the gap between SNG production and storage in the gas grid on the one hand, and to demonstrate the flexible re-electrification of CH₄/H₂ mixtures in combined heat and power (CHP) systems, on the other hand, the ESI platform has been complemented with a micro gas turbine module in 2018. The system is currently qualified for natural gas/CH₄ but will be subsequently tested with CH₄/H₂ mixtures with increasing H₂ content. If it can be shown – with moderate modifications to the CHP systems – that end-use applications are available for CH₄/H₂ mixtures with significant amounts of H₂, the transition to a low carbon/hydrogen energy economy can be simplified considerably. By allowing significant addition of H₂ (20 to 40 vol%) to the existing public networks, storage of large amounts of H₂ even on a seasonal basis, becomes feasible at moderate cost. Current legislative limits and fuel specifications of gas turbine OEMs typically allow only very low amounts of H₂ (less than 2 vol% resp. 5 vol%) in the fuel gas.

**Outlook for 2019**

A moderate expansion of the platform activities will continue to happen also in the coming years (2019/2020). The platform infrastructure still has significant flexibility and capacity to accommodate additional technologies (e.g., battery storage systems).

Additional features could also be added on a virtual basis within the recently launched project ReMaP (coordinated by the Energy Science Center (ESC) of ETH Zurich). ReMaP has the ambition to link the demonstration platforms at Empa and PSI (and possibly some test hardware at 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.

The ReMaP project has been officially kicked-off just at the end of 2018, and the first task related to the ESI platform is now to set up a platform control system which enables all the features of data transfer envisioned in the ReMaP project.

The efforts are supported by joint activities of several SCCERs (Coherent Energy Demonstrator Assessment — CEDA), which have been starting to develop intra-platform data handling procedures and data evaluation standards.
Appendix
Conferences

• 5th Swiss Symposium Thermal Energy Storage, January 26, 2018, HSLU, Horw, Switzerland.
  [> 130 participants; Audience and presenters composed of a mixture of companies and researchers gathered
to promote the dissemination of scientific results and foster collaboration between industry and academia.]

• LATSIS Symposium: 12th International Symposium Hydrogen & Energy, February 11–16, 2018, SwissTech
  Convention Center, EPFL, Lausanne, Switzerland.
  [Hydrogen & Energy Award for Michael Grätzel, Best Poster Award for Stavroula (Alina) Kampouri, organised
  by Noris Gallandat and Andreas Züttel.]

• AA-CAES Symposium, May 15, 2018, Biasca and Bellinzona, Switzerland.
  [About 35 participants from academia, industry, and federal agencies from Austria, Germany, and Switzerland.]

• Swiss and Surrounding Battery Days, May 22–24, 2018, Baden, Switzerland, organized by SCCER WP2.

• 1st International Symposium on Solid-State Batteries, May 28–29, 2018, organized by Empa, Dübendorf,
  Switzerland.

  [~ 100 participants]

• Inauguration Symposium «Small Scale Demonstrator for Sion», September 14, 2018, Energypolis, Sion,
  Switzerland.
  [80 participants]

• Delegation of the full project meeting of the EU project Pentagon, September 2018.
  [~ 30 participants]

• Inauguration of the HEPP facility, October 2018, Rapperswil, Switzerland.
  [~ 70 participants]

• HSR hosting the SCCER HaE Storage Annual Conference, November 6, 2018, Rapperswil, Switzerland.
  [~ 130 participants]

• BFH Conference with Swiss Battery Industry, November 12, 2018, Olten, Switzerland.
  [20 participants]

• Guided tours on the HEPP facility, September until December 2018, Rapperswil, Switzerland.
  [~ 300 participants]
Presentations

Work Package «Heat – Thermal Energy Storage»

