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SCCER Networked Research – a Base for Success

The Swiss Competence Center for Energy Research (SCCER) «Heat and Electricity Storage» (HaE) is one of eight centers, which have been established in the research fields of mobility (SCCER Mobility), efficiency (SCCER FEEB+D, SCCER EIP), power supply (SCCER SoE), grids (SCCER FURIES), biomass (SCCER Biosweet), energy storage (SCCER HaE), as well as economy and environment (SCCER CREST) in light of the Swiss Government’s Energy Strategy 2050.

The declared aim of this energy strategy is the transition from nuclear power to a power supply system based on renewable sources to meet the CO₂ emission targets. An important factor is to expand and strengthen the knowledge in the energy field through the increase of personnel resources, e.g., scientists, engineers, technicians alongside with technology development. The centers are organized as virtual consortia of industrial and academic institutions (cantonal universities, universities of applied sciences and federal universities and research centers) distributed all across Switzerland with the intension to maximize the outcome by combining the strongest competencies in each area of expertise.

To maintain a long-lasting effect on the Swiss power supply system, the competence centers will receive financial support until 2016 with a perspective of a second period until 2020.

Energy storage is a key element in this venture since energy, sourced from renewables like wind and solar energy, is only available on an intermittent, stochastic basis. Storing excess energy in times of low energy demand and releasing it in times of high energy demand is not only useful from an energetic perspective, it also may create an economic value within the energy market.

With an increasing contribution of the aforementioned renewable energy sources to the electricity mix, the significance of energy storage increases. This is clearly demonstrated by countries having installed a lot of wind and photovoltaic power, e.g., Germany and Denmark. Large intermittent discrepancies between electricity production and demand are being observed with the consequence of strongly fluctuating electricity prizes, causing also challenges to the stability of the power supply system.

In order to stabilize the grid, an increase in short term electricity storage capacity (hrs) with high response time is needed within the next years. In the long run, seasonal storage becomes important to ensure constant electricity supply without conventional fossil based power generation.

Heat, aside from electricity, is one of the most required type of energy today. About 50% of the primary energy carriers are transformed to heat by modern industrialized societies – required for space heating, hot water and process heat. Thus, it becomes obvious that a sensible use of energy must not neglect the questions related to heat.

The research and development within the SCCER Heat and Electricity Storage concentrates on five different fields with the involvement of more than 20 research groups from eleven public institutions as well as from the private sector.

With this «Annual Report 2014», we would like to invite you to learn more about the different areas of research and development carried out in the SCCER Heat & Electricity Storage within its first year of operation.

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

Advanced Batteries and Battery Materials
First-Principles Crystal Structure and Property Prediction of Compounds for Electrode Applications

Scope of project

Designing new materials with specific properties implies a detailed understanding of their structure and electronic properties at atomic level. Quite often structure and exact composition of compounds are extremely difficult to determine precisely from the experiments. The prediction of the possible crystal structures at different compositions represents indeed the very basic knowledge for any further electronic structure property investigation.

Status of project and main scientific results of workgroups

By employing a first-principle methodology, which couples cluster expansion, random searching and simulated annealing algorithms with total energy calculations at Density Functional Theory level [1, 2], Li- and Na-containing compounds relevant for battery applications were studied. The electrochemical discharge/charge processes of ions (Li, Na) at the electrodes is studied as a variable composition problem of the type atom (Li, Na)-host phase space, during which the lattice of the host compounds undergoes to structural changes at different degrees. In fact, the energy-composition and the energy-volume curves, derived from total energy calculations and geometry optimization of the modelled compounds, are important for understanding how much the discharge/charge reactions can be reversible.

The predicted local minima and global minima structures, either unknown or not-yet determined experimentally, localized on the energy-composition curve of the A(Li, Na)-host phase space, are checked for the lattice stability via phonon calculations.

The host systems investigated, as potential electrode materials, are:
- elemental tin,
- tetragonal phase Sn(t),
- elemental antimony with the trigonal symmetry space group, Sb(r),
- binary phases containing iron, FeSn2, FeF3, FeS2.

A-Sn and A-Sb are the typical examples of the electrical potential as a function of the composition across the binary phase diagrams. The A-FeXn systems are examples of intercalation followed by terna-

Figure 1: The calculated XRD patterns of Na xSn, modelled via discharge of Na in Sn(t).

Figure 2: The calculated potential of lithiation (left) and sodiation (right) of Sb(r) as a function of composition (x).

List of abbreviations

\begin{itemize}
  \item F Fluorine
  \item Fe Iron
  \item Li Lithium
  \item Na Sodium
  \item S Sulfur
  \item Sb Antimony
  \item Sn Tin
  \item TM Transition Metals
\end{itemize}

Authors

Riccarda Caputo¹
Maksym V. Kovalenko¹

¹ ETHZ
Batteries

First-Principles Crystal Structure and Property Prediction of Compounds for Electrode Applications

ry phase formation and then phase decomposition.

Sn(t) and Sb(r) were investigated as anode for A-ion batteries (A stands for alkali metal element, in the following Li and Na). The theoretical specific charges are 847.7 mAhg\(^{-1}\) and 660.4 mAhg\(^{-1}\), respectively, upon full discharge leading to the formation of Na\(_{15}\)Sn\(_4\) and Li\(_3\)Sb (Na\(_3\)Sb). The first-principles crystal structure prediction can serve as a complementary and important tool for predicting possible structures and understanding the structure-composition relationships, as reported in the running joint work with PSI lab on the Na-Sn system.

In fact, and this is of general validity, the discharge/charge processes in the electrochemical cell can visit not only the thermodynamic states of the phase space of the Na-Sn system but also pass through local minima and accordingly show the formation of unknown phases. The calculated energy-composition relationship of Na\(_x\)Sn, for x in (0, 3.75), suggested that the first steps of sodiation are endothermic, for x ≤ 0.063, followed by a plateau-like region, for 1 < x < 2, and then by a step down to the final state for x = 3.75, leading to the formation of Na\(_{15}\)Sn\(_4\). In terms of the calculated potential, the discharge reaction occurs at 0.25 volts for 1 < x < 2 and 0.143 volts for x = 3.75 [3].

The structural differences of A\(_x\)Sb, for x < 3 between Li- and Na-antimonides is reflected into the discharge/charge reactions. In fact, while in the Na-Sb system there exists a global minimum energy state at x = 1, in Li-Sb the lithiation using Sb as cathode readily leads to the formation of Li\(_3\)Sb passing through the local minima state at x = 2. The calculated average potential of the discharge reaction xLi + Sb → Li\(_x\)Sb for 1 < x < 3 is in the range (0.82, 0.93) volts down to 1.01 volts at x = 3.

The calculated discharge potentials leading to the formation of the hexagonal structures Li\(_2\)Sb and Li\(_3\)Sb are very close: 1.00 V and 1.01 V, respectively [4-5]. Differently, the calculated average potential of sodiation of antimony falls in the range (0.44, 0.52) volts for 1 < x < 3 and is 0.62 volts for the formation of Na\(_3\)Sb(h) [6]. Interestingly, the energy-volume curves of the two systems, Li-Sb and Na-Sb, as a function of the composition, show that while in Li-Sb the cell volume doubles at the final point, x = 3, in Na-Sb the cell volume of Na\(_3\)Sb(h) is almost four times that of elemental Sb(r) and a larger hysteresis is found along the structure-composition curve [6].

Among the iron-based cathode materials, FeF\(_3\), the trigonal phase, was investigated for the lithiation process. Two phases have been found for Li\(_x\)FeF\(_3\), x = 0.5 and x = 1. The calculated potentials are 0.89 volts and 2.91 volts, respectively, to discharge 0.5 and 1 mole of lithium in FeF\(_3\)(t) [7]. The other two iron-based compounds, FeSn\(_2\) and FeS\(_2\), are still under study in order to investigate the phase space of the ternary systems A-FeX\(_2\), and then extend the study to other convenient transition metals (TM) forming (di)-stan- nides, sulphides, and fluorides of type A-TMX\(_2\).

References

Scope of project

The high demand for advanced energy storage systems has resulted in increased research into novel battery systems. Na-ion batteries are a promising candidate for large-scale energy storage due to the abundance and low cost of Na. As Na is also an alkali metal, the electrochemistry and basic principles of Na-ion batteries are analogous to the well-known Li-ion batteries.

Status of project and main scientific results of workgroups

Experimental

XRD measurements were performed with a PANalytical Empyrean diffractometer using Cu Ka radiation. A self-standing electrode was used in the setup composed of 70 wt% Sn, 20 wt% PVDF binder and 10 wt% Super-P carbon. The electrode was cast from an acetone suspension onto Teflon film and then dried in air. It was cycled against sodium metal at a C/30 rate in the electrolyte NaClO₄ in PC + 5% FEC; 250 μL of electrolyte were used to soak the glass fibre separator in the cell.

Results

The phase diagram of Na-Sn reports nine possible binary phases, of which one, NaSn, can be found in two different polymorphs. The in situ XRD patterns of the sodiation process are shown in Figure 1 (left). The crystalline phase of the tetragonal Sn is clearly visible at open circuit voltage (OCV). As the sodiation proceeded, new phases were formed. In the Sn-rich region, for x<1, none of the phases reported in the Inorganic Crystallographic Structure Database (ICSD), NaSn, and NaSnₓ, matched the scanned diffraction patterns (Figure 1, middle), thus an unknown phase is seen. As regimes are shifted from the tin rich to the sodium rich phases (>1 Na per Sn atom) the unknown phase disappears and is replaced by NaSn phase reached after Na1.125–Na1.25. This extra 0.25 sodium can be attributed to the solid electrolyte interphase (SEI) formation identified around 0.55 V. The NaSn phase rapidly shows amorphization as the sodiation proceeds (i.e., Na1 → Na2.5) and new peaks appear. As with the first intermediate phase formed these new peaks belong to an unknown phase. They could not be matched to the thermodynamically stable phase Na₅Sn₅ (Figure 1, right).

As sodiation progresses an interesting feature becomes visible during the second and third sodiation steps. Careful examination of the peak at 19.07° reveals an increasing intensity around x = 2, a maximum around x = 2.5, and then a decreasing intensity and shift to lower angles at x = 3, where the final phase Na₁₅Sn₄ is formed. In literature an additional phase Na₂₉.₅Sn₈ which crystallizes in an orthorhombic system has been mentioned, however we didn’t identify this phase in our experiments.

Conclusion and outlook

The Na-Sn system has been studied via in situ XRD measurements during the cycling...
Bulk Analysis of Sn-Electrodes in Sodium Ion Batteries

The material undergoes a range of phase transitions. Three known phases as well as two unknown phases have been observed. The determination of the reaction mechanism of Sn with Na is a crucial step to be able to understand and further develop this promising anode material and its derivatives.

Figure 1:
Left – In situ XRD of the first sodiation of Sn electrodes.
Middle – In situ XRD corresponding to NaSn₂ with three references from the ICSD.
Right – In situ XRD corresponding to Na₉Sn₄ with two references from the ICSD.

References
Batteries

Tin/Carbon Composite Anode Material for Lithium Ion Batteries and Polyanionic Cathode Material for Sodium Ion Batteries

Scope of project

This is a collaborative project between the group of Prof. H.-G. Park from ETHZ and Prof. K.M. Fromm from the University of Fribourg, dedicated to study the Li-air batteries.

Status of project and main scientific results of workgroups

During the first year of this SCCER, members of this work group were busy in project acquisition for 3rd party funding, which was successful for an NRP-70 project of the SNSF, which started on October 1st 2014. A PhD student has been hired at University of Fribourg as of December 1st 2015 for the synthesis of new electrolytes. Given the late start of this PhD student, no results have so far been obtained for this part of the project. However, S. Maharajan started to work on February 1st 2014 and contributed to the research interactions within WP 1.

Sn/C composite anode material for Li-ion batteries

The current commercial anode material, graphite, has a low energy density (375 mAh/g⁻¹) and safety problems due to lithium deposition [1]. Alloy anodes (Li₅Sn or Li₅Si) are found to be interesting in terms of high energy density, enhanced safety and long cycle life. The theoretical specific capacities of alloy anodes are 2–10 times higher than that of graphite and 4–20 times higher than that of lithium titanate anodes (1.5V vs. Li/Li⁺) [2]. In essence, these alloy based anodes are eligible candidates in terms of high energy density and safety. However, the main hurdle faced in commercializing these alloy anodes is the huge volume variation (up to 300 %) during lithium insertion and extraction, which leads to the rupture of the active alloy particles and poor cycling, caused by the poor electrical contact [3].

In order to overcome the poor contact in the electrode due to the pulverization following volume expansion, we apply a yolk-shell structure using a carbon shell and Sn nanoparticles as yolks. The carbon shell will prevent the aggregation of Sn and has good electronic conductivity. In addition, creating a void inside the carbon shell will accommodate the volume change of Sn nanoparticles upon Li-insertion. A reverse micelle approach is known to yield yolk-shell type metal nanoparticles inside SiO₂ shells [4] as shown in Figure 1. In analogy, we obtained Sn nanoparticles in a SiO₂ shell (Sn@SiO₂ yolk-shell, Figure 2, left). Afterwards, the yolk-shell particles were covered with an organic coating, leading to carbonization via a heat treatment to obtain the carbon-coated Sn@SiO₂ particles (Figure 2, right). The etching of the SiO₂ layer and a thermal treatment will provide the formation of Sn-encapsulated hollow carbon with void in near future.

Polyanionic cathode material for Na-ion batteries

The source of lithium may be limited to apply in the automotive market. Thus, using sodium instead of lithium for rechargeable batteries is considered as an alternative high-energy battery. Polyanion (PO₄³⁻, P₂O₇⁴⁻) based cathode materials (NaMPO₄, M = Mn, Fe, Co) for sodium ion batteries are good candidates on grounds of cycle stability, thermal stability, safety, environmental friendliness and cost [5]. NaMnPO₄ exists in both olivine and maricite phases with

List of abbreviations

Co Cobalt
Fe Iron
Li Lithium
Mn Manganese
Na Sodium
O Oxygen
P Phosphorus
Sb Antimony
Si Silicon
Sn Tin
TEM Transmission Electron Microscopy
Ti Titanium
XRD X-ray Powder Diffraction

Authors

Katharina M. Fromm¹
Nam Hee Kwon¹
Sivarajakumar Maharajan¹

¹ University of Fribourg
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Tin/Carbon Composite Anode Material for Lithium Ion Batteries and Polyanionic Cathode Material for Sodium Ion Batteries

Figure 2: TEM images of Sn@SiO₂ (left) and carbon coated on SiO₂ shell (right).

