Posters

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Ni$_2$SnP as Negative Electrode Material for Na-ion Batteries

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Na-ion batteries are a promising battery technology which could be a reasonable alternative to Li-ion batteries. For Li-ion batteries, graphite is widely used as negative electrode material due to its very good stability upon lithiation/delithiation and its relatively high reversible specific charge (360 mAh/g). However, graphite presents a lower electrochemical activity in Na cells$^1$. Researches are focusing on looking for a new negative electrode with stable and reasonable performance. Ni$_2$SnP, synthesized by mechanochemistry, is described in the literature as a tetragonal structure and was tested as negative electrode for Li-ion batteries$^2$. In a half cell versus Li metal, Ni$_2$SnP provides a starting specific charge of 500 mAh/g but after 10 cycles, it decreases to 320 mAh/g. A conversion mechanism was suggested. Fig. 1a) shows the charge/discharge curve of Ni$_2$SnP electrode for the 1$^{\text{st}}$ and 2$^{\text{nd}}$ cycles in a sodium battery (versus Na metal). It can be noticed that the desodiation process is similar for both cycling. The 1$^{\text{st}}$ sodiation process presents a slight difference with a plateau at 0.5 V which might be related to SEI formation. The evolution of the specific charge upon cycling at C/20 rate is presented on Fig.1b). Without any further electrode and electrolyte formulation, a reversible specific charge of 150 mAh/g can be obtained and maintained for few cycles. The electrochemical mechanism of sodiation/desodiation processes in Ni$_2$SnP electrode will be also presented.

Fig.1a) Evolution of potential vs. Na upon 1$^{\text{st}}$ and 2$^{\text{nd}}$ cycle of Ni$_2$SnP electrode – b) Performance of Ni$_2$SnP electrode at C/20 rate with the electrolyte 1M NaClO$_4$ in PC.

Acknowledgment:

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References:

MSn$_2$ (M=Fe, Co) Intermetallics as Anode Materials for Na-ion Batteries

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Tin is a promising anode material for the storage of large amounts of lithium and sodium, it currently boasts one of the highest specific charges: 990 mAh/g and 846 mAh/g in lithium-ion and sodium-ion batteries upon conversion to Li$_{2.4}$Sn or Na$_{3.75}$Sn, respectively.$^1$ However, storing such large quantities of these ions is typically accompanied by large volume expansions of up to 400%, which leads to particle fracture and thus electrical isolation resulting in rapid capacity fade with cycle number. Here, we alloy the active Sn with inactive transition metals Co and Fe to form the tetragonal intermetallic MSn$_2$ (I4/mcm, Figure 1, left). Since neither Co nor Fe form alloys with Na, they are expected to be inactive in the storage of sodium; however, preliminary results show their presence influences the reaction of Sn with Na. What is the cause of this interaction? How does the electronic configuration of the inactive metal affect the reaction mechanism and cycling properties? These questions are addressed through studies of the electrochemical behavior, in situ and ex situ X-ray Powder Diffraction data (XRD) and X-ray Absorption Spectroscopy (XAS) studies (Figure 1, right). The insight gained through these studies will provide a framework from which the most effective combinations of active and inactive metals may be selected as suitable alloy hosts for the next generation of novel battery materials.

![Tetragonal Structure of the MSn$_2$ family](image)

Fig.1: Left: Tetragonal Structure of the MSn$_2$ family. Blue spheres represent M atoms, the green spheres represent the Sn atoms while the small grey spheres mark inert electron pairs on the tin atoms$^2$. Right: Galvanostatic Curves for the 1$^{st}$ sodiation and desodiation of CoSn$_2$ and FeSn$_2$.

Acknowledgment:

The Swiss National Science Foundation is thanked for financial support (Project 200021 156597). This work was performed within the Swiss Competence Center of Energy Research Heat and Storage (SCCER) framework.

References:


May 5, and May 6, 2015
1D Ionic Diffusion Direction vs the Shape and Size of Nano-LiMnPO₄

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Advanced lithium ion batteries require higher safety, lower cost, longer durability and lower toxicity to apply larger applications¹. LiMnPO₄ can be an alternative cathode material due to its stable structure, low material cost, lower toxicity, high theoretical capacity (170 mAh/g), high operating voltage (4.1 V vs. Li) and good capacity retention. However, it suffers from poor electronic and ionic conductivity⁵. Its poor ionic conductivity can be overcome by employing nano-particles in order to shorten Li-ion path lengths⁶. Enhancement in electron transport is achieved by carbon coated nanocomposite cathode material. Most high-performing LiMnPO₄ materials were so far achieved by adding a large amount of carbon (15 – 30 wt%) in order to increase the electronic conductivity⁶.⁷ Recently, we reported < 30 nm sized nano-LiMnPO₄ reached 97% of theoretical capacity with 10 wt% of carbon additive in total in the electrodes⁸. We investigated further to study the favorable direction for lithium ions in different shapes of nano-LiMnPO₄ and the desired composite structure to improve the electrochemical properties. We will show the updated results about the ionic diffusion direction vs the various shapes and sizes of nano-LiMnPO₄. The electrochemical tests and the electron diffraction patterns of different shapes of nano-LiMnPO₄ were also investigated.

<table>
<thead>
<tr>
<th>LiMnPO₄ particle</th>
<th>Li⁺ diffusion direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shape</td>
<td>Surface area (cm²/g)</td>
</tr>
<tr>
<td>![image]</td>
<td>51.38</td>
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<td>26.77</td>
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<td>![image]</td>
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Table 1 Summary of synthesized nano-LiMnPO₄ and the Li⁺ diffusion directions.

References:
Sn/C Composite Anode Materials for Lithium Ion Batteries

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Much interest has been flowing towards the trending high energy density batteries for wide applications including the most vital grid storage, electric vehicles and portable electronics. Alloy-type anodes (Si, Ge, Sn, Al, Sb, etc.) have much higher Li storage capacity than the intercalation-type graphite anode that is currently commercially used in Li-ion batteries [1]. The theoretical capacities of alloy anodes are 2-10 times higher than that of graphite and 4-20 times higher than that of the lithium titanate anode. Also, these alloy based anode materials have a moderate onset potential ranging between 0.3-0.4 V above Li/Li+, gaining safety advantages over low potential graphite anode and avoiding energy penalty over LTO anode.

Metallic tin (Sn) is one of the most promising anode materials for next-generation LIBs due to its high theoretical capacity of 991 mAhg⁻¹ or 7313 mAhcm⁻³, multiple times that of commercialized graphite anode materials (372 mAhg⁻¹ or 833 mAhcm⁻³). However, the huge volume expansion (up to 360%) consequently leading to the dramatic mechanical stress of Sn during cycling cause cracking and pulverization of the active material (refer Fig. 1). This also leads to the loss of conductivity at the electrode, resulting in quick capacity fading, which greatly hinders the practical application of Sn as anode material and thereby letting down its application in LIBs[9]. Another impactful problem is the rupture of the SEI layer due to volume change during cycling, causing the electrode surface exposed to the electrolyte. This causes excessive growth of SEI ending up with low Coulombic efficiency, ionic and electronic resistivity[10].

Figure 1: Pulverization of the active material

It is therefore essential to control the volume expansion and thereby preventing the loss of active materials. The idea of a composite electrode which could facilitate a buffer volume to survive the volume expansion will be the call of the moment. We have adopted a novel synthesis method to control the volume expansion by engineering a composite Sn/C electrode which serves as a buffer volume to the volume expansion.

Reverse micelle micro emulsion synthesis:
A reverse micelle micro emulsion technique has been developed which can synthesize Tin nanoparticles into Carbon shell with a void in between to accommodate the volume expansion[4].
We have achieved tiny Sn nanoparticles within the Silica shell in 20-30 nm range. The TEM image in Fig. 2 shows the tiny Sn nanoparticles encapsulated into SiO$_2$ shell. The SEM image in Fig. 3a shows the SEM image of the Sn nanoparticles and SiO$_2$ shell as well. The EDX spectrum (Fig. 3b) proves the existence of Sn$^0$ and SiO$_2$ shell.

Figure 2: TEM image showing yolk shell core particles of Sn nanoparticles and SiO$_2$
Conclusion:
A composite anode material is proposed and synthesized by reverse micelle micro emulsion technique. The sequential steps of self-polymerization, forming Carbon layer, removal of SiO2 shell and the electrochemical testing will be done after further quantification analysis in near future.

References:
Low Temperature Synthesized-Processed Garnet-Type Fast Li-Ion Conductor, Li$_{0.25}$Al$_{0.25}$La$_3$Zr$_2$O$_{12}$, for All Solid State Li-Ion Batteries

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Li-ion batteries (LIBs) are the most common battery type for consumer electronics. Their high energy densities, long cycle lives and variable charge-discharge rates make them the ideal choice for portable electronics and electric vehicles over other battery technologies. However, conventional liquid electrolytes used in LIBs present safety issues in terms of poor chemical stability, flammability and leakage. Solid inorganic electrolytes could solve these issues by having better chemical and thermal stabilities and at the same time could increase practical energy densities of LIBs by reducing the amount of packaging needed. In addition, ceramic electrolytes may enable the use of high capacity electrode materials (e.g. sulphur$^1$ and vanadate$^2$ based cathodes) which often pose safety and stability issues in combination with liquid electrolytes. In particular the garnet-type cubic Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) and doped variants are promising solid electrolytes with high Li-ion conductivities in the range of $\sim 10^{-4}$ S/cm at RT, chemical stability against metallic Li anode, and an enlarged thermal operation window. However, in order to obtain the high Li$^+-$conducting cubic phase, conventional solid-state and sol-gel syntheses are usually employed, requiring synthesis-processing temperatures above 1000 °C. Consequences of these high temperatures are poor control over the Li content due to Li loss and relatively large particle sizes in the micron range, which are unfavorable for further processing.

Here, we report a novel low temperature synthesis-processing route for cubic Li$_{0.25}$Al$_{0.25}$La$_3$Zr$_2$O$_{12}$, which results in smaller particle sizes and relatively lower sintering temperatures. Nano crystallites of cubic Li$_{0.25}$Al$_{0.25}$La$_3$Zr$_2$O$_{12}$ in the range of $\sim 300$ nm to $1 \mu$m (Fig. 1) are obtained at temperatures as low as 850 °C by a modified sol-gel synthesis – combustion method using mostly nitrate precursors. After simple isostatic pressing at a pressure of 1000 kN and sintering at 1075 °C of green bodies, pellets with high relative densities up to 90 % and high bulk Li-ion conductivities in the range of 0.5 x$10^{-4}$ S/cm are achieved. Similar high density and conductivity values are normally reachable using much more elaborate techniques (e.g. hot-pressing, high-energy ball milling, special protective atmospheres, etc.$^3$). As a proof-of-concept, batteries are assembled using LiCoO$_2$ as cathode and metallic Li as anode. All solid state batteries assembled with Li$_{0.25}$Al$_{0.25}$La$_3$Zr$_2$O$_{12}$ electrolyte show reversible charge and discharge at slightly elevated temperatures of 70-95 °C. The new synthesis-processing method shown here enables new pathways by using simplified methods, giving enhanced sintering activity because of the smaller particle size, and reducing Li loss due to lower processing temperatures.

![Fig. 1] Scanning electron microscopy (SEM) images of a)-b) a pellet cross-section of cubic c-Li$_{0.25}$Al$_{0.25}$La$_3$Zr$_2$O$_{12}$, and c)-d) cubic c-Li$_{0.25}$Al$_{0.25}$La$_3$Zr$_2$O$_{12}$ powder, at two different resolutions respectively.

References:


Many persons in R&D believe that the technical & economic properties of new products determine their commercial potential. The following 3 litigation cases show however the reality and the problems to solve:

A. Lithium Ion Batteries Antitrust Lawsuit

A lawsuit class action was filed 2012, at the U.S. District Court of California against GS Yuasa, NEC, Sony, Panasonic, Hitachi, Toshiba, Maxell and Sanyo having collectively controlled between 2000 and 2011 60 to 90 percent of the worldwide market for Li-Ion batteries: they fixed and artificially raised the prices of the batteries inflating the cost of portable computers - in violation of U.S. antitrust laws. Sales revenue 2011 in the worldwide Li-Ion rechargeable battery market was approximately $14 billion - In the late 1990s, two manufacturers from South Korea, LG Chem and Samsung, entered the market. Prices for Li-Ion batteries began to drop sharply, by nearly 50%. – In the process the 8 companies pled guilty and had to pay significant fines. Case Status of October 2, 2014: the Court denied defendants’ request to close the case.

B. BASF's vs. Umicore/Belgium for infringement of NMC patents

Umicore’s (Belgium) has infringed BASF’s and Argonne’s patents related to the chemical compositions of cathode active materials used in lithium-ion batteries: Ni-Mn-Co called NMC. Patent infringement, however, is just one piece of the unlawful conduct. Umicore has used to maintain its position as a primary supplier of such cathode active materials in this industry at the expense of BASF. Thus, this case is about Umicore’s willful and knowing infringement of patents as well as the anticompetitive, tortious, and deceptive conduct Umicore has used for its benefit and BASF’s detriment of a billion EURO (complaint filed on 20.02.15 at District Court of Delaware).


C. Litigation on the use of nickel-metal-hydrides in energy storage

Battelle-Geneva R&D Center[BG] filed in 1970 under contract for Daimler-Benz an international patent to protect a pioneer invention [by K.D. Beccu] for using Ni-Ti-Mn/Cr hydrides for reversible energy storage. The battery company VARTA filed an opposition claiming their previous use of Ti-Ni hydrides as catalysts. Their opposition was however dismissed by the Patent Court in Munich because of the different storage mechanism and substantial difference in hydrogen density in catalyst- and energy storage applications

In 1985 the US company Energy Conversion Devices / Ovonic Batteries[ECO-OBG] continued development of metalhydrides using rare earth metals instead of Ti-Ni. The patents filed were then opposed by the Japanese company Matsushita who finally lost the case and had to pay 35 mio US$ to ECD-OBG.

The NiMH system is currently used in lowcost, safe and high-performance storage batteries in over 7 mio Hybrid powered cars by Toyota, Honda, Ford, VW, BMW, Porsche. [Li-Ion only 0.6 mio E-cars]. Development under DOE/ARPA contract may increase the energy density to values depassing Li-Ion.
Improving Energy Storage Density of Carbon-Nanotube-based Supercapacitors by a Pseudocapacitive Coating

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An increase in clean energy demand drives the development of highly efficient devices for electrical energy storage, such as supercapacitors and new beyond-Li-ion-type batteries, creating research opportunities\textsuperscript{3}. Vertically aligned carbon nanotubes (VACNTs) have been conceived as ideal architecture for supercapacitor electrodes, and yet practical electrodes constructed out of VACNTs are often suffering from performance loss in energy density. We present in this work an enhancement in the energy density by a pseudocapacitive manganese oxide coating on the VACNT arrays. Results of the measured cell performance display that the pseudocapacitance effect increases energy density by as much as 15 times from the bare VACNT electrodes while retaining power density, hinting a supercapacitor that potentially outperforms commercial electrochemical capacitors. Further efforts towards the improvement of the supercapacitor energy density are on the way.

![Graph showing energy density vs. power density comparison between MnO₂/VACNT and VACNT supercapacitors](image)

Ragone plot of a MnO₂/VACNT supercapacitor cell (red) showing one-order-of-magnitude increased energy densities from a bare VACNT supercapacitor cell (black) yet at retained power density.

References:

\textsuperscript{1} Simon, P.; Gogotsi, Y. Nature Materials 2008, 7, 845.
\textsuperscript{2} Gogotsi, Y.; Simon, P. Science 2011, 334, 917.
\textsuperscript{3} Simon, P.; Gogotsi, Y.; Dunn, B. Science 2014, 343, 1210.
Encapsulations for Aluminum Alloys in High Temperature Energy Storage

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$^1$Laboratory for Renewable Energy Science and Engineering, École Polytechnique Fédérale de Lausanne, Switzerland

Aluminum Alloys (AA) have received a lot of attention as high temperature phase change materials (PCM) for thermal energy storage (TES), due to low sub cooling, high thermal conductivity, etc. $^1$. The encapsulating material for these alloys has received little attention with the exception of $^2$, showing that considerable degradation of the PCM in unprotected steel containers is to be expected. This is in accordance with fundamental research as shown in $^3$ and in its contained references.

![Intermetallic evolution graph]

Fig.1 Left: Evolution with time of high melting intermetallic reaction product between PCM and steel encapsulation. Right top: SEM image of intermetallic layer between encapsulation and PCM after 8 days at 700 °C. Right bottom: Boron nitride coated PCM without intermetallics after 61 days at 700 °C.

In our lab we verified that the evolution of intermetallic phases poses a problem to the application of AA in steel encapsulation for TES. We go on to show that ceramic coatings can efficiently protect the PCM against chemical degradation (see Fig. 1). Additionally, chemical and calorimetric analysis will further serve to validate our approach in this ongoing study.


$^3$Pasche, G. Interaction between liquid aluminium and solid iron. Al-rich intermetallics formation PAR. 2013, 8044.
Phase Change Material Systems for High Temperature Heat Storage

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The development of technologies for energy storage has been intensified in recent years driven by the disparity between energy availability and demand, which is expected to increase further as an increasing amount of energy is provided from renewable and intermittent sources. A large fraction of the end energy is used in heating applications, in Switzerland amounting to about 50\% of which an estimated 14\% is used in high temperature applications (temperatures > 400°C). In order to cover this, the need for continuous availability of thermal energy with renewable sources or waste heat, advanced heat storage technologies are required. Latent heat storage by means of phase change materials (PCM) has proven to be an attractive heat storage technology. Key advantages include the high energy storage density, applicability to high temperatures, and the ability to store and release heat at a constant temperature. A suitable heat storage system can consist of a porous structure of encapsulated PCM, as depicted in figure 1.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{phase_change_materials.png}
\caption{Generic latent heat storage system, (a) charging phase and (b) discharging phase.}
\end{figure}

A detailed model is developed which will support the choice of the PCM material, interlayer and encapsulation materials, the design of the structure, and the operating conditions, for a variety of up and downstream applications. This model is approached by i) implementing codes focusing on the melting/solidification, and ii) codes focusing on the coupled heat transfer (radiation, conduction, convection) and fluid flow. Eventually, these codes will be combined into a complete, transient and 3D heat storage model which will allow for an in-depth analysis of different material combinations and structures to be used for encapsulation.
Si-infiltrated SiC composites for High Temperature Applications: 
A Thermo-Mechanical Analysis

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Si-infiltrated SiC porous composites exist in different forms and are composed of cores of cellular ceramic and skin plates of ceramic matrix composites. Due to high thermal conductivity, low coefficient of thermal expansion, high elastic modulus and high strength, the final product can be a promising candidate for applications in temperatures up to 1500 K such as heat exchangers, recuperators and solar receivers.

In all these applications, high thermal loadings induce stresses in the structure, which can lead to severe damage and failure of the material. On the other hand, the structure of cellular core can be well designed to allow for a better heat exchange while preserving the integrity of the whole structure. Due to high cost of experiments, numerical models must be well developed to give a better understanding of the behavior of these architectures. The complex geometry of the cellular structure leads to huge numerical models, which in some cases is impractically time consuming. To resolve this problem, a method is developed using a combination of numerical homogenization and sub-modeling to simplify the geometry while having high resolution of results in zones of interest. The results show that the method can be used to analyze the thermally induced stresses in severe conditions in these structures. Future works will be focused on developing this model by assessing a model validation using experimental data.
High-Temperature Combined Sensible/Latent Storage for AA-CAES

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²Airlight Energy Manufacturing SA, Via Industria 10, 6710 Biasca, Switzerland

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At present, electricity storage with advanced adiabatic compressed air energy storage (AA-CAES) is considered to the only large-scale alternative to pumped hydro storage. Thermocline storage has gained increasing interest as a solution for thermal energy storage with potentially high efficiency and low costs. The present research aims at enhancing the concept using an experimental-numerical approach to study combined sensible/latent heat storage, which is based on placing a limited amount of steel-encapsulated AISI12 on top of a packed bed of rocks. The primary motivation for combining sensible and latent heat storage is to reduce the decrease in outflow temperature during discharging of sensible heat storage, which is favorable for downstream applications such as chemical reactions or thermodynamic power cycles. Air is used as heat transfer fluid and the storage may be operated at ambient pressure or at high pressure for the use in AA-CAES. At this stage, the work is focused on air at ambient pressure. An unsteady one-dimensional heat transfer model was verified using exact solutions and validated with experimental data from a labscale combined storage, see Fig. 1. Simulations are used to compare the performance of industrial-scale combined and sensible storages of different sizes. The simulations showed that the combined storage can not only reduce the drop in outflow temperature during discharging, but also reduce the total material costs for a given outflow temperature drop during discharging, see Fig. 2. The simulations further demonstrated that the combined storage achieves exergy efficiencies greater than 95% and material costs below $15/kWh, meeting the goals of the U.S. Department of Energy's Sunshot Initiative.

Fig 1 Comparison of simulated and measured PCM temperature of labscale storage ($E_{th}=42$ kWh).

Fig 2 Comparison of material costs for combined storage and sensible only storage as function of the maximum temperature drop during discharging ($E_{th}=100$ MWh).

Future work will focus partly on simulating storage units with air at high pressures. In addition, experiments will be carried out with an AA-CAES pilot plant that was constructed by Airlight Energy SA in Pollegio (CH).
CFD Modeling and Experimental Validation of a High-temperature Pilot-scale Combined Sensible/Latent Thermal Energy Storage

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Single-tank, or thermocline, thermal energy storage (TES) systems, with a packed bed of low cost filler material, represent a valuable alternative to the commonly exploited two-tank solution in nowadays conventional concentrating solar power (CSP) plants. However, an intrinsic drawback of this solution is the decrease of the heat transfer fluid (HTF) outlet temperature, towards the end of the discharge phase, leading to a detrimental effect on the power block efficiency. To avoid the HTF temperature decrease during discharging, a latent heat TES, based on phase change material (PCM), might be exploited instead. However, the high cost of the PCM, along with the relatively low efficiency for large temperature ranges\textsuperscript{1}, are strong limiting factors on the integration of a latent TES into a CSP plant. For this reason, the idea of adding a small amount of encapsulated PCM on top of the packed bed was proposed with the aim of mitigating the HTF temperature decrease during discharging limiting, at the same time, the increment of the overall TES system cost\textsuperscript{2}. To evaluate the capability of the combined sensible/latent heat storage, a 42.3 kWh\textsubscript{th}, pilot-scale storage has been built and tested under representative conditions of CSP plants, such as charging temperatures of around 600°C, which uses air as HTF. A packed bed of gravel, with average diameter of 32 mm and a total mass of 245 kg, was exploited as sensible heat storage section. Because of its melting temperature range suitable for CSP application, between 573°C and 577°C with a measured latent heat of fusion of 466 kJ/kg, the alloy AlSi\textsubscript{12} was selected as proper PCM material. It was encapsulated in steel tubes, 18 mm external diameter, positioned on top of the packed bed. The total mass of PCM was about 9 kg. Pebbles and encapsulated PCM were positioned into a 1.68 m high cylindrical stainless steel tank, 0.4 m external diameter, leading to a total height of 1.27 m and 0.09 m of the former and the latter respectively. The tank was insulated by means of Microtherm and rockwool layers. During charging, hot air is fed through the TES from top delivering its thermal energy to the PCM and rocks leaving then the system from the bottom. Conversely, during discharging, the energy stored is recovered by reversing the airflow direction with the HTF entering the TES from the bottom and leaving it from top. The proper flow direction during charging, and discharging respectively, allows to exploit buoyancy forces to create and maintain a thermocline zone which separates the hot region on top and the cold region at the bottom of the tank. The present study aims at modeling, by means of computational fluid dynamics (CFD) simulations, the thermo-fluid dynamics behavior of the pilot-scale combined sensible/latent TES. A simplified 2D axisymmetric numerical model was developed; both the packed bed of rocks and the PCM layers were modeled exploiting the porous media approach under the assumption of local thermal non-equilibrium (LTNE).\textsuperscript{3} The PCM phase transition was modeled as sensible process, i.e. non-explicit phase change tracking, with an increased material heat capacity, as the phase change occurs, accounting for its latent heat of fusion. Navier-Stokes, energy, turbulent kinetic energy and turbulent dissipation rate transport equations were numerically solved with the finite volume method (FVM) approach by means of Fluent 15.0 code from ANSYS. The results of the time-dependent CFD simulation were successfully validated with experimental data gathered from the pilot-scale prototype.

References:
Modeling and Simulation of High-Temperature TES Systems

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High temperature Thermal Energy Storage (TES) is one of the key technologies for energy conservation. Initially exploited by solar energy plants for backup and dispatch purposes, it is nowadays a technological sector generating a renewed interest, a field where future energy production, distribution and management scenarios are bringing new research challenges. TES systems are usually large-scale apparatuses and hence their experimental testing is a very expensive process. Therefore, numerical modeling and simulation are of paramount relevance to push forward R&D activities in this field.

The speech will deal with modeling and simulations of single tank TESs. These are systems in which a thermocline region exists, i.e., systems where there is a relatively thin horizontal layer separating high and low temperature regions of the heat storage media. Modeling challenges related to TES based on packed bed of solid materials with air as Heat Transfer Fluid (HTF) will be presented. Void fraction distribution, packed bed transport properties, and time dependent fluid dynamics models will be illustrated in details and their application results will be shown for some specific test cases. Furthermore, a special case of a TES exploiting a combination of sensible and latent heat storage will also be discussed.
Catalytic Chemical Discharge of an All-vanadium Redox Flow Battery to Generate Hydrogen from Renewable Energy Sources

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Recently, our laboratory has developed the concept of a dual-circuit redox flow battery in order to improve the energy density of conventional redox flow batteries (RFBs)¹. The battery is adapted with an external circuit that enables chemical discharge of the electrolytes on demand. This chemical discharge is a fast alternative to electrochemical discharge and enables the production of useful products simultaneously to the regeneration of the discharged electrolyte. On the negative side of the all-vanadium RFB the V(II) electrolyte is discharged to V(III) when passed over a Mo₂C catalytic bed: this reaction generates hydrogen from the protons present in the solution. On the positive side, if the charged redox species has a potential high enough to oxidise water, it is possible to generate oxygen, thus achieving indirect water splitting. Alternatively, the oxidation of SO₂ or H₂S may also be considered. The key advantage of this system over a conventional RFB is that it is able to store electricity beyond the standard capacity of the battery, as is often the case in a surplus of renewable energy, in the form of hydrogen. Consequently its storage capacity is increased. Moreover, it can deliver either hydrogen or electricity on demand, increasing the functionality of the system. This unique technological concept has recently been scaled to a 10 kW demonstrator system. Using a commercial all-vanadium RFB (Fig. 1) the design has been adapted to include the secondary external circuit. Some aspects of this demonstrator will be presented in this poster, including the design and synthesis of the catalyst and the design of the catalytic reactor. Discussions on the performance of the all-vanadium RFB will also be included, in terms of efficiency and flexibility of use.

Fig.1: (left) The 10kW/40kWh all-vanadium RFB used for the demonstration system. (right) A catalytic bed (horizontal tube) for the chemical discharge of the V(II) electrolyte leading to the formation of hydrogen.

References:
Inkjet Printing of Catalyst Layers for Electrochemical Energy Conversion Devices

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The fabrication and screening of efficient state-of-the-art, optimized or novel electrocatalysts and catalyst layers gains continuously in importance due to the foreseen changes in the power grid, in particular with the integration of various electrochemical energy conversion and storage systems including polymer electrode membrane fuel cells, metal air batteries and redox flow batteries. In such systems, the underlying electrochemical reactions, such as the oxygen reduction reaction or the hydrogen oxidation reaction, are located in so-called catalyst layers. Electrocatalysts represent the active sites and currently precious metals (e.g. Pt) and precious metal oxides (e.g. IrO₂ and RuO₂) are used as state-of-the-art materials. They are supported as nanoparticles on electron conducting materials (e.g. carbon black). In addition, a binder that also acts as an ion conductor complements the catalyst layer. A porous, three dimensional network is formed where the reactants meet at three phase boundaries (gaseous reactants, solid electrocatalyst and liquid electrolyte). Many efforts are made to reduce the amount or to replace precious metals and/or to increase the catalyst utilization. One promising material deposition technique that has recently demonstrated its potential is inkjet printing. It is a digital, mask-less and contact-less ink deposition technique with micrometer resolution. The process is up-scalable from the prototyping to the industrial level by increasing the number of applied nozzles within a printhead. The thickness of the printed structures can be controlled by printing several layers on top of each other. Even multilayer inkjet printing processes can be applied by depositing consequently different materials. A printable ink has to fulfill certain requirements mainly in terms of the dimensions of dispersed nanoparticles and/or aggregates (generally they have to be <400 nm in diameter), surface tension and viscosity. The jetting parameters of mostly piezoelectric driven printheads have to be optimized for the generation of stable and reproducible droplets and the ink/substrate interaction has to be considered as well. A post-processing step, normally thermal curing, transforms the deposited ink into the solid functional material.

In this contribution, LEPA introduces its inkjet printing facilities (Fig. 1a) and two approaches to prepare by multilayer inkjet printing catalyst layers for energy conversion systems based on Pt/C (Fig. 1b) and Co₃O₄/N-rGO.

Fig.1 a) Ceradrop X-Serie inkjet printer with integrated PulseForge 1300 photonic curing module from Novacentrix in LEPA. b) Inkjet printed Pt/C and Nafion based catalyst layer on a Nafion NR-212 membrane.
Selective Hydrogen Production from Formic Acid: Development of Homogeneous Iron Catalysts in Aqueous Solution

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An important challenge for the scientific community is the development of new hydrogen storage methods. Currently, hydrogen is stored in pressurized vessels that present safety hazards and are inconvenient to handle.1–3 In 2008, our group presented a novel approach for hydrogen generation from formic acid; H2 release on demand using a robust and effective ruthenium catalyst.4 Iron based catalyst were later proven to be active in propylene carbonate.5 Herein we present the results concerning the development of first row transition metal based, non-noble metal catalysts for selective aqueous phase formic acid dehydrogenation.

A new, water soluble phosphine ligand, the trisulfonated-tris[2-(diphenylphosphino)ethyl] phosphine sodium salt (PP3TS) has been synthesized. New catalysts, based on iron(II), were formed in situ with this PP3TS ligand and produce pure H2 and CO2 mixture from an aqueous FA solution, requiring no organic co-solvents or bases. Manometry, NMR and FT-IR techniques were used to follow the dehydrogenation reactions, determine kinetic parameters, and analyze the gas mixtures. These water soluble catalysts are completely selective and the gaseous products are free from CO contamination. To best of our knowledge, these represent the first examples of common transition metal based homogeneous catalysts that dehydrogenate selectively formic acid in aqueous solution.

Acknowledgement: EPFL and SCCER are thanked for financial support.

References:


Enabling Hydrogen Production via Water Splitting in Basic Electrolyte using Renewable Energy

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There is nowadays a tremendously growing interest in developing an energy vector, i.e. a fuel, that can be produced from renewable and clean sources of energy. For this purpose, water electrolysis is an attractive process as it can convert excess electrical or solar energy into the chemical products of hydrogen and oxygen. Indeed, hydrogen is considered as a promising fuel due to its high energy density, the several possible storage and transportation methods as well as the efficient energy conversion into electricity within fuel cells.

Electrochemical water splitting consists of two separate half reactions: the oxidation producing O\textsubscript{2} at the anode and the reduction generating H\textsubscript{2} at the cathode. Because the kinetically more difficult oxidation process proceeds best with catalysts in basic conditions, research is now focusing on the development of an efficient catalysts for the water reduction reaction in similar conditions.

Here, we present our investigations of hydrogen evolution catalysts for electrodes in basic conditions. The integration of these catalysts with photoelectrodes for the direct conversion of solar energy into a renewable fuel is also investigated. Two promising catalysts, Nickel-Molybdenum (NiMo) and Molybdenum Sulphide (MoS\textsubscript{2}), deposited with scalable and inexpensive techniques such as electrodeposition and sol-gel processes, are particularly scrutinized. In addition, a new method to produce 2-dimensional metal dichalcogenides nano-flakes (MoS\textsubscript{2} for example) is detailed. The different morphologies of the thin films obtained with the materials mentioned above are then related to the electrode performance for hydrogen evolution at different pH.
Hydrogen/Energy Storage in Formic Acid/Carbon Dioxide Systems: Enthalpy of Mixing for Formic Acid under Neutral and Basic Conditions

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It is now generally accepted that the current way of living is not sustainable and harms our environment in a greater extent than it can compensate.[1] Fossils fuels account for the majority of our energy needs, such as heat, electricity, and transportation.[2, 3] On this way, vast amounts of carbon dioxide are generated. The reduction of carbon dioxide with hydrogen, using renewable energy sources, to formic acid (FA) offers a simple and promising way to transform the waste CO2 gas into a valuable chemical s. The chemical industry has strong demand for formic acid and its high content of stored hydrogen (53 g/L) makes it attractive as a secondary energy vector for a future hydrogen-based society.[4-6]

When synthesizing FA from CO2 and H2, basic conditions in the reaction mixtures have an advantageous effect on the reaction rate and the yield, for kinetic and thermodynamic reasons.[7-9] Beller et al.[10, 11] developed several iron [10, 11] and ruthenium [12] catalysts, working with formic acid-amine mixtures. A drawback of these methods is the more laborious purification of produced FA due to the strong intermolecular interactions[13] or the lower exploitable hydrogen content when used directly - 2.3 wt% H2 for a typical 5(HCOOH):2(NEt3) mixture. Recently, we have produced unprecedentedly high concentrations of FA (2.2 M) with a Ru based catalyst in dimethyl sulfoxide without any additives.[14]

In presented work, we quantify the heat, which is released when mixing formic acid under the above mentioned conditions with solvents and additives. The goal is to characterize the energy, it takes to obtain pure formic acid from these reaction mixtures.

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References:

Perovskites have recently shown the potentials of relatively high electrocatalytic activity towards oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in alkaline media. Therefore they can represent potential low cost cathode materials for low temperature alkaline fuel cell and electrolyzer applications.

The basic perovskite oxide structure can be represented as ABO3, where A is the larger cation, such as a rare earth or an alkaline earth element, and B is the smaller cation, generally a transition metal. Generally, the perovskite electronic properties are considered to be determined mostly by the B-site cation. When the B-site cation is a transition metal, the major contribution to the material physical properties derives from the B-site cation d-band electrons.

In the present work we have investigated the ORR and OER activity of composite electrodes made of Ba0.5Sr0.5Co0.8Fe0.2O3- δ (BSCF) perovskite and acetylene black carbon. The processing of BSCF with carbon black has been found to modify the oxidation state of the B-site cations in the BSCF structure and also the activity towards both the ORR and the OER compared to the unprocessed catalyst.
Study of the Oxygen Evolution Mechanism and Activity of Perovskite La$_{1-x}$Sr$_x$CoO$_3$-based Electrodes in Alkaline Media by Thin Film Rotating Ring Disk Electrode Measurements

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Fuel cell and electrolyzers can represent a mid-term solution to the present need for a sustainable energy economy; they can be combined with renewable energy resources to build up a novel and sustainable energy based on power grids. One of the main drawbacks which hinders low temperature fuel cells and electrolyzers commercialization is the high costs of these devices. A considerable decrease in their cost can be achieved by developing non-noble metal electrocatalysts which are able to provide high catalytic activity towards the oxygen reduction and evolution reaction (fuel cell and electrolyzer mode, respectively). Particularly, perovskite oxides have recently shown the potentials of high electrocatalytic activity towards oxygen evolution reaction (OER) [1] and oxygen reduction reaction (ORR) [2-3] in alkaline media.

The basic perovskite oxide structure can be represented as ABO$_3$, where A is the larger cation, such as a lanthanide or an alkaline earth element, and B is the smaller cation, generally a transition metal. The ABO$_3$ structure can accommodate cation substitution in a wide range by partial substitution of either the A and the B cation with another element giving (A$_{x}$A'$_{1-x}$)(B$_{y}$B'$_{1-y}$)O$_3$ compositions. Even though the A-site ion does not really contribute to the electronic conduction, its size and valence were found to be important factors controlling the perovskite crystal structure and as a consequence also the electronic properties. A particular interesting case is La$_{1-x}$Sr$_x$CoO$_3$ at low values of x these oxides are p-type semiconductors while x>0.2 the conductivity changes in semimetallic or metallic type [4].

In the present work we have investigated the OER/ORR mechanism and activity of single and composite electrodes based on La$_{1-x}$Sr$_x$CoO$_3$ (x=0, 0.2, 0.6, 1) perovskite by thin film rotating ring disk electrode (RRDE) technique. La$_{1-x}$Sr$_x$CoO$_3$ powders were synthesized using a modified sol gel process, starting from an aqueous solution containing La, Sr and Co nitrate precursors. Citric acid and nitric acid were added to the nitrate solution as a complexing agent and oxidant additive, respectively. The solution was then heated under stirring to evaporate water until it changed into a viscous gel and finally ignited to flame, resulting in a black ash. To obtain single phase material, the La$_{1-x}$Sr$_x$CoO$_3$ powder was calcined at 1000 °C for 2 h in air. The specific surface of the oxide catalysts was determined by Brunauer-Emmett-Teller (BET) analysis. Most of the perovskite oxides show low surface area, since their synthesis requires relatively high calcination temperatures. Furthermore, they possess relative low conductivity and for this reason carbon is often added to the perovskite electrode to eliminate any possible concern about their electrical conductivity. However, carbon is known to possess a significant activity towards ORR in alkaline media reducing O$_2$ to peroxide via a two electron process [5]. Differently, in the typical oxygen evolution potential range carbon is expected to be strongly oxidized. Therefore, the influence of carbon addition to perovskite catalysts on the ORR and the OER should be systematically studied.

For the electrochemical characterization, thin films were prepared by drop-coating a cathode ink on glassy carbon disks. The cathode inks were prepared from a suspension made of La$_{1-x}$Sr$_x$CoO$_3$, Na$^+$-exchanged Nafion solution, and acetylene black (Alfa Aesar) in isopropanol. RRDE measurements were performed at room temperature in 0.1M KOH electrolyte, applying different rotation speeds and with a scan rate of 5 mV/s$^{-1}$. A new method was also applied to investigate the chemical/electrochemical activity of La$_{1-x}$Sr$_x$CoO$_3$ perovskite towards peroxide decomposition [6].

References:

Novel Iridium Pyrochlore Materials for the Anodic Oxygen Evolution Reaction in PEM Water Electrolyzers

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Nowadays energy storage becomes a significant issue due to the continuous growth of power production from intermittent renewable sources, e.g. wind and solar energy. Polymer Electrolyte Membrane (PEM) electrolyzers provide an opportunity to convert renewably generated electrical excess energy into chemical energy carriers, particularly hydrogen. While the cathodic reaction of PEM electrolyzers (hydrogen evolution reaction, HER) proceeds with fast electrochemical kinetics on Pt electrodes, the concomitant anodic process (oxygen evolution reaction, OER) faces sluggish kinetics and produces substantial yields only at high overpotentials. Moreover, due to the corrosive environment produced by high potentials, high temperature and acidic media, stability of the anode becomes another major issue of PEM electrolyzers. The pool of possible OER catalysts is therefore strongly limited to a few noble metal (mixed) oxides, particularly IrO₂ and IrₓRu₁₋ₓO₂. As a consequence, the large scale implementation of PEM electrolyzers can only be cost-effective if the amount of noble metals contained in the oxygen evolution catalysts is significantly reduced. A promising way to address this problem is the development of novel complex oxide materials containing lower amounts of noble metals. Recently, pyrochlore materials (of general formula A₂B₂O₆(O')ₓ, where A – rare earth or transition metal and B – Ir or/and Ru) were shown to be promising electrocatalysts for OER in acidic media.

The present work is focused on the synthesis and characterization of iridium pyrochlores obtained via a modified Adams fusion method: formation of oxide nanoparticles from molten sodium nitrate. Using this method iridium pyrochlores of Bi, Pb and Y were synthesized and afterwards characterized by powder X-Ray diffraction, electron microscopy, X-ray photoelectron spectroscopy, nitrogen absorption/desorption measurements and by electrochemical methods. Powder diffraction studies confirm that all materials crystallized in the pyrochlore cubic structure and microscopy studies indicate that they have a broad particle size distribution of 10 to 100 nm. The surface areas of materials were determined to be in the range of 15-30 m²/g. Electrochemical activities in OER of the investigated catalysts are comparable to high surface area IrO₂ and their electrochemical stabilities, measured with respect to repeated potential cycling (that resembles the intermittent input of renewable power sources) are remarkable.

References:
Two-step Approach for the Conversion of CO₂ into CH₃OH

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Increasing CO₂ level in the atmosphere has strong impact on climate and one strategy to address this problem involves the capture of CO₂ with subsequent sequestration in underground geological formations, which is termed as "carbon capture and sequestration" (CCS). An attractive and complimentary approach would be to use captured CO₂ as a C1 source for the synthesis of fuels such as methanol. Over the past 40 years, there has been significant progress in the development of heterogeneous catalysts for the conversion of CO₂ to CH₃OH.¹ However, these systems generally operate at high temperatures (>200 °C), which limits conversion in this entropically unfavorable reduction and performing this reaction under mild reaction conditions is a major challenge. For this purpose homogeneous catalyst may offer an attractive alternative since they tend to operate at low temperatures.

Two step conversion of CO₂ into methanol via the formation of carbonate and organic formate

Several ruthenium-based homogeneous catalysts have been evaluated in the direct reduction of CO₂ into methanol.² So far, the highest TON value for this reaction is 550, which is considerably lower than that observed with heterogeneous catalysts. Alternatively, different organic carbonates, carbamates, formates can be converted into methanol with TONs up to 5000.³ Therefore, we decided to develop catalysts for this two-step procedure to fix CO₂, at first diols to carbonates or amines to organic forms, and in a second step reduce these carbonates and formats to methanol.⁴ We have discovered an organo-catalyst that fixes CO₂ into amines at 50°C. We have also prepared a palladium-based nanoparticle catalyst which can transform organoformates under very mild condition. We believe, combining these systems will lead to a two-step procedure to generate methanol, comparable to heterogeneous catalysts with the added advantage of operating under mild reaction conditions.

References:

Ionic Liquid-Mediated Electrochemical Reduction of CO₂

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Ionic liquids (ILs) are fascinating materials with properties unlike most organic solvents. They typically possess high ionic conductivities, wide electrochemical windows, and negligible vapor pressure.¹ These features make them ideally suited for various electrochemical applications, for example, as electrolytes in dye-sensitized solar cells, batteries, and supercapacitors.²⁻⁴ In recent years, ionic liquids have also been found to be helpful in lowering the overpotential required for the electrochemical reduction of carbon dioxide.¹ Work in our research group has focused on determining the factors responsible for the beneficial effects of the ionic liquid, by thoroughly and systematically screening different ILs. Our results show that not all cation families are able to mediate the electrochemical reduction of CO₂, as some cations are inherently unstable at such reducing potentials. Among the cation families that are stable at the potentials required for CO₂ reduction, we find that the imidazolium salts perform much better than the tetraalkylammonium salts. Furthermore, we can conclude that residual water impurity in the ILs is not responsible for the observed catalytic effect.

References:
Methanol synthesis via direct hydrogenation of CO₂ is a key reaction, towards a future based on sustainability and responsible use of fossil materials. Numerous experimental and theoretical studies have been performed on Cu-based catalysts, especially Cu/ZnO/Al₂O₃ developed by ICI in 1960s. However, the structure of active sites as well as size/morphology/oxidation state of Cu particles in Cu-based catalysts remains elusive. In this study, Cu nanoparticles on several metal oxides were prepared, and the effect of Cu particle size and support materials on CO₂ hydrogenation over Cu-based catalysts was investigated.

Using metal nitrate precursors, Cu/SiO₂, Cu/ZnO, Cu/ZrO₂, Cu/CeO₂, and Cu/TiO₂ were prepared by an incipient wetness impregnation (IWI) method. In addition, 7.8% Cu/SiO₂ was also prepared by grafting of [CuO\(\text{tBu}\)]₄ on SiO₂, as described by Roussey et al. Particle size of Cu on each catalyst was estimated from N₂O titration technique. The catalytic performance for CO₂ hydrogenation was evaluated in a 9-mm I.D. tubular reactor. A mixture of 500 mg of catalyst powder and 5 g of SiC was placed in the reactor, and then reduced at 500 °C for 3 h in H₂/N₂ flow. The gaseous mixture (CO₂/H₂/N₂ = 2/6/2) was fed at a space velocity of 20 ml min⁻¹ gcat⁻¹ at 25 bars. The gas composition at the reactor outlet was analyzed with a GC equipped with a TCD and a FID. Fig. 1 (a) shows the TOFs of MeOH production over Cu/SiO₂ increases with an increase in Cu particle size, consistent with the need of large faceted nanoparticles. Fig. (b) illustrates the MeOH production rate over 10wt% Cu/MOₓ catalysts. The order of the rate was Cu/ZrO₂ > Cu/SiO₂ >> Cu/CeO₂ > Cu/ZnO > Cu/TiO₂. In addition, the yields of MeOH at 230 °C over Cu/SiO₂ and Cu/ZrO₂ were 9 and 35%, respectively. Thus, ZrO₂ is a suitable and promising support material for the title reaction.

Fig.1 (a) Cu Particle size effect on TOF of MeOH production over Cu/SiO₂ catalysts prepared by IWI and grafting method. (b) Support material effect on MeOH production rate over 10wt% Cu/MOₓ catalysts. Reaction temp: 230 °C.

References:
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Oxygen Reduction at PdPt(111) Alloy Single Crystal Electrodes in Aqueous Electrolytes

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Cyclic voltammetry (CV) was used for the characterization of (111) oriented surfaces of PdₓPtᵧ bulk alloys. PdₓPtᵧ(111) surfaces of various Pd content were prepared by inductive heating in Ar gas atmosphere leading to highly reproducible electrochemical properties. Characteristic peaks in cyclic voltammograms clearly identified Pd contribution¹³. Oxygen electroreduction reaction (ORR) was systematically studied in 0.1 M sulphuric and 0.1 M perchloric acid aqueous solutions using rotating disc electrode (RDE) and CV methods. The RDE data was analyzed using both Levich and Koutecky-Levich approaches and the reaction mechanism was discussed as a function of potential and surface composition.

References:

Energy-Efficient Co-Electrolysis Configurations for CO₂ Electrochemical Reduction

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Although the electrochemical reduction of CO₂ has been extensively studied over the past decades, with a renewed interest in the past 5 years, this topic has been tackled so far only by using a very fundamental approach, i.e., mostly by trying to understand and improve faradaic efficiencies, kinetics and selectivities toward certain products in half cell configurations and liquid based electrolytes (such as KHCO₃) (1). The main drawback of this approach is that, due to the low solubility of CO₂ in water, the maximum current which could be drawn falls in the range of 10-20 mA/cm² even under the most optimized convection conditions. In this work package from the Swiss Competence Center for Energy Research (SCCER) Heat & Storage, CO₂ is intended to be electrochemically reduced in a co-electrolysis system, i.e., a device similar to a water electrolyzer where the hydrogen evolving cathode is substituted by a CO₂ reduction one. By making the analogy with state-of-the-art water alkaline electrolyzers, such co-electrolysis system starts to be interesting from an energy efficiency point of view only if large currents (>100 mA/cm²) can be drawn from the anodic and cathodic electrochemical reactions (2). Due to the additional difficulty to prepare heavy metal impurity free pure liquid carbonate based electrolytes (below the ppm level to avoid cathodic metal plating and facilitated hydrogen evolution), the motivation is the development of a membrane-based cell using liquid electrolyte free gas diffusion electrodes for the CO₂ reduction reaction. This strategy is proven to enable operation at cell current densities > 1 A/cm² in Proton Exchange Membrane (PEM)-electrolyzer and Polymer Electrolyte Fuel Cells.

Only very few reports have already investigated the use of gas diffusion electrodes for the CO₂ reduction reaction (3, 4). In what we identified as the most promising co-electrolysis approach, unsupported gold or silver assembled in the CO₂ reduction electrode were separated from the oxygen evolution electrode through an 800 µm thick buffer layer filled with a 0.5 M KHCO₃ solution and a 50 µm thick cation exchange membrane (3, 4). These were the first experimental reports showing that CO₂ reduction currents of ≈140 mA/cm² for forming CO could be achieved at an overpotential of ≈0.5 V. Nevertheless, in this cell configuration, the CO₂ reduction electrode is in contact with a buffer layer consisting of a concentrated KHCO₃ solution, and therefore the question whether such configuration could sustain high CO₂ reduction currents over time due to contamination issues is questionable. In this contribution, we will report alternative liquid electrolyte free cell configurations for co-electrolysis operation. The most promising configurations will be characterized using a small scale electrolysis cell (1cm² active area), and the CO₂ reaction products will be analyzed by using an on line mass spectrometer (MS) coupled to the gas outlet of the electrolysis cell. Since only gaseous products can be detect by MS, unsupported Cu and Au nanoparticles which produce mostly CH₄/C₂H₄ and CO species respectively will be used as catalysts in the CO₂ reduction electrode.

References:
ECSA determination of Cu electrodes by Pb under potential deposition.

Application for CO₂ reduction

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Carbon dioxide is a major contributor to global warming and, beyond the mandatory reduction of our emissions, the possibility of recycling this greenhouse gas is becoming increasingly attractive. The electrochemical reduction of CO₂ is an interesting pathway, since a broad range of useful products can be formed such as methanol and formic acid (fuels for PEFC), methane and ethylene (reactants for synthesis or combustion process), CO and H₂ (syngas), etc. [1]. Nevertheless, on top of the high overpotential required to drive this reaction, the electrochemical reduction of CO₂ suffers from a poor yield/selectivity of valuable products [2, 3]. Copper-based electrocatalysts seem to be the most efficient to overcome these kinetic and barriers [3], but it has been shown that the size of the Cu (nano)particles envisaged for practical applications can influence the reaction selectivity [4]. In order to clarify this particle size effect, one needs to determine the electrochemically active surface area (ECSA) of the catalysts of interest that, for Cu, can be derived in-situ by lead underpotential deposition (Pb-UPD) [5]. Additionally, the selectivity of the CO₂-reduction reaction on these well-characterized materials needs to be determined with an appropriate technique.

With this motivation, we have performed Pb-UPD measurement on polycrystalline Cu and on carbon-supported Cu nanoparticles (NPs) of several particle sizes in a 3-electrode glass cell filled with 0.01 M of HClO₄ with 500 μM of Pb(ClO₄)₂ and 500 μM of KCl. In these measurements, we have used rotating ring disk electrode (RRDE) voltammetry to quantify the amount of Cl⁻ (typically ≈ 10%) co-adsorbed with Pb²⁺ and we could then estimate the ECSA of each catalyst [5]. Moreover, the characterization of the carbon-supported Cu-nanoparticles with X-ray photoelectron spectroscopy showed that NP-surface was covered with Cu-oxides. We therefore attempted to galvanostatically remove or reduce this oxide layers by partial dissolution (oxidation) or in-situ H₂-evolution, respectively, and quantified the resulting changes in the ECSA using this Pb-UPD RRDE-approach.

In summary, this contribution will introduce an RRDE-based methodology for the determination of the ECSA of Cu-based electrocatalysts that we have applied to the characterization of polycrystalline Cu and carbon-supported Cu nanoparticles of different sizes and of different oxidation states.

References:

Pilot and Demonstration Plant Power-to-Methane, HSR

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Power-to-Gas is a new technology allowing the synthesis of gas from renewable electricity. If the gas is hydrogen, the technology is also called Power-to-Hydrogen. If the hydrogen is further processed to methane, the technology is called Power-to-Methane. Methane can be injected into the existing gas grid, stored over several months and be used as a replacement for natural gas from fossil sources including mobility with existing gas engine technology.¹

In the current project a facility is built and operated which demonstrates that existing technology allows using water, air and renewable electricity to generate methane for renewable mobility. As a university of applied science we focus on the application side of Power-to-Methane systems, use technologies available from other parties and – most important – co-operate closely with industry and include it in the application of Power-to-Gas. The project focuses on the following goals:

- To demonstrate Power-to-Gas to laypersons and to host courses on the subject to people from the industry, mainly from the gas industry
- To understand the behaviour of subsystems and systems from a technical and economic point of view in order to assess the future role of power-to-gas in the Swiss energy supply.
- To gain data from the facility serving as a basis for simulation models and plant design.
- To start discussions in society, in politics and in industry on Power-to-Gas and supply the discussion with real facts.

The pilot and demonstration plant consists of components from several suppliers: Photovoltaic panels, a CO₂ capturing device from Climeworks, the methanation plant consisting of electrolyser, methanation reactors and filling station from Etogas using the same technology as used in the 6 MW plant in Werlte² and a car provided by Audi.

This project is a co-operation between the following partners:

- IET Institute for Energy Technology, HSR Hochschule für Technik Rapperswil
- Audi AG, Ingolstadt, Deutschland
- Climeworks, Zürich
- Erdgas Obersee, Rapperswil-Jona

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References:

Fig.1 Impressions from the Pilot and Demonstration Plant Power-to-Methane, HSR showing a) view onto the entire demonstration plant, b) photovoltaic panels, c) methanation reactors, d) CO$_2$-capturing device, e) filling station and f) car with gas engine.
Combined Storage of Electricity, Heat, and Cold

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A promising storage system based on the combination of a heat pump, heat engine, cold and hot storage is presented (see Figure 1). This site-independent technology can provide flexibility between power and heat while supplying electricity efficiently in the interesting power range of approximately 0.3–100 MW for several hours.

The underlining operating principle is that during periods of excess electricity generation, a heat pump is operated to charge a hot and in some cases also a cold storage. In periods of excess electricity demand, the system can be operated in reverse as a heat engine, using the stored temperature difference to generate electricity. In a thermally open variation, the storages can be used to additionally cover heating and cooling demands. This technology has been the subject of several independent academic and industrial investigations with varying system specifications (working fluid, temperature levels, storing material, etc.). Each investigator named the system differently (e.g. DESC, ETES\textsuperscript{1}, PHES, CHEST\textsuperscript{2} etc.), making the identification of relevant projects challenging.

The thermodynamic characterization of two promising variations of the storage system are presented, which are based on transcritical CO\textsubscript{2} cycles and subcritical isobutan cycles. Additionally two implementation concepts of the technology in a super-market and a factory in the food & beverages industry are introduced.

![Fig.1 Schematic of the process comprising a heat pump, a heat engine, a hot and a cold storage.](image)

References:
Life Cycle Assessment of Power-to-Gas for Integrated Energy System

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Power-to-Gas is a storage technology that enables long-term storage of fluctuating renewable energy, by producing hydrogen through water electrolysis, and reacting hydrogen with carbon dioxide to produce synthetic natural gas.

When designing a Power-to-Gas storage for an integrated energy system, there are many considerations that need to be taken into account. For example, although the processes such as electrolysis, methanation, carbon dioxide capture within a Power-to-Gas system are not new technologies, once combined with various process options, the performances of the entire systems vary. Besides process options, the scale of the system, the supply of electricity, the operation condition, will all have their impacts on the system performance. This study will focus on investigating the environmental impact of Power-to-Gas using the approach of Life Cycle Assessment (LCA) and parameterization of Life Cycle Inventory (LCI), to explore how these system parameters will affect the environmental performance. A general methodology (fig. 1) is also developed to construct scenarios for assessing storage technology, which could be applied to any other storage technologies in SCCER Heat and Electricity Storage (Hae).

The study has compared the Greenhouse Gas (GHG) emissions of Power-to-Gas with that of conventional gas production technologies for hydrogen and natural gas. In Power-to-Hydrogen, the associated GHG emissions of electricity generation for electrolysis will to a great extent determine the GHG emissions of hydrogen production, whereas in Power-to-Methane, the source of CO₂ (whether it is captured from biogenic or fossil-based emissions) will be a more important factor to consider in order to reduce the system emissions (fig. 2). The operation condition of electrolyzer has also an impact on efficiency and GHG emissions: the larger the load density of electrolyzer (operation point on polarization curve) is, the higher the GHG emissions. But this should be considered with its trade-off on capital investment. Lifetime and size of electrolyzer do have impact on GHG emissions, but are less influential than electricity supply in electrolysis and CO₂ source.
Fertigung von Lithium-Ionen Batterien

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Der Herstellungsprozess der Lithium-Ionen-Batterie beinhaltet die Fertigung der Batteriezelle, der Aufbau der Module sowie des Batteriepacks.

Abb. 1 Prozesskette für Lithium-Ionen-Batterien

Flachzelle:

Prismatische Zelle:

Rundzelle:

Um Forschungsarbeiten zum Thema der Fertigungstechnologien von Batteriezellen durchzuführen, kann auf Erfahrung aus verwandten Gebieten aufgebaut werden. Als Infrastruktur stehen die Labore für Maschinen­technik, Steuerungstechnik und Lasertechnik zur Verfügung. Das neue BFH-CSEM Energy Storage Research Center ESReC im InnoCampus Biel bündelt Fachkenntnisse und Kompetenzen aus verschiedenen Forschungsbereichen und macht Synergien nutzbar.

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Developing a Coupled Numerical Model for Underground Gas Storage

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Energy storage is an essential component of future energy systems that use large amounts of variable renewable resources.¹ Apart from pumped-storage hydropower, large scale energy storage is mainly provided by underground energy storage systems, where energy can be stored mechanically, chemically or by means of thermal energy. The focus of this work lies on the storage of synthetic natural gas in underground aquifers (chemical storage). So called wind gas or solar gas is used for mid- to long-term energy storage by transferring electric surplus energy from renewable power plants to synthetic natural gas by hydrolysis and a methanation reaction.

Underground gas storage poses a risk to humans and the environment. There is the possibility of the substances leaking to the surface or into the groundwater. Groundwater contamination can be caused by brine displacement as well. Mechanical stress can have an impact on the mechanical stability of the underground. Especially energy storage in shallow depths can influence groundwater quality and flow pattern. To assess these risks and to improve understanding of the complex and coupled processes of subsurface energy storage, efficient, consistent and adequate numerical models for multiphase flow, transport and energy processes are required.

Simulating underground gas storage requires robust models which are able to account for the specific dynamic boundary conditions and processes associated with the application on a large domain, including local features such as fault zones and a representation of the transient saline front. Within acceptable computational time this cannot be achieved by full three-dimensional multiphase multicomponent models due to limited computational resources. In contrast to that, less computational resources are required by numerous simplified mathematical models. One class of these models is based on the assumption of vertical equilibrium.² ³ ⁴ However, this assumption only holds after a certain timescale in the whole domain and such simplified models do not provide the accuracy desired. To overcome this obstacle, an adaptive model approach is chosen, that adjusts the model complexity in accordance with the required accuracy to achieve an increase in efficiency. For this purpose a multidimensional model is developed, that couples a simplified vertical equilibrium model to a full-dimensional model. This allows to adapt the model complexity locally during simulation according to the area of interest and the changing area of the domain where the vertical equilibrium assumption is valid.

The overall concept will be introduced and first results showing the benefits of the coupled model for the application of storing synthetic natural gas will be presented.

References:
SCCER Heat and Electricity Storage

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