- B. Fumey, «Application specific temperatures for storage material and component testing», invited talk, 3rd IEA SHC Task 58/ECES Annex 33 Experts Meeting, April 9–11, 2018, Ljubljana, Slovenia.
- B. Fumey, «Inventory of sorption heat storage component and system designs currently under investigation by task and annex partners», invited talk, 4th IEA SHC Task 58/ECES Annex 33 Experts Meeting, October 1–3, 2018, Graz, Austria.
Presentations


Work Package «Batteries – Advanced Batteries and Battery Materials»

• K.V. Kravchyk, S. Wang, L. Piveteau, F. Krumeich, M.V. Kovalenko, «Non-Aqueous Aluminium-Graphite Batteries: Status, Prospects and Future», MRS Spring Meeting & Exhibit, April 2–6, 2018, Phoenix, USA.


• 1st International Symposium on Solid-State Batteries, May 28–29, 2018, Empa, Dübendorf, Switzerland.

• C. Marino, «Is there a future for Na-ion batteries?», invited talk, 1st Swiss and Surrounding Battery Days, May 23–25, 2018, Baden, Switzerland.

• E. Marelli, «How to overcome the P2-phases Na deficiency: a proof of concept», talk, 1st Swiss and Surrounding Battery Days, May 23–25, 2018, Baden, Switzerland.

• M. Schuster, «Investigation of carbonophosphonates as cathode material for water-in-salt sodium-ion batteries», talk, 1st Swiss and Surrounding Battery Days, May 23–25, 2018, Baden, Switzerland.

• C. Marino, M. El Kazzi, E.J. Berg, M. He, C. Villevieille, «Interface and safety properties of Phosphorus-based negative electrodes for Li-ion batteries», poster, 1st Swiss and Surrounding battery days, May 23–25, 2018, Baden, Switzerland.


• J. Conder, C. Villevieille, «How reliable is the Na metal as a reference electrode?», poster, 19th International Meeting on Lithium Batteries, June 17–22, 2018, Kyoto, Japan.

• C. Battaglia, «Forschung Energiepeicherung an der Empa», invited talk, Briefing Kantonsrat Zürich, July 2, 2018, Zurich, Switzerland.


• C. Marino, «Biowaste lignin-based carbonaceous materials as anodes for Na-ion batteries», talk, 69th Annual Meeting of the International Society of Electrochemistry, September 2–5, 2018, Bologna, Italy.


• E. Cuervo Reyes, F. Pagani, C. Battaglia, «Ion Transport in (Low-Dimensional) Ionic Conductors», invited talk, ECS AiMES Meeting, October 3, 2018, Cancun, Mexico.

• «Advanced Li-ion Batteries», ILmac, October 3–4, 2018, Lausanne, Switzerland.
Appendix

Presentations

- R. Dubey, K.V. Kravchyk, M.V. Kovalenko, «High Mass Loading Graphite Anodes for Li-ion Batteries», poster, 7th Symposium SCCER Heat and Electricity Storage, November 6, 2018, Rapperswil, Switzerland.
- J. Vidal Laveda, J.E. Low, C. Battaglia, «Stabilizing NMC811 in Full Cells with High Areal Capacity», poster, 7th Symposium SCCER Heat and Electricity Storage, November 6, 2018, Rapperswil, Switzerland.
- C. Battaglia, «Materials Innovation for Next-Generation Batteries», talk, 7th Symposium SCCER Heat and Electricity Storage, November 6, 2018, Rapperswil, Switzerland.
- C. Marino, C. Bolli, E. Marelli, E. Kendrick, C. Villevieille, «Though the Electrochemical Mechanisms of the O3-Na(Ni0.5Mn5/16Sn1/16Ti1/8)02 Phase used as Cathode Material for Na-ion Batteries», poster, 7th Symposium SCCER Heat and Electricity Storage, November 6, 2018, Rapperswil, Switzerland.
- D. Reynard, C. Dennison, A. Battistel, H. Girault, «Low-Grade Heat Recovery Using All-Vanadium Redox Flow Battery», poster, 7th Symposium SCCER Heat and Electricity Storage, Nov. 6, 2018, Rapperswil, Switzerland.
- C. Villevieille, «Electrode materials, electrolyte or the engineering – what is the key to successful development of Na-ion batteries?», invited talk, 5th International Conference on Sodium Batteries, November 12–15, 2018, Saint-Malo, France.