Figure 3: XRD pattern (left) and TEM image (right) of maricite NaMnPO₄.

References

the former being preferable in terms of Na ion conductivity and the low temperature formation while the latter is thermodynamically stable at higher temperatures [6]. Also the maricite phase has a blocked structural arrangement, which hinders the pathway of Na⁺ ions. Consequently, the maricite phase is electrochemically inactive. Therefore, an effective synthesis method is needed now to synthesize olivine NaMnPO₄ at the nanometer scale.

The polylol synthesis was used, a precipitation method to synthesize NaMnPO₄ nanoparticles in a high-T° boiling organic medium [7]. However, after the synthesis, the maricite phase was obtained, which is not the desirable phase for Na⁺ ion insertion/extraction. Figure 3 shows the XRD pattern and TEM image obtained after the polylol synthesis. When heated, the synthesized material retained the phase until 600°C, but new peaks appear above 900°C. The nature of this material is being investigated.

In order to obtain the desired olivine phase of NaMnPO₄, olivine-LiMnPO₄ was synthesized via the polylol method [7]. Then, lithium will be removed by electrochemical techniques. As a next step, it is planned to make electrochemical sodiation of MnPO₄ to obtain olivine NaMnPO₄.
Heat

Thermal Energy Storage
High-Temperature Sensible TES Based on a Packed Bed of Pebbles

Scope of project

The integration of high-temperature thermal energy storage (TES) systems into concentrating solar power (CSP) plants, besides being a valuable solution to economically compete against solar photovoltaics (PV), allows to make solar energy dispatchable, increasing substantially its value to the grid. According to the TES systems in operation, sensible heat is by far the most exploited solution for storing thermal energy. Packed beds of gravel, as low-cost filler material, are a valuable and reliable option to sensibly reduce the cost of the storage system. Furthermore, this solution may found a large applicability in the case the CSP plant uses air as heat transfer fluid (HTF). Being a single-tank solution, the buoyancy-driven effects of the HTF are exploited to establish and maintain a thermocline zone which separates the hot region on top and the cold region at the bottom of the tank. The thinner the thermocline, the higher the thermodynamic quality of the stored energy, i.e. higher exergy content. However, the extent of thermal stratification may vary sharply during cycles especially during start-up when the TES is charged for the first time.

Status of project and main scientific results of workgroups

Computational fluid dynamics (CFD) is a useful tool which allows, during the design phase, to analyze the thermo-fluid dynamics behaviour of the TES system focusing on the optimization of its thermal stratification capability. In the present work, an industrial-scale rock bed TES system has been analyzed by means of accurate 3D CFD simulations with the aim of evaluating the transient evolution of thermal stratification into the packed bed. A total of 30 consecutive cycles, constituted by 12 hours of charging followed by 12 hours of discharging, were simulated computing, for all of them, a stratification efficiency index based upon the second law of thermodynamics.

Industrial-scale TES system

The single-tank TES system under investigation was designed to fulfill the round-the-clock energy requirement of a reference 80 MW, CSP plant which uses air as HTF. The latter is fed through the storage at 650°C; whereas, after the power block heat exchangers (HEs), the HTF temperature is reduced down to 270°C. On the basis of the reference operating temperatures, a packed bed of natural rocks, 3–4 cm average particles diameter, was exploited as low-cost filler material. The pebbles are contained into a concrete vessel, buried into the ground, with a truncated-cone shape in order to minimize the effect of thermal ratcheting on the lateral walls.

During the charge phase, the HTF at high temperature flows downward through the packed bed delivering its thermal energy to the gravel. Conversely, during the discharge phase, the energy stored can be recovered by reversing the air-flow direction with the HTF coming from the heat exchangers of the power block. Hence, 650°C and 270°C were assumed as reference charging and discharging temperatures respectively. With the given CSP plant dimensions, and considering the case of largest available DNI (in the month of June), calculations showed that a total of 7 TES units, 25.7 m and 21.7 m the upper and the lower diameter respectively and 9.5 m packed bed height, are required to hold the whole volume of about 30,000 m³ of rocks [1]. The thermal capacity of each TES unit, defined as the total energy stored in the packed bed when charged from ambient temperature to isothermal conditions at the inlet air flow temperature of 650°C, is about 1 GWh. The air mass flow rate through each TES unit is about 89.6 kg/sec for both the charging and discharging.

With the aim of obtaining a proper velocity distribution of the HTF through the packed bed, as similar as possible to a plug flow, each TES unit was equipped with four pipes on top, and four pipes at the bottom respectively, rather than a single pipe located in the centre. Furthermore, two calm chambers were also designed on top and at the bottom of the packed bed.

CFD model

Continuity, Navier-Stokes, energy, turbulent kinetic energy and turbulent dissipation rate
transport equations were numerically solved with the finite volume method (FVM) approach [2] by means of Fluent 14.5 code from ANSYS. The left-hand side of figure 1 shows the CAD model of one of the seven units. The computational domain considered for the analysis is a quarter of the whole geometry. It was discretized with a grid of almost 1,150,000 hexahedral elements. The right-hand side of figure 1 shows the computational domain with the main boundary conditions applied to the numerical model.

Thermal energy losses by means of conduction through the ground and convection/radiation from the lid towards the external environment were accounted for. The environment temperature was assumed equal to 35 °C and 20 °C during the charge phase and the discharge phase respectively. The layers of concrete and insulating materials, constituting the containing vessel, were numerically modelled with a single material of equivalent thermo-physical properties. At the beginning of the time-dependent CFD simulation, i.e. at time t = 0 sec, the TES system unit was considered in its dead state, i.e. thermal equilibrium with its environment. The dead-state temperature was assumed to be 17 °C.

The rock-bed was treated as a continuum and hence it was modelled exploiting the porous media approach [3]. An effective thermal conductivity (ETC), based upon the Kunii & Smith’s model [4][5], was considered to account for all the non-convective heat transfer mechanisms occurring into the packed bed. The ETC was implemented into the CFD code by means of a purpose-built user defined function (UDF), i.e. a «C» routine properly written to be linked to the CFD solver. Thermal radiation heat transfer was accounted for by the ETC itself and hence none radiation model was activated for the computation. A quadratic void-fraction distribution was also implemented in order to replicate the different particles arrangement, numerically and experimentally observed [6, 7] in the axial direction of the packed bed.

Air was treated as incompressible ideal gas with temperature-dependent thermo-physical properties assigned as piecewise linear interpolations of tabulated data. Conversely, the thermal properties of the solid materials (rocks and concretes) were experimentally measured and extrapolated afterwards, to cover a wider temperature range [7]. The extrapolated values were then assigned to the relative materials as piecewise linear profiles.

Results and discussion

The CFD simulations results are presented in terms of temperature distribution at different time spans. Non-dimensional quantities were exploited to describe the results obtained; non-dimensional position and temperature of unity indicate the upper surface, and the highest temperature respectively, of the packed bed.

Figure 2 shows the result obtained in terms of temperature distribution into the packed bed as a function of the axial position. The left-hand side of figure 2 focuses on the temperature distribution at the end of some of all the charge phases analyzed; instead, the right-hand side of figure 2 depicts the end of the relative discharge phases. As clearly visible from the graphs, during the initial cycles, the TES undergoes a sharp variation of thermal stratification. This is due to the fact that, at the beginning of the CFD simulation, the TES system was assumed to be in its dead-state; the effect of having both the charg-
High-Temperature Sensible TES
Based on a Packed Bed of Pebbles

ing and discharging temperatures different from that of the initialization led to the creation of two separate thermocline zones into the packed bed.

From a graphical standpoint, figure 3 shows the temperature contours of the TES system at the end of several consecutive charge phases. An important consideration that can be drawn, looking at the result obtained, is that about 28–30 cycles are required by the system before achieving a stable thermal stratification into the packed bed. Considering that a single cycle corresponds to one day, the transient behaviour of the TES system is in the order of one month. Pre-charging the TES system, i.e. charging the storage for a certain time before the beginning of the cyclic operation, might be a valuable solution to reduce the long time required to achieve a stable condition.

**Thermocline TES – thermal stratification**

For thermocline TES, thermal stratification is among the key parameters to maximize the overall efficiency of the system: the thinner the thermocline, the higher the thermodynamic quality of the stored energy, i.e. higher exergy content. Exergy is a measure of the work potential of a given amount of energy or, in other words, the maximum amount of energy that can be extracted from the system, at the specified state, as useful work.

Thanks to the advantage of being directly applicable in conjunction with a CFD-based analysis, the stratification efficiency, given by the so-called entropy generation ratio [8], was exploited to evaluate the transient evolution of thermal stratification into the industrial-scale TES unit. The qualitative information obtainable by using this second-law based approach is the extent to which the real TES system under investigation approaches the ideal case of perfectly stratified TES, i.e. zero-thickness of the thermocline zone with the two regions into the packed bed, at high and low temperature, adiabatically separated. Stratification efficiency close to unity indicates that the real TES is operating with a sharp thermal stratification, i.e. the entropy generation is minimized, and the thermal energy is stored at the highest thermodynamics quality.

Figure 2: Non-dimensional temperature as a function of non-dimensional packed bed height at the end of some charge (left) and discharge (right) phases.

Figure 3: Temperature contours of the TES system at the end of several consecutive charge phases. Temperature values are [°C].
References

Evaluation of stratification efficiency

With the aim of characterizing the stratification efficiency of the industrial-scale TES system proposed, a UDF was developed and implemented into Fluent. Once executed, the UDF allows to perform a loop over all the computational cells of the packed bed in order to collect information such as temperature, volume and absolute position of each cell.

Based upon an arbitrary number of divisions, the packed bed is virtually divided in the axial direction into a multilayer zone of constant thickness. All the cells information are automatically stored into the proper layer according to the axial position of each cell. The temperature of each layer is then computed by means of a volume-averaging technique. The resulting array, containing the temperature and the volume of each layer, is automatically exported and post-processed.

The gathered values were exploited to compute the total amount of energy and exergy available into the packed bed along with the entropy change of the TES during the process.

Results obtained

The methodology to qualitatively evaluate the stratification efficiency was applied to the 30 consecutive cycles analyzed. The result obtained in terms of transient evolution of thermal stratification is reported in figure 4. The markers represent the average value of the stratification efficiency of all the phases analyzed. To obtain these average values, six instantaneous stratification efficiency indexes were computed for each phase corresponding to an interval of about two simulation hours between one instant of time and the following.

The highest value of stratification efficiency, of about 0.93 on average, was achieved during the first charge indicating that the thermal stratification of the TES system is comparable to the ideal case of perfectly stratified TES. The stratification efficiency sensibly decreases down to 0.58, on average, already for the consecutive discharge phase indicating an entropy generation increment given by the creation of the two thermocline zones into the packed bed. A minimum value of stratification efficiency can be observed, for both the charge and discharge phases, between the 5th–6th cycle.

The difference between the average stratification efficiency of the charge and discharge phases reduces with consecutive cycles, disappearing towards the 19th–20th cycle wherein a maximum is also achieved and the two thermocline zones merge with each other into a single one. From this point forward, the stratification efficiency slightly decreases until reaching a stable condition of about 0.65.

Conclusions

The 3D CFD simulation results of the TES system, analyzed under 30 consecutive cycles of charging and discharging, were exploited to observe the effect of the initial cycles on thermal stratification. The latter, qualitatively evaluated with a second-law based figure of merit, showed a strong variation lasting for 20–22 cycles. A stable thermal stratification into the packed bed was achieved towards the end of the 30 cycles analyzed. The long transient behaviour is the result of the two thermocline zones, observed into the packed bed for the first 19–20 cycles, due to the fact the TES was considered in its dead state at the beginning of the test. Pre-charging the TES system before the first cycle might be a valuable solution to sensibly reduce the long time required to achieve a stable thermal stratification.
Low-Temperature Latent TES with Encapsulated PCM

Scope of project

Over the last two decades, the electricity consumption of the residential sector in the European Union (EU-27) showed a remarkable 40 % increment from about 600 TWh in 1990 up to almost 843 TWh in 2010 which is, so far, the highest amount of the last century [1]. After industry, the residential sector is the second most important consumer accounting for almost 30 % of the total electricity consumption. For this reason, the efficient use of energy by domestic appliances, along with the possibility of recovering and reusing their waste heat, is becoming more and more relevant. Waste heat usually refers to the fraction of energy that is lost, in the form of heat, by industrial processes, machines, electrical and domestic equipments. Within a typical household, the potential energy savings from waste heat recovery can be up to 25 % and, since appliances do not necessarily operate sequentially, a proper thermal energy storage becomes essential to enable the recovery and reuse on-demand of the harvested energy [2]. Given the requirements of system integration into a kitchen environment, a latent thermal energy storage (TES) system, based on a packed bed of macro-encapsulated organic phase change material (PCM), was selected as most suitable and promising solution. In the present work, a computational fluid dynamics (CFD) based approach was exploited to evaluate the performance of the TES system under investigation. Furthermore, an experimental campaign was also conducted on a purpose-built full-scale TES prototype in order to obtain useful data for validating the CFD model developed.

Status of project and main scientific results of workgroups

Latent TES system

The latent TES developed is composed by an insulated cylindrical polymeric container exploited to hold the PCM capsules (3–4 mm diameter range) constituting the packed bed (left-hand side of figure 1). The PCM selected is a paraffin, manufactured and provided by Microtek laboratories, with a nominal melting temperature of 32 °C.

During charging the wasted energy produced by the household appliances is harvested and transported by the heat transfer fluid (HTF) to the TES system feeding it from top. Percolating through the packed bed, the HTF delivers its thermal energy to the capsules, causing hence the PCM to melt. Conversely, during discharging the flow direction of the HTF is reversed and the energy stored in the capsules can be recovered and reused. Air was exploited as HTF for several economical and practical reasons. For instance, air is already exploited by various appliances as waste heat source (i.e. electric ovens, microwave ovens, refrigerators); furthermore, it is particularly suitable for the packed bed based TES system proposed.

CFD model

The TES system was analyzed by means of accurate 3D time-dependent CFD simulations with the twofold aim of evaluating its thermo-fluid dynamics behaviour and developing a robust and reliable model to predict its performance under different working conditions.