Work Package «Hydrogen – Production and Storage»

- «50th Anniversary of GAZNAT – Gaznat and EPFL a successful collaboration for future energy technology», invited talk, May 18, 2018, Rolex Learning Center EPFL, Switzerland.
Presentations

• «Storage of Renewable Energy by Reduction of CO₂ with Hydrogen», invited talk, South China University of Technology, June 19, 2018, Guangzhou, China.
• «Achievements on Hydrogen Storage from the Collaboration between Switzerland and Korea», invited talk, Europe-Korea Conference on Science and Technology (EKC), August 20, 2018, Glasgow, Scotland, Great Britain.
• «Storage of Renewable Energy by Hydrogen and Reduction of CO₂», invited talk, Materials.it 2018, October 22–26, 2018, Area della Ricerca CNR – Centro congressi, Bologna, Italy.
• «Hydrogen storage in solids, analysis and limits», invited talk, The 190th Committee on Hydrogen Function Analyses in Materials, Tohoku University, Advanced Institute for Materials Research (WPI-AIMR), Sendai, Japan.
• «The 20 Years of Complex Hydrides for Hydrogen Storage», invited talk, Metal H2018, November 1, 2018, Guangzhou, China.
• D. Reynard, C.R. Dennison, A. Battistel, H.H. Girault, «Harvesting low-grade heat using all-vanadium redox flow batteries», poster, 7th SCCER HaE Symposium, November 6, 2018, Rapperswil, Switzerland.
• N. Autissier, G. Laurenczy, «CO₂ as Hydrogen Vector & Formic Acid Power Supply Prototype», SCCER HaE Storage 7th Symposium, November 6, 2018, Rapperswil, Switzerland.
• G. Laurenczy, «Carbon dioxide to formic acid and to methanol: Homogeneous catalytic ways in aqueous solution at room temperatures», Conference: 256th National Meeting and Exposition of the American-Chemical-Society (ACS), August 19–23, 2018, Boston, MA, USA.
• L. Lombardo, H. Yang, A. Züttel, «Ionic Liquids as Efficient Destabilizing Agents of Sodium Borohydride», poster, 7th Symposium SCCER Heat and Electricity Storage, November 6, 2018, Rapperswil, Switzerland.
• H. Yang, L. Lombardo, A. Züttel, «Carbon Based Materials for Hydrogen Storage», poster, 7th Symposium SCCER Heat and Electricity Storage, November 6, 2018, Rapperswil, Switzerland.
• D. Lebedev, R. Ezhov, N. Kaeffer, M. Willinger, X. Huang, Y. Pushkar, C. Copéret, «From Nanoparticles to Single Sites – Decreasing the Noble Metal Content in Anodic Water Oxidation Catalysts», poster, 7th Symposium SCCER Heat and Electricity Storage, November 6, 2018, Rapperswil, Switzerland.
• «Gas solid interaction, the key for renewable energy storage», invited talk, XIX. Workshop über die Charakterisierung von feinteiligen und porösen Festkörpern, November 14, 2018, Niedernhausen, Germany.

• D. Aegerter, E. Fabbri, T.J. Schmidt, «The Effect of Fe in Ba$_{0.5}$Sr$_{0.5}$Co$_x$Fe$_{1-x}$O$_{3-δ}$ Towards the Oxygen Evolution Reaction in Alkaline Media», poster, 7th Symposium SCCER Heat and Electricity Storage, November 6, 2018, Rapperswil, Switzerland.

Work Package «Synthetic Fuels – Development of Advanced Catalysts»

• T.J. Schmidt, «Application of Synchrotron Based Methods to Study Electrochemical Energy Conversion Processes», invited talk, TU Munich, January 8, 2018, Munich, Germany.