Thanks to the symmetric characteristic of the TES system, only half of the whole model was assumed as computational domain. It was then discretized with a grid of almost 1,251,000 hexahedral elements. The right-hand side of figure 1 shows the computational domain considered for the CFD analysis along with the main boundary conditions applied.

List of abbreviations

- CFD: Computational Fluid Dynamics
- DSC: Differential Scanning Calorimetry
- FVM: Finite Volume Method
- HTF: Heat Transfer Fluid
- LTNE: Local Thermal Non-Equilibrium
- PCM: Phase Change Material
- TC: Thermocouple
- TES: Thermal Energy Storage

Authors

Simone Zavattoni¹
Maurizio Barbato¹
Marco Fossati¹
Antonio Gaetano¹
Jonathan Roncolato¹
John Doyle²
Nelson Garcia Polanco²
Joaquin Capablo²

¹ SUPSI
² Whirlpool R&D

Figure 1: Schematic of the TES system (left) and boundary conditions applied to the model (right).
Mass, momentum and energy conservation equations were numerically solved in transient regime with the finite volume method (FVM) approach [3] by means of Fluent 14.5 code from ANSYS. Thermal energy losses by means of convection and radiation from the external surfaces towards the environment were accounted for. The polymeric container, along with the layers of insulating material, was numerically modelled with a single material of equivalent thermo-physical properties. The packed bed was treated as a continuum and it was modelled exploiting the porous media approach [4]. Local thermal non-equilibrium (LTNE) was assumed and hence two different energy equations, for the solid and the fluid phases respectively, were solved. The so-called dual cell approach was exploited. In such an approach, a solid zone that is spatially coincident with the porous fluid zone is defined, and this solid zone only interacts with the fluid with regard to heat transfer.

As far as concerning the PCM, its phase transition was modelled as a sensible process, i.e. non-explicit phase change tracking with an increased material specific heat, as the phase change occurs, accounting for its latent heat of fusion. This so-called effective heat capacity was defined as piecewise linear profile as a function of temperature. The specific heat of the PCM in both the solid and the liquid states, along with the latent heat of fusion, were determined according to the results of the differential scanning calorimetry (DSC) analysis performed on purpose.

Because of the relatively low operating temperatures, radiative heat transfer into the computational domain was considered negligible with respect to other heat transfer mechanisms and thus none radiation model was activated for the computations.

The TES prototype was equipped with several K-type thermocouples (TCs) with the aim of continuously monitoring and recording the temperature evolution into the system. The ambient temperature, the inlet and the outlet HTF temperatures were measured along with the temperature of both the internal and external surfaces of the container to evalu-
Heat

Low-Temperature Latent TES with Encapsulated PCM

ate the heat losses. However, the majority of the TCs were positioned on layers at different heights into the packed bed: one at the centre of the layers and the others radially distributed at precise locations on a cross-like plastic framework.

The HTF mass flow rate was computed knowing both the HTF temperature and velocity. The latter was measured by means of a hot-wire anemometer probe (AP471 S3 DelthaOhm) with a resolution of 0.01 m/sec and an accuracy of ±0.3 m/sec. The measurements were taken from the bottom pipe during charging and from the upper pipe during discharging at different distances from the pipe wall in the radial direction to obtain an indicative description of the air flow velocity profile. This allowed to compute an average HTF velocity for a more accurate mass flow rate evaluation. The pressure drop through the packed bed was also measured by means of differential pressure sensors (DelthaOhm PP473 S1) with a resolution of 0.01 mbar. The measured data were collected, every 10 seconds, with a DO 2003 DeltaOhm data logger.

Among the various tests performed, a charge phase was selected as reference experimental result to validate the numerical model developed. For this reference test only a reduced fraction of capsules, approximately 16 kg or 20 cm of packed bed height, was considered with the aim of reducing the time required to fully charge the TES system. Figure 3 shows the temperature evolution into the packed bed during the reference test. The TCs were positioned on three layers as follows: 2 on the upper surface of the capsules, 9 on the middle plane at 10 cm from the upper layer, and 5 at the bottom layer in contact with the metallic grid (right-hand side of figure 3).

The evolution of the inlet temperature, along with that of the mass flow rate, is reported in figure 4. As visible from the graph, the inlet temperature of the HTF was well beyond the design value of 37 °C in order to ensure that the complete phase change of the material takes place during the test. A strong transient behaviour of both inlet temperature and mass flow rate was observed during the whole charge phase. Because of that and to accurately replicate the real experimental conditions, the time variation of these quantities was implemented into the numerical model by means of purpose-built user-defined functions.

Results and discussion

Figure 5 shows the comparison between the experimental data (red lines) and CFD simulation results (blue lines) of the central TCs on the three levels into the packed bed. The results obtained show that the numerical model reacts more slowly than the experimental prototype, probably indicating an underestimation of the heat transfer coefficient into the packed bed. Conversely, the offset between the curves of the upper central TC might be due to an uncertainty of the exact TC location during the experimental test.

The left-hand side of figure 6 shows the HTF velocity magnitude contours on the symmetry plane of the TES system. The effect of the flow distributor is well visible; the HTF in the entrance region is spread over the whole container cross-section. Only a minor fraction of mass flow rate passes through the 25 holes (1 cm diameter) in the central region of the distributor. Since the majority of the HTF flows outward from the latter, the formation of two separate toroidal eddies, above and below the flow distributor, can be observed in the upper fluid region. This effect is more clearly visible looking at the vectors plot reported in the right-hand side of figure 6.

Figure 7 shows the temperature distribution into the TES system at different time steps. As the charge phase proceeds,
the fraction of capsules above the PCM melting temperature increases. After about 1.5 hrs, half of the capsules underwent the phase change. In the second half of the test, a thermal gradient in the radial direction of the packed bed can be observed. This is due to the heat losses towards the external environment. An additional layer of insulation can be of help in further reducing the amount of thermal energy that is lost through the container walls. At the end of the test, almost all the capsules are above the melting point of the PCM and therefore, the TES system can be considered fully charged.

Conclusions

A latent TES system was analyzed by means of transient 3D CFD simulations with the aim of evaluating its thermofluid dynamics behaviour under different working conditions. The numerical model was validated with experimental data gathered from the purpose-built full-scale prototype.

Despite some differences between CFD simulation results and experimental data, given the various assumptions and simplifications introduced, the general temperature evolution of the real prototype is fairly well described by the numerical model developed.

References

Thermo-Mechanical Characterization of Cellular Ceramics in High-Temperature Environments

Scope of project

Cellular ceramics are attractive materials for high temperature applications such as thermal energy storage systems, thermal protection systems, porous burners, reformers, and volumetric solar radiation absorbers [1–3]. These material structures are able to withstand oxidative environments at high temperatures and are particularly resistant to thermal shock. This work presents our recent studies on thermal and mechanical behavior of Si-SiC porous ceramics including both numerical and experimental approaches.

Status of project and main scientific results of workgroups

Mechanical and thermal simulations

Numerical simulations showed the influence of cell morphology on thermal conductivity and mechanical properties of reticulated ceramic foams. We used tetrakaidecahedron cells to approximate the real foam structures. Effective thermal conductivity, effective elastic modulus and stress concentration factor were calculated using a parametric study considering foams with different porosities, cell inclination angle and ligament tapering. Figure 1 shows the effect of one of these parameters (cell inclination angle) on effective elastic modulus and effective thermal conductivity.

Mechanical testing

Si-SiC open-celled foams were produced by EngiCer, Switzerland. A Replica technique followed by Si infiltration was used. In the case of lattice structures the polymeric template was designed using a parametric MATLAB code and then manufactured using a 3D printer. The final product was a macro-porous reticulated ceramic, microscopically made of reaction bonded β-SiC, α-SiC powders, Si, and a low amount of residual carbon.

Flexural tests were conducted on both random and lattice structures in order to better understand their mechanical behavior. Acoustical emission (AE) and electrical resistance (ER) were recorded during the tests to gain more information on the fracture of individual struts in the samples, exemplarily shown in Figure 2 for a random foam of size 15 × 25 × 170 mm. Data were then processed using Weibull statistics. AE and ER monitoring techniques show to be practical means to detect the crack initiation in these foams. An increased amount of Si in the material resulted in higher strength, favouring Si-SiC foams, especially if passive oxidation conditions are met and therefore excess silicon oxidation is mitigated at high temperatures.

Thermal conductivity

Effective thermal conductivity of lattices and foams were measured using a custom-made experimental set-up (Figure 3, left). Cubic speci-
Heat

Thermo-Mechanical Characterization of Cellular Ceramics in High-Temperature Environments

Figure 2:
ER (upper) and AE (lower) measurements and corresponding measured forces.

Figure 3:
Left: Test set-up to measure effective thermal conductivity in lattices and foams.
Right: Thermal conductivity of foam samples after oxidation in 1600°C in air.

References


Heat men were placed between two plates held at constant temperatures. The thermal conductivity was measured after the system reached steady state. The thermal conductivity of a tetrakaidecahedron lattice sample (cubic with 4 cells in each edge) after oxidation in 1600 °C is displayed in figure 3 (right).

Conclusion

Si-SiC porous ceramics are special materials with unique properties that find applications in very high temperatures (above 1000 °C).

Direct modeling of foams can be a very accurate method to predict the properties of these materials in different applications. However due to the complex geometry of foams, a direct modeling is a very expensive and impractical approach. New methods must be developed to allow for coupled thermo-mechanical characterization.
High-Temperature Combined Sensible/Latent-Heat Thermal Storage

Scope of project

Our primary interest in high-temperature thermal energy storage (TES) stems from its use in advanced adiabatic compressed air energy storage (AA-CAES). In AA-CAES, electricity is used during periods of low demand to power an electric motor that drives a compressor. The thermal energy contained in the compressed air is stored, and the cooled air is stored in a sealed reservoir. To generate electricity during periods of high demand, the air is released from the reservoir, absorbs heat from the storage, and is expanded through a turbine that drives a generator. With a well-designed TES, the efficiency of an AA-CAES plant is projected to reach about 75%.

AA-CAES is of interest for two main reasons. First, it is at present the only alternative to pumped hydro energy storage (PHES) that can be competitive in terms of capacity and efficiency [1]. CAES is unique in that it is the only alternative to PHES that has been proven in practice at utility scale with the power plants in Huntorf, Germany and McIntosh, USA. The second reason why AA-CAES is of interest is cost. AA-CAES plants are estimated to be cheaper to construct and operate than PHES plants [2]. Efficient heat storage is the key enabling technology for AA-CAES and therefore the central focus of this project.

Status of project and main scientific results of workgroups

Sensible-heat TES units are often based on thermal oils or molten salts. Their disadvantages make them unattractive for AA-CAES.

Thermal oils are not only flammable and toxic, but also unstable above temperatures of about 400°C, far below the target compressed air temperature of about 550–600°C. The high freezing points of molten salts mean that a heating system must be used as a safeguard, incurring an energy penalty and complicating the power plant.

A further disadvantage common to thermal oils and molten salts is that their use in an AA-CAES plant requires heat exchangers, thereby reducing the overall efficiency and complicating the plant design.

To avoid these disadvantages, we use a packed bed of rocks as the sensible storage medium and air as the heat transfer fluid (HTF) [3]. Rocks are an abundant and economical stor-

The primary disadvantage of any sensible-heat TES is that the outflow temperature of the HTF decreases during discharge. This negatively impacts the turbine in an AA-CAES plant because it is not continuously operating at its design point. One possibility of avoiding the temperature decrease is to add a limited amount of phase change material (PCM) to the sensible-heat storage, resulting in combined sensible/latent-heat storage.

Preliminary experimental results with AlSi12 as the PCM, encapsulated in stainless steel tubes and placed on top of the packed bed of rocks, indicated that the combined storage could indeed stabilize the outflow temperature of the HTF [4]. More importantly, the preliminary experiments showed that as little as a few volume percent of PCM was sufficient to stabilize the outflow temperature. This result is significant because AlSi12 is about 1200 times more expensive per unit mass than the rocks.

Over the first year of this research project, the primary focus has been on additional measurements with an improved lab-scale TES, more accurate simulations using a quasi-one-dimensional model, and a detailed comparison of the combined sensible/latent-heat and sensible-heat-only TES.

A comparison of measured and simulated temperatures at various axial locations in the combined sensible/latent-heat lab-scale TES is shown in Figure 1 over three charge-discharge cycles. Given the simplicity of the quasi-one-dimensional representation, the agreement is good. In the right subfigure, the empty circles indicate the outflow temperature of the air, which can be seen to be nearly constant during the solidification of the PCM.

List of abbreviations

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<tr>
<td>AA-CAES</td>
<td>Advanced Adiabatic Compressed Air Energy Storage</td>
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<tr>
<td>HTF</td>
<td>Heat Transfer Fluid</td>
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<tr>
<td>PCM</td>
<td>Phase Change Material</td>
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Authors

L. Geissbühler¹
M. Kolman¹
A. Haselbacher¹
A. Steinfeld¹
G. Zanganeh²

¹ ETHZ
² Airlight Energy SA
In Figure 2 the combined and sensible-only concepts are compared for a large-scale TES unit with a diameter of approximately 10 m and a minimum height of 4 m using simulations. The comparison is based on the maximum outflow temperature drop during discharging. The results in the left subfigure indicate that the exergy efficiency after 20 charge/discharge cycles (when quasi-steady cycling behavior is achieved) for both concepts is greater than 95%, which is the target of the U.S. Department of Energy’s SunShot Initiative. Furthermore, the right subfigure shows that the combined storage has lower material costs per unit storage capacity for a given outflow temperature drop despite the much higher material costs per unit mass of the PCM compared to that of the rocks. This is because only a small amount of PCM is required to stabilize the outflow temperature and because the sensible-only storage must be increased substantially to reduce the outflow temperature drop. The costs per unit capacity of the combined storage are found to be lower than the U.S. Department of Energy’s SunShot Initiative’s target of 15 $/kWh.

Plans for future work include the evaluation of alternative PCMs and encapsulations, comparison of our results with two- and three-dimensional simulations, and experiments with a large-scale pressurized combined and sensible TES.

References
Phase Change Material Systems for High Temperature Heat Storage

Scope of project

The development of technologies for energy storage has been intensified in recent years driven by the disparity between energy availability and demand, 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 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.

Status of project and main scientific results of workgroups

Heat storage system

A suitable heat storage system can consist of a porous structure of encapsulated PCMs, as depicted in figure 1. During charging a heat transfer fluid (HTF) at high temperatures (above the melting temperature of the PCM) flows through the porous structure and transfers its thermal energy to the PCM by convective, conductive, and radiative heat transfer. During discharging, the HTF is below the melting temperature of the PCM and heat is transferred back. The HTF is heated up to the melting temperature of the PCM, thus guaranteeing a constant exit temperature of the HTF.

System modelling

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. The latent heat storage material system modelled is composed of a metallic PCM and a metal-ceramic PCM encapsulation. Using a metallic PCM with high material bulk conductivity compared to materials commonly used as PCMs, such as salts, automatically alleviates challenges connected to inefficient charging and discharging. The multi-component encapsulation allows for robustness via the chemically inert and thermally stable ceramic layer while ensuring mechanical stability and enhanced heat transfer by the metallic layer. This model is approached by

- implementing simpler 1D codes focusing on the melting/solidification, and
- more complex 3D 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.

1D numerical model focusing on melting/solidification

The 1D numerical model focusing on the melting/solidification is based on the solution of the Stefan problem [1] for materials with different specific heats, given latent heat and density. Time dependent boundary conditions of Dirichlet or Von Neumann type can be imposed.

Figure 2 illustrates results obtained for the one-dimensional setup where SiC was used as encapsulating material and copper as PCM. Figure 2 (a) illustrates the discharging phase modelled by removing a constant heat rate of 50 kW for 83 minutes, and the resulting inward movement of the solidification front and decrease in temperature. Figure 2 (b) illustrates the charging, modelled by addition of the same heat rate for the same amount of time. The melting starts from the outside with the melting front moving inwards. We observed the simultaneous ap-
Heat

Phase Change Material Systems for High Temperature Heat Storage

The appearance of two melting/solidification fronts, pointing to the need of a detailed understanding of the coupled fluid flow and heat transfer for an optimal PCM material usage and heat transfer.

The numerical method used is based on liquid mass fraction and works well for the one-dimensional cases. The generalization of the model into two and three dimensions adds the challenge of determining the orientation of the melting fronts. This is currently being implemented for a 2D unsteady case using the volume of fluid method to simulate the evolution of the free boundaries [2]. This algorithm will be included in the aforementioned code applicable to 3D unsteady cases and unstructured meshes.

3D model focusing on coupled heat transfer and fluid flow

The 3D model for coupled heat transfer and fluid flow focuses on investigating the effects of coupled conductive, radiative, and convective heat transfer in combination with phase change by means of numerical simulations. The numerical code developed is capable of performing parallelized full 3D unsteady simulations on unstructured grids obtained from an in-house [3] and other commercial mesh generators. An efficient Monte Carlo (MC) ray tracing algorithm is implemented to simulate the radiative heat exchange and coupling algorithms are investigated. The ray tracing algorithm is based on an algorithm previously used for particle tracing [4]. A fully path length based approach is chosen to obtain optimal results. Reflection and refraction at phase boundaries is accounted for by splitting incoming rays into two rays with corresponding intensities.

Exemplary results are depicted in figure 3 for a simplified geometry consisting of a solid phase in a non-absorbing, stagnant void phase. The distribution of the normalised absorbed radiation internally emitted from the cell highlighted is shown. For the solid phase, properties of a ceramic material were used and for the void phase those of air. The coupling of the radiation with the conduction is achieved by iteration.

The developed code will allow to investigate different geometries and materials, and to assess which material combinations and which kind of heat exchanger setup are high performing candidates for several specific applications.

Additionally, the code in combination with advanced volume averaging theory [5] will be used to determine effective transport properties for the coupled problem, allowing for their subsequent use in continuum models of the heat storage process. Particularly, we focus on the effect of the coupled heat transfer modes, which are commonly assessed separately, but expected to be inaccurate when coupling effects are strong. Leroy et al. [6] recently derived the volume averaged equations for the case of coupled radiative-conductive heat transfer. Understanding the coupling will contribute to the process of evaluating macroporous media as potential structures to be used as heat exchanger in the context of high temperature heat storage.

References

Aqueous Sodium Hydroxide Seasonal Thermal Energy Storage: Reaction Zone Design and Optimization

Scope of project

In a previous project at Empa (2002 to 2010) experience was gained in the handling/treatment of sodium lye and in the corrosion behaviour of sodium lye containing components and tanks. The horizontal plate (dish) heat and mass transfer components – applied in this project – did not show the expected effect of heat release in the absorption process step. This and the assumption of some available data as well as the ambitious COMTES (COMpact Thermal Energy Storage) proposal led to the identification of the concept of falling film absorption and desorption as a promising technology to be applied in the storage development.

With the concept of separating the power (the reaction zone – absorption/desorption and evaporation/condensation) and the capacity (storage of sorbent and sorbent in individual tanks) a power and capacity scaling can be done separately. The merger of the seasonally shifted process steps absorption (winter) and desorption (summer) in one falling film unit and the process steps evaporation (winter) and condensation (summer) in a second falling film unit is reducing the volume of the system and thus leads to a high volumetric energy density. Both, heat and mass transfer, are directly correlating with the area [1]. We also identified this concept because of the application of the technology in thermally driven absorption cooling machines.

Status of project and main scientific results of workgroups

Modelling of the heat and mass exchangers

For the tube bundles constituting the reaction zone of the thermal storage system, new heat and mass exchanger models have been set up [2]. They could successfully be used for design purposes and will be validated with experimental work. The modelling of the heat and mass exchanger tries to be representative for the reality of the system in regard of the operation set points. In the simulation, the coupled heat, mass and momentum equations are solved in the steady state conditions.

In order to reduce the volume of the facility, the falling film heat-exchanger and heat/mass-exchangers have to fulfill a dual function: absorber/desorber (A/D) and evaporator/condenser (E/C). The present model considers only one vertical tube column and the scaling of the power is done linearly (fluid distribution inside and outside of the tubes in parallel). For each tube (or tube row/column), the temperature is calculated inside and outside of the tube, and on the tube wall with the same indexes as shown in Figure 1.

Besides sizing the two combined units (tube bundle ge-
Aqueous Sodium Hydroxide Seasonal Thermal Energy Storage: Reaction Zone Design and Optimization

The mass flow rate of fluid spreading on the tubes is envisaged fairly lower for thermochemical seasonal storage applications than encountered in usual application fields of this kind of heat and mass exchangers. In fact, the main goal here is to avoid fluid recirculation in the A/D unit so that the target concentration is directly reached at the reaction zone. Furthermore, the A/D falling film tube bundle has to perform well in a large range of mass flow rate and fluid viscosities i.e. in a large sodium hydroxide concentration range. For these reasons, investigations were carried out concerning tube bundle surface wetting and fluid distribution, focused on reaching a high wetted surface (sodium lye covering the heat transfer surfaces) [3].

Following this design and sizing phase, a prototype is being built. It’s commissioning will lead to a validation of the heat and mass exchanger modelling and/or develop new correlations especially suited for calculating the heat transfer coefficient on horizontal smooth tube bundles using low mass flow rates of caustic soda as working fluid under reduced pressure.

Experimental results obtained on small scale experiments

The tube surface wetting was measured with water, a substitution fluid and sodium lye in order to assess the manifold performances under various mass flow rates and lye concentrations (experimental setup see Figure 3). Once the basic design of the tube bundle and manifold is set, the surface wetting is also a function of the materials in contact (chemical interaction, corrosion) and surface roughness (texturing). Therefore, a contact angle measurement campaign was started to compare the wetting potential of the substitution fluid (used for the preliminary experiment) to those of sodium hydroxide. During this campaign, the influence of the surface roughness of the 316L stainless steel used for the tubes (choice linked with corrosion issues) was highlighted. In this relation we also observed that a initial wetting of the tubes with sodium lye leads to a higher wetting in the following (process) cycles. So, a high enough «plug flow» at the beginning of a cycle followed by a lower flow rate can improve the process on the absorber/sesorber side.

Outlook

This work will go on and has to be linked with the surface wetting measurements on tube bundles as well as heat and mass transfer enhancement. In the future several options will be tested. These are encompassing further work on the surface structure and materials like coatings and surfactants.
Sustainable Electrocatalysts for Hydrogen Production Using Renewable Energy

Scope of project

One challenge in the production of hydrogen from renewable energy using water electrolysis at low current density (i.e. at ca. 10 mA cm\(^{-2}\)) for photoelectocatalytic applications is the identification of inexpensive and scalable catalyst materials to reduce the overpotential required to drive the water oxidation and reduction reactions. While Platinum is traditionally used for the water reduction half-reaction, it is not scalable to the terawatt range necessary. Abundant transition metal dichalcogenides (TMDs), MoX\(_2\) or WX\(_2\) (X = S or Se), have been identified as promising replacements for Pt in this application [1, 2]. However, the further development of high performance energy conversion devices using these materials, and their ultimate practical application, is hindered by the lack of a controllable method to fabricate large-area and continuous thin films with controllable 2D layer orientation and suitable contact to the electrode substrate. While physical or chemical vapor deposition techniques can offer good control over thin-film preparation [3, 4], these methods require high temperatures and vacuum, which are less suitable for the economical production of large-area energy conversion devices. Solution-based processing methods, in contrast, offer a viable route. Indeed, the chemical exfoliation of TMDs (using lithium intercalation) can afford stable dispersions of 2D flakes suitable for controllable film formation [5]. However, the concurrent change from the 2H-phase to the 1T-phase during chemical exfoliation is undesirable for many applications [6, 7]. Alternatively solvent-assisted exfoliation [8, 9, 10] can yield 2D flakes, though, due to the defect-free flake surfaces produced, obtaining stable dispersions at high concentration and processing them into uniform thin films without layer restacking remain significant challenges.

This year we have achieved advances in the exfoliation and solution processing of 2D MoS\(_2\) that were subsequently leveraged to prepare and electronically probe homogeneous multi-flake thin-film devices [11]. We first found that a polymer formed when using 1,2-dichlorobenzene (DCB) as a solvent is produced from the decomposition of the solvent during the sonication-assisted solvent exfoliation of MoS\(_2\). To examine the role of the SP on the exfoliation we added pre-synthesized SP to NMP, however no increase in MoS\(_2\) concentration after sonication was observed. In addition, when 1% ethanol was added to the DCB to inhibit SP formation [12], a similar concentration to that of the NMP exfoliation was observed. These observations clearly indicate that sonopolymer formation itself during exfoliation is an essential process for high yield of exfoliated MoS\(_2\). Indeed, stable dispersions up to 0.5 mg ml\(^{-1}\) of few-layer MoS\(_2\) flakes in the 2H phase were obtained after only 6 h of low-power sonication. After removing the sonopolymer using a washing procedure, alkyl-trichlorosilane surfactants were used to prevent the restacking of 2D MoS\(_2\) layers and create stable dispersions with concentrations as high as 85 mg ml\(^{-1}\).

To enable the use of these solvent-dispersed 2D flakes of TMDs the development of deposition methods that can offer precise control over film thickness and morphology is a remaining challenge. Generally in solution-based nanoparticle thin-film formation, precipitation and aggregation lead to poor uniformity and inadequate contact with the substrate. While partial control over these aspects can be achieved using appropriate surfactants or nanoparticle surface ligands, conventional solution based coating techniques (drop coating, spin coating or dip coating) still typically give rise to agglomerated structures after solvent evaporation, especially for 2D materials [13].

As such, much work has focused on applying the 2D template of a fluid/fluid interface for the assembly of nanomaterials, followed by transfer to a solid substrate to achieve thin-film formation in a controlled manner. The self-assembly of nanoparticles at a liquid/air interface (the so-called Langmuir-Blodgett technique) is the prototypical example of this approach [14, 15], and employing a liquid/liquid interface is a promising extension suitable for large-aspect ratio 2D materials [13]. Typically

Status of project and main scientific results of workgroups

List of abbreviations

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<tr>
<td>DCB</td>
<td>1,2-Dichlorobenzene</td>
</tr>
<tr>
<td>EG</td>
<td>Ethylene Glycol</td>
</tr>
<tr>
<td>LSV</td>
<td>Linear Scanning Voltammetry</td>
</tr>
<tr>
<td>NMP</td>
<td>N-Methylpyrrolidone</td>
</tr>
<tr>
<td>SP</td>
<td>Sodium Palmitate</td>
</tr>
<tr>
<td>SCSA</td>
<td>Space-Confined Self-Assembled</td>
</tr>
<tr>
<td>TMD</td>
<td>Transition Metal Dichalcogenide</td>
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Author

Kevin Sivula¹

¹ EPFL
in liquid/liquid self-assembly techniques, nanoparticles dispersed in a hydrophilic phase are driven to a hydrophilic/hydrophobic interface using mechanical agitation or an inducing agent [16, 17]. For example in seminal work by Vanmaekelbergh and coworkers, ethanol was used as an inducer for the self-assembly of gold nanoparticles at a water-heptane interface [18].

Recently, Jia et al. presented a similar approach with 2D sulphonated graphene by first dispersing the particles in the inducing solvent (ethanol) and injecting them into the water layer [19]. However, solvent-exfoliated semiconducting TMD flake dispersions show poor stability in most solvents.

Indeed, our attempts to apply traditional liquid/liquid self-assembly techniques were unsuccessful even with alkyl-trichlorosilane functionalized TMDs, as we observed aggregation rather than homogeneous film formation. Therefore, to enable the self-assembly of 2D TMDs we developed an approach to spatially confine the particles at the interface of two immiscible non-solvents for the TMD flakes, i.e. ethylene glycol (EG) and hexane. Our space-confined self-assembled (SCSA) thin film deposition method proceeds as follows. First, the WSe₂ dispersion is injected into the hexane layer near the EG/hexane interface. As the hexylamine rapidly dilutes into the hexane layer the flakes become confined by the two non-solvents and quickly align with the 2D interface. Increasing the loading of flakes leads to in-plane self-compression and generates a compact 2D self-assembly of the TMD. Next, the hexane layer is removed from the top leaving the self-assembled thin-film floating on the surface of the EG. The EG can then be removed from the bottom (through a fritted glass) affording the deposition of the SCSA WSe₂ film on a chosen substrate (e.g. conductive F:SnO₂ coated glass). Finally, the film is dried at 150 °C to remove any residual EG and improve film adhesion. Thin film electrodes, prepared with MoS₂ (ca. 20 nm) on F:SnO₂ coated PET plastic, revealed an overpotential of ca. 0.4 V for 10 mA cm⁻² water reduction current density. However, subsequent scanning of the electrode afforded a significant reduction of the overpotential to only 0.2 V for 10 mA cm⁻². While this initial result is promising, a further understanding of the electrochemical performance of these electrodes is needed to further reduce the overpotential.