• C. Copéret, «Molecular understanding and controlled functionalization of surfaces towards single-site catalysts and beyond», invited talk, SAOG 2018, February 1, 2018, Fribourg, Switzerland.


• A. Comas Vives, «What can Bonding Analysis and Ab Initio Molecular Dynamics tell us from Heterogeneous Catalysts?», invited talk, Young Faculty Meeting of the Chemistry Platform of the Swiss Academy of Sciences, June 5, 2018, Bern, Switzerland.

• E. Fabbri, «Oxygen Evolution Reaction – The Enigma in Water Electrolysis», invited talk, Young Faculty Meeting of the Chemistry Platform of the Swiss Academy of Sciences, June 5, 2018, Bern, Switzerland.

• C. Copéret, «Isolated Sites at Surfaces and Interfaces for Efficient Catalysis», invited talk, The 14th Young Faculty Meeting, June 5, 2018, New London NH, USA.

• T.J. Schmidt, «The Oxygen Evolution Reaction – From the Catalyst to the Cell Level», invited talk, Gordon Research Conference on Fuel Cells, August 2, 2018, Smithfield, RI, USA.

• C. Copéret, «Molecular understanding and controlled functionalization of surfaces towards single-site catalysts and beyond», invited talk, TOCAT8, August 5, 2018, Yokohama, Japan.


Presentations

- Y. Hou, R. Erni, R. Widmer, M. Rahaman, H. Guo, R. Fasel, P. Moreno-García, Y. Zhang, P. Broekmann, «Electrocatalytic CO₂ Reduction on Robust Cu@CuPd Core-shell Nanowires», contributed talk, 69th annual meeting of the International Society of Electrochemistry (ISE), September 3, Bologna, Italy.
- J. Zhang, W. Luo, A. Züttel, «Electrochemical CO₂ Reduction Toward CO and Ethanol», poster, 7th Symposium SCCER Heat and Electricity Storage, November 6, 2018, Rapperswil, Switzerland.
- K. Zhao, L. Wang, M. Calizzi, E. Moioli, A. Züttel, «Evolution of Adsorption Species During CO₂ Hydrogenation on Ru/Al₂O₃: Intermediates or Byproducts?», poster, 7th Symposium SCCER Heat and Electricity Storage, November 6, 2018, Rapperswil, Switzerland.
Appendix

Presentations

- P. Moreno-García, Y. Hou, M. Rahaman, P. Broekmann, «Towards Efficient Electrochemical N₂ Reduction at Room Temperature and Pressure through Hydride Transfer Mechanism on Cu@CuPd Nanowires», poster, 7th Symposium SCCER Heat and Electricity Storage, November 6, 2018, Rapperswil, Switzerland.
- J. Roth, «Energiespeicherung im Energiesystem von Morgen», invited talk, Aargauer Energie Aperos, November 27, 2018, Zofingen, Switzerland.
Presentations

- D. Perego, J. Herranz, T.J. Schmidt, «Differential Electrochemical Mass Spectrometry (DEMS) for Electroca-
talyis: An Overview», invited seminar, Politecnico di Milano, December 13, 2018, Milan, Italy.
- P.J. Dyson, «Valorizing waste to produce sustainable chemicals via catalytic routes», European Sustainable
Chemistry Award Lecture, 7th EuCheMS Chemistry Congress, Liverpool, UK.
- P.J. Dyson, «Improving the sustainability of reactions by modifying the environment of the catalyst», Clariant
CleanTech Lecture, University of Basel, Switzerland.
- F.D. Bobbink, «Design of ionic polymer catalysts for the synthesis of carbonates from CO2 and epoxides», ACS National Meeting, New Orleans, USA.
- F.D. Bobbink, «A Catalytic CO2 scrubber that generates cyclic carbonates from simple epoxide: ionic liquid
mixtures», SCS Fall Meeting, Lausanne, Switzerland.
- M. Hulla, G. Laurenzcy, P.J. Dyson, «N-Formylation of Amines with CO2 and Hydrosilanes Reactivity, Scope and Mechanism», SCS Fall Meeting, Lausanne, Switzerland.