Figure 1 includes the study of the surface (catalytic) sites on the surface of the TMD catalysts by electrochemical impedance spectroscopy and the optimization of the electrode fabrication procedure. Overall, the ability to make MoS₂ thin films enabled by our material processing techniques can be a valuable tool to aid the understanding and improvement of charge transport and transfer in these materials for application in other electrochemical and optoelectronic devices. Thus, extension of our methods to other TMDs and additional devices is also under development.
Demonstration of a Redox Flow Battery to Generate Hydrogen from Surplus Renewable Energy

Scope of project

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

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

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

Status of project and main scientific results of workgroups

Once the proof-of-concept system was established in the laboratory, a larger system aiming at the demonstration of the feasibility of the process of chemical discharge for production of hydrogen in real conditions was planned, financed, designed and built.

This demonstration system was installed on the site of the the water treatment facility (STEP), in Martigny. This project has been conducted in collaboration with Sinergy, the utility company of Martigny, and CREM, a research center on energy conversion also based in Martigny. The project was also funded by the Federal Office of Energy, Switzerland, under the energy conversion expertise programme, and the Energy Institute of the Canton of Valais.

Figure 1: Concept of the dual-circuit RFB. Hydrogen is generated by the chemical discharge of the negative electrolyte.

Authors

Amstutz Véronique¹
Heron Vrubel¹
Pekka Peljo¹
Kathryn E. Toghill¹
Hubert H. Girault¹

¹ EPFL
Demonstration of a Redox Flow Battery to Generate Hydrogen from Surplus Renewable Energy

Office of Energy and the district of Martigny and was planned to last for two years, starting from January 2014. Its specific goals were primarily to define the potential of the dual-circuit RFB for larger scale applications and to establish its feasibility, but also to provide some time for a proper design and scaling-up of its catalyst and catalytic beds.

In a first step, a commercially available 10 kW/40 kWh all-vanadium RFB was bought and installed (Figure 2), which was in a second step fully characterised in order to understand in details its modes of operation. The design of the catalytic bed lead to a horizontal, segmented configuration (horizontal tubes of Figure 3) of the reactor in order to facilitate a maximum use of the catalyst, but, more importantly, to favour convection of hydrogen bubbles from the liquid phase to the gas.

The design of the catalyst was also an essential aspect of the scale-up of the dual-circuit RFB. Indeed, the commercial Mo2C powder used in the bench-scale system could not be employed as it was leading to a strong resistance to the electrolyte flow through the catalytic bed, but also to trapped H2 bubbles in the catalytic bed itself. We developed therefore a catalyst consisting of Mo2C nanoparticles deposited on a ceramic bead support. These catalytic beads and this catalytic bed were successfully tested for the chemical discharge of the negative electrolyte of the RFB. However, some optimization will still be required to have a long-term stable catalytic bed.

In the framework of the demonstration project in Martigny, an open-day was organized on 12th November 2014. The same day, an official opening ceremony for the site and the project was celebrated with about 60 participants. A previous less official opening ceremony, taking place on 26th May, gathered about 20 participants for a thorough visit of the site and a dinner.

In terms of public outreach, the project was featured on Canal 9 news on 26th May. On 12th November the project was included in the news on RTS and Canal 9, and an article about the project appeared in the newspaper 24Heures. The project was also featured on the EPFL Mediacom website, and in a Youtube video produced by Mediacom at EPFL.

References
Solvation Studies of Formic Acid in Water and in Organic Solvents for Mechanistic Investigations of Formic Acid Formation and Decomposition

Scope of project

At present, our civilisation depends on fossil fuels as primary energy source. They account for the majority of our energy needs like heat, electricity, and transportation. The massive and irresponsible use of fossil fuels has its price: The emission of vast quantities of carbon dioxide into the earth’s atmosphere. There it acts, undoubtedly, as a greenhouse gas and CO₂ is primarily responsible for the profound changes in the world’s climate. One promising way to decrease the release of carbon dioxide into the atmosphere is to capture it directly at the sources [1]. Thereafter, it can be utilised as primary carbon source for the synthesis of fuels and feedstock chemicals by reducing it with hydrogen, derived from alternative energies. In this respect, the direct hydrogenation of carbon dioxide into formic acid (FA) is a simple and practical technique. Nowadays, formic acid is mainly used as feedstock chemical [2, 3], but the compound has also huge potential as a replacement energy vector [4, 5]. Properties that render formic acid attractive for this purpose are the high volumetric density of H₂ (53 g/L), moderate environmental toxicity, and that it is a liquid under ambient conditions. The combination of all these favourable properties in this compound makes formic acid an eligible candidate as future energy carrier in a hydrogen-based society [6–9].

Status of project and main scientific results of workgroups

Our research focusses on different aspects in the cycle of hydrogen storage and generation.

One core area is the interaction of formic acid with various organic solvents, another is the identification of catalytic active intermediates in the process of FA formation from carbon dioxide and hydrogen respectively in the decomposition of formic acid back to CO₂ and H₂.

Hydrogen delivery
HCOOH → CO₂ + H₂

Energy/hydrogen storage
H₂ + CO₂ → HCOOH

There are many suitable techniques for examining the interactions between formic acid and organic solvents e.g. calorimetric measurements, NMR spectroscopy, and FT-IR spectroscopy.

The search for catalytic active species is almost exclusively done with various NMR spectroscopy techniques.

Solvation of formic acid in water and in organic solvents

An important aspect for reaching high FA concentrations is that newly formed molecules are quickly stabilised from the surrounding solvent molecules. This step is also a crucial factor for hydrogen evolution since the same amount of energy is required to remove the solvation shell from the molecule to decompose it to hydrogen and carbon dioxide.

A proven technique to examine solvent-solute interactions is calorimetry [10]. The calorimetric measurements were performed with an EasyMax 102 Basic Synthesis Workstation. The mixing enthalpies for various organic solvents and water with formic acid were assed. The operating temperature of the measuring chamber was set to 25 °C and the compounds were added in small portions. At the end of each experiment the system was allowed to reach equilibrium state. All occurring temperature changes were carefully monitored and used for the calculations of the enthalpies of mixing [11] (Figure 1).

Figure 1: Calorimetric measurements (EasyMax 101): Enthalpies of mixing from selected solvents with formic acid.

Authors

Cornel Fink¹
Sergei Katsyuba¹
Gábor Laurenczy¹
¹ EPFL
Another established method to observe molecular interactions is NMR spectroscopy. Again, several FA/solvent systems were examined carefully. Exemplarily for others, the findings of the water/formic acid studies will be discussed in greater detail. 1H, 13C and 17O NMR spectra of numerous mixtures, ranging from pure water to pure formic acid, were recorded. A sensitive indicator for the changes in the chemical interactions at different mixing ratios is the chemical shift of the proton linked to the carbon of the FA (HCOOH, Figure 2). An external standard (benzene-d6) [12] was used for locking and referencing the samples. Chemical shifts can be used to calculate how the solvent molecules are co-ordinated around a formic acid molecule.

To gain more information about the solute-solvent interactions of FA in aqueous solutions, we carried out FT-IR spectroscopic studies. The interactions between formic acid and water were measured at different concentrations (Figure 3). Varied concentrations cause alterations in the chemical interactions. These alterations can be seen as characteristic changes in the FT-IR absorption spectra. Indicative are the frequencies of isolated IR bands, mainly caused by molecular vibrations of the νC=O and νC-H bond (Table 1).

Mechanistic studies on formic acid formation and decomposition

In catalytic reactions intermediates are of special interest. Difficulties in their observation arise from their short life times and generally low abundance – not seldom close to the detection limit of NMR spectroscopy. Therefore, sophisticated techniques are required to reveal catalytic processes [13]. For example, to investigate the formation of formic acid, a carefully measured amount of solvent and catalyst are added into medium pressure sapphire NMR tubes. Then, the tubes are pressurized with hydrogen and carbon dioxide (up to 100 bar) and exposed to heat. The decomposition of formic acid can be either observed at ambient conditions or at elevated pressures (maximal 100 bar), depending on the experimental design.

Last year, we published the results [14] of the very promising catalyst [RuCl₂(PTA)₄]. It produces unprecedented high concentrations of formic acid in DMSO (2.2 M) without any additives necessary. Our research is now concerned with the analysis of the catalytic intermediates of these reaction. The mechanistic studies

Table 1:

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<thead>
<tr>
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<th>νC-H</th>
<th>νC=O</th>
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<tr>
<td>Gaseous FA</td>
<td>2943</td>
<td>1770</td>
</tr>
<tr>
<td>FA monomer in Ar matrix</td>
<td>1767</td>
<td></td>
</tr>
<tr>
<td>FA acyclic dimer in Ar matrix</td>
<td>1747</td>
<td></td>
</tr>
<tr>
<td>FA cyclic dimer in Ar matrix</td>
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<td>FA-water 1:1 cluster in Ar matrix</td>
<td>1737</td>
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<tr>
<td>FA-water 1:2 cluster in Ar matrix</td>
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<tr>
<td>Liquid (98%) FA</td>
<td>2953</td>
<td>1719</td>
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<tr>
<td>X(FA) = 0.8</td>
<td>2950</td>
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<td>X(FA) = 0.5</td>
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<td>X(FA) = 0.2</td>
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<tr>
<td>X(FA) = 0.1</td>
<td>2941</td>
<td>1717</td>
</tr>
</tbody>
</table>

References
are carried out with a 400 MHz NMR spectrometer and the measurements are performed in a hydrogen atmosphere in 5 or 10 mm sapphire NMR tubes. To study hydride species, the catalyst gets dissolved in purified, deionized water (640 µL) and pressured with pure hydrogen. As before, an external standard (benzene-d$_6$) is used. The hydride region revealed two distinct signals: A doublet at -8.78 ppm and a triplet at -11.91 ppm (Figure 4). Both hydride signals collapse to single peaks in case of phosphorus decoupling. We know from structural analysis that the phosphorus is directly bound to the central ion. Hence, the two hydrides are most certainly located in the first coordination sphere of the complex, which is a strong support for identifying them as catalytically active species. Further research is necessary to improve our understanding of the mechanisms behind these catalytic processes.

**Acknowledgement**

SCCER, CTI and EPFL are thanked for financial support.

Figure 4: 1H NMR: The two dominating signals in the hydride region of [RuCl$_2$(PTA)$_4$], an indicator for a catalytically active species (400 MHz 1H spectrum, 5 mm sapphire tube at 91 bar H$_2$ pressure, water suppression, external standard (DMSO-d$_6$)).

**References**


Hydrogen Storage in Hydrides

Scope of project

The main achievements of our work in 2014 are the description of the reaction mechanism of the hydrogen desorption from alanates and first experiments for the analysis of the reduction of CO₂ on metal hydride surfaces.

Status of project and main scientific results of workgroups

Complex hydrides

In 1996 Bogdanovic presented [1, 2] first results of hydrogen sorption experiments on Ti-catalized NaAlH₄. Pressure-concentration isotherms were measured in a temperature range of 150 °C to 244 °C and two distinct and flat plateaus were found. The corresponding reactions are:

- \(3\text{NaAlH}_4 \rightleftharpoons \text{Na}_3\text{AlH}_6 + 2\text{Al} + 3\text{H}_2\)
- \(\text{Na}_3\text{AlH}_6 \rightleftharpoons 3\text{NaH} + \text{Al} + \frac{3}{2}\text{H}_2\)

The corresponding enthalpies for the reactions, determined by the Van’t Hoff plot are, \(\Delta H_1 = 111\text{ kJ}\) and \(\Delta H_2 = 70.5\text{ kJ}\), respectively.

This finding has initiated a new research field and hydrogen storage in complex hydrides became feasible. The Ti catalyst shows a reduction of the activation energy for the two reactions from 118 kJ/mol \(\text{H}_2\) to 80 kJ/mol \(\text{H}_2\) and from 124 kJ/mol \(\text{H}_2\) to 96 kJ/mol \(\text{H}_2\), respectively. Some years later first results on hydrogen desorption from borohydrides were presented. Borohydrides are similar compounds like alanates, however, no hexahydride phase is observed and until now no catalyst was found for the hydrogen sorption reaction in borohydrides.

Borohydrides contain up to 20 mass% of hydrogen and, therefore, store an order of magnitude more hydrogen as compared to metal hydrides. Despite the large number of publications [3] on the function of the catalyst in alanates only recently a new and consistent model for the mechanism of the Ti catalyst in alkali alanates was described, based on the local structure and thermodynamic considerations [4].

The mechanism is based on the fact, that in both reaction steps of the hydrogen desorption from NaAlH₄, the ions Na⁺ and H⁻ have to be moved from the complex (Na⁺[AlH₄]⁻) to the neighboring NaAlH₄ and from the hexahydride (3Na⁺[AlH₆]³⁻) to the elemental hydride NaH (Figure 1). The activation energy is determined by the charge separation, i.e. the role of the catalyst is to bridge between Na⁺...Ti...H⁻ and, therefore, allow the two ions to be moved simultaneously without forming NaH. The abundant AlH₃ spontaneously decomposes and releases hydrogen.

The hydrogen desorption mechanism of borohydrides is still not known. Due to the absence of a hexahydride phase, the elemental hydride is directly formed during the hydrogen desorption reaction, e.g. LiBH₄ → LiH + BH₃. The BH₃ molecules in analogy to AlH₃ spontaneously decompose (at \(T > 200\text{°C}\)) or two BH₃ can form the volatile B₂H₆ [5, 6]. The later reaction should be avoided, because it leads to a loss of boron from the material and diborane is poisonous gas for humans and fuel cells.

Reduction of CO₂ on metal hydrides

To store renewable energy in synthetic hydrocarbons, two major challenges have to be overcome:

- Extraction of CO₂ from the atmosphere close to the thermodynamic limit of energy need.
- Reduction of CO₂ with hydrogen to specific hydrocarbons in a controlled end energy efficient reaction [7, 8].

The catalytic reduction of CO₂ is determined by the local availability of hydrogen atoms and the orientation of CO₂ molecules. To control formation of C-C bonds and reaction paths
to synthesize specific energy-dense hydrocarbons from CO₂, a new approach is CO₂ reduction on a modified substrate based on metal-hydrogen systems (including metal clusters and nanoparticle compounds) (Figure 2). The aim is to elucidate the CO₂ reduction process in metal-hydrogen systems and to develop new reaction paths for formation of synthetic hydrocarbon as energy carriers.