Work Package «Assessment – Interactions of Storage Systems»

- M. Beuse, T.S. Schmidt, X. Zhang, B. Steffen, S.F. Schneider, A. Pena Bello, C. Bauer, D. Parra Mendoza,
«Life Cycle Emissions and Life Cycle Cost Analysis for Stationary Batteries in Different Geographies», EnIn-
nov 2018: 15th Symposium Energieinnovation, February 14–16, 2018, TU Graz, Graz, Austria.
- P. Schütz, D. Gwerder, A. Stamatiou, R. Waser, D. Sturzenegger, M. Aprire, A. Armijo, B. Arregi, P. Elguezab-
- T.S. Schmidt, M. Beuse, B. Steffen, colleagues from PSI and UNIGE, «Economic and environmental assessment of different battery technologies for different grid network applications», Discussion Forum Life-Cycle Assessment, April 16, 2018, Zurich, Switzerland.
- P. Schütz, D. Gwerder, A. Stamatiou, R. Waser, D. Sturzenegger, J. Worlitschek, M. Aprire, A. Armijo, B. Ar-
- A. Malhotra, H. Zhang, T.S. Schmidt, «The influence of selection pressures on technological evolution in com-
- M. Patel, Finanz und Wirtschaft Forum «Smart Energy 2018: Welche Energiespeicher sind rentabel? Die öko-
nomische Sicht», invited talk, Gottlieb Duttweiler Institut, July 2018, Rüschlikon, Switzerland.

• M. Berger, J. Worlitschek, «Feedback between anthropogenic factors and climate: energy consumption for space heating», 17th Annual CMAS Conference, October 10, 2018, Chapel Hill, NC, USA.


• A. Malhotra, H. Zhang, M. Beuse, T.S. Schmidt, «Windows of Opportunity in the Lithium-Ion Battery Industry – A Patent-Citation Network Analysis», 7th SCCER HaE Symposium, November 6, 2018, Rapperswil, Switzerland.

• M. Beuse, B. Steffen, T.S. Schmidt, «Competitive Dynamics of Stationary Electricity Storage», 7th SCCER HaE Symposium, November 6, 2018, Rapperswil, Switzerland.


• S.F. Schneider, E.J. Berg, C. Bauer, P. Novák, «A Techno-Economic and Environmental Assessment of Future Na-Ion Batteries», poster, 7th Symposium SCCER Heat and Electricity Storage, November 6, 2018, Rapperswil, Switzerland.


• X. Zhang, T. Terlouw, S.F. Schneider, C. Bauer, «Life Cycle Assessment of Batteries – the Environmental Perspective», poster, 7th Symposium SCCER Heat and Electricity Storage, November 6, 2018, Rapperswil, Switzerland.


• M. Berger, S. Frehner, J. Worlitschek, «HVAC design based on Swiss Climate Scenarios CH2018», 16th Swiss Geoscience Meeting, November 11, 2018, Bern, Switzerland.
Work Package «Heat – Thermal Energy Storage»


Work Package «Batteries – Advanced Batteries and Battery Materials»


• E. Marelli, C. Villevieille, S. Park, N. Hérault, C. Marino, «Co-Free P2–Na0.67Mn0.6Fe0.25Al0.15O2 as Promising Cathode Material for Sodium-Ion Batteries», ACS Applied Energy Materials, 1, 11, 5960–5967, 2018.

• C. Marino, E. Marelli, S. Park, C. Villevieille, «Impact of Water-Based Binder on the Electrochemical Performance of P2–Na0.67Mn0.6Fe0.25Co0.15O2 Electrodes in Na-Ion Batteries», Batteries, 4 (4), 66, 2018.


Work Package «Hydrogen – Production and Storage»


• PhD thesis of Cornel Fink, No 8739 (2018) EPFL, «High-pressure NMR spectroscopic and calorimetric studies on formic acid dehydrogenation and carbon dioxide hydrogenation».

• PhD thesis of Mickael Montandon-Clerc, No 8594 (2018) EPFL, «Hydrogen storage in the carbon dioxide/formic acid system, using homogeneous iron(II)-phosphine catalysts in aqueous solution».


Work Package «Synthetic Fuels – Development of Advanced Catalysts»


Appendix

Publications

- F.D. Bobbink, F. Menoud, P.J. Dyson, «Synthesis of methanol and diols from CO₂ via cyclic carbonates under metal-free», ACS Sustainable Chemistry & Engineering, 6 (9), 12119–12123, 2018.
Work Package «Assessment – Interactions of Storage Systems»

- M. Friedl, HSR: In 2018, the focus was to inform the public about our research activities, because scientific publications are expected after the construction of the HEPP demonstrator in the years 2019–2020. Many articles about project HEPP have been published by journalists and by ourselves in the following media: Aargauer Zeitung, Aqua&Gas, Bulletin.ch, die Baustellen, ee-news, Erdgas, ET Elektronik, Folio, Höfner Volksblatt, Leader Special, Linth-Zeitung, NZZ am Sonntag, Panorama/ Bildung Beratung Arbeitsmarkt, Punkt 4 Info, Rundschau Ausgabe Süd, Schweiz am Wochenende, St.Galler Tagblatt, Südostschweiz, Youtility, Zug Kultur, Zürichsee Zeitung. 2018.
- S. Schneider, C. Bauer, E. Berg, «A modeling framework to assess performance, costs and environmental impact of Li-ion and Na-ion batteries», submitted to Environmental Science and Technology, 2019.
Patents

Organized Events

7th Annual Symposium, SCCER «Heat and Electricity Storage»

The 7th Annual Symposium «SCCER Heat & Electricity Storage» was held on November 6, 2018, in Rapperswil.

Organizers
Thomas J. Schmidt, Jörg Roth, Ursula Ludgate, Astrid Busa, Sandra Moebus, Paul Gantenbein

Speakers
Dr. Kerry-Ann Adamson, Jacobs Consultancy, UK
Dr. Enrique Troncoso, Systeng Consulting, UK
Dr. Tom Kober, PSI, CH
Sandra Moebus, HSR, CH
Dr. Luiz Carlos Reichenbach de Sousa, HSR, CH
Dr. Alexandra Pâtru, PSI, CH
Prof. Dr. Gabor Laurenczy, EPFL, CH
Dr. Nordahl Autissier, GRT, CH
Giorgio Crugnola, FZ Sonick, CH
Dr. Corsin Battaglia, Empa, CH
Cornelia Jahnel, PECEM, D
Klaus Borrmann, PECEM, D
Dr. Paul Gantenbein, HSR, CH

Oral Presentations
- E. Troncoso, «Hydrogen & Local Energy Systems, a Case Study: The BIG HIT Project».
- T. Kober, «Power-to-X Technologies and Market Environment in Switzerland».
- A. Pâtru, «Design Principles of Bipolar Electrochemical Co-Electrolysis Cells for Efficient Reduction of Carbon Dioxide from Gas Phase at Low Temperature».
- G. Laurenczy, «Carbon Dioxide as Hydrogen Vector».
- N. Autissier, «HyForm-PEMFC 1 kW Demonstrator Unit – Results and Perspectives».
- G. Crugnola, «The Swiss Experience in Cell and Battery Manufacturing for EV, Grid Operation and Back-up Power».
- C. Battaglia, «Materials Innovation for Next-Generation Batteries».
- C. Jahnel, K. Borrmann, «Heat Storage to Go. We move heat to where it’s needed.»