The Ce-Co system was investigated in view of the change of thermodynamic potential for CO₂ reduction. Co is a catalytically active metal, for example, for the Fischer–Tropsch process. The formation of the Co hydride is an endothermic process. However, the formation of the intermetallic compounds, for example CeCo₃, lead to exothermic hydrogen absorption, forming the interstitial hydride CeCo₃H₄, and to ready hydrogen desorption (endothermic) at ambient pressures (Figure 2). The catalytic CO₂ reduction was prepared by repeating a hydrogen absorption/desorption cycle. The hydrogen desorption kinetics in various CO₂ and CO atmospheres, as well as the catalytic activity, was analysed by using a fixed bed quartz tube reactor. At the surface of the hydride, CO adsorption significantly retards recombination of hydrogen and the subsequent hydrogen release, compared to CO₂. CO₂ conversion commenced at 200 °C and found higher at the reduced surface by CO + H₂.

In the course of the CO₂ reduction, CH₄ was formed under our experimental conditions. The formation of C₂H₆ was lower by one order of magnitude. In the formation of CH₄, commencing at 200 °C, there are two distinct regions. At the higher temperatures, the formation of CH₄ was enhanced by pre-reduction of ceria and other oxides. On the other hand, the formation of CH₄ commenced at 200 °C in both reactions. In the initial stage at 200 °C, CO molecules and the adsorbates, dissociated from CO₂, retard recombination of hydrogen. There, the high availability of hydrogen might lead to a local C-H bonding in the catalytic CO₂ reduction [10].

The understanding of the mechanism of the catalytic hydrogen desorption from the alanates is an excellent basis for the further development of new hydrogen storage materials. First results on the investigation of the CO₂ reduction on metal hydrides and the detection of C-C compounds represent a very important step forward in the development of new catalysts for the synthesis of hydrocarbons.

**Figure 2:**
Left: Catalytic CO₂ reduction reaction on the surface of a metal or metal hydride.
Right: Potential curves for activated chemisorption of hydrogen on a metal surface covered with a surface layer and exothermic solution in the bulk (schematic).

**References**
Synthetic Fuels
Development of Advanced Catalysists

Illustration: BeholdingEye / iStock
New Catalysts for the Transformation of CO₂ into Fuels

Scope of project

We are currently studying the reduction of CO₂ into fuels such as formic acid, methane and methanol. Among these different fuels methanol is the most versatile and several heterogeneous catalysts have been reported for the direct hydrogenation to methanol. In all the cases harsh reaction conditions (over 200 °C) along with low turnover numbers (TON) are major drawbacks. In contrast homogeneous catalyst systems that operate under relatively milder conditions (140 °C) with higher TONs of up to 221 have been reported [1]. Although promising, none of the catalysts reported are commercially viable. We have developed ultrathin sheets of palladium (figure 1) that catalyze the formation of methanol when dispersed in solution. These sheets may be a single palladium layer thick and their full characterization is in progress. We intend to use these thin palladium sheets to coat various surfaces to generate highly dispersed heterogeneous catalysts that may be superior in activity to those currently reported. We also intend to apply the route used to generate these nanosheets to other metals such as nickel and bimetallic systems and explore their activity in methane and methanol forming reactions. Others in the working group may find uses for these nanosheets, e.g. in preparing electrodes for the electrocatalytic reduction of CO₂.

Status of project and main scientific results of workgroups

We are also working on the reduction of CO₂ to methanol using a two-step, one-pot method (figure 2) based on homogeneous catalysis, although it should be possible to immobilize the molecular catalysts later in the study to give heterogeneous systems. The initial step involves CO₂ fixation into diol compounds followed by in situ hydrogenation to generate methanol. We believe, in this way we will be able to generate methanol under mild reaction conditions with higher TONs. Advantageously, this reaction needs only one equivalent of diol and once methanol is generated from the system the diol compound will again fix another equivalent of CO₂ thereby generating a cyclic process. The substrates could also be heterogenized, e.g. by attaching a vinyl group to the arene ring and then transforming them into a functional polymer, which should lead to the simple isolation of methanol.

We are also exploring non-volatile frustrated Lewis pair-type systems to trap hydrogen and CO₂ and then convert them into fuels. The first system we have prepared affords formic acid, but only under harsh conditions. We have also discovered metal free catalyst (NHC) for N-methylation reactions using CO₂ as the carbon source and hydrosilane as the source of hydrogen [2] (figure 3). Notably, the catalyst showed excellent chemoselectivity and substrates scope for this reaction. We are now developing this strategy to fuel production using ionic liquid amines.

References


Figure 1 (upper left): Ultrathin palladium nanosheet catalysts
Figure 2 (upper right): Two step one pot generation of methanol from CO₂ under mild condition.
Figure 3 (below): Functional group tolerance: nitro, keto, nitrile, alkene, alkyne, ether, ester.

Author
Paul J. Dyson¹
¹ EPFL

List of abbreviations

NHC Nucleophilic Heterocyclic Carbene
TON Turnover Number
Molecular Control and Understanding of Surface Chemistry

Scope of project

Heterogeneous catalysts, including photo and electrocatalysts, are essential to the development of cleaner and more efficient processes, a key for sustainable development of our society. On heterogeneous catalysts, all – catalytic – events take place at the surface of the materials. However, despite years of research and many advances in characterization methods, the rational development of heterogeneous catalysts is often impeded by the lack of understanding of the surface chemistry. Our strategy has thus focused on the preparation of well-defined surface sites through the controlled functionalization of material surfaces and their detailed characterization – at the molecular level – by combining experimental and computational approaches (Scheme 1). Our ultimate aim is a predictive approach towards the design of functional materials with desired catalytic properties.

Status of project and main scientific results of workgroups

To this end, we work on:

- the preparation of metal oxide materials with controlled composition and homogeneity;
- the control of site density and surface chemistry of these materials, including the understanding of detect sites [1] and the controlled growth of metal particles on top of oxide supports [2].

We also introduce organic functionalities in order to immobilize highly active homogeneous catalysts and to capitalize on the rational development of homogeneous catalysts [3].

In addition, we have developed nuclear magnetic resonance (NMR) methods to obtain expedient and yet detailed information of surface sites through dynamic nuclear polarization [4].

This approach has been very successful for the development of highly active single-site catalysts with catalytic performances (e.g. olefin polymerization and metathesis), often surpassing both homogeneous and classical heterogeneous catalysts.

Within the aim to convert the excess electricity and CO₂, a greenhouse gas, into fuels, our goal is to develop more efficient catalysts for chemical (hydrogenation) and electrochemical conversion processes.

References


(b) F. Héroguel et al., «Simultaneous generation of mild acidic functionalities and small supported Ir NPs from alumina-supported well-defined iridium siloxide», J. Catal., 321, 81 (2015).
We therefore focus our research on:

- the development of hybrid materials for the immobilization of highly active homogeneous CO₂ hydrogenation catalysts [3,5]. With this project, we have developed new platform molecules, which will be used to prepare hybrid materials to immobilize a new generation of immobilized CO₂ hydrogenation catalysts.
- the development of heterogeneous catalysts for the conversion of CO₂ into methanol. With this project, we are developing more selective catalyst through the controlled growth of supported Cu nanoparticles and better (computational) models to improve these catalysts through a structure-activity relationship.
- the development of processes for the capture and the conversion of CO₂ [6].

We are developing so-called Sorbent Enhanced Reforming to capture CO₂ and produce pure H₂.

- the development of electro-catalysts for the formation of H₂ and the direct conversion of CO₂ into fuels. We are developing methods to control the shape and composition of colloids towards the preparation of selective electro-catalysts for the conversion of CO₂ to fuels.

References


(b) D. Baudouin et al., «Nickel-silicide colloid prepared under mild conditions as a versatile Ni-precursor for more efficient CO₂ reforming of CH₄ catalysts», J. Am. Chem. Soc., 134, 20624 (2012).
Electrochemical CO₂ Reduction

Scope of project

The electrochemical reduction of CO₂ to hydrocarbon is a promising pathway for the recycling of this greenhouse gas. Nevertheless, on top of the high overpotential typically required to drive this reaction, the electrochemical reduction of CO₂ suffers from a low faradaic efficiency (it is kinetically more favorable to evolve hydrogen in the hydrogen evolution reaction (HER) from water than to reduce CO₂), and from a poor and/or uncontrolled yield of valuable products such as methanol or methane [1]. In this work package, several strategies will be employed at PSI’s Electrochemistry Laboratory in order to:

- develop measurement tools for online and in operando detection of the reaction products in the electrochemical reduction of CO₂,
- find the origin of the selectivity of specific electrode materials,
- design electrocatalyst systems with high selectivity in the CO₂ reduction towards valuable products such as methanol or methane.

Status of project and main scientific results of workgroups

In this first annual report, the focus is made on the development of online and in operando electrochemical tools, following two pathways.

Liquid electrolyte based electrochemical cell

The first approach makes use of a liquid electrolyte based electrochemical cell. In this setup, the identification and quantification of produced volatile species such as methanol, formic acid, carbon monoxide, methane or ethylene. In addition, a similar type of electrochemical cell coupled to a Fourier transform infrared spectroscopy (FTIR) setup for the detection of reaction products and intermediates adsorbed onto the electrode surface was also built. This first approach offers a high flexibility when screening multiple parameters, such as the nature or structure (single crystal electrodes vs. nanoparticles) of the electrode on which the electrochemical reduction occurs or the experimental operating conditions (pH and temperature).

While still working on improving the design of the electrochemical cell and setup, preliminary CO₂ reduction results followed by DEMS were obtained on a polycrystalline Cu disk in 0.1 M KHCO₃ saturated with CO₂. In this setup, the working electrode is pressed on the PTFE membrane of the DEMS setup representing the inlet to the vacuum system as to allow the direct collection of the volatile reduction products. Even if this approach results in poorly-defined diffusion conditions near the electrode, it allows for the observation of qualitative reactivity trends described in the following.

In an exemplary experiment, the potential profile depicted in Figure 1 (A) is applied to the Cu disk electrode. Figure 1 (B-D) displays the time evolution of the mass fragment signals m/z = 2 (H₂⁺), m/z = 15 (CH₃⁺) and m/z = 44 (CO₂⁺). Both H₂ and hydrocarbon products are generated, in good agreement with the literature [1], while CO₂ gets progressively consumed, confirming the viability of the vacuum and DEMS-setup.

Solid polymer electrolyte based electrochemical cell

The second approach for online and in operando detection of CO₂ reduction reaction products makes use of a solid polymer electrolyte based electrochemical cell, in a similar way of how a water electrolysis cell is operating. It consists of a two compartment/electrode cell, each of them supplied with its own gas and separated from each other by an anion or cation exchange membrane. The cathode compartment is operating in a CO₂ rich atmosphere, and the outlet of this compartment is connected to a mass spectrometer. The main advantage of this approach over the one cited above is that it is operating in a dry state with a defined amount of water vapor entering each compartment of the cell. Since the presence of water is identified to be the main reason for the high HER activities, high faradaic efficiencies for CO₂ conversion are expected to be reached using this approach. This could then also boost the selectivity toward certain products and offer completely

List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>DEMS</td>
<td>Differential Electrochemical Mass Spectrometry</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>HER</td>
<td>Hydrogen Evolution Reaction</td>
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<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
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References


Authors

Julien Durst¹
Yohan Paratcha¹
Juan Herranz¹
Mehtap Özbasan¹
Thomas Gloor¹
F.N. Bäch¹
Thomas J. Schmidt¹

¹ PSI
different insights on this reaction, compared to what could be learned from classical liquid electrolyte based electrochemical measurements. In an actual CO₂ co-electrolysis operation, CO₂ is reduced at the cathode side, while O₂ is produced at the anode (from the water splitting reaction), the overall cell voltage of a co-electrolysis cell being then the thermodynamical potential calculated from the Nernst equation plus the sum of the overpotentials for these anodic and cathodic reactions. Nevertheless, in the first stage of this work package the anodic reaction will be the hydrogen oxidation, known to be a few orders of magnitude faster than the oxygen evolution, so that no additional overpotential is required to activate this anodic reaction.

Designs of electrodes fulfilling the criteria of an optimal operation in such an electrochemical cell are different than in the first approach proposed here (the liquid electrolyte cell), and offer less flexibility in terms of the electrode structures which can be tested. Gas diffusion electrodes in the form of carbon supported metal particles in the nanometer range, with a high open porosity (>60%), are typically used for such type of operation so as to allow a high fraction of active sites (due to the nanometric size of the electrocatalysts) and a fast diffusion of the reactants and removal of the products.

Coupling of the two approaches

It seems clear why coupling both of the two approaches presented here is pivotal: the first will allow a fast screening of several electrode materials/structures in order to find design criteria for electrocatalysts with high selectivity toward production of hydrocarbons, which should then be applied in the synthesis of carbon supported metal nanoparticles to be used in an actual co-electrolysis cell.

To evaluate the viability of this second approach, a carbon supported platinum catalyst (Pt/C) was tested as a CO₂ reduction catalyst. It is known that Pt is a catalyst with one of the lowest faradaic efficiencies for CO₂ reduction, since only H₂ is being released [1]. Nevertheless, this result has been derived from measurements performed in liquid electrolytes, where it is known that due to the very fast HER kinetics and the limited diffusivity of H⁺/H₂ in liquid phase, it is impossible to polarize a Pt electrode at potentials low enough, i.e. significantly below 0 V RHE where the CO₂ reduction reaction is thermodynamically possible. This could actually be solved by using the solid polymer electrolyte based electrochemical cell approach, operating in a gas phase type of environment, where 3 orders of magnitude larger current densities (in A/cm²) can be reached compared to a classical liquid electrochemical cell due to faster H⁺/H₂ diffusivities. This approach has already been used before to quantify HER kinetics [2], where low Pt loadings (in cm²/g) have been employed to reach large specific currents (in A/cm²).

The same strategy as in reference [2] has been applied here, and potentiostatic voltammograms (Figure 2 A) have been recorded in 1 atm of N₂ (black trace) and CO₂ (red trace). The voltammogram recorded in the N₂-sat. environment, where only H₂ evolution occurs on the Pt/C electrode, leads to similar performance than those evaluated elsewhere [2]. Under CO₂-sat. conditions, the electrolysis performance is 4-times lower than under N₂-sat. conditions (Figure 2 A). This can be rationalized by the partial adsorption of CO₂ onto the Pt catalyst surface [3], which lowers the number of active sites for the hydrogen evolution. The time-dependent MS profile recorded during electrolysis (Figure 2 B) allows concluding that only H₂ was generated during both electrolysis modes, even in the CO₂-rich atmosphere (no signals on the mass fragments m/z = 15, 27, 31 for methane, ethylene or methanol were observed). As a conclusion, even under conditions where Pt could be polarized at low potentials (here below 0.6 V RHE), its faradaic efficiency toward CO₂ reduction remains negligible.

Outlook

After demonstrating the viability of both approaches, the focus will be set on finding the origin of the selectivity of specific electrode materials, with a special care on Cu-based catalysts.
Towards a Mechanistic Understanding of the Electro-Reduction of CO₂

**Scope of project**

The atomic structure of a single-crystalline copper electrode has been studied under in operando conditions by scanning tunnelling microscopy (STM) during hydrogen evolution which is considered as an important parasitic side-reaction of the CO₂ electro-reduction. It is demonstrated that the hydrogen evolution reaction (HER) leads to significant changes in the electronic and geometric structure of the copper electrode due to H-intercalation.

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

The focus of this current SC-CER project is on the conversion of the environmentally unfriendly green-house gas CO₂ into hydrocarbons (ethylene, methanol etc.) by means of (photo-)electrochemical processing (Figure 1). The particular technological challenge is related to the extraordinary stability of the CO₂ molecule thus requiring extremely high over-potentials for the electrochemical reduction. Only by the use of proper reaction catalysts the CO₂ reduction can be accelerated so that the process might become feasible in future from an economic point of view. Up to now, only copper-based catalysts have shown a promising activity towards the CO₂ conversion into the desired hydrocarbons [1, 2]. However, their selectivity towards specific reaction products (e.g. ethylene) still remains rather poor. In addition, a molecular level understanding of the particular activity of copper-based catalysts as the basis for a tailored design of new catalyst materials is still lacking.

The first step of the project is therefore aimed at gaining a deeper atomistic understanding of the electro-catalytic conversion of CO₂ into hydrocarbons at copper-based catalysts by using a surface-electrochemical approach. This approach will make use of well-defined, single-crystalline model catalysts (Figure 2) where high-resolution scanning probe techniques (STM and AFM) can be applied not only under in situ but also under in operando conditions during an ongoing (electro-reduction) reaction.

What often limits the overall current efficiency of the CO₂ reduction in an aqueous environment is a hydrogen evolution reaction (HER) that is superimposed on the CO₂ reduction. In the current electrocatalysis literature the HER is discussed only as a parasitic side-reaction of the CO₂ reduction. However, we will demonstrate that the HER plays an important role for the activation of the copper surface by forming surface-confined (intercalated) hydrogen intermediates that are probably needed in the course of CO₂ reduction to form hydrocarbons.

**Results and discussion**

Figure 3 gives an overview of the surface structure of a Cu(111) electrode in dilute 5 mM H₂SO₄ [3]. The potential regime close to the on-set of the copper dissolution reaction is dominated by the specific adsorption and lateral ordering of (bi)sulfate anions from the supporting electrolyte whereas the copper surface remains anion-free at the on-set of the HER.
Our high-resolution STM images (Figure 1 g-j) give clear experimental evidence of an H-mediated Cu(111) surface reconstruction/relaxation that affects both the in-plane and out-of-plane structure of the copper surface while the overall atom surface-density remains unaltered. Figure 1 j reveals the presence of anomalous, square structure motifs of Cu next-neighbours inside such a (4 × 4) unit-cell besides trigonal structure motifs that are common for the ideal (1 × 1) lattice (in-set of Figure 2 a). It is not only the local coordination which deviates from the hexagonal Cu(111)-(1 × 1) lattice under HER conditions but also the corresponding nearest-neighbour distances (NNDs). These range from about 2.1 Å to 3.6 Å. Compared to the ideal value for the Cu(111)-(1 × 1) lattice of NND = 2.56 Å we observe both local expansion and local compression effects within the topmost copper layer under HER conditions. The resulting (4 × 4)-xH superstructure can be rationalized as the lateral ordering of sub-surface hydrogen in conjunction with the concerted reconstruction and relaxation of the surrounding copper lattice.

It is this structural impact of the hydrogen evolution and the subsequent H-intercalation on the copper lattice which is actually imaged in the STM under such in operando conditions (Figure 3). Not only the geometric but also the electronic structure is significantly affected by the presence of sub-surface hydrogen as evidenced by bias/tunneling current dependent STM experiments (Figure 4).

Identical reconstruction phases have been observed in other acidic media such as 10 mM HCl solution indicating that the observed structural effects are independent from the chemical nature of the anion species in the electrolyte. Shifting the HER towards more negative potentials (e.g. by increasing the pH in (bi)carbonate solution) leads to a disappearance of the (4 × 4)-xH superstructure within the potential range of -250 mV to -350 mV proving that the appearance (4 × 4)-xH is indeed directly linked to the HER.

Conclusions and next steps

Former studies considering the bare (unreconstructed) copper surface as the electrocatalytically active one for the CO2 reduction need to be reconsidered in the light of our recent in operando STM results [4]. It is most likely that the hydrogen intermediates intercalated into the copper during the superimposed HER/CO2 reduction play a crucial role rationalizing the particularly high activity of copper towards CO/CO2 conversion into hydrocarbons.

References

A Uniform Techno-Economic and Environmental Assessment for Electrical and Thermal Storage in Switzerland: Development and Case Studies

Scope of project

The aims of the task «Integrated Assessment of Storage» are to develop a uniform techno-economic and environmental assessment method for electrical and thermal storage and to apply this method to different energy storage technologies and applications. This report describes the work undertaken at the University of Geneva, at Paul Scherrer Institut (PSI) and at Lucerne University of Applied Sciences (HSLU) in 2014 considering research activities, work in progress and scientific outputs. So far, work at the University of Geneva is focused on techno-economic assessment and at the PSI on environmental assessment applying life cycle assessment (LCA). All institutions contribute as a team to the development and assessment of different energy storage (ES) technologies and applications.

Status of project and main scientific results of workgroups

The goals of the task «Integrated Assessment of Storage» have been achieved according to the project proposal:

- Analytic design and characterization of ES technologies by means of the uniform assessment methodology.
- Reference energy systems specified by the consideration of relevant case studies linked with other work packages within SCCER-Storage.

Uniform assessment methodology

The first subtask is to develop a uniform techno-economic and environmental assessment for ES which is applied to different ES technologies (electricity and heat), applications and sectors. As shown in Figure 1, the methodology currently being developed integrates different levels including the ES unit, ES application and the economic/regulatory context. A time-dependent approach is considered accounting for the dynamics of ES, the stochastic nature of renewable energy generation, demand loads and variable energy prices. Figure 2 shows a first selection of indicators foreseen to assess the performance (including the impact on the energy system), economic benefits and environmental impact of ES technologies depending on the application.

The uniform assessment method can be applied with different purposes including ES technologies characterization and comparison, comparison of ES with a reference scenario and/or competitors, analysis of the impact of ES on the energy system, optimisation of ES technologies for any given application and/or identify research priorities.

The assessment method has been applied to four ongoing case studies as explained below.

Energy storage case studies

Battery storage for single home PV units and demand management

The performance and the economic benefits brought by battery systems managing photovoltaics (PV) generation without feed-in tariffs but selling electricity to the wholesale market under dynamic retail tariffs is being assessed. This work adds value to the literature because the analysis is time-dependent considering two different scales. Firstly, a dynamic tariff based on the wholesale market i.e. one price value per hour for every day of the year is compared with a...
A Uniform Techno-Economic and Environmental Assessment for Electrical and Thermal Storage in Switzerland: Development and Case Studies

Integration

Flat rate and a double profile tariff with a temporal resolution of one minute. Secondly, the battery model simulates the reduction of battery capacity and annual discharge throughout the battery lifetime for lead-acid (PbA) and lithium-ion (Li-ion) batteries. These two facts make this analysis different to previous studies which were based on constant assumed parameters [1]. According to simulation results, the dynamic tariff was able to increase the value of PbA and Li-ion batteries by 47% and 64% respectively regarding the simple tariff as shown in Figure 3.

Power-to-gas

A prototype power-to-methane plant is being commissioned in Rapperswill with a 25 kW alkaline electrolyser. The methanation reactor is based on thermochemical catalysis while CO₂ is supplied with industrial pressurized cylinders. The generated methane will be used as a fuel for a fleet of vehicles. The PSI is currently performing a life cycle assessment to quantify the environmental impact of the plant and the University of Geneva will conduct the techno-economic assessment. The scope of the analysis will be extended beyond the prototype unit and further evaluate different sources of electricity and CO₂ as well as different electrolyser and methanation technologies (Figure 4). The economic impact of adding other applications (in addition to generate fuel for vehicle) will be investigated and differences between an analysis based on nominal values as considered in [2] and a time-dependant analysis will be quantified.

Preliminary LCA results indicate that using synthetic methane from excess renewable electricity and CO₂ extracted from the atmosphere as vehicle fuel leads to a substantial reduction of greenhouse gas emissions compared to natural gas vehicles.

Pumped-hydro and battery storage for energy arbitrage

The University of Geneva has started to compare pumped-hydro and battery storage performing energy arbitrage using the Monte-Carlo method to tackle the uncertainty associated with energy prices.

This work is expected to be expanded by incorporating different energy price scenarios according to the day-ahead market, intraday market, renewable energy diffusion, etc, in collaboration with HSLU and the University of St. Gallen.

Thermal storage for the industry

In order to apply the assessment method to heat storage, the final heat energy demand for the Swiss industry was broken down by temperature level (based on temperature data from the European Union) as represented in Figure 5. Further improvement of the analysis would require physical production data which do not seem to be publicly available.
Electro-thermal energy storage

Electro-thermal energy storage (ETES) refers to the technology which allows converting electricity into heat and cold and vice versa, via a combination of heat pump and heat engine cycle processes (Figure 6).

The output of the most flexible type of the system, currently in development by HSLU under the name of DESC (dual energy storage converter) can be pure electricity or a combination of electricity, heat and cold.

The system has a functionality of an energy storage in that it contains high and low temperature sources that can be utilized to meet fluctuating demands of electricity and thermal energy.

During 2014 the ETES concept has been investigated by HSLU in terms of process design and a modified DESC version has been proposed that has generated preliminary design data as input for the LCA analysis conducted by PSI. The conceptual design will be further evaluated in 2015 through computer simulations and experimental campaigns.

In parallel to the development of the technical concept an evaluation of the operational requirements has been initiated in December 2014 by investigating potential applications (one industrial partner established) and market value propositions. The output of this analysis will also provide input for other technologies such as battery and thermal storage.

References


Storages for Flexibility of Power and Heat

Scope of project

The aim of this task «Storages for flexibility of power and heat» is the advancement of a novel storage technology called dual electricity storage converter (DESC). DESC is a thermodynamic electricity storage technology which can be used both in bulk electricity storage applications as well as in combined electricity/heating and cooling applications. During periods of excess electricity generation or low-price electricity availability, a heat pump is operated to charge a hot and a cold storage. In periods of low electricity production or high power prices, DESC can be operated as a heat engine, using the stored temperature difference to generate electricity which can be consumed locally or fed to the grid. Furthermore, DESC can be open, thermally meaning that heat and cold can be directly extracted from the storages, to cover process heat and cold demand for industries (e.g. pasteurization, product cooling) as well as the space heating and cooling demand in building blocks. The hot storage can be also charged directly from a hot stream (e.g. solar collectors, waste heat etc.). The overall principle of DESC can be seen in Figure 1.

Status of project and main scientific results of workgroups

This report describes the work undertaken from the Thermal Energy Storage (TES) group at Lucerne University of Applied Sciences (HSLU) during the year 2014. The main focus of the work in 2014 was the review and evaluation of existing projects by 3rd parties that are similar to DESC, the understanding of a possible market for this product and the acquisition of industrial partners.

The goals of this task for 2014 have been achieved according to the project proposal:
- In depth evaluation of critical parameters of existing ABB concept finalized.
- Alternative DESC concepts compared.

Review and evaluation of existing concepts

A first comparative review of previous similar storage concepts has been performed. The review included both literature research and discussions with groups with experience in this technology.

A steady-state thermodynamic model has been developed to verify the concept and parameters reported by ABB using transcritical CO₂ as the working fluid.

Figure 2 shows an example of a T-S diagram of the ABB process, as it was generated by the thermodynamic model.

After the model and the critical parameters were verified, the model was used to theoretically assess alternative concepts (subcritical isobutene and ammonia cycles).

A 5 kW isobutane DESC test-rig was designed based on the thermodynamic model combined with market research for existing components.
Identification of DESC market and acquisition of industrial partners

The acquisition of industrial partners already from the early stages of the technology development is considered of great importance.

A series of strategic meetings were arranged with Mayekawa Intertech AG, a Zug-based company, specialized in refrigeration systems and automation and interested in developing a DESC product.

The meetings resulted in collaboration for two projects where HSLU will be the scientific developer and Mayekawa will provide funding and expertise. The projects concern the development of an ammonia DESC test-rig at HSLU and a latent heat storage at 95 °C to be used as the hot temperature storage in DESC as well as in independent industrial applications.

Additionally, a scanning of the Swiss food & beverages sector was performed to identify possible factories were the DESC pilot plant could be installed. A list of 70 possible sites with energy needs at suitable temperature levels was put together and the most interesting candidates will be contacted. The goal is to understand the energy system and the needs of relevant industries which will help define the DESC specifications and recognize the possible DESC market.

References/Literature

Applied Power-to-Gas Systems

Scope of project

Power-to-gas is a process for storing the energy from renewable electricity from summer to winter in the form of chemical energy as hydrogen or methane. The required technologies and the main infrastructures required for its implementation already exist today. New and improved technologies from research laboratories and start-up companies will appear on the market in the next few years. The Institute for Energy Technology at the University of Applied Sciences Rapperswil (HSR) has used the funds from SCCER to establish a competence centre for the implementation of power-to-gas.

HSR has organised the first event in Switzerland on the topic power-to-gas: «Expertengespräche Power-to-Gas» on 13th May 2014, where more than 40 experts met at the HSR campus. The presentations gave an overview on the current status of power-to-gas. Additionally, HSR is chairing a group of all parties in Switzerland, planning or operating a power-to-gas facility.

Status of project and main scientific results of workgroups

New projects in 2014:
- Scientific and technical consulting of the power-to-hydrogen facility of Regio Energie Solothurn.
- «Renewable Methane for Transport and Mobility»: Project funded by the National Science Foundation within the Swiss National Research Programme NFP70 and in co-operation with EPFL, Empa, HSR and ZHAW. The entire value chain power-to-gas for using the renewable gas in long distance professional transport is analysed from a technical point of view and an economic point of view.
- Pilot- and demonstration facility power-to-methane at HSR, where an electric power of 25 kW can be used to produce synthetic methane. The facility was operational end of 2014 and is using existing technology mainly from the company Etogas. It enables HSR to learn quickly on how to operate power-to-gas facilities and on how to model them.

New industrial co-operations in 2014:
- Erdgas Obersee, www.erdgasobersee.ch
- Erdgas Regio, www.erdgasregio.ch
- Verband der Schweizerischen Gasindustrie (VSG), www.erdgas.ch
- Schweizerischer Verein der Gasindustrie, www.svgw.ch
- Elektrizitätswerk Jona-Rapperswil, www.ewjr.ch
- Regio Energie Solothurn, www.regioenergie.ch
- St. Galler Stadtwerke, www.sgsw.ch
- Etogas, www.etogas.com
- Postauto Schweiz AG, www.postauto.ch

New academic co-operations in 2014:
- Prof. Dr. Andreas Züttel, Swiss Federal Institute of Technology Lausanne, Physical Chemistry
- Christian Bach, Swiss Federal Laboratories for Materials Science and Technology, Laboratory Internal Combustion Engines
- Prof. Dr. Karl Frauendorfer, University of St.Gallen, Institute for Operations Research and Computational Finance (ior/cf-HSG), www.iorcf.unisg.ch
- Prof. Dr. Urs Baier, Zürich University of Applied Sciences, Institute of Biotechnology, www.ibt.zhaw.ch
Performance, Lifetime, Safety and Reliability of Battery Systems

Scope of project

The goal of this task for 2014 was the evaluation of cells, batteries and battery management electronics.

Status of project and main scientific results of workgroups

Survey on industrial state of the art

The Empa Reliability Laboratory has contracted access to the large data base of Shmuel De-Leon Energy Ltd.

This on-line data base includes 29'000 updated records of industry vendors, batteries, cells, fuel cells and super capacitors datasheets. It provides detailed specifications about energy storage cells and batteries: fuel cells (121), military batteries (391), primary batteries (58), primary cells (4'626), rechargeable batteries (135), rechargeable cells (19'906) and ultracapacitors (1'884).

A survey on battery management electronics provided by LiIonBMS.com gives an excellent overview about industrial issues relating to Li-ion cells and batteries such as charging types, balancing, battery pack design, cell protection and battery management systems. It provides detailed specifications about available battery management systems (BMS) hardware solutions from 48 industrial developers. A parametric selector enables to evaluate solutions for large Li-ion battery packs with off-the-shelf battery management systems.

Moreover 31 different BMS chipsets of 14 semiconductor manufacturers are characterized in detail by:
- maximum single string voltage,
- BMS technology (digital/analog),
- BMS topology (wired/distributed),
- diagnostics development effort required to fulfill safety standards (ISO26262),
- series cells / # of ICs,
- # of temperature sensors,
- balancing method (internal resistor / internal FET / external FET / active),
- standby and operating current,
- min. and max. cell voltage, voltage accuracy (@ 3.6 V, 25 °C),
- reading interval,
- current sensor type,
- SOC calculation method,
- communication protocol,
- wiring demand,
- cost and availability.

These data bases, surveys and tools will be useful for the design of battery packs and high voltage batteries with reliable battery monitoring and management systems.

Cell experiments and material analysis

Ageing and characterisation experiments and materials analysis were continued on a variety of commercial cells. Standard charge and discharge cycles as well as fast charging and application power profiles were used to characterise capacity fade, increase of resistance and shift in impedance spectra.

Figure 1 shows the capacity fade of high power LiFePO4-nanophosphate cells stressed with

1) application power cycles where state of charge (SOC) remained between 42 % and 100 %,
2) standard cycles with 100 % degree of discharge with the same average charge and discharge power as in 1).

Cell 1 thereby had a total energy throughput of 284 kWh in 6920 operational hours, cell 2 only 38 kWh in 1040 hours. Cell 1 can perform about 7 times more power cycles to degrade to 80 % of initial capacity than cell 2 even though energy throughput and operational time for cell 1 is a factor of 7 higher than for cell 2.

This is a clear indication that at least for this cell type the degree of discharge contributes much more to ageing pro-
Focused ion beam (FIB) cross sectioning was used to observe structural changes on the surface and in the bulk of graphite anodes aged with fast charging cycles.

Figure 2 shows increased cracking and prevalence of porous areas after 2000 fast charging cycles. Time-of-Flight FIB-SIMS analysis of the same samples shows a large difference in concentration of Li+ ions on the graphite anode indicating changes in the structure and compound of the solid electrolyte interface layer and the underlying bulk material, figure 3.
Appendix
Conferences

1st Annual Symposium, SCCER Heat & Electricity Storage, November 4, 2014

Oral Presentations

- M. Kovalenko, «Advanced Electrode Materials for Li-ion and Na-ion batteries and beyond».
- P. Häring, «Batteries in the Challenge of Expectations and Realizations».
- A. Haselbacher, «Overview of SCCER Heat-Storage Research and Development Efforts».
- G. Zananeh, et. al. «Industrial Packed Bed of Rocks Thermal Energy Storage».
- A. Züttel, et. al. «Advances in Hydrogen Production and Storage».
- M. Uffer, et al. «Megawatt Scale PEM Electrolysis for Energy Storage Applications».
- P. Dyson, et al. «Catalytic and Electro-catalytic CO\textsubscript{2} Reduction: the Genesis of Working».
- J. Worlitschek, et al. «Technology Interaction of Storage Systems - Gaining Flexibility between the Energy Grids».
- M. Rindlischbacher «Das Hybridwerk Aarmatt».
- F. Krysiak, «Socio-economic energy research and its potential relevance for storage».

Posters

- Y. Paratcha, J. Durst, J. Herranz, T.J. Schmidt, «Electrochemical setup for online FTIR and differential electrochemical mass spectrometry studies of CO\textsubscript{2}-electroreduction on model metal surfaces».
- K. Waltar, D. Lebedev, E.Fabbri, A. Fedorov, C. Copéret, T.J. Schmidt, «High-surface area catalysts for the anodic oxygen evolution reaction in PEM electrolyzers».
- E. Fabbri, M. Nachttegaal, X. Cheng, T.J. Schmidt, «Insights into d-band perovskite catalysts for application as oxygen electrodes in low temperature alkaline fuel cells and electrolyzers».
- C. Villevieve, L. Vogt, M. El Kazzi, E. Berg Jämstorp, S. Pérez Villa, P. Novák, «Sn anode for Na-ion batteries: A bulk and interfacial study».
- L. Vogt, P. Novák, C. Villevieve, «MSn\textsubscript{x} (M=Fe, Co, Mn) intermetallics as anode materials for Na-ion batteries».
- M. Reichardt, C. Villevieve, P. Novák, S. Sallard, «Lithium chromium pyrophosphate as new insertion material for Li-ion batteries».
- M. Rahaman, A. Dutta, T. Wandlowski, P. Broekmann, «Compositional dependence of CuAu alloy nanoparticles towards electrochemical reduction of CO\textsubscript{2}».
- N.H. Kwon, H. Yin, T. Vavrova et. al., «Particle size and shape dependence of the ionic diffusivity in LiMnPO\textsubscript{4} cathode for lithium ion batteries».
- X. Cheng, E. Fabbri, T.J. Schmidt, «Study of the oxygen evolution mechanism and activity of Perovskite La\textsubscript{2-x}Sr\textsubscript{x}CoO\textsubscript{3} -based electrodes in alkaline media by thin film rotating ring disc electrode measurements».
- K.D. Beccu, «Technologie- und Marktsituation des Hochenergie-Speichersystems Metallhydrid [NiMH]».
- D. Parra, M. Patel, «A uniform techno-economic and environmental assessment methodology for electrical and thermal storage development and integration in Switzerland».
- P.J. Dyson, S. Das, F. Bobbink, «Metal free catalyst for chemoselective methylation of amines using CO\textsubscript{2} as a carbon source».
- M. Montandon-Clerc, G. Laurenczy, «Formic acid dehydrogenation catalyzed by non-precious metal based catalysts in aqueous solution».
- G. Laurenczy, «Hydrogen storage and generation with CO\textsubscript{2}-formic acid systems».
- T.M. Trung, Huynh, P. Broekmann, «Intercalation of hydrogen into Cu(111) under reactive conditions studied by in-situ STM».
Conferences

- C. Fink, G. Laurency, «Solvation of formic acid in water and in organic solvents».
- A. Dutta, T. Wandloski, P. Broekmann, M. Rahaman, «Synthesis of SnO₂ nano particles on PVP function-
alized reduced graphene oxide by self-capping function of hexanoate ligands: An application for electro-
chemical CO₂ reduction in aqueous medium».
- P. Peljo, V. Amstutz, K. Toghill, H. Vrubel, H. Girault, «Conversion of electricity into hydrogen using a dual-
circuit redox flow battery».
- E. Rezaei, A. Ortona, S. Haussener, «Thermo-mechanical characterization of cellular ceramics in high-tem-
perature environments».
- D. Perraudin, S. Haussener, «Phase change material systems for high temperature heat storage».
- A. Stephan, C. Bening, T.S. Schmidt, V. H. Hoffmann, «A sectoral perspective on knowledge development
and diffusion in the lithium-ion battery technology in the US and Japan».
- J.-P. Brog, K. Fromm, «Nano-LiCoO₂: organometallic precursors as source of high Li-ion diffusion oxides for
battery purpose».
- S. Maharajan, N.H. Kwon, K. Fromm, «Polyanionic Cathode Materials For Sodium Ion Batteries».
- A. Kocabas, O. Zuleyha, S. Kato, E. Callini, A. Züttel, «Catalyzed H sorption mechanism in Alanates».

For full list of presenta-
tions, publications and
patents see website
www.sccer-hae.ch
Presentations

**Bulk Analysis of Sn-Electrodes in Sodium Ion Batteries**
- L.O. Vogt, C. Villevieille. Poster in ISE conference in Lausanne (Sep.14) «MSn$_2$ (M=Fe, Co, Mn) intermetallics as anode materials for Na-ion batteries».
- 2 posters in SCCER Heat and Storage workshop (Nov. 14) at PSI, same as ISE conference.

**Tin/Carbon Composite Anode Material for Lithium Ion Batteries and Polyanionic Cathode Material for High-Temperature Sensible TES Based on a Packed Bed of Pebbles**
- Annual symposium of SCCER, PSI, Switzerland, 4. Nov. 2014.
  - Polyanionic cathode materials for sodium ion batteries
- SCCER WP1, workshop, PSI, Switzerland, 27. Oct. 2014.
- SCCER WP1 meeting, Fribourg, Switzerland, 1. Oct. 2014.
- FriMat day, Poster, Fribourg, Switzerland, 27. June 2014.

**Thermo-Mechanical Characterization of Cellular Ceramics in High-Temperature Environments**

**Phase Change Material Systems for High Temperature Heat Storage**

**Aqueous Sodium Hydroxide Seasonal Thermal Energy Storage: Reaction Zone Design and Optimization**
Demonstration of a Redox Flow Battery to Generate Hydrogen from Surplus Renewable Energy

- «Adaptation of a redox flow battery to generate hydrogen from surplus renewable energy: principle and pilot project». 65th annual meeting of the International Society of Electrochemistry conference – Ubiquitous Electrochemistry, Lausanne (Switzerland), presented on the 5th of September 2014.
- «Adaptation of a redox flow battery to generate hydrogen from surplus renewable energy».
- 10th European Symposium on Electrochemical Engineering, in Chia (Italy), presented on the 2nd of October 2014.
- «Conversion of electricity into hydrogen using a dual-circuit redox flow battery». Poster at the SCCER Annual Conference, Villigen (Switzerland), presented on the 4th of November 2014.
- «Low-cost Mo₂C catalysts for Indirect Electrolytic Hydrogen Evolution». MRS Fall Meeting & Exhibit, in Boston (United States of America), presented on the 2nd of December 2014.
- «Hydrogen production by redox flow batteries». UNSW Materials and Electrochemistry Symposium, University of South Wales, School of Materials Science and Engineering (Australia), presented on the 5th of December 2014.
- «A demonstrator for the conversion of surplus renewable energy to hydrogen». 5th Euro-Mediterranean Hydrogen Technologies Conference (EmHyTeC 2014), in Taormina (Italy), presented on the 11th of December 2014.

Storages for Flexibility of Power and Heat

- Organization of 2nd Swiss Symposium Thermal Energy Storage at HSLU.

Other contributions

- T.J. Schmidt, «Electrocatalysis for the future energy system: Fuel cells, electrolyzers and more...». Symposium on Advances in Surface Chemistry, Ulm University, Germany, November 6, 2014.
- T.J. Schmidt, «Electrochemistry and the energy system: What the future may bring!». University of Cape Town, Chemical Engineering Department, Cape Town, South Africa, November 24, 2014.
Publications

**Bulk Analysis of Sn-Electrodes in Sodium Ion Batteries**
- P. Bleith, H. Kaiser, P. Novák, C. Villeuveille, «In situ X-ray diffraction characterisation of Fe$_{63}$TiOPO$_4$ and Cu$_{63}$TiOPO$_4$ as electrode material for Na-ion batteries». Submitted to *Journal Power Sources* (2015).

**Thermo-Mechanical Characterization of Cellular Ceramics in High-Temperature Environments**

**Demonstration of a Redox Flow Battery to Generate Hydrogen from Surplus Renewable Energy**

**Hydrogen Storage in Hydrides**

**Molecular Control and Understanding of Surface Chemistry**
For full list of presentations, publications and patents see website www.sccer-hae.ch


Towards a Mechanistic Understanding of the Electro-Reduction of CO₂


Applied Power-to-Gas Systems

• M.J. Friedl, B. Meier, Aqua & Gas, No 10, 14–21 (2014).
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

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