Posters

Thermal Energy Storage
- P. Roos, A. Haselbacher, «Multi-Tank TES System Analysis».
Organized Events


Battery and Materials

- R. Dubey, K. Kravchyk, M. Kovalenko, «High Mass Loading Graphite Anodes for Li-ion Batteries».
- J. Vidal Laveda, J.E. Low, C. Battaglia, «Stabilizing NMC811 in Full Cells with High Areal Capacity».
- C. Marino, C. Bolli, E. Marelli, E. Kendrick, C. Villevieille, «Though the Electrochemical Mechanics of the O3-Na(Ni_{0.5}Mn_{0.25}Sn_{0.15}Ti_{0.15})O_{2} Phase used as Cathode Material for Na-ion Batteries».
- M. Schuster, C. Villevieille, C. Marino, «Investigation on the Suitability of Manganese Carbonophosphate Compounds as Cathodes in Aqueous Na-Ion Batteries».
- A. Fuerst, A. Haktanir, M. Stalder, «Battery Cost Reduction through Production Simulation».
- D. Reynard, C. Dennison, A. Battistel, H. Girault, «Low-Grade Heat Recovery Using All-Vanadium Redox Flow Battery».

Hydrogen Generation and Storage

- L. Lombardo, H. Yang, A. Züttel, «Ionic Liquids as Efficient Destabilizing Agents of Sodium Borohydride».
- H. Yang, L. Lombardo, A. Züttel, «Carbon Based Materials for Hydrogen Storage».
- D. Lebedevc, R. Ezhow, N. Kaeffer, M. Willinger, X. Huang, Y. Pushkar, C. Copéret, «From Nanoparticles to Single Sites – Decreasing the Noble Metal Content in Anodic Water Oxidation Catalysts».
- D. Abbott, E. Fabbri, M. Borlaf, F. Bozza, R. Schäublin, Th. Graule, T.J. Schmidt, «Operando X-Ray Absorption Investigations into the Role of Fe in the Oxygen Evolution Activity and Stability of NiFe_{x}O_{y} Nanoparticles».
- D. Aegerter, E. Fabbri, T.J. Schmidt, «The Effect of Fe in Ba_{0.5}Sr_{0.5}CoFe_{1-x}O_{3-δ} Towards the Oxygen Evolution, Reaction in Alkaline Media».

Synthetic Fuels

- J. Zhang, W. Luo, A. Züttel, «Electrochemical CO2 Reduction Toward CO and Ethanol»
- K. Zhao, L. Wang, M. Calizzi, E. Moioli, A. Züttel, «Evolution of Adsorption Species During CO2 Hydrogenation on Ru/Al2O3: Intermediates or Byproducts?»
- G. Noh, E. Lam, K. Larmier, P. Wolf, C. Copéret, «The Role of Ti Supporting Cu Nanoparticles in the Selective Hydrogenation of CO2 to Methanol».

Y. Hou, R. Erni, R. Widmer, R. Fasel, P. Broekmann, “Synthesis and Characterization of Cu@CuPd Nanowire Catalysts for the Efficient Production of Formate and CO from CO₂”.


P. Moreno-Garcia, Y. Hou, M. Rahaman, P. Broekmann, “Towards Efficient Electrochemical N₂ Reduction at Room Temperature and Pressure through Hydride Transfer Mechanism on Cu@CuPd Nanowires”.


B. Pribyl, A. Pătru, T. Binninger, T.J. Schmidt, “Efficient CO₂ Reduction from Gas Phase at low Temperatures in a Bipolar like Co-Electrolysis Cell Configuration and Comparison to Liquid Phase CO₂ Reduction”.

**Assessment of Storage Systems**


M. Berger, S. Frehner, J. Worlitschek, “Temperature-Derived Heating and Cooling Loads”.


S. F. Schneider, E. J. Berg, C. Bauer, P. Novák, “A Techno-Economic and Environmental Assessment of Future Na-Ion Batteries”.


---

**Organized Events**
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

We thank the following industrial and cooperation partners: