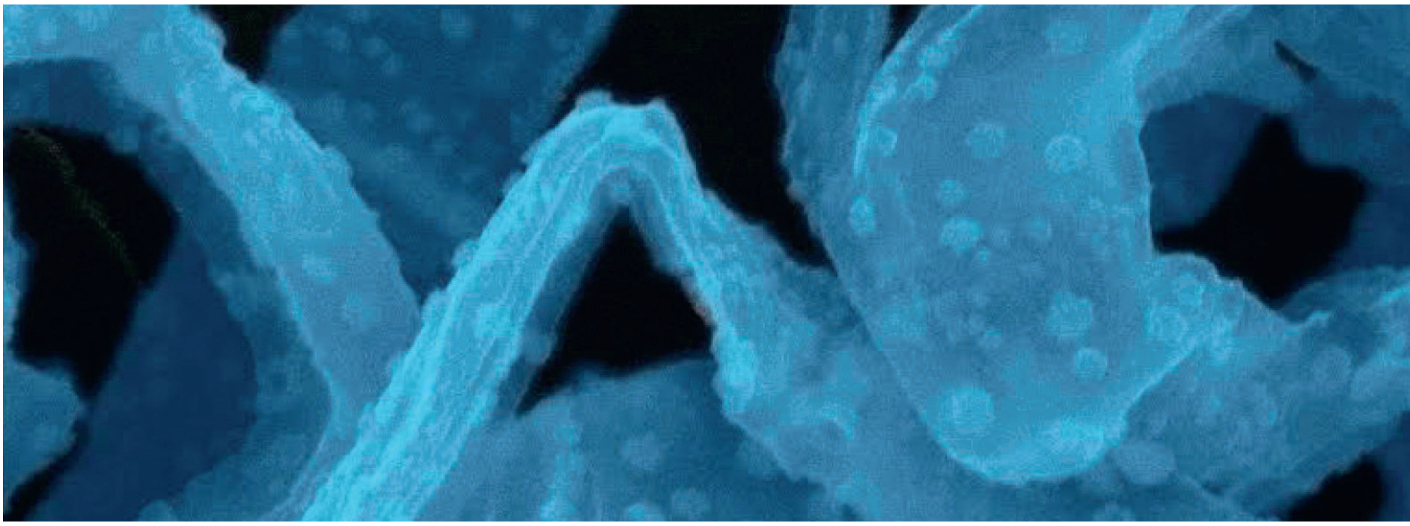
PAUL SCHERRER INSTITUT



Annual Report 2018

Electrochemistry Laboratory

Cover
Li dendrites, observed by scanning electron microscopy, forming on a Li substrate when using Li metal as a working electrode in lithium-ion batteries.

PAUL SCHERRER INSTITUT

Annual Report 2018

Electrochemistry Laboratory

Paul Scherrer Institut
Electrochemistry Laboratory
5232 Villigen PSI
Switzerland

Secretary
Phone +41 56 310 29 19
Fax +41 56 310 44 15

Hardcopies of this report are available from

Cordelia Gloor
cordelia.gloor@psi.ch
Paul Scherrer Institut
5232 Villigen PSI
Switzerland

A full version of this report is also available on the web
http://www.psi.ch/lec

Publisher
Electrochemistry Laboratory
Paul Scherrer Institut
5232 Villigen PSI
Switzerland

Editorial Team
Cordelia Gloor / Peter Lutz
Felix N. Büchi
Lorenz Gubler

Printing
Paul Scherrer Institut

ISSN 1661-5379
DOI: 10.3929/ethz-a-007047464
PSI Electrochemistry Laboratory : : Annual Report 2018

CONTENTS

EDITORIAL

PSI's Electrochemistry Laboratory is the leading center for research on electrochemical energy storage and conversion in Switzerland. The Lab bridges fundamental electrochemical science with applied electrochemical engineering, which is unique even on international standards. This allows us to keep a systemic view even when addressing basic scientific questions.

In this Annual Report 2018, you will not only find details on PSI's Electrochemistry Laboratory, but six reports on current topics of the Lab contributing to the grand challenge of electrochemical energy storage and conversion. Further, the Laboratories key facts and figures for 2018 are given, including a full list of our 53 peer reviewed publications and numerous talks demonstrating the leading role of PSI's Electrochemistry Laboratory on the national and international level.

In Mai 2018, the Lab held the 34th annual Electrochemistry Symposium *Pushing the Limits of Characterization in Electrochemistry* with world-class scientists as speakers attracting an audience of more than 120 participants. Details of this event you will find also in this annual report on page 42.

2018 was also a successful year for three of our PhD students who successfully defended their theses. All of the new PhDs were directly able to continue their careers either in an academic or industrial environment.

At this point it needs to be mentioned that all our projects and results could not have been achieved without the funding we received over the years from industrial partners and the different funding agencies in Switzerland and abroad. We, therefore, would like to take this opportunity to thank all our funding sources hoping to continue our successful collaborations in the years to come.

With the year 2018 ending, however, also important changes were implemented. The structure of the Lab has been reorganized, the Lab is now organized into six groups. The change secures a smooth transition into a successful future for the Lab.

Felix N. Büchi

THE ELECTROCHEMISTRY LABORATORY AT A GLANCE

Our Mission

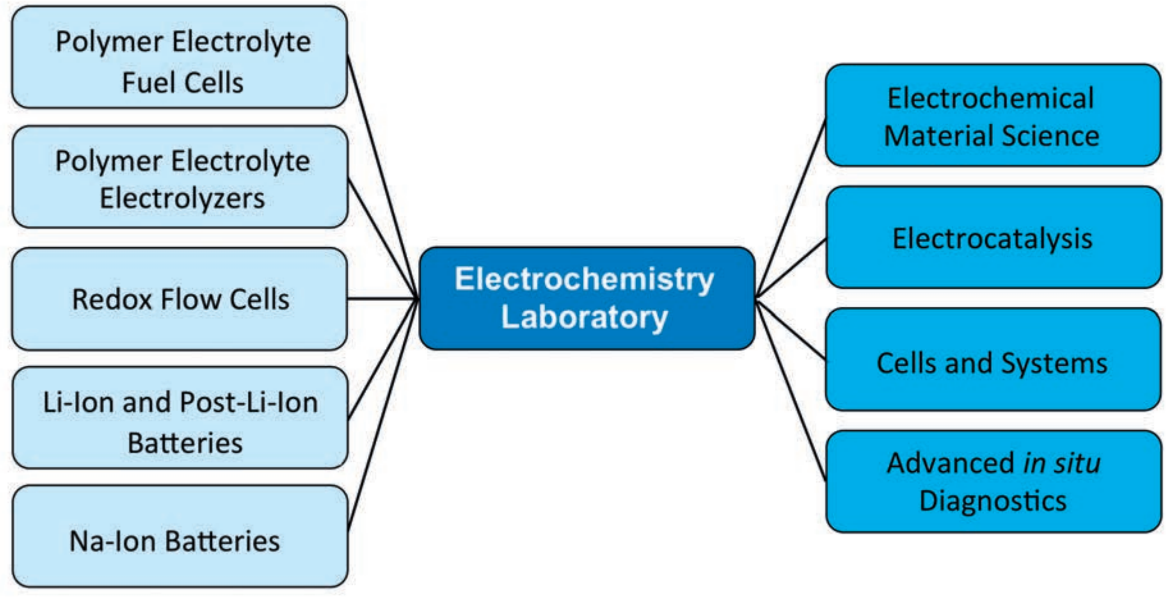
Advancement of electrochemical energy storage and conversion by

- **developing novel electrochemical materials, cells and devices;**
- **providing insights into electrochemical materials, cells and device properties.**

PSI's Electrochemistry Laboratory is Switzerland's largest Center for Electrochemical Research with about 70 employees. Our mission is to advance the scientific and technological understanding of electrochemical energy storage and conversion specifically in the context of a sustainable energy system, where renewable energy is required to be stored in secondary batteries or chemicals such as hydrogen and (re-)converted into electricity. The Laboratory's R&D, is hence focused on secondary batteries – specifically Li- and Na-based systems –, polymer electrolyte fuel cells and electrolyzers, as well as redox flow cells.

As a research institute's laboratory we are bridging the gap between fundamental science and applied engineering by combining both academically and industrially relevant questions. For the technologies under research, we not only develop fundamental understanding of materials on an atomic and molecular scale (electrochemical materials sciences and electrocatalysis), but also in the applied development of technical cells and devices, e.g., fuel cell systems.

On many technical complexity levels, we are developing and utilizing advanced *in situ* and *operando* diagnostic tools to gain insights in properties and processes from the nanometer to the centimeter scale, respectively, often making use of PSI's unique large scale facilities such as the Swiss Light Source (SLS) and the Swiss Neutron Spallation Source (SINQ).



Electrochemical energy storage

The vision in Electrochemical Energy Storage is to make significant contributions to the most advanced electrochemical energy storage systems.

The work is focused on rechargeable batteries, which are mainly lithium and sodium based. The scientific goal is a profound understanding of the electrochemical processes in complex non-aqueous systems. In particular, of utmost scientific interest are the numerous interactions of all components determining the safety and life time of such systems.

PhD Student Marta Mirolo running XPS experiment.

The work equally considers the synthesis of novel materials for electrochemical energy storage and the modification of known materials (e.g., carbon), and material characterization, keeping in mind the entire span from basic science to industrial applications. To answer the scientific questions, we develop various sophisticated *in situ* and *operando* methods for use in the field of non-aqueous solid-state electrochemistry and investigate the physical and electrochemical properties of insertion and conversion materials and electrochemical interfaces *in situ*. Also, we do electrochemical engineering work on three-dimensional electrodes and characterize industrial batteries.

Electrochemical energy conversion

A major focus of the Electrochemical Energy Conversion are the development and in-depth understanding of materials, processes and devices for the conversion of renewable power to hydrogen (or syngas) and back to power. Especially in the context of a sustainable energy system utilizing hydrogen as an energy carrier, these electrochemical energy conversion steps are of particular importance.

In this topical context the work is focused on Polymer Electrolyte Fuel Cells (PEFC) and Polymer Electrolyte Water Electrolyzers (PEWE) for water electrolysis and the co-electrolysis of CO_2 and water, respectively. In addition, work is devoted on the materials development for Redox Flow Cell systems.

The R&D strategy involves activities on four pathways:

- the development and application of advanced *in situ* and *operando* diagnostic imaging tools on stack, cell and component levels (X-rays and neutrons);
- membrane development based on PSI's own radiation-grafting technology;
- research in electrocatalysis and the reaction kinetics of the relevant reactions (e.g., the oxygen electrode reactions) for improved understanding of intrinsically limiting factors; and
- system, stack and cell engineering.

On the level of technology demonstration, we have designed and we develop and operate the so-called hydrogen path on PSI's Energy System Integration (ESI) Platform on the 100 kW level, i.e., operate a technical scale PEWE System including product gas clean-up and a H_2-O_2 PEFC reconversion system, which is based on a joint development with our collaboration partner Swiss Hydrogen SA.

Bridge Discovery team in the redox flow cell test lab.

CURRENT SCIENTIFIC TOPICS

Challenges and prospects for safer all-solid-state-batteries

Since the commercialization of the first Li-ion battery by Sony in the early 90s, the vast majority of electrode materials have been carbons and oxides. However, Li-ion batteries are starting to reach their limitations owing to recent concerns about the availability of Li and, in particular, recent issues regarding safety (Samsung S7, Boeing Dreamliner, etc.). One alternative for making safer batteries is to substitute the flammable organic-based liquid electrolyte with a solid one. Solid electrolytes based on ceramics and glasses have been investigated for more than 20 years, but to date, no commercially viable solution has been realised because of the multiple drawbacks associated with these materials. In the Battery Materials group, we decided to take a closer look at the challenges remaining for the development of solid state batteries and to develop solutions to tackle them.

Li-ion batteries are, to date, the most reliable and efficient commercial products that can store electric energy for different applications (e.g. medical devices, electric vehicles, and portable electronics). Over the last 25 years, most research has been dedicated to the development of novel electrode materials and their engineering, which has led to an increase in the energy density by a factor of three, from 90 Wh/kg in 1991 to 240 Wh/kg for the battery commercialised in the Tesla car in 2014. [1]

Unfortunately, this outstanding energy density increase coupled with improvements in electrode materials has not yet been accompanied by an improvement in the safety of the batteries. [2] The organic solvents present in liquid electrolytes are harmful to humans and the environment, but even worse, the low thermal stability, flammability, and toxicity of carbonate-based electrolytes pose significant safety challenges (several recently reported cases). Although intensive research is ongoing to make organic electrolytes less toxic and more stable, the best alternative is to replace liquid organic electrolytes with solid electrolytes. [3] This solution will provide drastically improved safety and reduce the size and the weight of the battery stack (Figure 1), thus improving the energy density of the storage system.

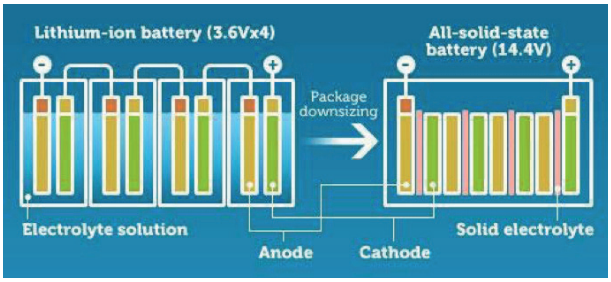


Figure 1. *Schematic comparison of a conventional Li-ion battery and the downsized battery realised by replacing the liquid electrolyte with a solid state electrolyte. Reprinted from Toyota website.*

In recent years, many solid electrolytes belonging to different material families have been investigated as promising candidates for fast Li^+ conducting electrolytes, as summarised in Figure 2. [4] Clearly, the most suitable candidates have very high ionic conductivities (as close as possible to that of organic electrolytes). In particular, sulfide-based electrolytes (e.g. $Li_{10}GeP_2S_{12}$ and $Li_7P_3S_{11}$) exhibit comparable ionic conductivities to liquid electrolytes. Unfortunately, for these electrolytes with promising ionic conductivities, there are severe concerns regarding

- their extremely narrow electrochemical stability windows (Figure 2) and
- their safety risk owing to the possible release of toxic H_2S gas during synthesis and upon exposure to air or moisture.

Other candidates are dense ceramic electrolytes that have attracted much interest owing to the possibility of combining relatively high ionic conductivities (for a solid at room temperature) with wide electrochemical stability windows. These materials follow the Arrhenius equation, i.e. their ionic conductivity increases with temperature, which opens new perspectives for all-solid-state batteries based on safe garnet-type solid electrolytes.

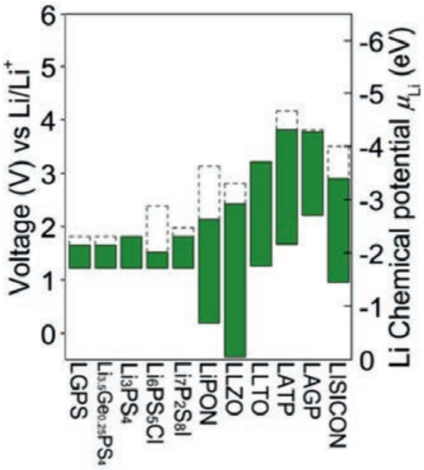


Figure 2. *Electrochemical stability windows for different solid state electrolytes obtained from DFT calculations. [5]*

Within the Electrochemistry Laboratory, we are investigating both systems to understand their limitations at the bulk, surface, and engineering level to develop solutions supporting the transition to safer Li-ion, all-solid-state batteries.

Sulfide-based solid electrolytes

The biggest advantage of sulfide-based electrolytes relies on their ability to be sintered at room temperature avoiding then a lot of engineering efforts to perform electrochemical tests. Unfortunately, it was reported that the electrochemical stability window is extremely narrow leading to questions about the chemical stability especially at the interface between the electroactive material and the solid electrolyte. Our first approach was to make an electrochemical test using electroactive materials out of the stability window. Thus, we selected one well-known negative electrode material ($Li_4Ti_5O_{12}$) and one positive electrode material ($LiCoO_2$), both tested versus Li-In alloy, a reference electrode buffering the Li dendrites formation. [6]

Negative electrode

The electrochemical performance obtained with $Li_4Ti_5O_{12}$ (LTO) as negative electrode is displayed in Figure 3. As can be seen, despite being out of the theoretical stability window, the LTO electroactive material can deliver almost its theoretical capacity (120 mAh/g instead of 150 mAh/g) for long-term cycling without any capacity fading. The difference between the experimental capacity and the theoretical one can be explained by

- the electrode engineering; since carbon Super P is decomposing the solid electrolyte, the active material was only mixed with the SE, and
- the particle size of LTO which might be too big to ensure fast enough Li^+ transport through the core.

As the results are promising for LTO despite being out of the theoretical stability window, we can conclude that the electrochemical performance is still sufficient and that so far no electrode engineering is required.

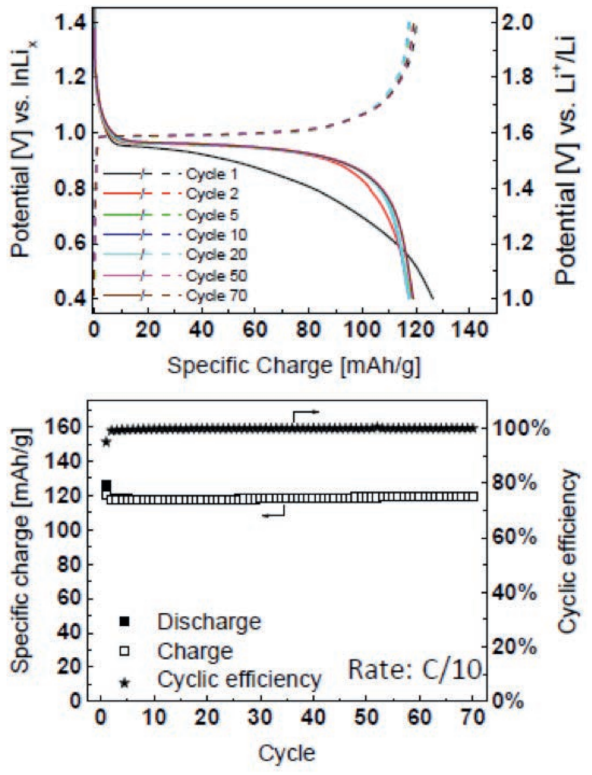


Figure 3. Top: Galvanostatic curves of LTO tested in half-cell configuration versus In-Li at a rate C/10 with CC protocol at room temperature. Bottom: Electrochemical performance of the LTO/LPS/In-Li cell during long-term cycling. The open squares represent the charge capacities whereas the solid squares represent the discharge capacities. The stars represent the Coulombic efficiency.

Following the same procedure, we decided to test another electroactive material but this time we selected a cathode material, again out of the theoretical stability windows (as reported in Figure 2).

Positive electrode

$LiCoO_2$ (LCO) was selected as cathode of choice to assess its stability in contact with LPS. As can be seen in Figure 4, LCO is unfortunately not cycling properly in contact with LPS. Indeed, we can notice a very large irreversible capacity along the first cycle (indicated by a yellow box in Figure 4). Additionally, the experimental specific charge is very low, ca. 80 mAh/g instead of 130 mAh/g for the theoretical values (Figure 4). Finally, we can notice also a relatively poor Coulombic efficiency and a fading during cycling, both indicating that LPS is most probably decomposing during oxidation.

In order to improve the electrochemical performance of LCO cathode material and knowing that the electrolyte is decomposing at high voltage (see *operando* surface contribution on page 13 in this report), we opted to a surface modification of the particles using sol-gel coating. As can be seen in Figure 5 and regarding the electrochemical performance obtained, we would like to highlight the importance of coating the active material LCO in order to deliver higher specific charges.

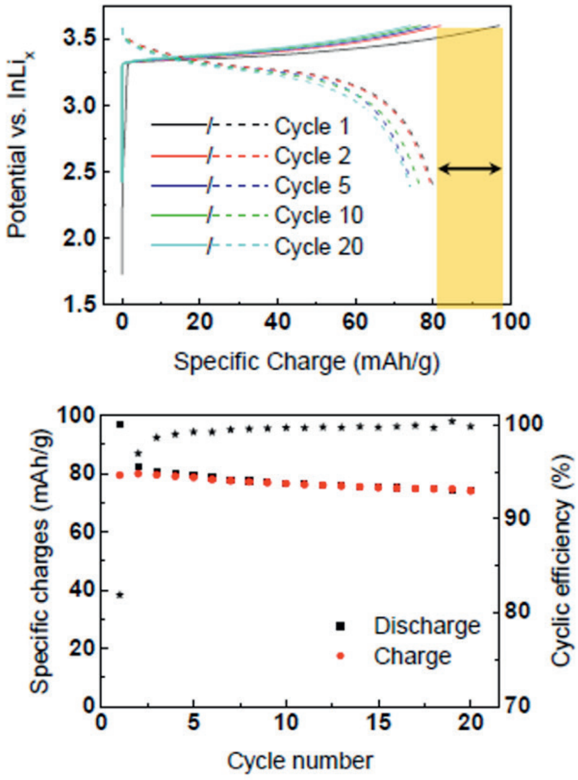


Figure 4. Top: Galvanostatic curves of LCO tested in half-cell configuration versus In-Li at a rate C/10 with CC protocol at room temperature. Bottom: Electrochemical performance of the LCO/LPS/In-Li cell during long-term cycling. The red circles represent the charge capacities whereas the black squares represent the discharge capacities. The stars represents the Coulombic efficiency.

When the electrodes, containing both 50 : 50 (in wt.%) LCO : LPS with and without coating and cycled at C/10, are compared (Figure 5), the initial specific charge is around 105 mAh/g and 91 mAh/g, respectively. These values are much lower than the specific charge of 140 mAh/g reached in conventional Li-ion cells. Besides, the loss of capacity during the first discharge is smaller for the coated electrodes as they reached 91 mAh/g and 74 mAh/g respectively, which represent a loss of 15 % and 19 %. The possible reason for the observed difference might come from the significant electrolyte decomposition at the interface of the uncoated oxide electrode/electrolyte. During the first cycle (Figure 5), a significant overpotential is noted for the uncoated sample which highlights the importance of a coating layer to limit the electrolyte decomposition when reaching high potentials.

Additionally, in order to deliver higher specific charges over many cycles, the optimal electrode composition (optimized ratio between LCO and LPS) needs to be found. As LCO is a semiconductor, a higher ratio will improve the electronic pathway over the electrode leading to higher specific charge. The sample containing the highest amount of active material delivered an initial capacity of 144 mAh/g which is 20 % higher than the 60 : 40 mixture and 30 % more than the 50 : 50 coated composite electrode. A similar trend can be observed for the discharge during the first cycle.

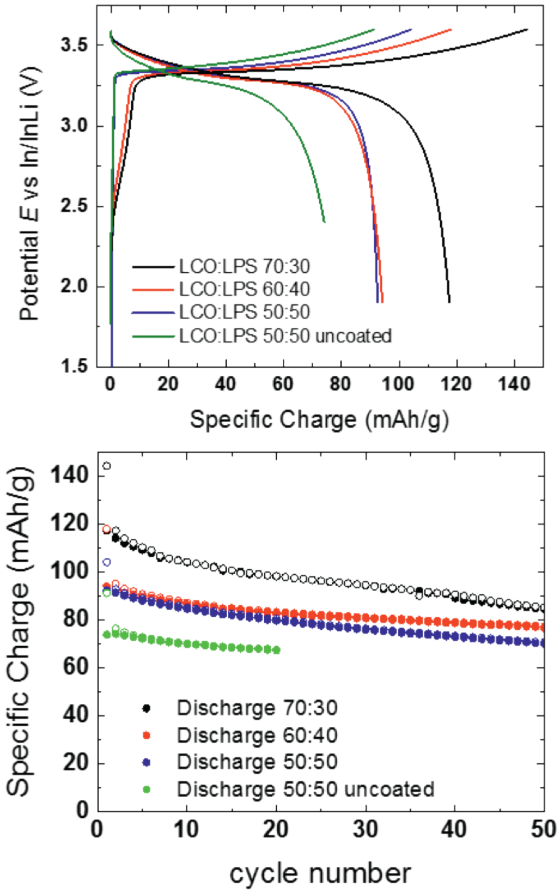


Figure 5. *Top: Galvanostatic curves of coated LCO : LPS (50 : 50; 60 : 40; 70 : 30) and uncoated LCO : LPS (50 : 50) tested in half-cell configuration versus In-Li at a rate C/10 with CC protocol at room temperature. Bottom: Electrochemical performance of the LCO/LPS/In-Li cell during long-term cycling. The open circles represent the charge capacities whereas the closed circles represent the discharge capacities.*

For the sulfide-based solid electrolyte, we demonstrated the importance of the proper engineering of the electrode materials to ensure optimal cycling. Indeed, surface protection (via coating methods) and appropriate electrode composition (amount of active material and electrolyte) are crucial for an improved long-term cycling performance of cathode materials for all-solid-state batteries.

Garnet-based solid electrolytes

Another alternative to sulfide-based solid electrolyte, relies on the development of ceramic oxide materials (Figure 2). Perovskite materials with the composition of (Li, La)TiO_3 show promising high Li^+ conductivity with good structural stability. Their conductivity properties are impressive for ceramic materials at room temperature (10^{-3} S/cm). Unfortunately, this perovskite solid electrolyte is unsuitable for all-solid-state batteries using Li metal counter electrodes owing to high reactivity of Ti and its reduction during cycling below 1.7 V vs. Li^+/Li.

Thus alternatives have been developed to overcome the limitations of the Ti/Li reaction. In 2007, Murugan et al. introduced the concept of a garnet-based solid electrolyte ($Li_7La_3Zr_2O_{12}$). This material exhibits temperature-dependent crystallization and forms two different polymorphs: cubic and tetragonal. Samples synthesized at elevated temperatures (> 1200 °C in air) show a cubic structure, whereas those prepared at lower temperatures (< 1000 °C) form a tetragonal phase. Advantageously, the Li-ion conductivity of the cubic phase is two orders of magnitude higher than that of the tetragonal phase (10^{-4} and ~10^{-6} S/cm at room temperature, respectively). In this context, LLZO was used as solid electrolyte in our group to show the advantages and limitations of such system.

Electrolyte preparation

Contrary to LPS solid electrolyte, garnet type electrolyte needs high temperature to be sintered. This step was successfully achieved at 1175 °C for 5 h in air. The LLZO solid electrolyte pellets were prepared with a relative density of 93 % measured by geometrical parameters. Unfortunately, the sintering is performed in air and, thus, the surface of the solid electrolyte pellet is then covered by impurities that need to be polished with silicon carbide grinding papers to obtain a mirror-like surface (Figure 6). The final polishing step reduced the pellet thickness to ca. 300 µm and achieved a flat surface, crucial for the electrode film deposition. [7]

Then, the usual way to obtain electrode materials turned to be inefficient with garnet solid electrolyte. Indeed, it was not feasible to «attach» the electrode to the pellet since the interface between the solid electrolyte/electrode was far away optimized. Drop casting of the electrode, on top of the solid electrolyte pellet, turned also to be unsuccessful since the solid electrolyte decomposed with the solvent used in the electrode preparation.

Alternatively, LLZO samples were inserted in a sputtering deposition chamber for the deposition of the 50 nm Si thin film. Beforehand, a plasma Ar^+ etching treatment of 30 sec was conducted in the sputtering chamber to obtain a «clean» surface (removal of surface species) without breaking vacuum. This step was followed by the Si thin film deposition. Figure 6c and 6d show the Si film deposited on one surface of the LLZTa pellet. Figure 6c shows the difference of color between the Si-coated area (pink) and the uncoated LLZTa pellet (pale yellow). Figure 6d shows the EDX analysis at interface of the coated/uncoated pellet. As can be seen, there is a net presence of carbon species on the uncoated area whereas almost none are detected on Si-coated area.

These results show the successful «in situ» treatment with initial removal of carbon-rich surface species and direct deposition of Si film on the «clean» surface.

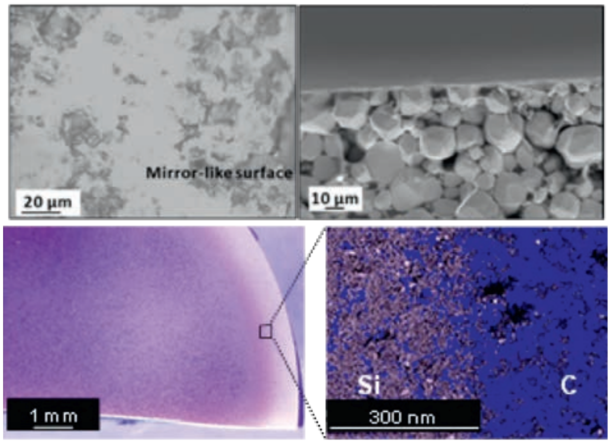


Figure 6. Top: Optical micrograph of LLZO pellet after sintering and polishing. Bottom: Image and EDX analysis after in situ Argon plasma etching and Si deposition.

Electrochemical performance

The Si/LLZO stack was then investigated electrochemically in half-cell vs. Li metal. The cell was maintained at 80 °C in a temperature controlled chamber to limit the resistivity of the bulk LLZO electrolyte. Figure 7 shows the potential profiles for the 1st, 2nd, 3rd, 5th, 10th, and 20th cycle at C/18 rate. During the first cycle an initial irreversible activity at ~0.4 V vs. Li^+/Li is detected. The first delithiation results in sloping potential plateau evolving smoothly from 0.2 V to 0.5 V vs. Li^+/Li.

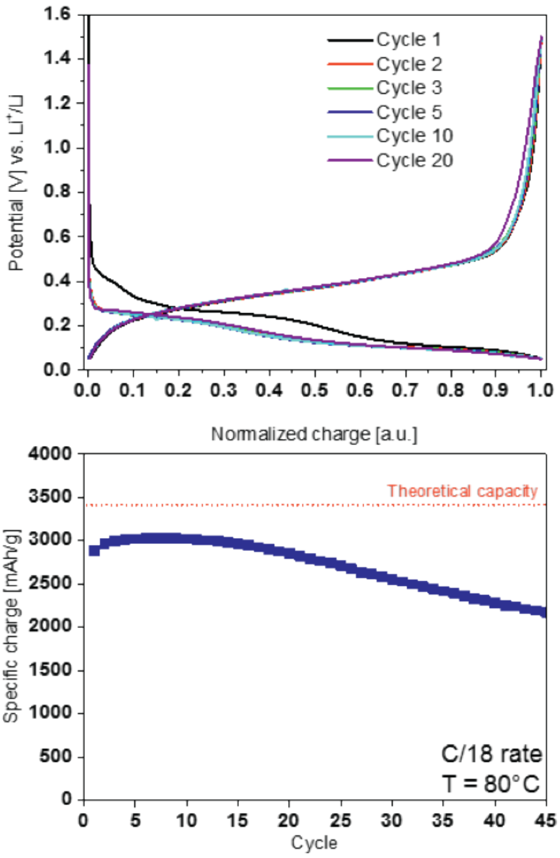


Figure 7. Top: Normalized galvanostatic curves of Si/LLZO tested in half-cell configuration versus Li at a rate C/18 with CC protocol at room temperature. Bottom: Electrochemical performance of the Si/LLZO/Li cell during long-term cycling.

From the 2nd to the 20th galvanostatic cycle, there are no relevant changes except the disappearance of the initial irreversible activity at 0.4 V vs. Li^+/Li during discharge. Figure 7 shows the cycling performance able to provide an initial delithiation capacity of 2885 mAh/g with an increase after few cycles up to 3023 mAh/g. High delithiation capacity above 3000 mAh/g was retained for at least twelve cycles before starting to fade down to 2174 mAh/g after 45 cycles. The overlapping of the potential profiles from 2nd to 20th cycle suggests that the capacity fades due to film «loss» rather than irreversible reactivity.

Conclusion

Along this report, we demonstrated that there still is a long way to go to obtain technically viable concepts for all-solid state batteries.

In the sulfide-based solid state electrolyte, we identified several problems at the interface that require proper engineering to ensure proper cyclability. Here the development of advanced *operando* techniques such as *operando* XRD and XPS will help us to address properly the question of the chemical stability at the interface. Additionally, other parameters such as the mechanical stability during cycling should be also investigated, as well as the Li-ion transport properties. To this point, new methodologies are currently being developed such as *operando* X-ray microscopic tomography and *operando* neutron imaging.

In the case of garnet-based solid electrolyte, we described a proof of concept enabling the cycling of solid state batteries using garnet LLZO electrolyte. We have demonstrated, that intimate contact at the interface between the electrode and the solid electrolyte can be obtained by a proper surface treatment. Based on this approach, we successfully deposited and cycled reversibly a thin film electrode used as a model system. High specific charge could be obtained for multiple cycles. Further engineering of the solid electrolyte and electrode will be conducted to ensure a cycling at room temperature and coupling to a bulk type electrode.

Contact

For further information on all-solid-state batteries, please contact Dr. Mario El Kazzi.

mario.el-kazzi@psi.ch

Contributors

The contributors for this particular research topic are Dr. Mario El Kazzi, Dr. Giulio Ferraresi, Ms. Laura Höltschi, Dr. C. Villevieille and Mr. Xiaohan Wu.

Funding

We thank our different funding sources for their support: Swiss National Science Foundation (SNSF), Prima Grant n° PR00P2_179766, SAFT SE Bordeaux France, Toyota Motor Europe.

Acknowledgement

We thank Prof. Dr. Petr Novák for fruitful discussions in the field of solid state batteries and electrochemistry. We also thank Dr. C. L. Tsai & Dr. S. Uhlenbruck from Forschungszentrum Jülich GmbH, IEK-1, Germany, for providing the raw powder of LLZO. Our thank goes also to Dr. L. Czornomaz from IBM Research Zürich, Switzerland, for the thin film deposition on LLZO.

References

[1] C.P. Grey, J.M. Tarascon, *Nat. Mater.* **16**, 45–56 (2017).

[2] A.L. Robinson, M.S. Whittingham, *Mrs Bulletin* **41**, 188–189 (2016).

[3] J. Janek, W.G. Zeier, *Nature Energy* **1**, 16141 (2016).

[4] J.C. Bachman, S. Muy, A. Grimaud, H.-H. Chang, N. Pour, S.F. Lux, O. Paschos, F. Maglia, S. Lupart, P. Lamp, L. Giordano, Y. Shao-Horn, *Chem. Rev.* **116**, 140–162 (2016).

[5] Y. Zhu, X. He, Y. Mo, *ACS Appl. Mater. Interfaces* **7**, 23685–23693 (2015).

[6] X. Wu, M. El Kazzi, C. Villevieille, *Journal of Electroceramics* **38**, 207–214 (2017).

[7] G. Ferraresi, M. El Kazzi, L. Czornomaz, C.-L. Tsai, S. Uhlenbruck, C. Villevieille, *ACS Energy Letters*, 1006–1012 (2018).

Operando XPS and Raman spectroscopies: Complementary techniques to investigate the surface and the near-surface evolution of Li-ion battery electrodes

Li-ion batteries (LIB) are nowadays considered serious contenders for electrochemical energy storage devices for electric mobility as well as backup power supply when batteries are connected to homes and/or intermittent power grids. Among the most important requirements for their large-scale commercialization are long autonomy, fast charging, stable battery cycle life, low cost per kW, and safety. To ensure the continuous increase of their electrochemical performance and safety a constant development of characterization techniques is needed to provide better insights into the physics and chemistry of the various parts of the battery and in particular of the working electrodes. Both the bulk and the surface structure modification of the battery materials need to be investigated upon cycling due to their direct impact on battery behavior. By combining *operando* XPS (chemical information) and Raman spectroscopy (structural information), both surface and near-surface changes can be monitored.

In the last few years, the expansion of *operando* techniques has tremendously helped to gain fundamental dynamic understanding of the structural and chemical evolution of the bulk electrode materials. [1] However, the processes taking place at the electrolyte-electrode interface and near the surface of the electrode remain elusive, even though they have been extensively studied in the last 30 years. [2] The reason is mainly related to the restrictive measurements using *post-mortem* surface techniques. This is due to the incompatibility of the liquid electrolyte with the ultra-high vacuum (UHV) environment, the limited depth analyses of the surface tools, the absence of appropriate *operando* cells, as well as the challenge of interpreting the data. Those limitations made the detailed comprehension of the surface electrochemical reaction mechanisms very challenging.

In this contribution, we show the recent methods' development of *operando* X-ray photoelectron spectroscopy (XPS; using the example of an all-solid-state lithium battery – SLiB) and Raman microscopy (using the example of a high voltage cathode material) to probe the surface and the near-surface, offering thus an unprecedented manner of real-time monitoring of the evolution of the electrolyte-electrode interface and the materials' structure during Li-ion battery operation. We will present as well the corresponding *operando* XPS and Raman electrochemical cells. Both *operando* XPS and Raman are unique techniques allowing direct detection of changes in the chemical, structural, and electronic properties as function of the applied voltage. Moreover, they overcome the limitations related to the *post-mortem* measurements such as relaxation processes, sample-to-sample deviations, risk of surface contamination, or modification during disassembly and transfer to UHV. [3]

Operando XPS in all-solid-state lithium batteries

SLiBs are a promising energy storage technology anticipated to offer high energy and power densities while ensuring safety during operation by replacing flammable liquid electrolytes with nonflammable solid electrolytes (SEs). [4] Understanding the degradation of the SE-electrodes' interfaces during cycling is currently one of the most challenging obstacles in the development of SLiBs. Here, we introduce *operando* X-ray photoelectron spectroscopy as an approach for real-time monitoring of the chemical interfacial reactions between different components of the composite electrodes. In the presented case study, amorphous $(Li_2S)_3$-P_2S_5 (LPS) [5] is used as SE, due to its high room temperature ionic conductivity. *Post-mortem* XPS measurement is compared here to *operando* XPS by investigating the interface reactivity and the electrochemical activity of the working electrode (WE) composed of a mixture of $Li_4Ti_5O_{12}$ (LTO) and LPS.

XPS operando cell

A dedicated electrochemical cell was developed for the purpose of *operando* XPS. [3] It is capable of maintaining high mechanical pressure and offers reliable electrochemistry and versatility in terms of materials' application. [3] Mechanical pressure during operation is crucial for reliable cell performance of bulk-type SLiB. Maintaining the pressure during XPS measurement is a particular challenge in the cell design, since the photoelectrons' pathway cannot be blocked.

We designed an *operando* XPS SLiB cell as shown in Figure 1. The implementation of the slit in the top cell lid ③ ensures maximum mechanical integrity of the structure whilst allowing the penetration of the X-rays with an incidence angle of 30°. On the surface of the WE, the interfaces between LTO, LPS, and vapor-grown carbon fibers (VGCF) particles are exposed to X-rays. The tri-layered cell stack ⑦ is fabricated inside the polyoxymethylene (POM) ring ② and subsequently transferred to the *operando* XPS cell base ①, thus eliminating any mechanical stress which could be induced if the cell stack would had to be removed from the mold. The top lid is pressed on the cell stack by screws ⑤ and contacted to the positive electrode ⑥. The screws were electrically insulated from the lid by a plastic washer ④ to avoid any internal short-circuit.

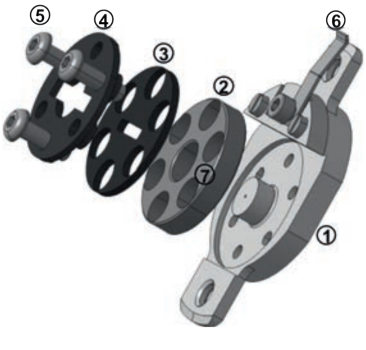


Figure 1. *Operando XPS cell design for an all-solid-state battery. Reproduced from Reference [3] with permission from The Royal Society of Chemistry.*

Post-mortem XPS measurement at the LTO-LPS interface

During the first lithiation, as depicted in Figure 2A, we observed from the Ti 2p core level spectra the reduction of Ti^{4+} (blue component at 459.0 eV) to Ti^{3+} (green component at 456.3 eV). [5] The LPS SE is characterized by the S 2p and P 2p core levels. The major contribution to the spectra comes from the typical Li-S-P bonds as in Li_3PS_4 (161.7 eV for S 2p and 132.0 eV for P 2p). Minor impurity in form of polysulfides (S-S_x, green component in S 2p core level spectra, at 163 eV) can also be observed. Besides the LTO activity, no electrolyte decomposition was detected in the S 2p or P 2p spectra. This finding is not in line with previous theoretical calculation predicting LPS reduction to occur at 1.7 V vs. Li^+/Li to form Li_2S. [6] However, as shown in Figure 2B, the C 1s spectrum in the lithiated WE presents a significant increase of the carbonate species on the surface. At the same time, the C 1s core level signal from the conductive carbon additive (C-C) decreases drastically. This suggests the formation of Li_2CO_3 on the electrode surface. The formation of Li_2CO_3 is surprising in this kind of electrodes and can be attributed to the reactivity of Li_2S. In particular, the surface of Li_2S is highly reactive and prone to the conversion to Li_2O and Li_2CO_3. [7]

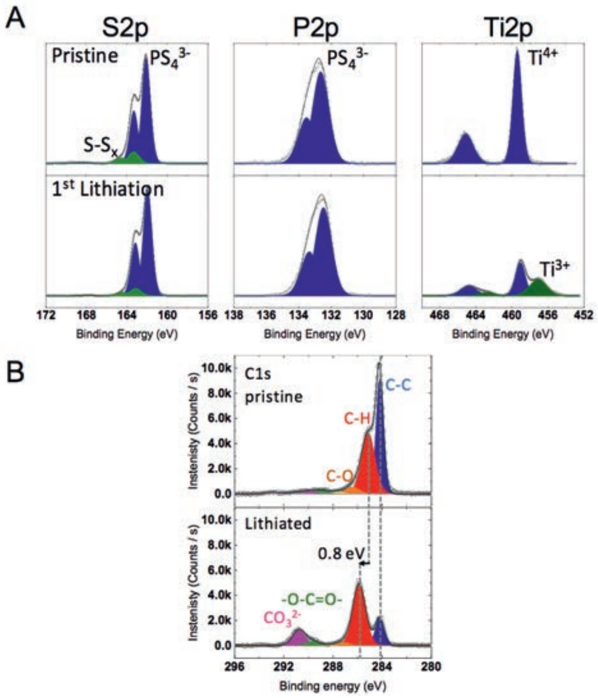


Figure 2. *(A) S 2p, C 1s, and Ti 2p XPS core levels acquired on pristine (top) and lithiated (bottom) LTO-LPS composite electrode. (B) C 1s core level spectra acquired on pristine (top) and lithiated (bottom) LTO-LPS composite electrode.*

Operando XPS at the LTO-LPS interface

Using *operando* XPS, cycling of SLiBs under ultra-high vacuum (UHV) conditions can minimize surface contamination and additional reactivity. LPS reduction is readily observed below 1.1 V cell voltage (1.7 V vs. Li^+/Li). In Figure 3, the component in orange located at 1.3 eV lower than the main component corresponds well to the BE to Li_2S, as reported in literature. [8] The formation of Li_2S appears to be irreversible within the cycling window of LTO (0.4–1.4 V cell voltage). These findings confirm the previous prediction of the anodic stability of LPS and highlight the importance of the *operando* XPS experiment with respect to *post-mortem* XPS to capture real-time electrode-electrolyte reactivity in SLiB.

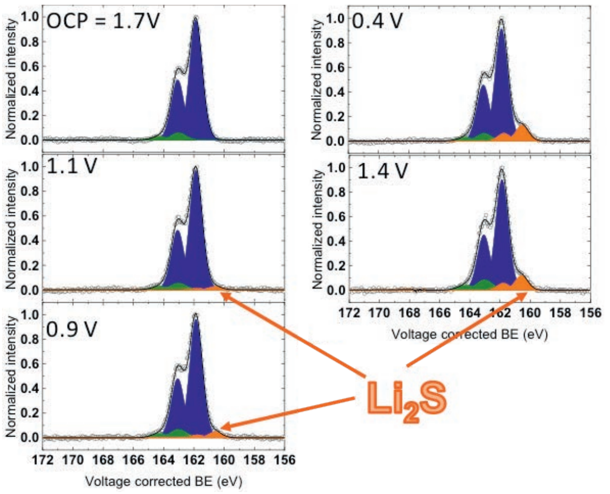


Figure 3. *Operando XPS measurement of the S 2p core level spectra at different cell voltages acquired on LTO-LPS WE. The voltages are measured against an $InLi_x$ counter electrode, which has a stable potential of 0.62 mV vs. Li^+/Li. [9]*

Raman spectra of cathode materials during cycling

Raman spectroscopy is a highly versatile technique widely used to characterize electrode materials via their inherent vibrations. Briefly, a monochromatic laser is shined upon the sample and the light scattered back contains inherent vibrations frequencies from the sample. A detailed analysis of the Raman spectra (Figure 4a) might reveal the lattice symmetries, atomic coordination geometries, oxidation states, the coexistence of several phases, the presence of defects, impurities, strains, and other phenomena relevant for the characterization of electrode materials and their degradation mechanisms. [10, 11]

Raman spectroscopy is particularly suited for studying materials within their working environment and while they operate. This is because

- the laser probe is potentially non-destructive,
- the spectrometer coupled to an optical microscope can resolve single oxide secondary particles in the composite electrode,
- the visible frequency of the laser enables the use of common transparent window materials for building *in situ* electrochemical cells,
- the spectrum acquisition time scales (in the order of seconds) available in standard instrumentation enable sufficient time resolution, and
- strong infrared absorbers such as electrolyte solvents feature moderate Raman signals and thus enable discerning vibrations from inorganic oxide particles.

Raman operando cell

The key challenge in the design of an *in situ/operando* cell for Raman spectroscopy is to incorporate an optically transparent window while keeping optimal electrochemical performance of the cell. The task is full of compromises that have been historically approached with diverse cell designs.

We have recently developed a custom-made coin-cell type configuration (Figure 4b) and we had identified many key parameters for achieving optimum performance. We use a 100 µm-thin microscope glass as window material in order to minimize the working distance and maximize the intensity of the Raman signals. Polytetrafluoroethylene (PTFE) O-rings and high-density polyethylene (HDPE) rings (Figure 4b, parts #1 and #7) are used to guarantee the cell remains gas and electrolyte tight during the experiment. More details about the cell design and the spectrum recording conditions can be found in reference [12].

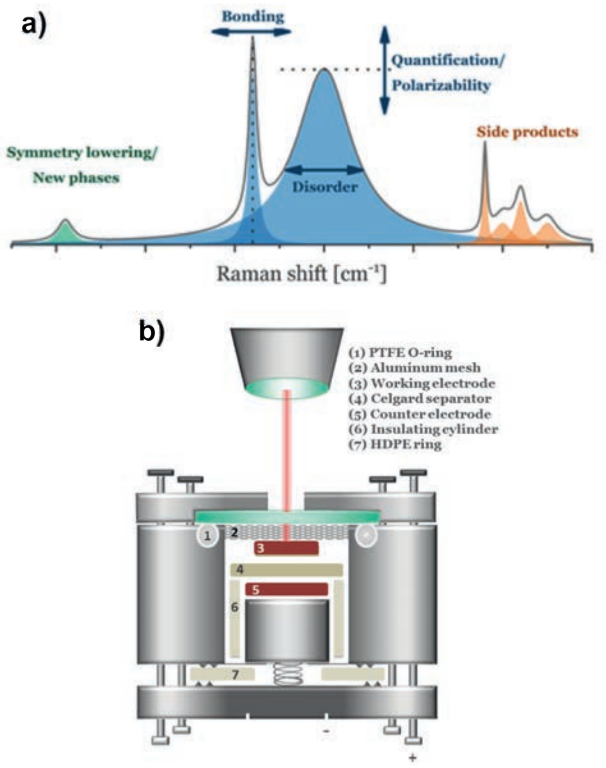


Figure 4. *(a) Reading a spectrum: representation of the information that can be interpreted from a Raman spectrum. (b) Recording spectra: our custom-made Raman-electrochemical operando cell, used to record the Raman spectrum of electrode materials while they cycle. Reproduced from Reference [12] under the Creative Commons Attribution License (CC BY).*

Operando Raman on high voltage NCA cathode

We have applied the developed Raman cell to record the *operando* Raman spectra of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA), one of the most attractive Li-ion cathode materials, already used in Tesla's EVs. [13] Figure 5a shows the evolution of the two main Raman active bands of NCA, i.e., the E_g and A_{1g} vibrational modes. The bands clearly feature a cycling-dependent evolution: they intensify on delithiation and return to their initially broad, weak profiles on relithiation.

A set of new bands above 600 cm^{-1} are resolved when the lithium content per formula unit drops below 0.6. These bands have been observed for the first time thanks to the improved signal-to-noise ratio enabled by the advanced cell design. DFT phonon calculations assign the new bands to new lattice symmetries introduced by lithium vacancies. The appearance of the bands coincides with the redox process observed at 3.73 V vs. Li^+/Li. Li-vacancy ordering was believed to occur in NCA in analogy to $LiNiO_2$ but was not observed using diffraction techniques. Raman spectroscopy has provided the first experimental evidence of configurational transitions between distinct Li orderings in NCA. [14]

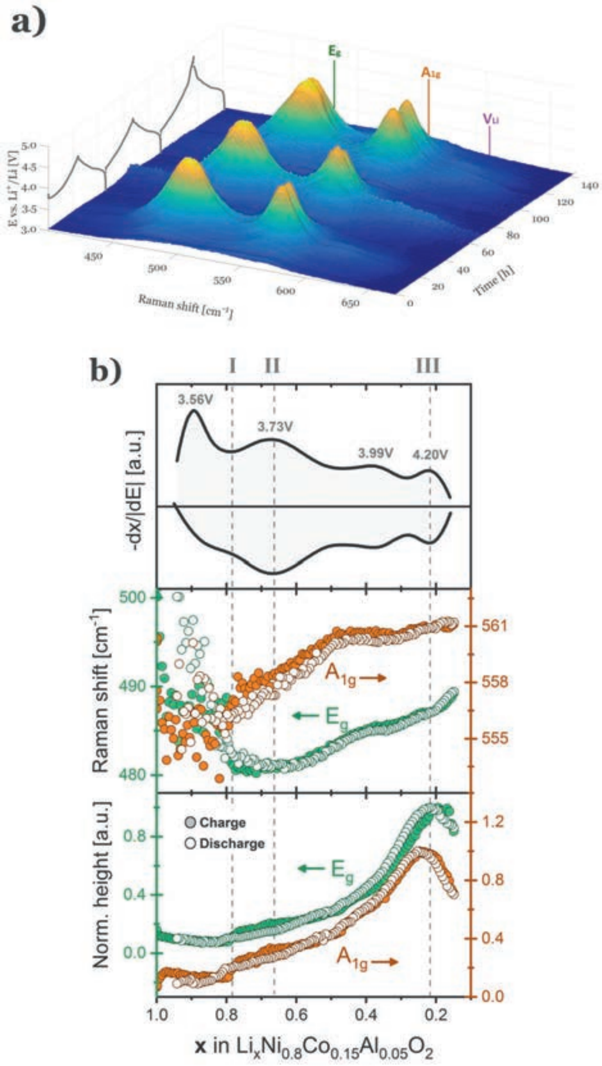


Figure 5. *(a) Three-dimensional map of the evolution of the Raman bands of NCA during three full cycles. The constant-current cycling profile used in the experiment is inserted in the left panel (3.0 -> 4.3 V vs. Li^+/Li, 10 mA/g, electrolyte: 1 M $LiClO_4$ in EC : DMC wt. 1 : 1). The positions of the main Raman bands (E_g, A_{1g} and lithium vacancy V_{Li}) are indicated in the back panel. (b) Differential charge plot of NCA together with the fitted peak positions and heights of the E_g and A_{1g} bands as a function of lithium content during the first galvanostatic cycle. Each data point results from the deconvolution of a single spectrum. Reproduced from Reference [12] under the Creative Commons Attribution License (CCBY).*

In addition, we have developed data-intensive analysis tools for automated treating and fitting of all spectra. Figure 5b shows the band positions and intensities retrieved by deconvoluting the spectral envelope into Lorentz-type peak profiles. The fitted parameters show remarkable reversibility on dis-/charge and clearly correlate to the redox activity of NCA.

The trends in Figure 5b are divided into three different stages indicating processes dependent on the lithium content x in the oxide. Early at x ~ 0.8 (Stage I), a steep increase in band intensities occurs, which coincides with the commonly reported dissolution of a native $=CO_3$ layer at the surface of NCA particles (observed at ~ 3.78 V vs. Li^+/Li). Later, at x ~ 0.67 (Stage II) the U-shaped trend of the E_g band positions reaches a minimum. DFT phonon calculations suggest the E_g band minimum to be also related to the formation of a local lithium vacancy ordering. Approaching the end of charge, at x ~ 0.2 (Stage III), the band intensities of both bands reach their maxima, which coincides with oxygen gas release from NCA. The evidence suggests that the redox process above 4.2 V vs. Li^+/Li originates from an $O^{2-} \rightarrow O^-/O$ oxidation, resulting ultimately in oxygen loss from the lattice. [14]

Conclusion

In conclusion, we describe an advanced development related to *operando* XPS measurements using the example of SLiBs and *operando* Raman using the example of a high voltage cathode material in a carbonate-based electrolyte. Both *operando* XPS and Raman cells employed here offer insights into the real-time evolution of

- the chemical states of the elements at the SE–electrode interface and configurational phase transitions, and
- of the electronic structure changes, respectively.

Those results highlight the importance of *operando* XPS and Raman experiments with respect to the traditional *post-mortem* ones. Combining those two techniques offers for any relevant material in-depth understanding of its interfacial and near-to-surface properties.

Contact

For further information please contact Prof. Dr. Petr Novák.

petr.novak@psi.ch

Contributors

The contributors of the described research are E. Flores, X. Wu, M. Mirolo, C. Villevieille, E.J. Berg, and M. El Kazzi.

Acknowledgement

E. Flores and E.J. Berg acknowledge the Swiss National Science Foundation (SNSF) grant No. 160540 under the Ambizione Energy funding scheme. X. Wu and C. Villevieille gratefully acknowledge CCEM project No. 911 for the funding.

References

[1] F. Lin, Y. Liu, X. Yu, L. Cheng, A. Singer, O.G. Shpyrko, H.L. Xin, N. Tamura, C. Tian, T.-C. Weng, X.-Q. Yang, Y.S. Meng, D. Nordlund, W. Yang, M.M. Doeff, *Chemical Reviews* **117,** 13123–13186 (2017).

[2] M. Gauthier, T.J. Carney, A. Grimaud, L. Giordano, N. Pour, H.-H. Chang, D.P. Fenning, S.F. Lux, O. Paschos, C. Bauer, F. Maglia, S. Lupart, P. Lamp, Y. Shao-Horn, *The Journal of Physical Chemistry Letters* **6**, 4653–4672 (2015).

[3] X. Wu, C. Villevieille, P. Novák, M. El Kazzi, *Phys Chem Chem Phys* **20**, 11123–11129 (2018).

[4] Y. Kato, S. Hori, T. Saito, K. Suzuki, M. Hirayama, A. Mitsui, M. Yonemura, H. Iba, R. Kanno, *Nat Energy* **1**, 16030 (2016).

[5] X. Wu, M. El Kazzi, C. Villevieille, *J. Electroceramics* **38**, 207–214 (2017).

[6] Y. Zhu, X. He, Y. Mo, *ACS Appl. Mater. Interfaces* **7**, 23685–23693 (2015).

[7] Y. Jung, B. Kang, *Physical Chemistry Chemical Physics* **18**, 21500–21507 (2016).

[8] S. Wenzel, S. Randau, T. Leichtweiß, D.A. Weber, J. Sann, W.G. Zeier, J. Janek, *Chemistry of Materials* **28**, 2400–2407 (2016).

[9] K. Takada, N. Aotani, K. Iwamoto, S. Kondo, *Solid State Ionics* **86**, 877–882 (1996).

[10] W.G. Fateley, N.T. McDevitt, F.F. Bentley, *Applied Spectroscopy* **25**, 155–173 (1971).

[11] R. Baddour-Hadjean, J.-P. Pereira-Ramos, *Chemical Reviews* **110**, 1278–1319 (2010).

[12] E. Flores, P. Novák, E.J. Berg, *Frontiers in Energy Research* **6**, (2018).

[13] G.E. Blomgren, *Journal of The Electrochemical Society* **164**, A5019–A5025 (2017).

[14] E. Flores, N. Vonrüti, P. Novák, U. Aschauer, E.J. Berg, *Chemistry of Materials* **30**, 4694–4703 (2018).

Membranes for redox flow batteries

Redox flow batteries are well suited to provide grid-scale energy storage solutions, for instance to support power generation from wind and solar farms. The technology is in the demonstration and early deployment phase and requires further improvements in performance and reduction of cost to be competitive in the energy storage market. The ion exchange membrane is a key component in flow batteries, as it influences cell performance and accounts for almost half of the hardware cost. Therefore, improvements in membrane technology are imperative to improve the economic viability of flow batteries.

A redox flow battery (RFB) is an electrochemical energy storage device that comprises an electrochemical conversion device, consisting of a cell stack or an array thereof, and external tanks to store the electrolytes containing redox-active species. Those compounds in the positive and negative electrolyte, respectively, can be reversibly oxidized and reduced. An RFB can thus be charged and discharged and used for energy storage applications. Owing to the design principle consisting of an electrochemical reactor separated from the electrolyte storage units, the power and energy rating of the battery can be independently scaled.

All-vanadium redox flow battery

Flow batteries with different chemistries have been commercialized, such as the Fe-Cr, Zn-Br_2 and H_2-Br_2 battery. [1, 2] The all-vanadium redox flow battery (VRFB) is technically the most advanced system. It uses vanadium-ions in different oxidation states as redox-active species in both electrolytes (Figure 1).

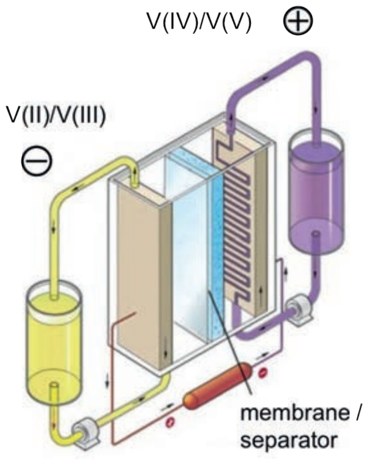


Figure 1. Schematic of an all-vanadium redox flow battery comprising electrolyte tanks with dissolved vanadium ions in different oxidation state and an electrochemical conversion device to perform charge and discharge reactions. (Source: Sandia National Laboratories, 2014).

The projects at PSI over the past 5 years have focused on this type of RFB. In addition, the development of flow battery chemistries based on organic redox couples has received growing interest over the past decade (e.g., the methylviologen/TEMPO combination), yet these systems are still in the early development stage.

The vanadium redox flow battery employs vanadium-ions in the oxidation states II, III, IV and V in the positive and negative electrolyte, respectively. The ions in the positive electrolyte are present as oxo-ions: VO^{2+} for V(IV) and VO_2^+ for V(V). The ions are most commonly dissolved as (bi)sulfate at a concentration of 1–2 M in a sulfuric acid solution of 2–4 M. The charge and discharge reactions at the two electrodes are as follows:

positive electrode:

$$\mathrm{VO_2^+} + 2\mathrm{H^+} + \mathrm{e^-} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} \mathrm{VO^{2+}} + \mathrm{H_2O}$$

negative electrode:

$$\mathrm{V^{2+}} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} \mathrm{V^{3+}} + \mathrm{e^-}$$

The electrochemical reactions take place at the surface of carbon felt electrodes separated by an ion exchange membrane in the cells of the stack. The ion exchange membrane is a dense polymer film that separates the two cell compartments physically, while it allows the passage of certain ions. Both cation and anion exchange membranes are used in VRFBs. Cation exchange membranes (CEMs) offer low resistance, because they take advantage of the high mobility of the acid protons, yet they also suffer from high crossover of vanadium-ions, as they are cations and therefore easily exchanged into the ionomer. This leads to poor coulombic efficiency of the cell. Anion exchange membranes (AEMs) on the other hand offer superior vanadium barrier properties, but their conductivity is lower, which leads to a low voltaic efficiency at high current densities of > 0.2 A/cm^2. In any case, the exclusion of coions («Donnan exclusion») is not complete at the ionic strengths used in the electrolytes (Figure 2). [3]

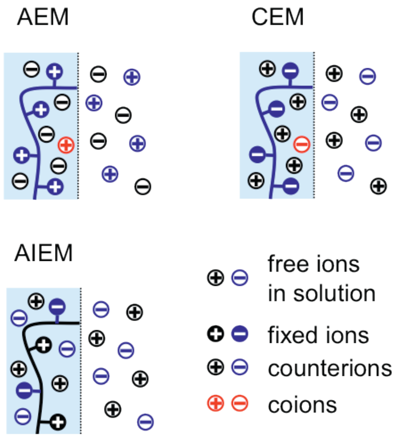


Figure 2. Schematic representation of the structure of an anion exchange membrane (AEM), a cation exchange membrane (CEM), and an amphoteric ion exchange membrane (AIEM).

Amphoteric membranes

With the aim of combining the favorable properties of a CEM and an AEM, we have developed an amphoteric ion exchange membrane (AIEM), which contains both fixed positive and negative charges (Figure 3). [4] The results indicate that this proves to be possible (Table 1): the cell resistance R_Ω using the AIEM is about halfway between that using Nafion® 212, a standard CEM, and FAP-450, a widely used AEM from Fumatech (Germany), while the vanadium crossover i_x is as low as that of the AEM. The tradeoff between resistance and crossover is characterized by the selectivity parameter α, which is higher in case of the AIEM compared to the other, commercial membranes.

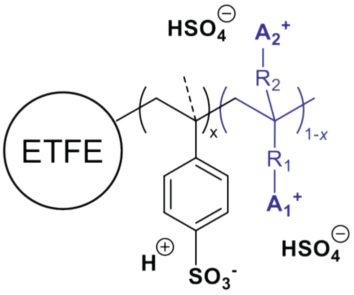


Figure 3. Structure of the radiation grafted PSI amphoteric ion exchange membrane. An ETFE film of 25 µm is used as base polymer. Sulfonated styrene units provide cation exchange sites, the anion exchange sites are provided by the comonomer units.

Property	Unit	PSI grafted	N212	FAP-450
Membrane Type →		AIEM	CEM	AEM
δ	µm	44	57	59
R_Ω	Ω·cm²	0.65	0.45	0.98
i_x	mA·cm⁻²	0.20	0.80	0.19
α	-	200	70	140
J_V	µL·h⁻¹·cm⁻²	-0.03	21	-38

Table 1. Membrane properties relevant to the use in an all-vanadium redox flow battery. δ: thickness; R_Ω: ohmic resistance measured in the cell; i_x: VO^{2+} crossover measured ex situ in a diffusion cell, expressed as current density equivalent; α: selectivity parameter $\alpha = (R \cdot T) / (F \cdot R_\Omega \cdot i_x)$ [5], where T is taken as 298 K; J_V: net vanadium flux across the membrane (+ value: towards positive electrolyte, – value: towards negative electrolyte).

The AIEM developed at PSI is prepared by pre-irradiation induced graft copolymerization («radiation grafting») of radically polymerizable monomers onto an ethylene-tetrafluoroethylene (ETFE) film of 25 µm thickness. The styrene based monomer unit yields, after sulfonation, cation exchange sites, the comonomer unit provides anion exchange sites. [4]

Tackling capacity fading

In the context of the use of ion exchange membranes as polymer electrolyte in VRFBs, it is important to understand the transport properties of the different species: vanadium-ions in the 4 different oxidation states, background electrolyte ions, and water. Transport is caused by various driving forces, i.e., concentration, pressure and potential gradients, and transport coefficients are strongly concentration dependent as well as coupled. [3] For instance, the movement of water is coupled to the movement of ions (electroosmosis). The voltage drop ΔU across the membrane caused by the finite mobility of ions is given by Ohm's law:

$$\Delta U = R_\Omega \cdot i \qquad (1)$$

where R_Ω is the area resistance of the membrane and i the current density. Minimizing ohmic losses equates to increasing the mobility of ions in the membrane. This means, however, that also the passage of unwanted ions, i.e., V-ions, is facilitated. The diffusive flux J_{diff} of a species / ion across the membrane, according to Fick's law, is proportional to its concentration difference Δc between the positive and negative side:

$$J_{\text{diff}} \propto \Delta c \qquad (2)$$

The migrative flux J_{migr} only applies to ions. It is proportional to the charge of the ion z_i and the current density i:

$$J_{\text{migr}} \propto z_i \cdot i \qquad (3)$$

At low current densities, the transport of vanadium-ions across the membrane is dominated by diffusion. Differences in the diffusivities of the different vanadium ions leads to the net transport of vanadium across the membrane, which causes capacity fading of the battery owing to the imbalance of vanadium content between the positive and negative electrolyte. This is exactly what is observed for CEMs and AEMs: for CEMs net vanadium flux J_V from the negative to the positive electrolyte is observed (Table 1). This is a consequence of the higher diffusivities of V^{2+} and V^{3+} compared to VO^{2+} and VO_2^+, leading to a net flux of vanadium-ions towards the positive electrolyte. In contrast, the net vanadium flux across an AEM is directed towards the negative side. Here the uptake of the higher charged vanadium species V^{2+} and V^{3+} is disfavored due to a stronger Donnan exclusion compared to VO^{2+} and VO_2^+. Therefore, the use of a CEM or an AEM leads to the buildup of volumetric and hence capacitive imbalance between the negative and positive electrolyte. To recover the capacity, electrolyte rebalancing is required. With an AIEM, which contains both fixed anionic and cationic groups, vanadium transport through the membrane is much more balanced (cf. net vanadium flux J_V in Table 1). Electrolyte imbalance is therefore minimized over extended charge-discharge cycles and capacity fading drastically reduced (Figure 4).

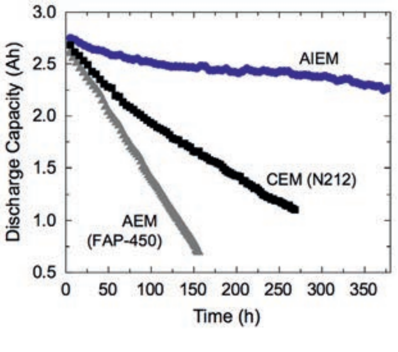


Figure 4. Capacity fading over 80 charge-discharge cycles at a current density of 40 mA·cm⁻² using a commercial AEM and CEM and an AIEM developed at PSI. [6]

Bilayer architecture

In an AIEM, the positive and negative fixed charges are located in close proximity on the copolymer chain. This has been found to lead to effects of «charge cancellation», i.e., the measured cation and anion ion exchange capacity, respectively, is lower than the theoretically expected value. [7] This indicates that not all the charge carriers in the membrane are effectively contributing to the conductivity of the material. Therefore, we have adopted an alternative membrane architecture, where individual layers of a cation exchange polymer and an anion exchange polymer are combined in the form of a bilayer membrane (Figure 5).

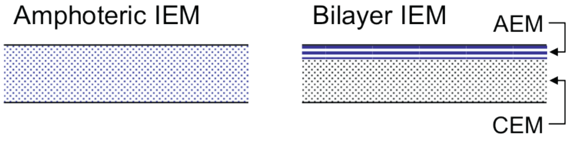


Figure 5. *Architectures of ion exchange membranes containing both cation and anion exchange functionalities.*

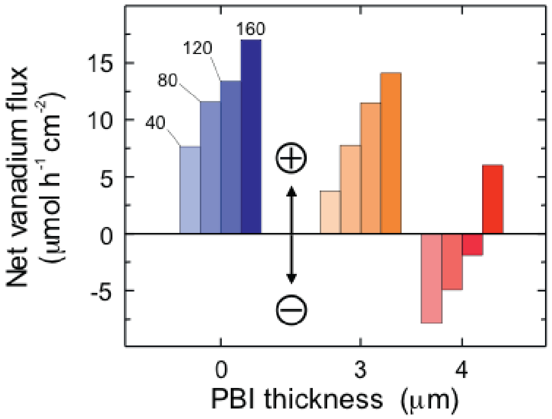


Figure 6. *Influence of PBI layer thickness on the net vanadium flux across the membrane as a function of current density (from 40 to 160 mA·cm^{-2}). [8]*

As a model system, Nafion® 212 (N212) with a thickness of ~ 55 µm is chosen as the cation exchange ionomer, and polybenzimidazole (PBI) as anion exchange polymer. [9] Neat PBI is uncharged, yet exposure of the polymer to an acid, as in our case, leads to acid uptake and protonation of the benzimidazole units, yielding fixed cationic charges. The thickness of the PBI layer was in the range of a few micrometers. Figure 6 shows the influence of the presence of a PBI layer on N212 and its thickness on the net vanadium crossover through the membrane. With neat N212, a pronounced net crossover from the negative to the positive side is observed (as already highlighted above). Moreover, the flux towards the positive electrolyte increases with increasing current density. This is a consequence of the migrative flux term (Equation 3), which increases with current density. Introducing a thin layer of PBI leads to a shift of the net vanadium flux towards the negative side. At a PBI film thickness of 4 µm the flux at low current density is reversed towards the negative side, as in a neat AEM (cf. Table 1). At a current density of ~ 130 mA·cm^{-2}, the net flux switches to the positive side. Hence, at this current density, the vanadium transport rates are balanced and the capacity fading thus minimized. The ohmic cell resistance with N212 is measured at 0.45 Ω·cm^{2}, and the addition of a PBI layer with a thickness of 3 and 4 µm leads to an increase of the ohmic resistance to ~ 0.7 Ω·cm^{2}. For comparison, the ohmic resistance of the FAP-450 AEM from Fumatech is 0.98 Ω·cm^{2}.

The combination of an AEM and a CEM in the form of a bilayer membrane therefore represents a straightforward approach to adjust the transport properties of vanadium in the membrane to target balanced flux conditions. Further work is aimed at using alternative materials to N212 to lower the cost of the bilayer membrane.

Conclusion

The ion exchange membrane used in all-vanadium redox flow batteries as electrolyte is a key component regarding performance and cost. Membrane research and development is aimed at minimizing the ohmic resistance of the material concurrently with maximizing the blockage of the transfer of vanadium ions. The research at PSI aims at accomplishing this with two approaches using low-cost membrane preparation methods. In the first approach, amphoteric membranes have been designed, which were shown to exhibit higher ion transport selectivity than pure anion or cation exchange membranes. In the second approach, anion and cation exchange polymer are combined in a bilayer membrane architecture. This allows the tuning of net vanadium transport across the membrane in straightforward manner via the thickness of the two layers. Thus, capacity fading can be minimized.

Acknowledgement

Research Funding by the Swiss Federal Office of Energy (contract no. SI/501421-01) and Bridge Discovery, a joint program of the Swiss National Science Foundation and Innosuisse (project no. 176653), is gratefully acknowledged. We thank Aaron Schneider for technical support.

Contact

For further information, please contact Dr. Lorenz Gubler, Head of Research Group *Membranes & Electrochemical Cells.*

lorenz.gubler@psi.ch

Contributors

The contributors of the described research are F.J. Oldenburg and D. Vonlanthen.

References

[1] J. Noack, N. Roznyatovskaya, T. Herr, P. Fischer, *Angew. Chem. Int. Ed. Engl.* **54**, 9776–809 (2015).
[2] B.R. Chalamala, T. Soundappan, G.R. Fisher, M.R. Anstey, V.V. Viswanathan, M.L. Perry, *Proceedings of the IEEE 102*, 976–999 (2014).
[3] L. Gubler, *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering (2018)*. DOI: 10.1016/B978-0-12-409547-2.14285-4
[4] F.J. Oldenburg, A. Albert, L. Gubler, *Patent Application No. 2018P11960EP*, Paul Scherrer Institut (2018).
[5] W. Xie, R.M. Darling, M.L. Perry, *J. Electrochem. Soc.* **163**, A5084–A5089 (2016).
[6] F.J. Oldenburg, T.J. Schmidt, L. Gubler, *J. Power Sources* **368**, 68–72 (2017).
[7] O. Nibel, T.J. Schmidt, L. Gubler, *J. Electrochem. Soc.* **163**, A2563–A2570 (2016).
[8] F.J. Oldenburg, E. Nilsson, T.J. Schmidt, L. Gubler, submitted.
[9] L. Gubler, A. Arndt, F.J. Oldenburg, *Patent Application No. 2018P00973EP01*, Paul Scherrer Institut (2018).

Optimizing porous materials for fuel cells and electrolysers

The use of hydrogen as an energy vector for renewable primary energy relies largely also on economic factors. For automotive fuel cells, the key number is the cost per peak power, which can be reduced either by lowering the cost per cell area (e.g. using lower catalyst loadings) or by increasing the maximum power density. For electrolysers, operation costs are dominant, and they can be reduced by improving the efficiency. In all these cases, improvement requires a better understanding of the losses related to mass transport, and the design of new strategies to mitigate them. Advanced porous materials play a key role in achieving these goals.

Porous materials in electrochemical energy converters (fuel cells and electrolysers) play a key role in determining the performance and, subsequently, the viability of a device for a given application. As they cumulate several functions, such as the supply of reactants, the removal of products, and the thermal and electrical conduction, there is neither a single parameter nor an easy to calculate «figure of merit» to determine the suitability of a material. This is particularly true in the presence of two-phase flow, which strongly increases the complexity of transport phenomena.

In fuel cells, water occupying pores of the gas diffusion layers (GDLs) is known to reduce the oxygen diffusivity and to induce mass transport losses. The topic of transport losses in electrolysers is much less explored, and the mechanisms leading to transport losses are not as straightforward. In both cases, a material with a homogeneous distribution of parameters is probably far from optimal: due to the different requirements mentioned above, dedicating separate sections of the material to separate functions can result in a significant improvement. Here, we will summarize our recent research in this field, using modifications of either the structure or the wetting characteristics on the way to realize optimized porous materials for fuel cell and electrolyser applications.

Playing with the structure …

The structure of porous media is of utmost importance to determine the distribution of water and gas in operation. As shown previously [1], they can, under certain circumstances, be the dominant factor determining whether a given pore will be invaded with water. Hydrophilic pores will not spontaneously wick water if the gas/water interface needs to pass through a constriction inducing a capillary barrier. Reversely, large pores can provide a very effective pathway for water removal, even if they are hydrophobic.

In this context, several researchers have explored the possibility of modifying the structure of fuel cell gas diffusion layers by laser perforation in order to provide specific pathways for water removal. [2] A known problem is the heat spread around the perforation, resulting in the removal of hydrophobic coating around the holes, rendering the adjacent region prone to flooding. A solution to this problem, as illustrated in Figure 1, is to reverse the order of processing steps. The material is first perforated, and the hydrophobic treatment is subsequently applied. The SEM-EDX analysis shown in the bottom part of Figure 1 clearly shows that the fluorine (only present in the FEP coating) is distributed until the edge of the perforation.

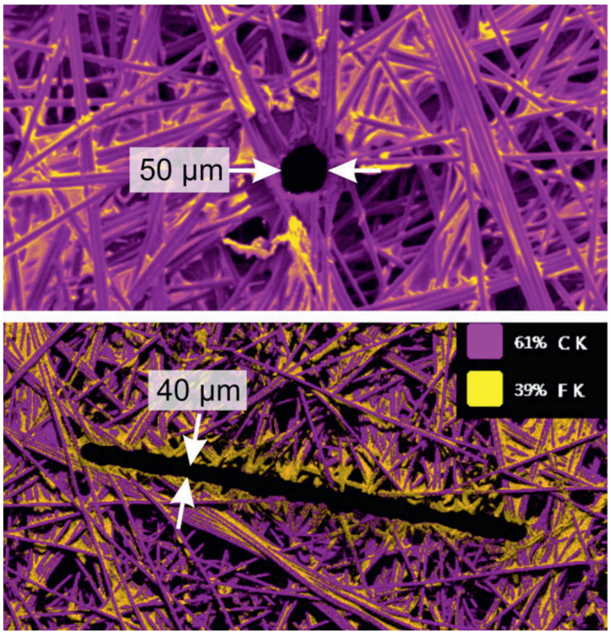


Figure 1. *Laser perforated water pathways in fuel cell GDL materials (Toray TGP-060). Top: circular hole cut into the material previously hydrophobized with PTFE (SEM image). Bottom: Elongated hole cut on the bare material, which was subsequently hydrophobized with FEP (SEM-EDX image).*

Furthermore, the use of elongated slits instead of circular holes as published elsewhere is expected to improve not only the water transport through the material, but also the lateral water transport, e.g. to remove the water from under the fuel cell lands. While the topic of mass transport losses and their relation to two-phase flow is widely documented for fuel cells, this field remains largely unexplored for electrolysers. The reason to this discrepancy can be found in the consequences that mass transport overpotentials have for these different devices. For fuel cells operating at around 0.7 V, a loss of 100 mV is a matter of life and death. For electrolysers operating at around 2 V, the same loss represents an efficiency loss of only 5 %.

Nevertheless, if the application of water electrolysis is to move from the niche market of high value, high purity hydrogen production to mass storage of energy, even these limited losses have to be tackled. In previous neutron imaging studies [3], we observed that the gas produced by the electrolysis reaction does not disrupt the water supply, even at high current densities. On the other hand, loss breakdown studies [4] indicate a significant mass transport loss term. A likely hypothesis is that these mass transport limitations are not related to the bulk of the PTL, but to the interplay between the catalyst layer and the adjacent PTL structure. To further understand this, the structure of electrolyser PTLs was analysed using X-ray tomographyic microscopy (see Figure 3). The obtained 3D structural data was further processed to evaluate the contact area of the PTL structure with the catalyst layer, as a function of the penetration depth of the MEA.

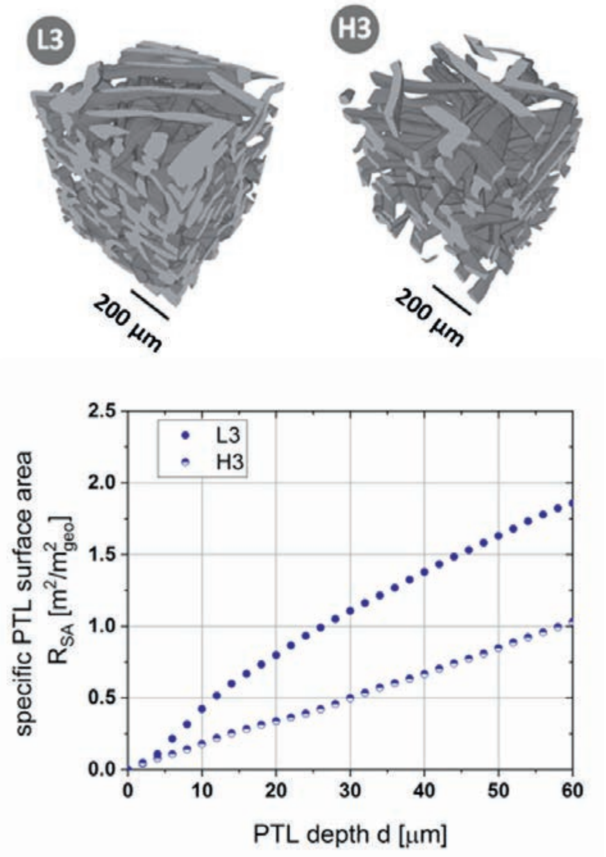


Figure 2. Structure of electrolyser PTLs measured using X-ray tomographic microscopy and computed geometric contact area as a function of the penetration depth of the MEA for two samples with low and high porosity. The «L3» sample has a porosity of 56 % and the «H3« sample a porosity of 75 %.

The results show that a PTL structure with high porosity results in a contact area approximately twice lower than a similar sample with low porosity, which may have an important impact on transport losses. The developed methodology and the corresponding findings are currently being used to develop advanced PTL structures in order to optimize the mass transport at the PTL–catalyst interface.

... and with the surface properties

While structural modifications can provide very effective pathways for water in fuel cells, using local modifications of the contact angle to the same purpose [5] allow a higher design flexibility – as the mechanical integrity of the porous media is not affected, and permits the creation of highly hydrophilic regions which spontaneously wick liquid water. The latter possibility was used in a novel design for evaporative cooling of fuel cells, where water is injected in the anode side through a single channel and is spread over the whole active area with the help of a GDL with patterned wettability. Using this concept, a cooling power as high as 1.7 W/cm^2 was demonstrated [6]. A remaining concern is the risk of either water flooding of the gas channels or gas bubbling into the water supply channel. To elucidate within which range this concept can be used, a setup allowing a precise control of the capillary pressure was designed. The results (see Figure 3) indicate that with the material used (Toray TGP-060), water will invade the gas channels as soon as the capillary pressure is above 0 mbar. On the other hand, gas bubbling in the water supply channel does not occur before the capillary pressure reaches -15 mbar.

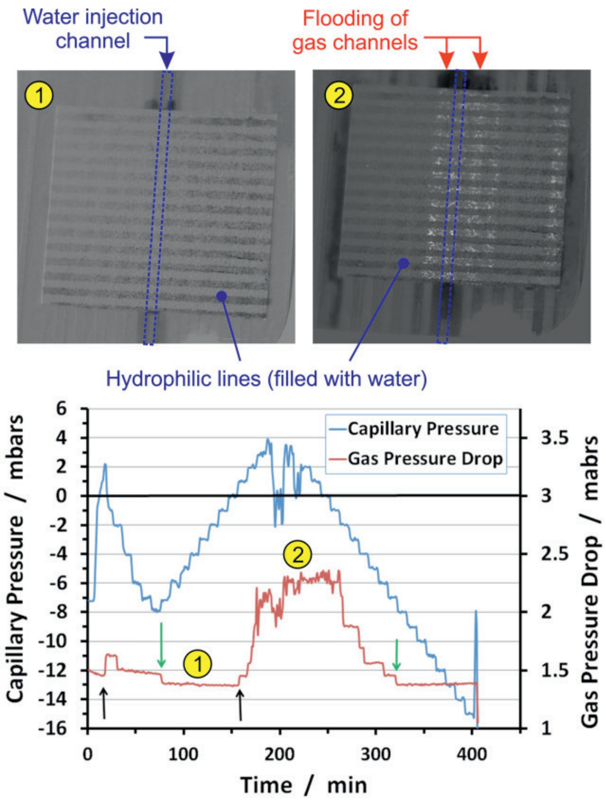


Figure 3. Evaporative cooling using GDLs with patterned wettability: limits of stable range as a function of capillary pressure. The optical images show the water in a stable condition and in a condition of excessive capillary pressure, resulting in flooding of the gas flow channels.

Therefore, the current material offers a stable operation range of 15 mbar for the capillary pressure, within which neither flooding or bubbling occurs. Current research aims at extending this range in order to ease the practical implementation of the concept in technical fuel cells. GDLs with patterned wettability can also be used in the cathode for reducing mass transport losses [7]. In this case, an important point to consider is the interplay between the flow field and pattern designs. A striking example of this is given by the combination of our GDLs with an interdigitated cathode flow field. Such a flow field design is of high interest for reducing mass transport losses, as the transport of oxygen to the regions under the lands does not rely on diffusion but is assured by convection. However, its application to real fuel cell stacks has been prevented so far by the fact that water tends to accumulate at the end of the inlet channels, inducing not only performance losses but also highly variable pressure drops rendering the parallel stack configuration impossible.

Our results (see Figure 4) combining performance analysis and high resolution neutron imaging demonstrate that GDLs with hydrophilic water pathways create a bypass for water from the inlet to the outlet channels, resulting in a much more stable operation and a constant pressure drop. These very promising results indicate that interdigitated flow fields might, after all, be suitable for fuel cell stack operation.

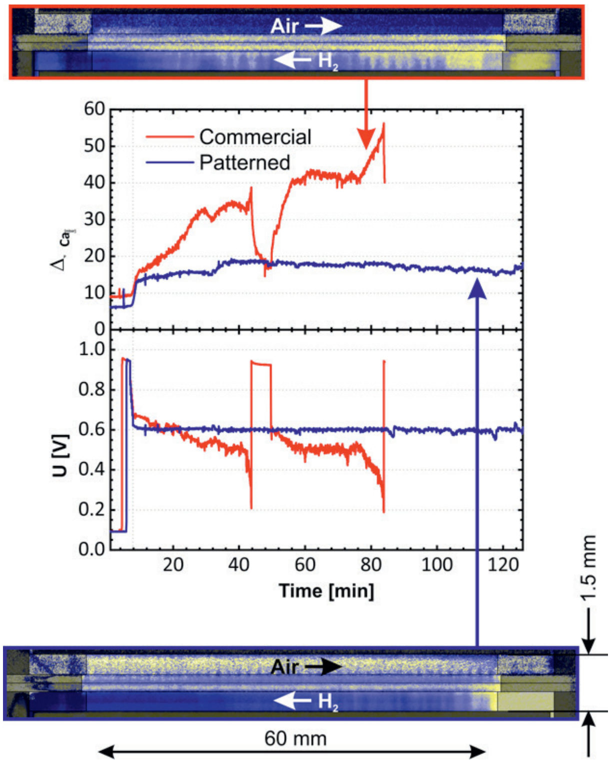


Figure 4. *Comparison of fuel cell operation with an interdigitated flow field with two different materials: one standard commercial hydrophobized GDL and our GDL with patterned wettability (water distribution measured with high resolution neutron imaging at the NEUTRA beam line of PSI). Operation at 1.5 A/cm^2, 70 °C, An / Ca stoichiometric ratios: 2.5 / 1.4, An / Ca humidity: 75 % / 50 %.*

Conclusions

Porous materials do play a crucial role in enabling fuel cell and electrolysers in energy related applications. Our research on optimized materials covers a wide range of topics from structural modifications to local tuning of the contact angle, and from novel cooling designs to performance improvement. Recent results indicate that, although extensive research was done on porous media – in particular for fuel cells –, a significant potential for improvement remains. A key to future research is the consideration of the interaction between the porous layers and the neighbouring components such as the catalyst layer on one side and the flow field on the other side.

Contact

For further information on porous materials for fuel cells or electrolysers, please contact Dr. Pierre Boillat, head of the Neutron Radiography of Electrochemical Systems group or Dr. Felix Büchi, head of the Fuel Cell Systems and Diagnostics group.

pierre.boillat@psi.ch
felix.buechi@psi.ch

Contributors

The contributors for this particular research topic are M. Cochet, C. Csoklich, V. Manzi, T.J. Schmidt, D. Scheuble, T. Schuler, M. Siegwart.

Acknowledgement

We kindly acknowledge the financial support from the Swiss National Science Foundation (grant no. 172474), from the Swiss Federal Office of Energy (contract no. SI/501635-01 and Si/501331-01) and from the Swiss Competence Center for Energy Research *Efficient Technologies and Systems for Mobility* (SCCER Mobility).

References

[1] A. Forner-Cuenca, J. Biesdorf, A. Lamibrac, V. Manzi-Orezzoli, F.N. Büchi, L. Gubler, T.J. Schmidt, P. Boillat, *J. Electrochem. Soc.* **163**, F1038–F1048 (2016).
[2] D. Gerteisen, T. Heilmann, C. Ziegler, *J. Power Sources* **177**, 348–354 (2008).
[3] J. Seweryn, J. Biesdorf, T.J. Schmidt, P. Boillat, *J. Electrochem. Soc.* **163**, F3009–F3011 (2016).
[4] M. Suermann, K. Takanohashi, A. Lamibrac, T.J. Schmidt, F.N. Büchi, *J. Electrochem. Soc.* **164**, F973–F980 (2017).
[5] A. Forner-Cuenca, J. Biesdorf, L. Gubler, P.M. Kristiansen, T.J. Schmidt, P. Boillat, *Adv. Mater.* **27**, 6317–6322 (2015).
[6] M. Cochet, A. Forner-Cuenca, V. Manzi, M. Siegwart, D. Scheuble, P. Boillat, *Fuel Cells* **18**, 619–626 (2018).
[7] A. Forner-Cuenca, J. Biesdorf, V. Manzi-Orezzoli, L. Gubler, T.J. Schmidt, P. Boillat, *J. Electrochem. Soc.* **163**, F1389–F1398 (2016).

Strategies towards efficient anodic electrodes for water electrolyzers

The development of energy storage systems is absolutely necessary to mediate the variable nature of energy generation from renewable resources in the course of supplanting fossil-fuel based energy technologies. Within this scenario, water electrolysis technologies have been at the center of the spotlight owing to their abilities to efficiently convert the renewable energy surplus into hydrogen, considered as the future energy vector. Water electrolyzers are electrochemical energy conversion devices that can produce hydrogen and oxygen from intermittent renewable energy sources. Stored hydrogen can be consequently reconverted to electricity by a fuel cell, or converted into other fuels. Therefore, water electrolyzers appear to be central to the development of a clean, reliable and emissions-free hydrogen economy, particularly for those countries which aim to invest in renewable energies.

The growing needs to store large amounts of energy produced from renewable sources have recently targeted substantial R&D efforts towards water electrolysis technologies. However, while possessing the advantages of flexibility, almost zero emission, and production of high purity gases, water electrolyzers need to be improved in terms of costs, efficiency and durability to become economically attractive. [1, 2]

Water electrolyzers are typically categorized by the basis of operating temperature and electrolyte nature. Low-temperature electrolyzers can be subdivided into polymer electrolyte water electrolyzers (PEWEs), which are based on an acidic, proton-conducting electrolyte, and alkaline water electrolyzers (AWEs).

The main advantages of PEWEs are fast kinetics of the cathodic hydrogen evolution reaction and high-voltage efficiencies at high current densities. Furthermore, they can produce pure hydrogen at relatively high pressures with over 150 bar being demonstrated, offering the possibilities of storing hydrogen directly without or only with small further mechanical compression. [3–6] However, under the typical operation condition of a PEWE, only few electrode materials present adequate stability. Therefore, the anodic and the cathodic reactions are generally catalyzed by noble metal-based catalysts, such as Pt and Ir.

The main advantage of AWEs, based on an alkaline electrolyte, is the possibility of using alternative catalysts to noble metals and cheap flow fields since several materials present adequate stability when exposed to an alkaline environment. [1]

The oxygen evolution reaction (OER) occurring at the surface of the anodic electrode is central to the development of efficient electrolyzers. Unfortunately this reaction is hampered by slow kinetics and significant overpotential losses both in acidic and alkaline environments, even using state-of-the-art (and expensive) materials such as IrO_2. [1, 2] Therefore, the development of cost-effective, robust, and highly active anodic catalysts for PEWEs is currently a great challenge and it has been a large focus of the research community during the last decade. This requires a deep understanding of the electrochemical reaction mechanism and of the key material features that facilitate fast reaction kinetics. In this regards, several candidate materials have been screened, and significant steps have been taken in understanding of the OER mechanism, activity descriptors (i.e., catalyst physico-chemical materials properties central to the OER), and materials design directions.

In the following, the main approaches undertaken by the Electrocatalysis and Interface group of the Electrochemistry laboratory towards the development of highly active and durable OER electrodes, both for application in PEWEs and AEWs, will be described. The Electrocatalysis and Interface group has acquired in the last 5 years a deep understanding of the OER mechanism at the surface of metal oxide catalysts.

Projects on oxygen evolution catalysts have been founded by an Ambizione Swiss National Science Foundation (SNSF) grant, by the Competence Center for Energy and Mobility (CCEM), and the Swiss Competence Center for Energy Research (SCCER) *Heat & Electricity Storage* as well as Swiss Federal Office of Energy.

In the field of water splitting electrocatalysis, our group has become a leader in *operando* techniques, such as *operando* X-ray absorption spectroscopy (XAS) and small angle X-ray scattering (SAXS). [7–15]

Anodic electrodes for PEWEs

It is currently widely accepted that IrO_2 represents the best catalyst in terms of activity and stability for the anodic reaction of PEWEs. However, one of the major cost inhibitors of PEWEs is the use of IrO_2 as an anode material. Iridium is not only an expensive noble metal, but it is also a non-abundant element which prevents its implementation as an anode material in PEWEs on a large scale. [2] Thus, the design of an efficient, stable, and cost-effective anodic electrocatalyst is in demand for the widespread market penetration of PEWEs. However, replacing Ir is very challenging due to the harsh requirements for the anodic electrode of PEWEs, which consist of

- stability in acidic environment at relatively high electrode potentials and
- reasonable oxygen evolution activity.

At the Electrocatalysis and Interface group, we have followed a multi-level approach in order to develop robust and efficient OER catalysts with reduced Ir-content, investigating not only the OER activity and stability, but also the key materials properties through *operando* XAS characterizations to further develop novel catalyst materials. Figure 1 illustrates the three different approaches undertaken for the goal of achieving the best compromise in terms of reduced costs, high activity, and stability for anodic PEWE electrodes.

The first approach consists of investigating the influence of the particle size, morphology, surface structure, and composition on the OER activity and stability of nano-crystalline IrO_2 catalysts with different surface area. In collaboration with the Coperet group at ETH Zürich, we have prepared and fully characterized IrO_2 electrodes with different particle sizes and Brunauer–Emmett–Teller (BET) surface areas ranging from 30 m^2g^{-1} up to 150 m^2g^{-1} (see Figure 2). IrO_2 nanoparticles with the highest surface area also display the highest mass activity ($E = 1.5\ V_{RHE}$ at 10 Ag^{-1}). [14] The high OER activity was correlated not only to the catalyst surface area but also to the presence of an initial iridium hydroxide layer. For the highest surface area sample, *operando* XAS shows that the initial fraction of Ir^{3+}, which is associated with the hydroxide layer, is reversibly converted to Ir^{4+}-oxide species as the OER proceeds. [14] Unfortunately, IrO_2 nanoparticles suffer from poor stability under OER conditions. Therefore, we have oriented our research towards other catalyst systems still containing reduced Ir-content.

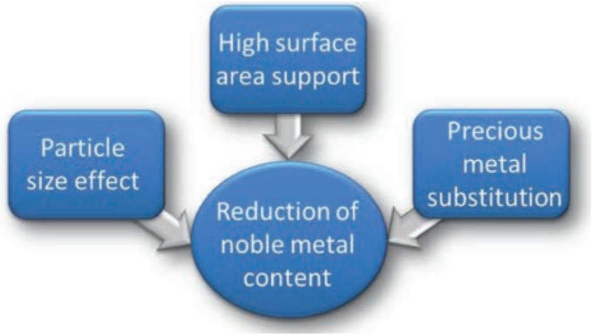


Figure 1. *Sketch representing the three main approaches undertaken by the Electrocatalysts and Interface group to develop cost effective, OER active and, stable anodic catalysts for PEWEs with a reduced noble metal content (mostly Ir) compared to state-of-the-art anodic electrodes.*

In a second approach, we have combined IrO_2 nanoparticles with a robust oxide under PEWE anodic conditions, TiO_2, which can act as an actual catalyst support. [10] IrO_2-TiO_2 composite electrodes with a total surface area of 245 m^2g^{-1} displayed a slightly higher OER activity than single, high surface area IrO_2 electrodes (150 m^2g^{-1}), but remarkably improved durability during a start-stop simulating stability test. [10]

In a third approach, towards the development of cost-effective, active and stable OER catalysts for PEWE anodes with reduced noble metal content, Ir-based pyrochlore oxides have been developed. Pyrochlores are a family of complex oxides with a general formula $A_2B_2O_{6.5+x}$, where noble metals can be partially replaced by earth-abundant elements. Pyrochlores of the general formula $(A, A')_2Ir_2O_{6.5+x}$ (A, A′ = Bi, Pb, Y) were synthesized via a modified Adams fusion method achieving surface areas in the range of 10–40 m^2g^{-1}. Electrochemical measurements in acidic media showed that yttrium and bismuth pyrochlore catalysts possess high OER activity approaching that of the state-of-the-art IrO_2 nanoparticles. [16] The high intrinsic activity and stability behavior of yttrium-iridium catalysts were correlated with a highly active IrO_x surface layer that forms due to leaching of the Y^{3+} cations into the electrolyte solution, the occurrence of which was revealed both experimentally and computationally using density functional theory calculations. The Ir-based pyrochlores present good stability over 500 start-stop cycles with activity loss under 20 %. Based on the activity and stability results, it can be concluded that $Y_2Ir_2O_7$ and $Bi_2Ir_2O_7$ pyrochlores are valid candidates as OER catalysts for application in PEWEs. [16]

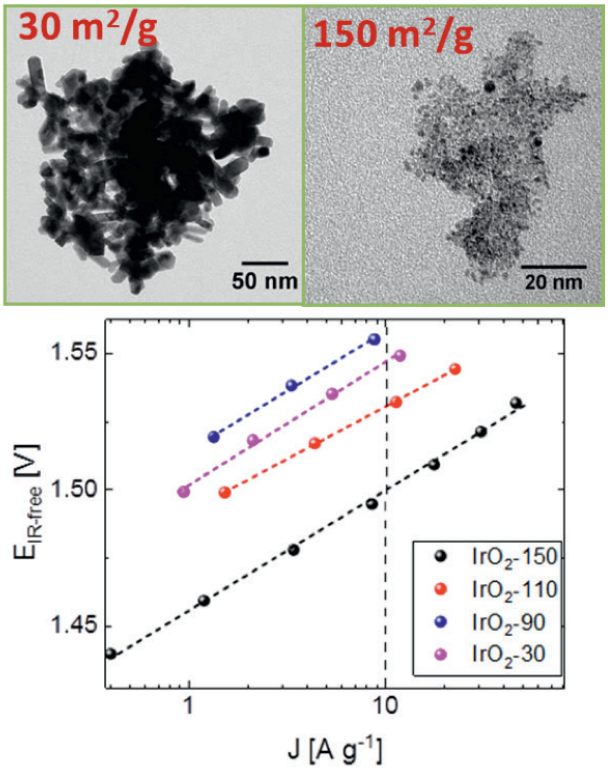


Figure 2. *Top: Transmission electron microscopy (TEM) of IrO_2 samples with BET surface areas of 30 and 150 m^2g^{-1}, respectively. Bottom: OER Tafel plots showing the steady-state current density recorded after 1 min in 0.1 M $HClO_4$ for sample with 150 (IrO_2-150), 110 (IrO_2-110), 90 (IrO_2-90) and 30 (IrO_2-30) m^2g^{-1}BET surface area. Reprinted (adapted) with permission from Chemistry of Materials 28, 6591–6604 (2016). Copyright (2018) American Chemical Society.*

Alkaline electrodes for AWEs

The main advantage of AWEs is that several materials present adequate stabilities when in contact with alkaline electrolyte, allowing the investigation of a wide range of catalyst materials as alternatives to noble metals. However, the efficiency of AWEs is still plagued by the slow kinetics of the OER occurring at the anode. Therefore, the development of highly active, stable, and cost-effective anode materials still remains a considerable challenge for the advancement of AWE systems. The state-of-the-art AWE anodic electrode is based on NiO due to its relatively good activity and stability. The high activity of NiO for the OER in alkaline media has already been recognized for several decades, but more recently the effect of Fe doping on the OER has been the subject of many intensive investigations since the incorporation of small amounts of Fe into NiO can greatly enhance its OER activity. [1] In a recent work, we have produced highly crystalline $Ni_{1-x}Fe_xO_y$ nano-powders by flame-spray synthesis (see Figure 3) with different Ni-to-Fe ratios to investigate how Fe incorporation influences the surface electronic properties and local coordination structures of Ni catalysts, and how this impacts the electrochemical stability and OER activity. [8] *Operando* XAS measurements (see Figure 3) show that the incorporation of Fe greatly stabilizes the Ni electronic structure and local coordination environment under OER conditions. Combined with electrochemical measurements, we find that the incorporation of Fe leads to an overall stabilization of the initially compact and crystalline rock salt structure of $Ni_{1-x}Fe_xO_y$ and thereby inhibits the transformation to more layered and disordered polymorphs. [8]

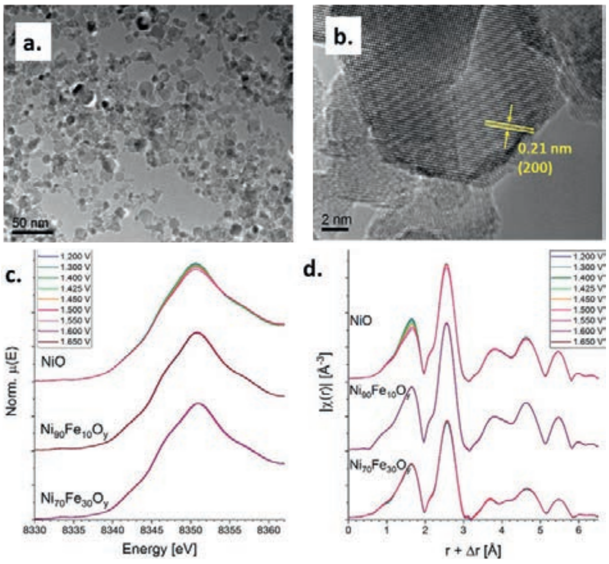


Figure 3. *TEM (a) and high resolution (HR) TEM (b) micrographs of $Ni_{0.9}Fe_{0.1}O_y$ catalysts. Normalized XANES spectra (c) and Fourier transformed Ni EXAFS spectra (d) recorded in operando for $Ni_{1-x}Fe_xO_y$ over a range of applied potentials. (Note: 1.600 V and 1.650 V were not measured for NiO). All Ni χ(k) functions were Fourier transformed over a k-range of 2.6–12.5 Å. Reproduced from Reference [8] with permission from The Royal Society of Chemistry.*

Beyond the state-of-the-art NiO-based catalysts, transition metal oxides with perovskite-related structures have recently emerged as promising electro-catalysts for the OER in AWEs.[1, 2] Given the immense compositional possibilities granted by the perovskite structure and the many open questions about the mechanism at the origin of their electrocatalytic activity, the research has been mostly focused on identifying catalytic descriptors able to predict the optimal physicochemical properties for maximizing the OER activity. In our recent work,[17] the correlation between *ex situ* electronic conductivity, oxygen vacancy content, flat-band potential (Efb), and the OER activity for a wide range of perovskite compositions have been investigated experimentally and theoretically (see Figure 4). It has been found that all of these pa-rameters can affect the OER activity; however, none of them alone plays a crucial role in determining the electrocatalytic activity.

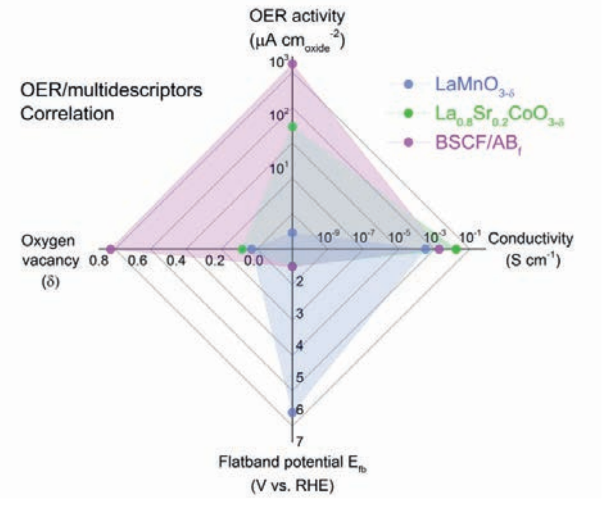
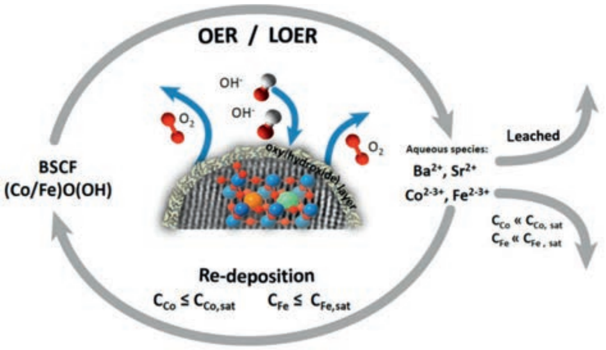


Figure 4. *Correlation between OER activity, conductivity, amount of oxygen vacancies, and flat-band potential for $LaMO_{3-\delta}$, $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ and, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ electrode processed with acetylene black carbon (BSCF/ABf). Reprinted with permission from Chemistry of CS Catalysis 8, 9567–9578 (2018). Copyright (2018) American Chemical Society.*

The correlation of one single physicochemical property with the OER activity always presents deviation points,[18] indicating that a limitation does exist for such 2-dimensional correlations. Nevertheless, these deviations can be explained considering other physicochemical properties and their correlations with OER activity. The novel concept of the OER multi-descriptor relationship, that we have introduced in our recent study [17] (see Figure 4), represents a significant advancement in the quest of searching for highly active oxygen evolution catalysts as an efficient anode catalyst for AWEs. A further development in the understanding of the dynamics on the catalyst surface under real operating conditions has been achieved by performing *operando* XAS for a series of nanocrystalline perovskite oxides.[7, 9] We have recently revealed, for the first time, that the perovskite electronic and local structure change during the water splitting reaction. Particularly, we could demonstrate that the key for highly active catalysts is a self-assembled (oxy)hydroxide top layer with a short range order. This is completely different from the message of several OER-related publications, which consider unstable (hence, of no value) perovskite oxides developing this superficial amorphous layer.[19]

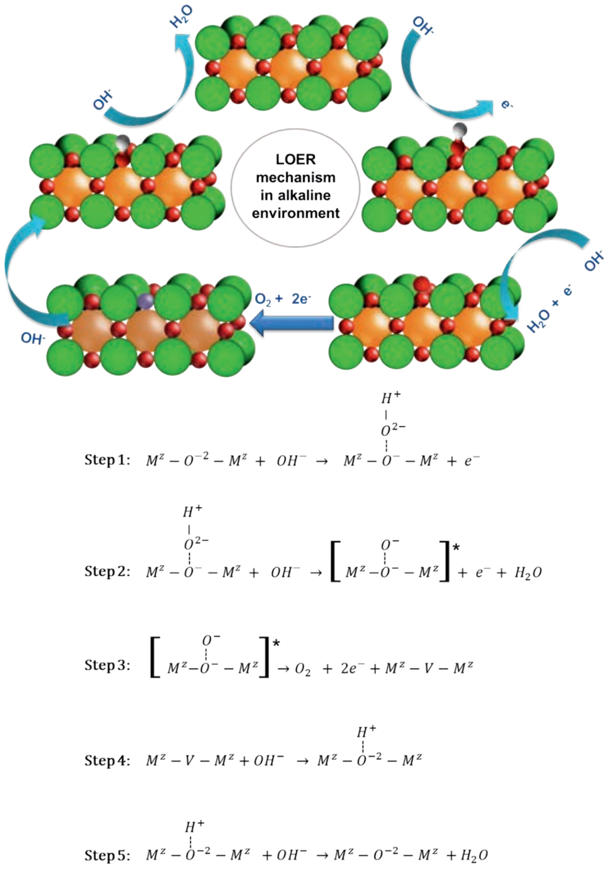
In particular, the growth of a CoO(OH) layer after the onset potential of the OER has been nicely observed by performing *operando* XAS on $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) perovskite nano-particles,[9] which is a highly active OER catalyst.[20] The formation of the self-assembled CoO(OH) and the great performance stability of the BSCF catalysts in alkaline environment have been explained by the reaction scheme depicted in Figure 5.[9] The lattice oxygen evolution reaction (LOER) process leads to the direct evolution of perovskite lattice oxygen, and it is accompanied by cation dissolution. Ba^{2+} and Sr^{2+} cations are highly soluble, and thus, they can easily leach out from the perovskite structure (see equation on the bottom). LOER also triggers dissolution of Co and Fe cations. However, being rather insoluble, Co and Fe redeposition on the catalyst surface can take place. Furthermore, the lattice oxygen consumed by the LOER can be replenished by OH^- from the electrolyte. Therefore, a stable dynamic cycle is established, permitting the coexistence of self-assembled active surface layer with the original BSCF perovskite structure.[9, 19]



$$ABO_{3-\delta} + OH^- \leftrightarrow BO(OH) + A^{2+}_{aq} + \frac{2-\delta}{2}O_2 + 3e^-$$

Figure 5. *OER/LOER and dissolution/redeposition mechanism leading to the formation of a self-assembled active surface layer on the surface of BSCF perovskite. Reprinted with permission from Chemistry of ACS Catalysis 8, 9765–9774 (2018). Copyright (2018) American Chemical Society.*

The possible occurrence of a different reaction mechanism than the conventional one, which foresees four concerted proton-electron transfer steps,[19] has been proposed in the very early OER literature, but was only recently rigorously formulated by our study.[21] Based on thermodynamics considerations, it is possible to demonstrate that if the conventional OER mechanism takes place, also metal cation dissolution and the LOER must occur. A possible mechanism involving the oxidation of the lattice oxygen (more precisely the lattice O^{2-} anions) has been recently proposed by Fabbri and Schmidt in Reference [19] and is represented in Figure 6.



$$\textbf{Step 1:}\quad M^z - O^{-2} - M^z + OH^- \rightarrow M^z - \overset{\substack{H^+ \\ | \\ O^{2-} \\ \vdots}}{O^-} - M^z + e^-$$

$$\textbf{Step 2:}\quad M^z - \overset{\substack{H^+ \\ | \\ O^{2-} \\ \vdots}}{O^-} - M^z + OH^- \rightarrow \left[M^z - \overset{\substack{O^- \\ \vdots}}{O^-} - M^z \right]^* + e^- + H_2O$$

$$\textbf{Step 3:}\quad \left[M^z - \overset{\substack{O^- \\ \vdots}}{O^-} - M^z \right]^* \rightarrow O_2 + 2e^- + M^z - V - M^z$$

$$\textbf{Step 4:}\quad M^z - V - M^z + OH^- \rightarrow M^z - \overset{\substack{H^+ \\ \vdots}}{O^{-2}} - M^z$$

$$\textbf{Step 5:}\quad M^z - \overset{\substack{H^+ \\ \vdots}}{O^{-2}} - M^z + OH^- \rightarrow M^z - O^{-2} - M^z + H_2O$$

Figure 6. *Proposed LOER mechanism in alkaline environment where lattice oxygen represents the reactions sites, leading to lattice oxygen evolution and consequent formation of oxygen vacancies in the metal oxide lattice, which can be replenished by a final step by reacting with OH^- in the electrolyte. Four electrons are overall exchanged in the LOER but decoupled proton electron steps take place. Step 2 and 3 are represented as formal reaction steps, but they would rather occur as a concerted process where H^+ and O_2 are released. Reprinted with permission from Chemistry of ACS Catalysis 8, 9765–9774 (2018). Copyright (2018) American Chemical Society.*

By the *operando* XAS analysis of different Co-based catalysts, it was suggested that the more important the growth of the assembled hydroxide layer is, the higher the OER/LOER activity of the catalyst. Flexible structures such as BSCF can be seen as an ideal precursor catalyst for the LOER because their highly defective surface can facilitate oxygen exchange and dynamic self-reconstruction of the surface. Flexibility in the structure can be associated with the oxygen vacancy concentration and ion mobility, and indeed, a direct correlation between the oxygen vacancy content and the OER activity has been revealed in Reference [17].

Contact

For further information, please contact Prof. Dr. T.J. Schmidt, head of the Electrocatalysis & Interfaces group.

thomasjustus.schmidt@psi.ch

Contributors

The contributors for this particular research topic are E. Fabbri, B.-J. Kim, X. Cheng, D.F. Abbott, M. Povia and T.J. Schmidt.

Acknowledgement

Kindly acknowledged is financial support from SNSF Ambizione grant and the Swiss Competence Center for Energy Research (SCCER) *Heat & Electricity Storage* as well as CCEM and the Swiss Federal Office of Energy.

References

[1] E. Fabbri, A. Habereder, K. Waltar, R. Kotz, T.J. Schmidt, *Catal. Sci. Technol. 4*, **3800–3821 (2014).**

[2] J. Herranz, J. Durst, E. Fabbri, A. Pătru, X. Cheng, A.A. Permyakova, T.J. Schmidt, *Nano Energy* **29**, 4–29 (2016).

[3] K.E. Ayers, E.B. Anderson, C. Capuano, B. Carter, L. Dalton, G. Hanlon, J. Manco, M. Niedzwiecki, *ECS Transaction* **33**, 3–15 (2010).

[4] P. Millet, R. Ngameni, S.A. Grigoriev, N. Mbemba, F. Brisset, A. Ranjbari, C. Etiévant, *International Journal of Hydrogen Energy* **35**, 5043–5052 (2010).

[5] U. Babic, M. Suermann, F.N. Büchi, L. Gubler, T.J. Schmidt, *Journal of The Electrochemical Society* **164**, F387–F399 (2017).

[6] M. Carmo, D.L. Fritz, J. Mergel, D. Stolten, *International Journal of Hydrogen Energy* **38**, 4901–4934 (2013).

[7] B.-J. Kim, X. Cheng, D.F. Abbott, E. Fabbri, F. Bozza, T. Graule, I.E. Castelli, L. Wiles, N. Danilovic, K.E. Ayers, N. Marzari, T.J. Schmidt, *Adv Funct Mater* **28**, 1804355 (2018).

[8] D.F. Abbott, E. Fabbri, M. Borlaf, F. Bozza, R. Schäublin, M. Nachtegaal, T. Graule, T.J. Schmidt, *Journal of Materials Chemistry A*, DOI: 10.1039/C8TA09336A (2018).

[9] E. Fabbri, M. Nachtegaal, X. Cheng, T. Binninger, B. Kim, J. Durst, F. Bozza, T. Graule, N. Danilocic, K.E. Ayers, T.J. Schmidt, *Nature Materials* **16**, 925–931 (2017).

[10] E. Oakton, D. Lebedev, M. Povia, D.F. Abbott, E. Fabbri, A. Fedorov, M. Nachtegaal, C. Copéret, T.J. Schmidt, *ACS Catalysis* **7**, 2346–2352 (2017).

[11] B.-J. Kim, D.F. Abbott, X. Cheng, E. Fabbri, M. Nachtegaal, F. Bozza, I.E. Castelli, D. Lebedev, R. Schäublin, C. Copéret, T. Graule, N. Marzari, T.J. Schmidt, *ACS Catalysis*, 3245–3256 (2017).

[12] T. Binninger, R. Mohamed, A. Pătru, K. Waltar, E. Gericke, X. Tuaev, E. Fabbri, P. Levecque, A. Hoell, T.J. Schmidt, *Chemistry of Materials* **29**, 2831–2843 (2017).

[13] E. Fabbri, D.F. Abbott, M. Nachtegaal, T.J. Schmidt, *Current Opinion in Electrochemistry* **5**, 20–26 (2017).

[14] D.F. Abbott, D. Lebedev, K. Waltar, M. Povia, M. Nachtegaal, E. Fabbri, C. Copéret, T.J. Schmidt, *Chemistry of Materials* **28**, 6591–6604 (2016).

[15] T. Binninger, E. Fabbri, A. Pătru, M. Garganourakis, J. Han, D.F. Abbott, O. Sereda, R. Kotz, A. Menzel, M. Nachtegaal, T.J. Schmidt, *Journal of the Electrochemical Society* **163**, H906–H912 (2016).

[16] D. Lebedev, M. Povia, K. Waltar, P.M. Abdala, I.E. Castelli, E. Fabbri, M.V. Blanco, A. Fedorov, C. Copéret, N. Marzari, T.J. Schmidt, *Chemistry of Materials* **29**, 5182–5191 (2017).

[17] X. Cheng, E. Fabbri, Y. Yamashita, I.E. Castelli, B. Kim, M. Uchida, R. Haumont, I. Puente-Orench, T.J. Schmidt, *ACS Catalysis* **8**, 9567–9578 (2018).

[18] X. Cheng, E. Fabbri, M. Nachtegaal, I.E. Castelli, M. El Kazzi, R. Haumont, N. Marzari, T.J. Schmidt, *Chemistry of Materials* **27**, 7662–7672 (2015).

[19] E. Fabbri, T.J. Schmidt, *ACS Catalysis* **8**, 9765–9774 (2018).

[20] E. Fabbri, M. Nachtegaal, X. Cheng, T.J. Schmidt, *Advanced Energy Materials* **5**, (2015).

[21] T. Binninger, R. Mohamed, K. Waltar, E. Fabbri, P. Levecque, R. Kötz, T.J. Schmidt, *Scientific Reports* **5**, 12167 (2015).

The SCCER «Heat and Electricity Storage» – Electrochemical Highlights 2018

Within the goal of the SCCER HaE to provide energy storage solutions to enable the Energy Strategy 2050 and the fulfilment of the Paris climate targets the SCCER in general progressed along the plans in 2018. Storage of heat, battery development, hydrogen production and storage, synthetic fuels and chemical feed stock sourced by CO_2 reduction and, as an overarching activity, the system assessment on three nested levels (technological, system and socio-economic) are the high level topics for this (second) phase of the SCCER. In this summary, a focus is set on electrochemistry relevant topics batteries, battery materials development, and electrochemical CO_2 reduction.

Batteries

The role of batteries in today's energy system (other than for transportation) is twofold. On smaller scale (order of magnitude 10 kWh), systems for residential self-consumption in combination with PV see an increasing market as PV becomes less expensive. On large scale (MWh – GWh) battery installations for ancillary services become more and more common.

With increasing share of renewables, the need for batteries will certainly further increase. Therefore, it is important to address the three major challenges: Cost, durability and safety.

Those three major aspects are related to material combinations and manufacturing processes. The SCCER addresses both, materials questions and manufacturing optimization.

In line with the current debate on the use of Cobalt, a study on material criticality was performed. All batteries containing Cobalt have an issue with regard to metal criticality, as well as lead acid batteries, which are especially problematic as well due to Zinc, Lead and Iron. Based on the economic & environmental assessment of Lithium-Ion vs Sodium-Ion cells it was concluded that, at the current state of development the Sodium system lacks behind the state of the art Lithium system in terms of cost and environmental impact due to their still significant difference in energy density (Figure 1).

The assessment results will be implemented in the future research strategy of the battery work team. The challenge is to find material combinations which work with abundant elements only (Co and Ni free).

The specific project goal along the innovation roadmap is to demonstrate full battery cells based on material sets following the previous requirements.

One milestone to get reliable results on self-developed material sets for battery full cells is the qualification of the electrode coatings at high mass loadings via benchmark materials. This milestone was achieved in the past year. Electrodes were coated with NMC111 and graphite, respectively, and tested in a full cell. The cell performed with a capacity retention of 75 % after 200 cycles at C/5. The obtained data allowed projecting a gravimetric energy density of 220 Wh/kg in a pouch cell with a stack of 11 anodes and 10 cathodes. Furthermore, an in-house material combination with NMC811 and graphite was tested. It surpassed the performance of the benchmark, but provides still room for improvement to meet the target performance of 275 Wh/kg (see Figure 2.).

On the manufacturing side of battery cells, the focus is mainly on a holistic (computer) model based analysis of manufacturing and on critical mechanical manufacturing steps (cutting and folding). The virtual production model was developed and

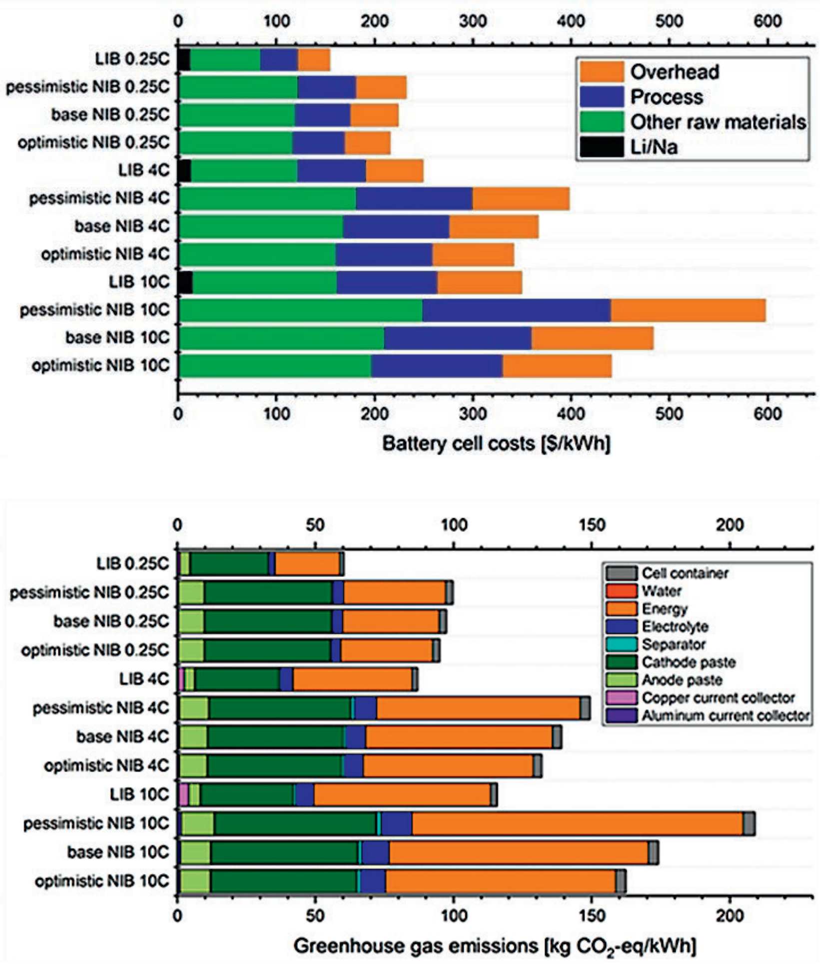


Figure 1. Production costs (top) and associated GHG emissions (bottom) of Na-ion and Li-ion batteries today [1] (Ch. Bauer et al. PSI).

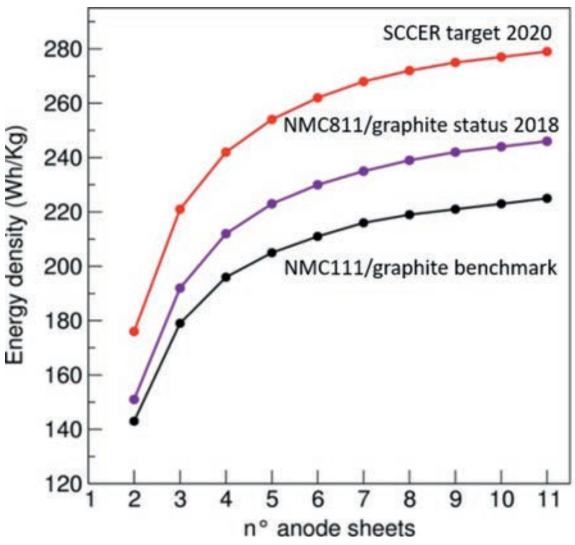


__Figure 2.__ Benchmark, status, and target values for projected stacked pouch cell based on lab-scale full cell results (C. Battaglia et al., Empa).

parametrized in the past year. One of the first promising results was the identification of a potential of 60 % cost reduction in manufacturing cost for pouch cells and 25 % cost reduction for cylindrical cells.

Similar to the activity benchmarking the electrode coating process, the first functioning pouch cell was assembled from commercial materials, using the manufacturing modules for laser cutting, stacking and ultrasonic welding.

The test of the cell with 6 anode sheets and 5 cathode sheets each sized 65 x 85 mm indicated that the design capacity of 1100 mAh was reached (Figure 3). The cell weighs 19.2 grams and has a measured capacity of 1054 mAh, which equals to a discharge energy of 3846 mWh at C/5.

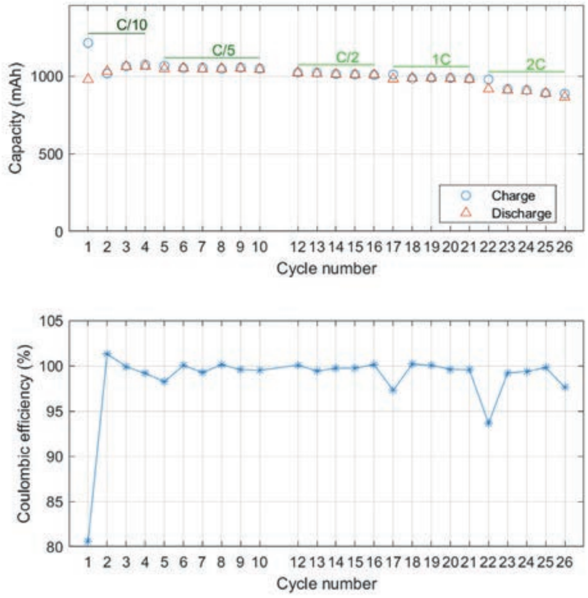


__Figure 3.__ Results of the stacked battery from commercial components to benchmark the manufacturing concept (Axel Fuerst et al., BFH).

This results in a gravimetric energy density of 200 Wh/kg and is close to the current state-of-the-art even without further design optimizations. The battery reached 80 % of initial capacity at about 200 cycles, which is in line with current state-of-the-art for NMC-based lithium-ion materials. Not only the electrode coating, but also the cell assembly processes passed the validation milestone allowing to take the next steps to a SCCER Battery demonstrator.

Electrochemical CO_2 conversion

Converting CO_2 and water with the help of (renewable) electricity into hydrocarbons offers the possibility to establish a fossil-free chemical industry. Admitting that this is a very ambitious goal for the future, the processes proved to be feasible, yet on a quite fundamental level.

In the past years of the SCCER Hae Cu based electro catalytic processes were explored to produce Format (annual production of formic acid today: several Mio tons [2]) and Syngas (global consumption in 2014: 100 000 MW_{th}, and about to double soon [3]).

In order to enhance the selectivity, other systems were explored to produce CO (syngas). Ag showed Faradaic efficiencies for CO (FE_{CO}) > 90 % –0.3 V to –1.2 V vs RHE, highly efficient Cu/Zn were studied (FE_{CO} = 90 % at -0.95 V vs RHE). Selective C2 and C3 alcohol production based on the system Cu-Ag

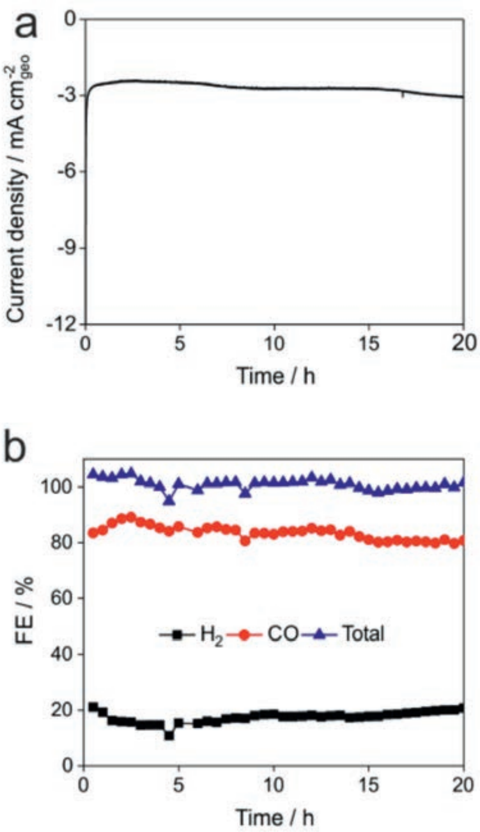


__Figure 4.__ Potentiostatic catalyst stressing experiments (on Cu@CuPd-NWs catalyst) carried out in CO_2-sat. 0.5 M $KHCO_3$ at –0.8 V vs RHE (CO formation regime); (a) Current density/time plot of continuous 20 h electrolysis and (b) Corresponding CO_2RR product distribution represented as FE vs time plot (P. Broeckmann at al., Uni Bern).

($FE_{EtOH} = 37\,\%$), and Formate formation with modified Cu metal foams and dendritic catalysts ($FE_{formate} = 49\,\%$ at –0.7 V vs RHE) have been identified. Furthermore, the carbon-supported SnO_x-based NP catalysts are also very promising candidates for the formate production ($FE_{formate} = 75\,\%$). While the investigation of the underlying mechanisms progressed, and selectivity of the electrodes significantly improved in the past years, the current approaches rely on aqueous alkaline solutions saturated with CO_2 as electrolyte which limits the current densities to few mA/cm^2 (see Figure 4).

The solubility and diffusion of CO_2 in the electrolyte limits the current density to 30 mA/cm^2. In addition, it was found that CO_2 is electrochemically pumped to the anode, which further reduces the performance of such electrolysis cells. To overcome this limitation, the gas phase reaction, rather than the liquid phase reaction is explored via a bipolar-like membrane assembly [4]. However, unlike a bipolar membrane system, this system does not contain two rigid and connected ionomer layers of similar thicknesses, but rather it contains a thin film alkaline ionomer layer, which is sprayed onto the cathode catalyst layer and Nafion® XL membrane separating the cathode from the anode side (see Figure 5).

By employing only a thin alkaline ionomer film, the CO_2 and H_2O molecules formed at the interface of the two layers can more easily diffuse towards the cathode and participate in the reactions once more. The preliminary results using Au black as the cathode catalyst show that this novel configuration successfully suppressed the formation of CO_2 on the anode side, while maintaining similar faradaic efficiency as the alkaline electrolyte system. In order to be able to detect the produced gases online during the tests, a new versatile multivariate calibration method for mass spectrometers was developed and employed during the experiments. [5]

These were just examples out of two work packages of the SCCER HaE summarized from the Annual Report of the SCCER HaE 2018. The report, which provides further details on all the topics of the SCCER HaE, is currently in press and will be available online at www.sccer-hae.ch in April 2019.

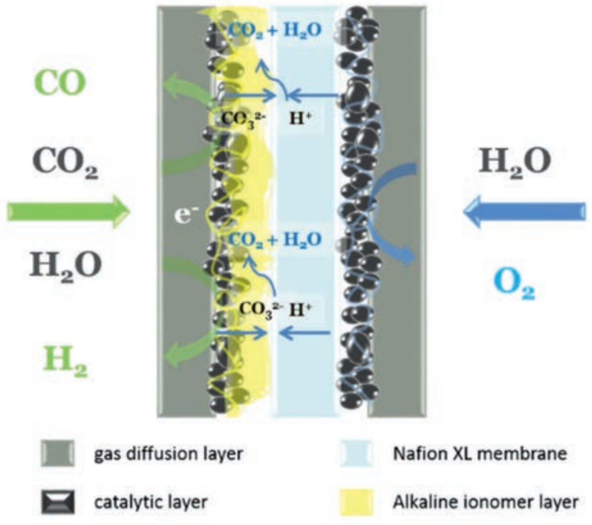


Figure 5. *Schematic for the new cell configuration used for the gas-phase CO_2RR (T.J. Schmidt et al., PSI).*

Contact

For further information on the SCCER Heat and Electricity Storage please contact Dr. Jörg Roth.

joerg.roth@psi.ch

Contributors

The contributors for this particular research topic are T.J. Schmidt[1], P. Broekmann[2], P. Novák[1], Ch. Bauer[1], C. Battaglia[3], M. Kovalenko[3, 4], A. Fuerst[5] and J. Roth[1].

References

[1] S. Schneider, C. Bauer, E. Berg, «A modeling framework to assess performance, costs and environmental impact of Li-ion and Na-ion batteries». Submitted to Environmental Science and Technology (2019).

[2] https://onlinelibrary.wiley.com/doi/10.1002/14356007.a01_045.pub3, 5.2.2019.

[3] https://www.globalsyngas.org/resources/the-gasification-industry/, 5.2.2019.

[4] A. Pătru, T. Binninger, B. Pribyl, T.J. Schmidt, J. Electrochem. Soc., 166 (2) F34–F43 (2019);
A. Pătru, T. Binninger, B. Pribyl, T.J. Schmidt, EP17182823.

[5] T. Binninger, B. Pribyl, A. Pătru, Peter Rüttimann, Saša Bjelić, T.J. Schmidt, J. Mass Spectrom., 53, 1214–1221 (2018).

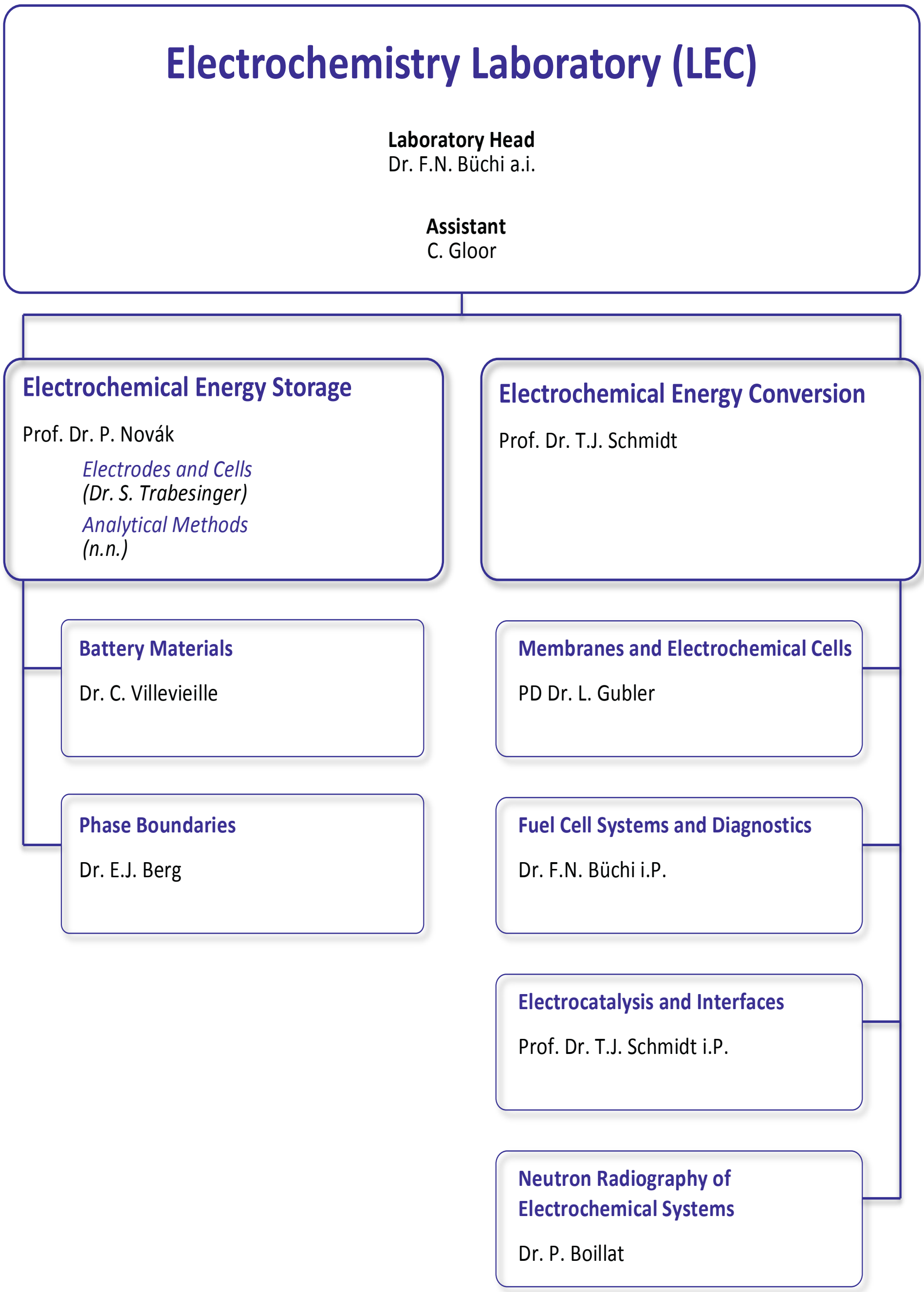
---

[1] PSI [2] University of Bern [3] Empa [4] ETHZ [5] BFH

THE ELECTROCHEMISTRY LABORATORY

FACTS & FIGURES

STRUCTURE 2018



Electrochemistry Laboratory (LEC)

Laboratory Head
Dr. F.N. Büchi a.i.

Assistant
C. Gloor

Electrochemical Energy Storage

Prof. Dr. P. Novák

Electrodes and Cells
(Dr. S. Trabesinger)

Analytical Methods
(n.n.)

Battery Materials
Dr. C. Villevieille

Phase Boundaries
Dr. E.J. Berg

Electrochemical Energy Conversion

Prof. Dr. T.J. Schmidt

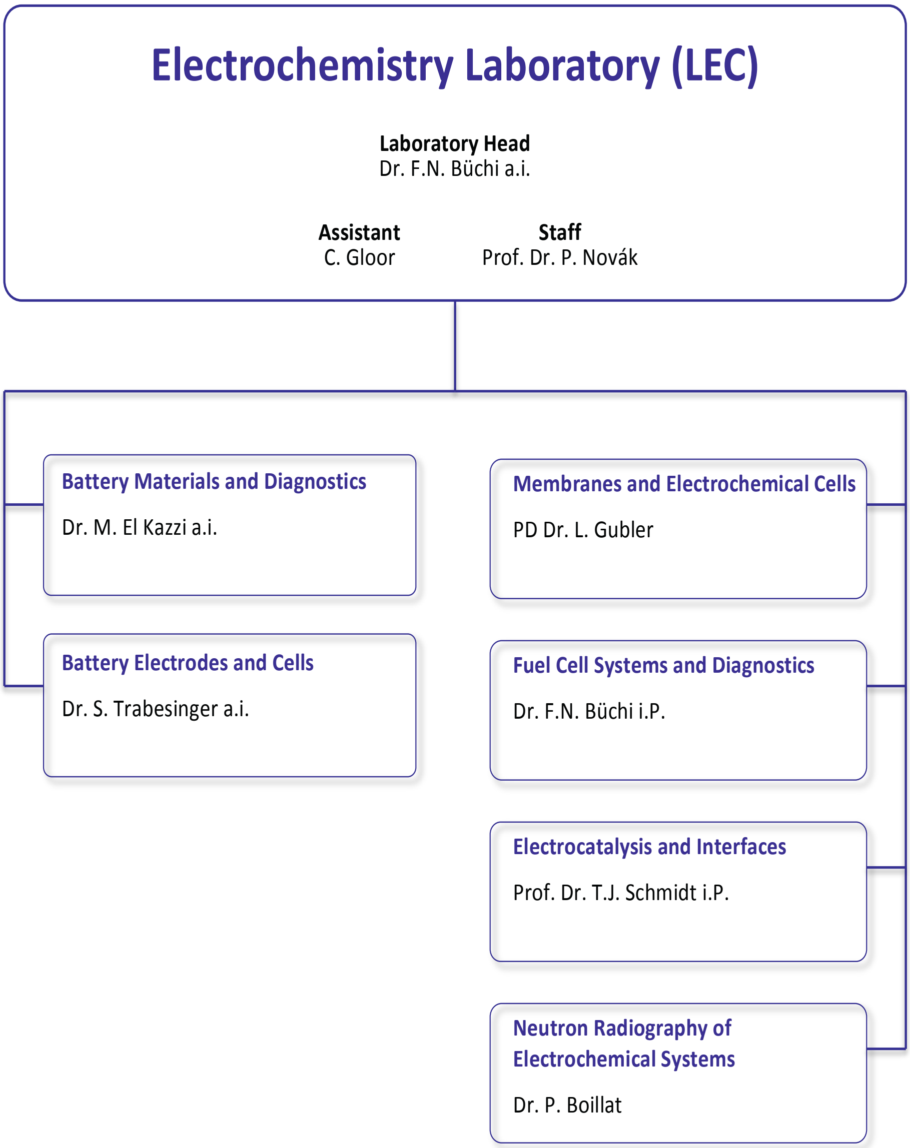
Membranes and Electrochemical Cells
PD Dr. L. Gubler

Fuel Cell Systems and Diagnostics
Dr. F.N. Büchi i.P.

Electrocatalysis and Interfaces
Prof. Dr. T.J. Schmidt i.P.

Neutron Radiography of Electrochemical Systems
Dr. P. Boillat

STRUCTURE 2019



Electrochemistry Laboratory (LEC)

Laboratory Head
Dr. F.N. Büchi a.i.

Assistant
C. Gloor

Staff
Prof. Dr. P. Novák

Battery Materials and Diagnostics
Dr. M. El Kazzi a.i.

Battery Electrodes and Cells
Dr. S. Trabesinger a.i.

Membranes and Electrochemical Cells
PD Dr. L. Gubler

Fuel Cell Systems and Diagnostics
Dr. F.N. Büchi i.P.

Electrocatalysis and Interfaces
Prof. Dr. T.J. Schmidt i.P.

Neutron Radiography of Electrochemical Systems
Dr. P. Boillat

PERSONNEL 2018

Staff

Dr. Daniel ABBOTT (Post Doctoral Researcher)
Martin AMMANN (Technician)
Dr. Erik J. BERG (Group Leader)
Dr. Juliette BILLAUD BOUVILLE (Post Doctoral Researcher)
Dr. Pierre BOILLAT (Group Leader)
Dr. Christoph BOLLI (Post Doctoral Researcher)
Dr. Anthony BOUCLY (Post Doctoral Researcher)
Dr. Felix BÜCHI (Laboratory Head a.i. & Group Leader)
Dr. Magali COCHET (Scientist)
Dr. Salvatore DE ANGELIS (Post Doctoral Researcher)
Dr. Mario EL KAZZI (Scientist)
Dr. Jens ELLER (Scientist)
Dr. Emiliana FABBRI (Scientist)
Cordelia GLOOR (Assistant)
Thomas GLOOR (Technician)
PD Dr. Lorenz GUBLER (Group Leader)
Dr. Aurélie GUÉGUEN (Scientist)
Dr. Fabian JESCHULL (Post Doctoral Researcher)
Michelle Locher (Technician)
Dr. Elena MARELLI (Post Doctoral Researcher)
Dr. Cyril MARINO (Scientist)
Christian MARMY (Technician)
Dr. David MCNULTY (Post Doctoral Researcher)
Dr. Tom NOLTE (Post Doctoral Researcher)
Prof. Dr. Petr NOVÁK (Section Head)
Dr. Alexandra PĂTRU (Scientist)
Dr. Daniele PEREGO (Post Doctoral Researcher)
Dr. Anastasia A. PERMYAKOVA (Post Doctoral Researcher)
Christian PETER (Engineer)
Dr. Rosa ROBERT SANCHEZ (Scientist)
Dr. Viktoriia SAVELEVA (Post Doctoral Researcher)
Dirk SCHEUBLE (Engineer)
Prof. Dr. Thomas J. SCHMIDT (Section Head & Group Leader)
Aaron SCHNEIDER (Lab Technician)
Dr. Bing SUN (Post Doctoral Researcher)
Dr. Yuri SURACE (Post Doctoral Researcher)
Dr. Sigita TRABESINGER-URBONAITE (Project Leader)
Stephan TSCHUMI (Engineer)
Dr. Claire VILLEVIEILLE (Group Leader)
Dr. David VONLANTHEN (Scientist)
Dr. Leiting ZHANG (Post Doctoral Researcher)

PhD Students

Dino AEGERTER
Ugljesa BABIC
Christoph CSOKLICH
Justus DIERCKS
Nataša DIKLIĆ
Kathrin EBNER
Eibar Joel FLORES CEDEÑO
Giulio FERRARESI
Steffen GARBE
Jonathan HALTER
Adrian HEINRITZ
Sebastian HENNING
Laura HÖLTSCHI
Baejung KIM
Paul KITZ
Daniela LEANZA
Maria Victoria MANZI OREZZOLI
Marta MIROLO
Adrian MULARCZYK
Fabio OLDENBURG
Mauro POVIA
Bernhard PRIBYL
Simon SCHNEIDER
Tobias SCHULER
Arnaud SCHULLER
Maximilian SCHUSTER
Muriel SIEGWART
Michael STRIEDNIG
Seçil ÜNSAL
Xiaohan WU
Hong XU
Mateusz ZLOBINSKI

The Electrochemistry Laboratory, December 2018.

DISSERTATIONS 2018

Sebastian Michael Henning

Characterization and polymer electrolyte fuel cell application of bimetallic aerogels

Ph.D. Thesis No. 24919, ETH Zürich, January 2018.

Examiners:	Prof. Dr. T.J. Schmidt, PSI Villigen/ETH Zürich Prof. Dr. M. Kovalenko, ETH Zürich Dr. J. Herranz, PSI Villigen

Giulio Ferraresi

From liquid to solid electrolyte: interface investigation of model negative electrodes for Li-ion batteries

Ph.D. Thesis No. 25215, ETH Zürich, June 2018.

Examiners:	Prof. Dr. P. Novák, PSI Villigen/ETH Zürich Prof. Dr. M. Kovalenko, ETH Zürich Dr. C. Villevieille, PSI Villigen Dr. M. El Kazzi, PSI Villigen

Ahmet Oguz Tezel

The effect of electrolyte structure on solid electrolyte interphase formation on graphitic anodes for Li-ion batteries

Ph.D. Thesis No. 2018:236, NTNU Norwegian University of Science and Technology, Trondheim, Norway, June 2018.

Examiners:	Prof. Dr A.M. Svensson, NTNU Trondheim Prof. Dr. S. Sunde, NTNU Trondheim Prof. Dr. P. Novák, PSI Villigen/ETH Zürich

BACHELOR AND MASTER STUDENTS

Alexander Arndt Humboldt Universität zu Berlin, Berlin, Germany	*Functionalization of polymer films for vanadium redox flow batteries with improved power density* September 2017 – April 2018 (Membranes and Electrochemical Cells).
Darryl Nater ETH Zürich	*Investigation of succinic anhydride as an electrolyte additive in lithium ion batteries* September 2017 – January 2018 (Electrochemical Energy Storage).
Elisabeth Nilsson KTH Royal Institute of Technology, Stockholm, Sweden	*Drivers and mitigation of gas crossover in polymer electrolyte water electrolyzers* November 2017 – April 2018 (Membranes and Electrochemical Cells).
Anastasiia Mikheenkova Université de Rennes, Rennes, France	*Further optimization for going to a Na-ion full cell system* May 2018 – July 2018 (Electrochemical Energy Storage).
Gong Cheng ETH Zürich	*All-solid-state Li-ion batteries based on garnet/sulfide solid electrolyte* July 2018 - January 2019 (Electrochemical Energy Storage).

AWARDS

Magali Cochet

Christian Friedrich Schönbein Medal
M. Cochet, A. Forner-Cuenca, V. Manzi-Orezzoli, M. Siegwart, D. Scheuble, P. Boillat
Best scientific contribution for a «Novel concept for evaporative cooling of fuel cells: an experimental study based on neutron imaging».

6th European PEFC & Electrolyser Forum 2017, Lucerne, Switzerland, July 7, 2017.

Kathrin Ebner

Best Contributing Talk
K. Ebner, J. Herranz, V.A. Saveleva, L. Ni, B.-J. Kim, U.I. Kramm, T.J. Schmidt
A novel synthesis approach for Fe/N/C-type ORR-catalysts - insights on composition and activity.

680th WE-Heraeus Seminar on «Materials Development for Automotive Propulsion», Bad Honnef, Germany, October 14–17, 2018.

Victoria Manzi

Best Poster Prize
V. Manzi-Orezzoli, T.J. Schmidt, P. Boillat
Modifying Microporous Layers for Polymer Electrolyte Fuel Cells

ModVal 2018 – 15th Symposium on Model and Experimental Validation of Electrochemical Energy Devices, Aarau, Switzerland, April 12–13, 2018.

Marta Mirolo

Best Poster Prize
M. Mirolo, C.A.F. Vaz, P. Novák, M. El Kazzi
Electrodes surface evolution and cross-talk processes in a full cell NCA vs. LTO revealed by XPEEM.

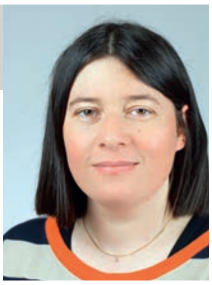
69th Annual Meeting of the International Society of Electrochemistry (ISE), Bologna, Italy, September 2–7, 2018.

Bernhard Prybil

2nd Poster Prize
B. Pribyl, A. Pătru, T. Binninger, T.J. Schmidt
Efficient CO_2 reduction from gas phase at low temperatures in a bipolar like co-electrolysis cell configuration.

International Summer School«Power to X: Fundamentals and Applications of Modern Electrosynthesis», Villars, Switzerland, August 27–31, 2018.

Claire Villevieille

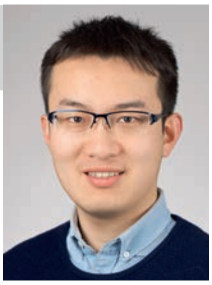


International Battery Association (IBA) Award 2018
Claire Villevieille

In recognition of her outstanding scientific accomplishments in fundamental electrochemical research at an early career stage.

IBA/International Battery Association 2018, Jeju Island, Korea, March 11–16, 2018.

Hong Xu



Best Poster Prize
H. Xu, M. Bührer, F. Marone, T.J. Schmidt, F.N. Büchi, J. Eller
Study of water distribution in GDLs of PEFC using X-ray tomographic microscopy.

ModVal 2018 – 15th Symposium on Model and Experimental Validation of Electrochemical Energy Devices, Aarau, Switzerland, April 12–13, 2018.

CONFERENCES – SYMPOSIA

ModVal 2018 – 15th Symposium on Modeling and Experimental Validation of Electrochemical Energy Devices, April 12–13, 2018.

ModVal 2018 is the 15th symposium in the series of annual events initiated in 2004 by the Swiss Federal Office of Energy.

The symposium provides a platform for idea exchange encompassing academic institutions as well as industry. ModVal aims at disseminating new results in research, promoting personal contacts, and stimulating new collaborations.

Venue:
Culture and Congress House/KuK, Aarau, Switzerland

Organizers:
Dr. Erik J. Berg
Dr. Felix N. Büchi
Dr. Jens Eller
Dr. Lorenz Gubler

Plenary Talks
Prof. Richard Hanke-Rauschenbach, Leibniz University of Hannover, Germany
Prof. Anthony Kucernak, Imperial College London, UK
Prof. Anton Van der Ven, University of California, Santa Barbara, USA

Scope

The program covers topics relevant to electrochemical energy conversion and storage devices, i.e., fuel cells, electrolyzers and batteries.

Modeling and Simulation:

- First-principles methods & quantum mechanics
- Electrode kinetics, electrocatalysis
- Mass transport phenomena
- Computational fluid dynamics
- Genetic algorithms

Validation:

- *In situ* chemical, electrochemical and microstructural characterization methods
- *Ex situ* model experiments to retrieve relevant parameters
- Imaging and spectroscopic techniques

1^{st} Swiss and Surrounding Battery Days, May 23–25, 2018.

This symposium was the first one of a planned series of annual events supported by the Swiss Competence Center of Energy Research (SCCER Heat and Electricity Storage).

This symposium provided a unique opportunity to bring the core European battery community together with the goal of exchanging ideas, discussing new approaches, networking, and initiating collaborations. The topic of the conference was rather broad as it included not only Li-ion batteries but also post-Li ones, the materials science approach combined with classic electrochemistry, the methodology used to understand complex reaction mechanisms, bulk & surface material modification, modelling, etc.

Venue:

Hotel du Parc, Baden, Switzerland

Organization committee:

- Dr. Claire Villevieille
- Dr. Cyril Marino

Scientific Committee:

- Prof. Dr. Petr Novák, PSI
- Dr. Corsin Battaglia, Empa
- Prof. Dr. Maksym Kovalenko, ETH Zürich & Empa
- Prof. Dr. Katharina Fromm, University of Fribourg
- Prof. Dr. Axel Fuerst, Bern University of Applied Sciences
- Dr. Jörg Roth, Scientific Coordinator of the SCCER HaE, PSI

Keynote Speakers

- Prof. Dr. Stefano Passerini, Laboratory of Electrochemistry for Batteries, Ulm, Germany
- Prof. Dr. Renaud Bouchet, Laboratoire d'Electrochimie et physicochimie des matériaux et des interfaces, Grenoble, France
- Dr. Alexandre Ponrouch, Institut de Ciència de Materials de Barcelona, Spain
- Prof. Dr. Valérie Pralong, Laboratoire de Cristallographie et Sciences des Matériaux, Caen, France
- Prof. Dr. Marie-Liesse Doublet, Institut Charles Gerhardt, Université de Montpellier, France
- Dr. Wolfgang Zeier, Laboratory of Materials by Design, Justus-Liebig-University Giessen, Germany

Invited Speakers

- Dr. Cyril Marino, PSI
- Dr. Lorenz Gubler, PSI
- Prof. Dr. Ali Coskun, University of Fribourg
- Dr. Sigita Trabesinger, PSI

34th PSI Electrochemistry Symposium, April 25, 2018.

Pushing the Limits of Characterization in Electrochemistry

Organizers:

Felix N. Büchi, Cordelia Gloor, Electrochemistry Laboratory

Contributions from (in order of appearance):

Anders Nilsson, Stockholm University, Stockholm, Sweden
Henrik Lemke, PSI Villigen
Andrea E. Russell, University of Southampton, United Kingdom
Vasiliki Tileli, École Polytechnique de Lausanne (EPFL)
Christian Masquelier, Université de Picardie Jules Verne, Amiens, France
Elena Savinova, Université de Strasbourg, France

From left to right: *Anders Nilsson, Henrik Lemke, Pierre Boillat, Thomas J. Schmidt, Elena Savinova, Lorenz Gubler, Andrea E. Russell, Felix Büchi, Claire Villevieille, Vasiliki Tileli, Christian Masquelier, Petr Novák, Cordelia Gloor.*

Plenary talks, poster session, lunch and discussions …

DOCUMENTATION

Collaborations with Industrial Partners

The Laboratory had the pleasure to collaborate with the following industrial partners during the year 2018:

ajusa

BASF
We create chemistry

IMERYS
Graphite & Carbon

MICHELIN

PROTON®
ON SITE

saft

simatec
smart technologies

TOYOTA

umicore

VOLKSWAGEN
AKTIENGESELLSCHAFT

Project Collaborations with External Partners

The Laboratory had the pleasure to collaborate with the following external partners during the year 2018:

Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Bundesamt für Energie BFE

Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Swiss Confederation

Innosuisse – Swiss Innovation Agency

SNF Sinergia

FNSNF
Swiss National Science Foundation

BRIDGE

Teaching Activities

Teaching

Prof. Dr. P. Novák	*Elektrochemie* ETH Zürich, HS 2018.
Prof. Dr. T.J. Schmidt / PD Dr. L. Gubler	*Renewable Energy Technologies 2* ETH Zürich, FS 2018.
Prof. Dr. T.J. Schmidt	*Physical Electrochemistry & Electrocatalysis* ETH Zürich, FS 2018.

Contributions to Courses

Dr. E. Fabbri	*Renewable Energy Technologies 2* ETH Zürich, FS 2018.
PD Dr. L. Gubler	*Energy Storage Systems* Lucerne University of Applied Sciences and Arts, May 23, 2018.

Publications

Peer Reviewed Papers

D.F. Abbott, E. Fabbri, M. Borlaf, F. Bozza, R. Schäublin, M. Nachtegaal, T. Graule, T.J. Schmidt	*Operando X-ray absorption investigations into the role of Fe in the electrochemical stability and oxygen evolution activity of* $Ni_{1-x}Fe_xO_y$ *nanoparticles* Journal of Materials Chemistry A **6**, 24534–24549 (2018).
M. Andersson, A. Mularczyk, A. Lamibrac, S.B. Beale, J. Eller, W. Lehnert, F.N. Büchi	*Modeling and synchrotron imaging of droplet detachment in gas channels of polymer electrolyte fuel cells* Journal of Power Sources **404**, 159–171 (2018).
U. Babic, T.J. Schmidt, L. Gubler	*Communication – Contribution of Catalyst Layer Proton Transport Resistance to Voltage Loss in Polymer Electrolyte Water Electrolyzers* Journal of The Electrochemical Society **165**, J3016–J3018 (2018).
E.J. Berg, S. Trabesinger	*Viability of Polysulfide-Retaining Barriers in Li–S Battery* Journal of The Electrochemical Society **165**, A5001-A5005 (2018).
T. Binninger, B. Pribyl, A. Pătru, P. Ruettimann, S. Bjelić, T.J. Schmidt	*Multivariate calibration method for mass spectrometry of interfering gases such as mixtures of CO,* N_2*, and* CO_2 Journal of Mass Spectrometry **53**, 1214–1221 (2018).
P. Boillat, C. Carminati, F. Schmid, C. Grünzweig, J. Hovind, A. Kaestner, D. Mannes, M. Morgano, M. Siegwart, P. Trtik, P. Vontobel, E.H. Lehmann	*Chasing quantitative biases in neutron imaging with scintillator-camera detectors: a practical method with black body grids* Optics Express **26**, 15769–15784 (2018).
L. Capone, P. Marmet, L. Holzer, J. Dujc, J.O. Schumacher, A. Lamibrac, F.N. Büchi, J. Becker	*An Ensemble Monte Carlo Simulation Study of Water Distribution in Porous Gas Diffusion Layers for Proton Exchange Membrane Fuel Cells* Journal of Electrochemical Energy Conversion and Storage **15**, 031005-031005-10 (2018).
R. Chattot, O. Le Bacq, V. Beermann, S. Kühl, J. Herranz, S. Henning, L. Kühn, T. Asset, L. Guétaz, G. Renou, J. Drnec, P. Bordet, A. Pasturel, A. Eychmüller, T.J. Schmidt, P. Strasser, L. Dubau, F. Maillard	*Surface distortion as a unifying concept and descriptor in oxygen reduction reaction electrocatalysis* Nature Materials **17**, 827–833 (2018).
X. Cheng, E. Fabbri, Y. Yamashita, I.E. Castelli, B. Kim, M. Uchida, R. Haumont, I. Puente-Orench, T.J. Schmidt	*Oxygen Evolution Reaction on Perovskites: A Multieffect Descriptor Study Combining Experimental and Theoretical Methods* ACS Catalysis **8**, 9567–9578 (2018).
M. Cochet, A. Forner-Cuenca, V. Manzi, M. Siegwart, D. Scheuble, P. Boillat	*Novel Concept for Evaporative Cooling of Fuel Cells: an Experimental Study Based on Neutron Imaging* Fuel Cells **18**, 619–626 (2018).
J. Conder, C. Marino, P. Novák, C. Villevieille	*Do imaging techniques add real value to the development of better post-Li-ion batteries?* Journal of Materials Chemistry A **6**, 3304–3327 (2018).
J. Conder, C. Villevieille	*Is the Li–S battery an everlasting challenge for operando techniques?* Current Opinion in Electrochemistry **9**, 33–40 (2018).

M. De Bardi, R. Müller, C. Grünzweig, D. Mannes, P. Boillat, M. Rigollet, F. Bamberg, T.A. Jung, K. Yang	*On the needle clogging of staked-in-needle pre-filled syringes: Mechanism of liquid entering the needle and solidification process* European Journal of Pharmaceutics and Biopharmaceutics **128**, 272–281 (2018).
J. Dujc, A. Forner-Cuenca, P. Marmet, M. Cochet, R. Vetter, J.O. Schumacher, P. Boillat	*Modeling the Effects of Using Gas Diffusion Layers With Patterned Wettability for Advanced Water Management in Proton Exchange Membrane Fuel Cells* Journal of Electrochemical Energy Conversion and Storage **15**, 021001-021001-14 (2018).
E. Fabbri, T.J. Schmidt	*Oxygen Evolution Reaction – The Enigma in Water Electrolysis* ACS Catalysis **8**, 9765–9774 (2018).
G. Ferraresi, M. El Kazzi, L. Czornomaz, C.-L. Tsai, S. Uhlenbruck, C. Villevieille	*Electrochemical Performance of All-Solid-State Li-Ion Batteries Based on Garnet Electrolyte Using Silicon as a Model Electrode* ACS Energy Letters **3**, 1006–1012 (2018).
G. Ferraresi, C. Villevieille, I. Czekaj, M. Horisberger, P. Novák, M. El Kazzi	*SnO_2 Model Electrode Cycled in Li-Ion Battery Reveals the Formation of Li_2SnO_3 and Li_8SnO_6 Phases through Conversion Reactions* ACS Applied Materials & Interfaces **10**, 8712–8720 (2018).
E. Flores, P. Novák, E.J. Berg	*In situ and operando Raman spectroscopy of layered transition metal oxides for Li-ion battery cathodes* Front. Energ. Res. **6** (82), (2018).
E. Flores, N. Vonrüti, P. Novák, U. Aschauer, E.J. Berg	*Elucidation of $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ Redox Chemistry by Operando Raman Spectroscopy* Chemistry of Materials **30**, 4694–4703 (2018).
A. Fluri, D. Pergolesi, A. Wokaun, T. Lippert	*Stress generation and evolution in oxide heteroepitaxy* Physical Review B **97**, 125412 (2018).
M. Goktas, C. Bolli, E.J. Berg, P. Novák, K. Pollok, F. Langenhorst, M.v. Roeder, O. Lenchuk, D. Mollenhauer, P. Adelhelm	*Graphite as Cointercalation Electrode for Sodium-Ion Batteries: Electrode Dynamics and the Missing Solid Electrolyte Interphase (SEI)* Advanced Energy Materials **8**, 1702724 (2018).
K.V. Greco, A. Forner-Cuenca, A. Mularczyk, J. Eller, F.R. Brushett	*Elucidating the Nuanced Effects of Thermal Pretreatment on Carbon Paper Electrodes for Vanadium Redox Flow Batteries* ACS Applied Materials & Interfaces **10**, 44430–44442 (2018).
L. Gubler	*Polymer electrolyte materials for electrochemical energy devices* Elsevier Reference Module in Chemistry, Molecular Sciences and Chemical Engineering, ISBN 9780124095472 (2018).
L. Gubler, T. Nauser, F.D. Coms, Y.-H. Lai, C.S. Gittleman	*Prospects for Durable Hydrocarbon-Based Fuel Cell Membranes* Journal of The Electrochemical Society **165**, F3100–F3103 (2018).
L. Gubler, T.M. Nolte, T. Nauser	*Antioxidant Strategies for Hydrocarbon-Based Membranes* ECS Transaction **86**, 369–379 (2018).
J. Halter, F. Marone, T.J. Schmidt, F.N. Büchi	*Breaking through the Cracks: On the Mechanism of Phosphoric Acid Migration in High Temperature Polymer Electrolyte Fuel Cells* Journal of The Electrochemical Society **165**, F1176–F1183 (2018).
J. Halter, S. Thomas, S.K. Kaer, T.J. Schmidt, F.N. Büchi	*The influence of phosphoric acid migration on the performance of high temperature polymer electrolyte fuel cells* Journal of Power Sources **399**, 151–156 (2018).

S. Henning, R. Shimizu, J. Herranz, L. Kühn, A. Eychmüller, M. Uchida, K. Kakinuma, T.J. Schmidt	*Unsupported Pt_3Ni Aerogels as Corrosion Resistant PEFC Anode Catalysts under Gross Fuel Starvation Conditions* Journal of The Electrochemical Society **165**, F3001–F3006 (2018).
A. Iranzo, P. Boillat	*CFD simulation of the transient gas transport in a PEM fuel cell cathode during AC impedance testing considering liquid water effects* Energy **158**, 449–457 (2018).
H. Ishikawa, S. Henning, J. Herranz, A. Eychmüller, M. Uchida, T.J. Schmidt	*Tomographic Analysis and Modeling of Polymer Electrolyte Fuel Cell Unsupported Catalyst Layers* Journal of The Electrochemical Society **165**, F7–F16 (2018).
B.J. Kim, X. Cheng, D.F. Abbott, E. Fabbri, F. Bozza, T. Graule, I.E. Castelli, L. Wiles, N. Danilovic, K.E. Ayers, N. Marzari, T.J. Schmidt	*Highly Active Nanoperovskite Catalysts for Oxygen Evolution Reaction: Insights into Activity and Stability of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{2+\delta}$ and $PrBaCo_2O_{5+\delta}$* Advanced Functional Materials **28**, 1804355 (2018).
S. Lal, A. Lamibrac, J. Eller, F.N. Büchi	*Determination of Water Evaporation Rates in Gas Diffusion Layers of Fuel Cells* Journal of The Electrochemical Society **165**, F652–F661 (2018).
D. Leanza, C.A.F. Vaz, I. Czekaj, P. Novák, M. El Kazzi	*Solving the puzzle of $Li_4Ti_5O_{12}$ surface reactivity in aprotic electrolytes in Li-ion batteries by nanoscale XPEEM spectromicroscopy* Journal of Materials Chemistry A **6**, 3534–3542 (2018).
E. Marelli, C. Villevieille, S. Park, N. Hérault, C. Marino	*Co-Free P2–$Na_{0.67}Mn_{0.6}Fe_{0.25}Al_{0.15}O_2$ as Promising Cathode Material for Sodium-Ion Batteries* ACS Applied Energy Materials **1**, 5960–5967 (2018).
C. Marino, J. Cabanero, M. Povia, C. Villevieille	*Biowaste Lignin-Based Carbonaceous Materials as Anodes for Na-Ion Batteries* Journal of The Electrochemical Society **165**, A1400–A1408 (2018).
C. Marino, E. Marelli, S. Park, C. Villevieille	*Impact of Water-Based Binder on the Electrochemical Performance of P2-$Na_{0.67}Mn_{0.6}Fe_{0.25}Co_{0.15}O_2$ Electrodes in Na-Ion Batteries* Batteries **4**, 66 (2018).
R. Mohamed, T. Binninger, P.J. Kooyman, A. Hoell, E. Fabbri, A. Pătru, A. Heinritz, T.J. Schmidt, P. Levecque	*Facile deposition of Pt nanoparticles on Sb-doped SnO_2 support with outstanding active surface area for the oxygen reduction reaction* Catalysis Science & Technology **8**, 2672–2685 (2018).
G. Nagy, V. Sproll, U. Gasser, T.J. Schmidt, L. Gubler, S. Balog	*Scaling the Graft Length and Graft Density of Irradiation-Grafted Copolymers* Macromolecular Chemistry and Physics **219**, 1800311 (2018).
F.J. Oldenburg, M. Bon, D. Perego, D. Polino, T. Laino, L. Gubler, T.J. Schmidt	*Revealing the role of phosphoric acid in all-vanadium redox flow batteries with DFT calculations and in situ analysis* Physical Chemistry Chemical Physics **20**, 23664–23673 (2018).
D. Pergolesi, E. Gilardi, E. Fabbri, V. Roddatis, G.F. Harrington, T. Lippert, J.A. Kilner, E. Traversa	*Interface Effects on the Ionic Conductivity of Doped Ceria–Yttria-Stabilized Zirconia Heterostructures* ACS Applied Materials & Interfaces **10**, 14160–14169 (2018).
M. Povia, J. Herranz, T. Binninger, M. Nachtegaal, A. Diaz, J. Kohlbrecher, D.F. Abbott, B.-J. Kim, T.J. Schmidt	*Combining SAXS and XAS To Study the Operando Degradation of Carbon-Supported Pt-Nanoparticle Fuel Cell Catalysts* ACS Catalysis **8**, 7000–7015 (2018).
A. Rabis, T. Binninger, E. Fabbri, T.J. Schmidt	*Impact of Support Physicochemical Properties on the CO Oxidation and the Oxygen Reduction Reaction Activity of Pt/SnO_2 Electrocatalysts* The Journal of Physical Chemistry C **122**, 4739–4746 (2018).

M. Raventos, E.H. Lehmann, M. Boin, M. Morgano, J. Hovind, R. Harti, J. Valsecchi, A. Kaestner, C. Carminati, P. Boillat, P. Trtik, F. Schmid, M. Siegwart, D. Mannes, M. Strobl, C. Grunzweig	*A Monte Carlo approach for scattering correction towards quantitative neutron imaging of polycrystals* Journal of Applied Crystallography **51**, 386–394 (2018).
M. Reichardt, S. Sallard, C. Marino, D. Sheptyakov, P. Novák, C. Villevieille	*Multiple redox couples cathode material for Li-ion battery: Lithium chromium phosphate* Journal of Energy Storage **15**, 266–273 (2018).
R. Robert, P. Novák	*Switch of the Charge Storage Mechanism of $Li_xNi_{0.80}Co_{0.15}Al_{0.05}O_2$ at Overdischarge Conditions* Chemistry of Materials **30**, 1907–1911 (2018).
M. Saito, Y. Tachikawa, T. Fujinami, K. Mikami, Y. Hayashi, H. Shiroishi, D. Streich, E.J. Berg, P. Novák	*Lanthanum Manganite-based Air Electrode Catalysts and Their Application to Lithium-air Batteries: Effects of Carbon Support Oxidation* Electrochemistry **86**, 265–271 (2018).
S. Schmidt, S. Sallard, C. Borca, T. Huthwelker, P. Novák, C. Villevieille	*Phosphorus anionic redox activity revealed by operando P K-edge X-ray absorption spectroscopy on diphosphonate-based conversion materials in Li-ion batteries* Chemical Communications **54**, 4939–4942 (2018).
M. Suermann, T.J. Schmidt, F.N. Büchi	*Comparing the kinetic activation energy of the oxygen evolution and reduction reactions* Electrochimica Acta **281**, 466–471 (2018).
B. Sun, M. El Kazzi, E. Müller, E.J. Berg	*Toward high-performance $Li(Ni_xCo_yMn_z)O_2$ cathodes: facile fabrication of an artificial polymeric interphase using functional polyacrylates* Journal of Materials Chemistry A **6**, 17778–17786 (2018).
S.M. Taylor, A. Pătru, D. Perego, E. Fabbri, T.J. Schmidt	*Influence of Carbon Material Properties on Activity and Stability of the Negative Electrode in Vanadium Redox Flow Batteries: A Model Electrode Study* ACS Applied Energy Materials **1**, 1166–1174 (2018).
L. Vitoux, M. Reichardt, S. Sallard, P. Novák, D. Sheptyakov, C. Villevieille	*A Cylindrical Cell for Operando Neutron Diffraction of Li-Ion Battery Electrode Materials* Frontiers in Energy Research **6**, Article 76 (2018).
X. Wu, C. Villevieille, P. Novák, M. El Kazzi	*Monitoring the chemical and electronic properties of electrolyte–electrode interfaces in all-solid-state batteries using operando X-ray photoelectron spectroscopy* Physical Chemistry Chemical Physics **20**, 11123–11129 (2018).
Y. Wu, J.I.S. Cho, T.P. Neville, Q. Meyer, R. Ziesche, P. Boillat, M. Cochet, P.R. Shearing, D.J.L. Brett	*Effect of serpentine flow-field design on the water management of polymer electrolyte fuel cells: An in-operando neutron radiography study* Journal of Power Sources **399**, 254–263 (2018).

Talks

Invited Talks

F.N. Büchi	*Elektromobilität mit Brennstoffzellen und Wasserstoff – Stand der Technik und Ausblick* AGVS beider Basel, Sissach, Switzerland, October 25, 2018.
F.N. Büchi	*Wasserstoff zur Energiespeicherung - Demonstrator ESI Plattform* Symposium elektrische Energiespeicherung, Biel, Switzerland, November 27, 2018.
F.N. Büchi	*Brennstoffzellen, Batterien, Energiespeicher - Labor für Elektrochemie am PSI* Park Innovaare – Visit Axpo, Villigen, Switzerland, December 18, 2018.
E. Fabbri	*Insights into Perovskite Nano-Catalysts as Oxygen Electrodes for the Electrochemical Splitting of Water* Advanced Materials Seminar, EPF Lausanne, Switzerland, February 26, 2018.
E. Fabbri	*Perovskite Nano-Catalysts as Oxygen Electrodes for the Electrochemical Splitting of Water* ModVal 2018 – 15th Symposium on Modeling and Experimental Validation of Electrochemical Energy Devices, Aarau, Switzerland, April 12–13, 2018.
E. Fabbri	*Oxygen Evolution Reaction – The Enigma in Water Electrolysis* The 11th Young Faculty Meeting, Bern, Switzerland, June 5, 2018.
E. Fabbri	*Insights into Perovskite Nano-Catalysts as Oxygen Electrodes for the Electrochemical Splitting of Water* 69th Annual Meeting of the International Society of Electrochemistry, Bologna, Italy, September 2–7, 2018.
L. Gubler	*Membranes for All-Vanadium Redox Flow Batteries – Current Development Trends* 1st Swiss & Surrounding Battery Days, Baden, Switzerland, May 23–25, 2018
L. Gubler	*Antioxidant Strategies for Hydrocarbon-based Membranes* 234th ECS Annual Fall Meeting, Cancun, Mexico, September 30 – October 4, 2018.
L. Gubler	*Speicher und Energie-Umwandlungen, Wasserstoff* Workshop SBB – Empa Dübendorf, Switzerland, November 2, 2018.
L. Gubler	*Brennstoffzellen: Eine Technologie vor dem Durchbruch ?* Naturwissenschaftliche Gesellschaft Winterthur (NGW), Winterthur, Switzerland, November 9, 2018.
J. Herranz	*New Diagnostic Methods and Materials for Pt-Based Fuel Cell Catalysts* Physical Chemistry Seminar, TU Darmstadt, Darmstadt, Germany, April 12, 2018.
J. Herranz	*Pt-Based Aerogels As Enhanced-Durability Electrocatalysts for PEFCs* 234th ECS Fall Meeting, Cancun, Mexico, September 30 – October 4, 2018.
P. Kitz	*Combined in situ EIS and EQCM-D: Insights into interphase formation in Li-ion batteries* Battery Seminar, Department of Chemistry - Ångström Laboratory, Uppsala, Sweden, March 11, 2018.
C. Marino	*Is there a future for Na-ion batteries?* 1st Swiss & Surrounding Battery Days, Baden, Switzerland, May 23–25, 2018.

P. Novák	*Silicon Upgraded Negative Electrodes* IBA 2018 – International Battery Association Meeting, Jeju, South Korea, March 11–16, 2018.
P. Novák	*In Situ Monitoring of F- Formation in Lithium Ion Batteries by OEMS* 1st Swiss & Surrounding Battery Days, Baden, Switzerland, May 23–25, 2018.
P. Novák	*Operando Characterization of Interfaces in Batteries* 19th International Meeting on Lithium Batteries, Kyoto, Japan, June 17–22, 2018.
P. Novák	*Operando Characterization of Battery Materials* Seminar at the Technical University of Braunschweig, Braunschweig, Germany, August 8, 2018.
P. Novák	*Battery Science: A Balancing Act between Fundamental Research and Applications* Seminar at the University of Ulm, Ulm, Germany, October 16, 2018.
D. Perego	*Differential Electrochemical Mass Spectrometry (DEMS) for electrocatalysis: an overview* Invited seminar at Politecnico di Milano, Milano, Italy, December 13, 2018.
T.J. Schmidt	*Application of Synchrotron Based Methods to Study Electrochemical Energy Conversion Processes* TU Munich, Munich, Germany, January 8, 2018.
T.J. Schmidt	*Noble Metal Aerogels as Highly Durable Catalysts for Polymer Electrolyte Fuel Cell Applications* Ecole Polytechnique de Lausanne, Sion, Switzerland, March 15, 2018.
T.J. Schmidt	*The Oxygen Evolution Reaction – From the Catalyst to the Cell Level* Gordon Research Conference on Fuel Cells, Smithfield, RI, USA, August 2, 2018.
T.J. Schmidt	*Noble Metal Aerogels as Highly Durable Catalysts for Polymer Electrolyte Fuel Cell Applications* Massachusetts Institute of Technology, Chemical Engineering Department, Cambridge, MA, USA, August 3, 2018.
T.J. Schmidt	*Application of Noble Metal Aerogels in Polymer Electrolyte Fuel Cells* International Workshop on «Single Nanostructures, Nanomaterials, Aerogels and their Interaction», Dresden, Germany, August 30, 2018.
T.J. Schmidt	*Energiespeicherung im Energiesystem von Morgen* Aargauer Energie Aperos, Baden, Switzerland, November 20, 2018.
T.J. Schmidt	*Energiespeicherung im Energiesystem von Morgen* Aargauer Energie Aperos, Zofingen, Switzerland, November 22, 2018.
T.J. Schmidt	*The Oxygen Evolution Reaction – Properties of* IrO_2 University of Cape Town, HySA Catalysis, Cape Town, South Africa, November 29, 2018.
S. Trabesinger	*Unappreciated Complexity of Li–S Battery* 1st Swiss & Surrounding Battery Days, Baden, Switzerland, May 23–25, 2018.
S. Trabesinger	*Materials Engineering Challenges for Viable Li–S Battery Electrodes and Cells* CIMTEC 2018, 8th Forum on New Materials, Perugia, Italy, June 10–14, 2018.
S. Trabesinger	*Direct proof of Oxidation-and-Transport Processes within Li-ion cells* 256th ACS Meeting & Exposition, Boston, USA, August 19–23, 2018.

S. Trabesinger	*Viability of Graphite Electrodes with Performance-Enhancing Additives* 69th Annual Meeting of the International Society of Electrochemistry, Bologna, Italy, September 2–7, 2018.
S. Trabesinger	*Materials Choices for Viable Li–S Batteries* Funam2, 2nd International Workshop on Functional Nanostructured Materials, Krakow, Poland, October 11–12, 2018.
C. Villevieille	*Bulk and surface investigations of all-solid-state batteries: garnet ceramic solid electrolyte vs. sulfide-based solid electrolyte* IBA 2018 – International Battery Association, Jeju, South Korea, March 11-16, 2018.
C. Villevieille	*Challenges to tackle in all-solid-state batteries: Sulfide-based glassy solid electrolyte vs. garnet ceramic solid electrolyte* 1st International Symposium on Solid-State Batteries Dübendorf, Switzerland, May 28–29, 2018.
C. Villevieille	*What can we really learn about batteries from operando techniques?* ILL & ESS User Meeting, Diffraction on energy materials Grenoble, France, October 10–12, 2018.
C. Villevieille	*Designing, synthesizing, and monitoring battery materials using advanced operando techniques* Center of Advanced Materials, Heidelberg, Germany, November 8, 2018.
C. Villevieille	*Electrode materials, electrolyte or the engineering – what is the key to successful development of Na-ion batteries?* 5th International Conference on Sodium Batteries, Saint-Malo, France, November 12–15, 2018.
D. Vonlanthen	*Redox-Flow-Batterien – grosse und leistungsstarke Batteriespeicher* Symposium elektrische Energiespeicherung Schweiz, Biel, Switzerland, November 27, 2018.

Contributed Talks

U. Babic, M. Zlobinski, T. Schuler, T.J. Schmidt, L. Gubler	*PSI Electrolysis Activities – PEM/CCM Manufacturing and Advanced Diagnostics* ESTORE meeting, Roskilde, Denmark, February 6, 2018.
U. Babic, M. Zlobinski, T.J. Schmidt, L. Gubler	*Degradation Mechanisms and Accelerated Stress-Test Protocols for Polymer Electrolyte Water Electrolyzers* 234th ECS Fall Meeting, 2018, Cancun, Mexico, September 30 – October 4, 2018.
P. Boillat, M. Cochet, D. Scheuble, V. Manzi-Orezzoli, M. Siegwart	*Neutron Imaging for Fuel Cells: Yesterday, Today and Tomorrow* 11th World Conference on Neutron Radiography, Sydney, Australia, September 2–7, 2018.
F.N. Büchi, P. Boillat, L. Gubler	*Developments in Electrolysis at PSI* 9th IEA Annex 30 workshop, NREL, Golden, CO, USA, September 27, 2018.
M. Cochet , L. Höltschi, C. Jordy, C. Villevieille, P. Boillat	*Neutron Imaging for Solid State Batteries* 1st Swiss and Surroundings Battery Days, Baden, Switzerland, May 23–25, 2018.
K. Ebner, V.A. Saveleva, J. Herranz L. Ni, B.-J. Kim, M. Nachtegaal, U.I. Kramm, T.J. Schmidt	*A novel, inexpensive synthesis approach towards composition-controlled non-noble metal O_2 reduction catalysts* 69th Annual Meeting of the International Society of Electrochemistry, Bologna, Italy, September 2–5, 2018.

K. Ebner, V.A. Saveleva, J. Herranz L. Ni, B.-J. Kim, U.I. Kramm, T.J. Schmidt	*A novel synthesis approach for Fe/N/C-type ORR-catalysts – insights on composition and activity* 680th Wilhelm and Else Heraeus Seminar on «Materials Development for Automotive Propulsion», Bad Honnef, Germany, October 14–17, 2018.
A. Forner-Cuenca, V. Manzi-Orezzoli, L. Gubler, T.J. Schmidt, P. Boillat	*Diffusion Layers with Localized Hydrophilic Domains: Influence of Electron Energy on Spatial Resolution* 234th ECS Fall Meeting, 2018, Cancun, Mexico, September 30 – October 4, 2018.
L. Gubler, F.J. Oldenburg, T.J. Schmidt	*Amphoteric Membranes with Bilayer Architecture for Vanadium Redox Flow Batteries* Workshop on Ion Exchange Membranes for Energy Applications (EMEA 2018), Bad Zwischenahn, Germany, June 26–28, 2018.
J. Herranz, M. El Kazzi, L. Mangani, J. Diercks, M. Povia, M. Horisberger, A. Pătru, T.J. Schmidt	*Disclosing the Oxidation State of Copper Oxides upon Electrochemical CO_2-Reduction* 234th ECS Fall Meeting, Cancun, Mexico, September 30 – October 4, 2018.
J. Herranz, V. Saveleva, M. Nachtegaal, L. Ni, U. I. Kramm, T.J. Schmidt	*Composition Effects on the Aqueous-Electrolyte & PEFC activity of Fe-Based O_2-Reduction Catalysts* 234th ECS Fall Meeting, Cancun, Mexico, September 30 – October 4, 2018.
L. Höltschi, C. Jordy, C. Villevieille	*Caractérisation électrochimique de cathodes à haut potentiel pour les batteries tout-solide à base de soufre* La réunion annuelle du Groupe Français d'Etude des Composés d'Insertion (GFECI), Le Touquet, France, March 26–29, 2018.
L. Höltschi, C. Jordy, C. Villevieille	*Electrochemical Performance of High Voltage Cathodes in Sulfur based All-solid-state Batteries* 1st Swiss and Surrounding Battery Days, Baden, Switzerland, May 23-25, 2018.
F. Jeschull, P. Novák, S. Trabesinger	*Silicon as a Capacity Enhancing Additive in Graphite Electrodes* Advanced Battery Power Conference, Münster, Germany, April 10–11, 2018.
F. Jeschull, P. Novák, S. Trabesinger	*Challenges and Limitations of Silicon as a Capacity Enhancing Additive in Graphite Electrodes* 1st Swiss & Surrounding Battery Days, Baden, Switzerland, May 23–25, 2018.
F. Jeschull, F. Scott, S. Trabesinger	*Understanding the Improved Capacity Retention of Si Electrodes Prepared in Buffered Electrodes Slurries* 69th Annual Meeting of the International Society of Electrochemistry, Bologna, Italy, September 3–7, 2018.
D. Leanza, C.A.F. Vaz, I. Czekaj, P. Novák, M. El Kazzi	*The controversial surface reactivity of Li4Ti5O12 in the aprotic electrolyte disclosed with XPEEM* ModVal 2018 – 15th Symposium on Modeling and Experimental Validation of Electrochemical Energy Devices, Aarau, Switzerland, April 12–13, 2018.
D. Leanza, C.A.F. Vaz, P. Novák, M. El Kazzi	*XPEEM reveals the local (electro-) chemical surface reactions of the NCM cathode and their impact on the LTO counter anode* 234th ECS Fall Meeting, Cancun, Mexico, September 30 – October 4, 2018.
V. Manzi-Orezzoli, T.J. Schmidt, P. Boillat	*Gas Diffusion Media with Optimized Water Transport* 234th ECS Fall Meeting, Cancun, Mexico, September 30–October 4, 2018.
E. Marelli, C. Villevieille, C. Bolli, C. Marino	*How to Overcome the P2-Phases Na Deficiency: a Proof of Concept* 1st Swiss & Surrounding Battery Days, Baden, Switzerland, May 23–25, 2018.

C. Marino, J. Cabanero, M. Povia, C. Villevieille	*Biowaste lignin-based carbonaceous materials as anodes for Na-ion batteries* 69th Annual Meeting of the International Society of Electrochemistry, Bologna, Italy, September 2–7, 2018.
M. Mirolo, C.A.F. Vaz, P. Novák, M. El Kazzi	*XPEEM nanoscale surface spectroscopy applied to Li-ion battery electrodes: the case of NCA cycled vs. LTO* 1st Swiss and Surrounding Battery Days, Baden, Switzerland, May 23–25, 2018.
A. Mularczyk, A. Lamibrac, F. Marone, F.N. Büchi, T.J. Schmidt, J. Eller	*Convection driven droplet detachment from gas diffusion layers* ModVal 2018 – 15th Symposium on Modeling and Validation of Electrochemical Energy Devices, Aarau, Switzerland, April 12–13, 2018.
A. Mularczyk, A. Lamibrac, F. Marone, T.J. Schmidt, J. Eller, F.N. Büchi	*Droplet detachment from gas diffusion layers* 234th ECS Fall Meeting, Cancun, Mexico, October 2, 2018.
A. Mularczyk, F.N. Büchi, T.J. Schmidt, J. Eller	*Effect of Heat Transfer Limitations on the in situ Study of Water Evaporation Rates in Fuel Cell Gas Diffusion Layers* 2018 Physics of Drying Conference, Ecole des Ponts Paris Tech, Marne la Vallée, France, November 5–7, 2018.
G. Nagy, V. Sproll, U. Gasser, S. Balog, L. Gubler	*Nano-Structure and Performance of Radiation-Grafted Fuel Cell Membranes* Neutrons for Biology. New Vistas: Monitoring Water and Hydrogen Bonds, Szeged, Hungary, January 16, 2018.
F.J. Oldenburg, T.J. Schmidt, L. Gubler	*Balancing Vanadium Transport in All-Vanadium Redox Flow Batteries* ModVal 2018 – 15th Symposium on Modeling and Validation of Electrochemical Energy Devices, Aarau, Switzerland, April 12–13, 2018.
F.J. Oldenburg, T.J. Schmidt, L. Gubler	*Tuning Electrolyte Transport with Amphoteric PBI-Nafion Bilayered Membranes* The International Flow Battery Forum (IFBF), Lausanne, Switzerland, July 10–12, 2018.
A. Pătru, S. Taylor, D. Perego, T.J. Schmidt	*Insights into Performance and Degradation of Carbon based Negative Electrode in the All Vanadium Redox Flow Cell* 1st Swiss & Surroundings Battery Days, Baden, Switzerland, May 23–25, 2018.
A. Pătru, C. Borca, D. Perego, T. Huthwelker, F.J. Oldenburg, L. Gubler, T.J. Schmidt	*Investigation of V(V)/V(IV) Redox Reaction in Mixed Acid Electrolyte Using X-Ray Absorption Spectroscopy* 234th ECS Fall Meeting, Cancun, Mexico, September 30 – October 4, 2018.
A. Pătru, S. Taylor, O. Nibel, D. Perego, C. Borca, M. Bohn, F.J. Oldenburg, T. Huthwelker, L. Gubler, T.J. Schmidt	*Insights into electrodes and electrolytes in the all vanadium redox flow batteries* 234th ECS Fall Meeting, Cancun, Mexico, October 1–6, 2018.
A. Pătru, B. Pribyl, T. Binninger, T.J. Schmidt	*New Co-Electrolysis Cell Design with Improved CO_2 Reduction Efficiency* 234th ECS Fall Meeting, Cancun, Mexico, October 1–6, 2018.
A. Pătru, T. Binninger, B. Pribyl, T.J. Schmidt	*Design Principles of Bipolar Electrochemical Co-Electrolysis Cells for Efficient Reduction of Carbon Dioxide from Gas Phase at Low Temperature* 7th Symposium SCCER HaE, Rapperswil, Switzerland, November 6, 2018.
D. Perego, J. Herranz, T.J. Schmidt	*CO_2 reduction to valuable products: a Differential Electrochemical Mass Spectrometry (DEMS) study* SCCER Meeting 2018, Villars-sur-Ollon, Switzerland, January 22–24, 2018.
D. Perego, J. Herranz, S. M. Taylor, A. Pătru, T.J. Schmidt	*Differential Electrochemical Mass Spectrometry (DEMS) for electrocatalysis* 69th Annual Meeting of the International Society of Electrochemistry, Bologna, Italy, September 2–7, 2018.

D. Perego, J. Herranz, S. M. Taylor, A. Pătru, T.J. Schmidt	*Differential Electrochemical Mass Spectrometry (DEMS) for electrocatalysis* 2018 MRS Fall Meeting, Boston, USA, November 25–30, 2018.
M. Povia, T. Binninger, M. Nachtegaal, A. Diaz, J. Kohlbrecher, B.-J. Kim, T.J. Schmidt	*Operando Electrochemical Characterization of Pt on Carbon Catalysts combining XAS and SAXS* 69th Annual Meeting of the International Society of Electrochemistry, Bologna, Italy, September 2–7, 2018.
M. Povia, J. Herranz, T. Binninger, D.F. Abbott, B.J. Kim, M. Nachtegaal, T.J. Schmidt	*A Combined SAXS and XAS Setup of Operando Electrocatalyst Degradation Studies* 234th ECS Fall Meeting, Cancun, Mexico, October 1–6, 2018.
V.A. Saveleva, J. Herranz, T.J. Schmidt	*Degradation of the Carbon Support in Fe/N/C Catalysts used for the Reduction of Oxygen in PEM Fuel Cells* 680th Wilhelm and Else Heraeus Seminar on «Materials Development for Automotive Propulsion», Bad Honnef, Germany, October 16, 2018.
M. Siegwart, M. Cochet, V. Manzi- Orezzoli, M. Zlobinski, T.J. Schmidt, J. Zhang, P. Boillat	*Time-of-flight Neutron Imaging for the Localization of Freezing Events during PEFC Cold Starts* ModVal 2018 – 15th Symposium on Modeling and Validation of Electrochemical Energy Devices, Aarau, Switzerland, April 12–13, 2018.
M. Siegwart, M. Cochet, V. Manzi-Orezzoli, T.J. Schmidt, J. Zhang, P. Boillat	*Time-of-Flight Neutron Imaging for the Distinction of Super-cooled Water and Ice during PEFC Cold-starts* 234th ECS Fall Meeting, Cancun, Mexico, September 30 – October 4, 2018.
X. Wu, C. Villevieille, P. Novák, M. El Kazzi	*Operando X-ray Photoelectron Spectroscopy Monitoring Electrolyte–Electrode Interfaces in All-Solid-State Batteries* 1st Swiss & Surrounding Battery Days, Baden, Switzerland, May 23–25, 2018.
X. Wu, C. Villevieille, P. Novák, M. El Kazzi	*Electrolyte–Electrode Interfacial reactivity in All-Solid-State Batteries Elucidated By Operando XPS* 234th ECS Fall Meeting, Cancun, Mexico, September 30 – October 4, 2018.
M. Zlobinski, T.J. Schmidt, P. Boillat	*Contamination of Proton Exchange Membrane and Regeneration Strategies* 69th Annual Meeting of the International Society of Electrochemistry, Bologna, Italy, September 2–7, 2018.

Patents

F.J. Oldenburg, A. Albert, L. Gubler	*Amphoteric Electrolyte Membrane and a Redox Flow Battery comprising an Electrolyte Membrane* EP 18175340.1, filed May 31, 2018.
U. Babic, M. Zlobinski, P. Boillat, L. Gubler	*Method for Removing Non-Proton Cationic Impurities from an Electrochemical Cell and an Electrochemical Cell* EP 18196579.9, filed September 25, 2018.
L. Gubler, A. Arndt, F.J. Oldenburg	*Bilayer Electrolyte Membrane and a Redox Flow Battery comprising a Bilayer Electrolyte Membrane* EP 18199911.1, filed October 11, 2018.

Posters

D. Aegerter, B.-J. Kim, E. Fabbri, T.J. Schmidt	*The Effect of Fe in* $Ba_{0.5}Sr_{0.5}Co_xFe_{1-x}O_{3-\delta}$ *Towards the Oxygen Evolution Reaction in Alkaline Media,* 7th Symposium SCCER HaE, Rapperswil, Switzerland, November 6, 2018.
U. Babic, E. Nilsson, A. Pătru, T.J. Schmidt, L. Gubler	*Cell Performance Determining Effects of the Anode Catalyst Layer Loading in Polymer Electrolyte Water Electrolyzers* ModVal 2018 – 15th Symposium on «Modeling and Experimental Validation of Electrochemical Energy Devices», Aarau, Switzerland, April 12–13, 2018.
C. Bolli, A. Guéguen, M.A. Mendez, E.J. Berg	*In Situ Study of the Reaction Mechanisms of TMSPi and TMSPa Additives in Lithium Ion Batteries by OEMS* 233rd ECS Annual Spring Meeting, Seattle, USA, May 13–17, 2018.
F.N. Büchi, A. Mularczyk, A. Lamibrac, F. Marone, T.J. Schmidt, J. Eller	*Synchrotron based characterization of droplet detachment from gas diffusion layers* Gordon Research Conference on Fuel Cells, Smithfield, RI, USA, July 29-August 2, 2018.
M. Cochet, M. Siegwart, D. Scheuble, P. Boillat	*Modeling Evaporation Cooled Fuel Cells* ModVal 2018 – 15th Symposium on «Modeling and Experimental Validation of Electrochemical Energy Devices», Aarau, Switzerland, April 12–13, 2018.
M. Cochet, U. Hannesen, P. Boillat	*Neutron Radiography Study of the Water Management in a Commercial-Size PEFC for the AutoStack-Core Project* 34th PSI Electrochemistry Symposium, Paul Scherrer Institut, Villigen, Switzerland, April 25, 2018.
J. Conder, C. Villevieille	*How reliable is the Na metal as a reference electrode?* 19th International Meeting on Lithium Batteries, Kyoto, Japan, June 17–22, 2018.
J. Conder, C. Villevieille, C. Marino, C. Ghimbeu	*Electrochemical investigation of hard-carbon materials for Na-ion batteries, role of the electrode formulation* 19th International Meeting on Lithium Batteries, Kyoto, Japan, June 17–22, 2018.
K. Ebner, B.-J. Kim, T.J. Schmidt	*A novel synthesis approach towards Fe-based non-noble metal oxygen reduction catalysts employing sodium carbonate as an inexpensive pore inducing agent* 34th PSI Electrochemistry Symposium, Paul Scherrer Institut, Villigen, Switzerland, April 25, 2018.
K. Ebner, V.A. Saveleva, L. Ni, B.-J. Kim, M. Nachtegaal, U.I. Kramm, T.J. Schmidt	*A novel, inexpensive synthesis approach towards composition-controlled non-noble metal* O_2 *reduction catalysts* 69th Annual Meeting of the International Society of Electrochemistry, Bologna, Italy, September 2–5, 2018.
E. Flores, U. Aschauer, P. Novák, E.J. Berg,	*Operando Raman spectroscopy study of* $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ 19th International Meeting on Lithium Batteries, Kyoto, Japan, June 17, 2018.
J. Halter, T.J. Schmidt, F.N. Büchi	*Phosphoric Acid Invasion in GDLs: Temperature and Concentration Dependence and Correlation to Contact Angles* ModVal 2018 – 15th Symposium on «Modeling and Experimental Validation of Electrochemical Energy Devices», Aarau, Switzerland, April 12–13, 2018.
L. Höltschi, X. Wu, C. Borca, T. Huthwelker, C. Jordy, C. Villevieille	*Soft X-Ray Absorption Spectroscopy to Elucidate the Solid Electrolyte Decomposition in Sulfide Based All-solid-state Batteries* 34th PSI Electrochemistry Symposium Paul Scherrer Institut, Villigen, Switzerland, April 25, 2018.

L. Höltschi, M. Cochet, C. Jordy, C. Villevieille, P. Boillat	*Operando Neutron Imaging to Investigate Li-ion Transport in All-solid-state Batteries* 1st International Symposium on Solid-State Batteries, Dübendorf, Switzerland, May 28–29, 2018.
L. Höltschi, M. Cochet, C. Jordy, C. Villevieille, P. Boillat	*Operando investigation of solid state batteries (Li3PS4 solid electrolyte) by neutron imaging techniques* 19th International Meeting on Lithium Batteries, Kyoto, Japan, June 17–22, 2018.
L. Höltschi, C. Jordy, C. Villevieille	*Electrochemical Performance of High Voltage Cathodes in Sulfur based All-solid-state Batteries* 69th Annual Meeting of the International Society of Electrochemistry Bologna, Italy, September 2–7, 2018.
P. Kitz, E. Berg	*Simultaneous in-situ EIS and EQCM-D: New insights into interphase formation in Li-ion batteries* 1st Swiss & Surrounding Battery Days, Baden, Switzerland, May 23–25, 2018.
P. Kitz, P. Novák, E.J. Berg	*Simultaneous in-situ EIS and EQCM-D: New insights into interphase formation in Li-ion batteries* 19th International Meeting on Lithium Batteries, Kyoto, Japan, June 17–22, 2018.
V. Manzi-Orezzoli, P. Boillat	*Modifying Microporous Layers for Polymer Electrolyte Fuel Cells* ModVal 2018 – 15th Symposium on «Modeling and Experimental Validation of Electrochemical Energy Devices», Aarau, Switzerland, April 12–13, 2018.
E. Marelli, C. Villevieille, C. Bolli, C. Marino	*How to overcome the P2-phases Na deficiency: a proof of concept* 34th PSI Electrochemistry Symposium, Paul Scherrer Institut, Villigen, Switzerland, April 25, 2018.
C. Marino, M. El Kazzi, E.J. Berg, M. He, C. Villevieille	*Interface and safety properties of Phosphorus-based negative electrodes for Li-ion batteries* 1st Swiss & Surrounding Battery Days, Baden, Switzerland, May 23–25, 2018.
C. Marino, C. Bolli, E. Marelli, E. Kendrick, C. Villevieille	*The electrochemical mechanisms of the* $O3\text{-}Na(Ni_{0.5}Mn_{5/16}Sn_{1/16}Ti_{1/8})O_2$ *(NNMST) phase used as cathode material for Na-ion batteries* 7th Symposium SCCER HaE, Rapperswil, Switzerland, November 6, 2018.
M. Mirolo, C.A.F. Vaz, P. Novák, M. El Kazzi	*XPEEM nanoscale surface spectroscopy applied to Li-ion battery electrodes: the case of NCA cycled vs. LTO* ModVal 2018 – 15th Symposium on «Modeling and Experimental Validation of Electrochemical Energy Devices», Aarau, Switzerland, April 12–13, 2018.
M. Mirolo, C.A.F. Vaz, P. Novák, M. El Kazzi	*Electrodes' surface evolution and cross-talk processes in a full cell NCA vs. LTO revealed by XPEEM* 69th Annual Meeting of the International Society of Electrochemistry, Bologna, Italy, September 2–7, 2018.
A. Mularczyk, F.N. Büchi, T.J. Schmidt, J. Eller	*Water Evaporation Induced Temperature Distribution in Gas Diffusion Layers of Polymer Electrolyte Fuel Cells* 69th Annual Meeting of the International Society of Electrochemistry, Bologna, Italy, September 2–7, 2018.
F.J. Oldenburg, T.J. Schmidt, L. Gubler	*Balancing Vanadium Transport in All-Vanadium Redox Flow Batteries* NES-ENE PhD-Day, Paul Scherrer Institut, Villigen, Switzerland, April 26, 2018.
D. Perego, M. Porto, J. Herranz, C. Marmy, P. Rüttimann, T.J. Schmidt	CO_2 *reduction to valuable products: a Differential Electrochemical Mass Spectrometry (DEMS) study* PSI Catalysis Seminar, Paul Scherrer Institut, Villigen, Switzerland, February 1, 2018.

D. Perego, J. Herranz, T.J. Schmidt	*Differential Electrochemical Mass Spectrometry for electrocatalysis* 34th PSI Electrochemistry Symposium, Paul Scherrer Institut, Villigen, Switzerland, April 25, 2018.
D. Perego, J. Herranz, T.J. Schmidt	*Differential Electrochemical Mass Spectrometry (DEMS) for electrocatalysis* 7th Symposium SCCER HaE, Rapperswil, Switzerland, November 6, 2018.
B. Pribyl, T. Binninger, T.J. Schmidt	*Efficient CO_2 reduction from gas phase at low temperatures in a bipolar like co-electrolysis cell configuration* 34th PSI Electrochemistry Symposium, Paul Scherrer Institut, Villigen, Switzerland, April 25, 2018.
B. Pribyl, T. Binninger, T.J. Schmidt	*Efficient CO_2 reduction from gas phase at low temperatures in a bipolar like co-electrolysis cell configuration* PSI Catalysis Seminar, Paul Scherrer Institut, Villigen, Switzerland, June 14, 2018.
B. Pribyl, T. Binninger, T.J. Schmidt	*Efficient CO_2 reduction from gas phase at low temperatures in a bipolar like co-electrolysis cell configuration* Summer School «Power-to-X: Fundamentals and Applications of Modern Electrosynthesis», Villars-sur-Ollon, Switzerland, August 27–31, 2018.
B. Pribyl, T. Binninger, T.J. Schmidt	*Efficient CO_2 reduction from gas phase at low temperatures in a bipolar like co-electrolysis cell configuration* 69th Annual Meeting of the International Society of Electrochemistry, Bologna, Italy, September 2–7, 2018.
B. Pribyl, T. Binninger, T.J. Schmidt	*Efficient CO_2 reduction from gas phase at low temperatures in a bipolar like co-electrolysis cell configuration and comparison to liquid phase CO_2RR* 7th SCCER HaE Symposium, Rapperswil, Switzerland, November 6, 2018.
V.A. Saveleva, J. Herranz, M. Nachtegaal, U.I. Kramm, T.J. Schmidt	*Fe/N/C Oxygen Reduction Catalysts for PE Fuel Cells: Composition and Performance* Summer School «Power to X: Fundamentals and Applications of Modern Electrosynthesis», Villars-sur-Ollon, Switzerland, August 28, 2018.
S. Schneider, P. Novák, E.J. Berg	*Performance modeling of Li-ion and Na-ion batteries* ModVal 2018 – 15th Symposium on «Modeling and Experimental Validation of Electrochemical Energy Devices», Aarau, Switzerland, April 12–13, 2018.
S. Schneider, P. Novák, C. Bauer, E.J. Berg	*Could Na-ion batteries be more suitable than Li-ion batteries for high-power applications?* 69th Annual Meeting of the International Society of Electrochemistry, Bologna, Italy, September 2–7, 2018.
S. Schneider, E.J. Berg, C. Bauer, P. Novák	*A Techno-Economic and Environmental Assessment of Future Na-Ion Batteries* 7th Symposium SCCER HaE Rapperswil, Switzerland, November 6, 2018.
T. Schuler, T.J. Schmidt, F.N. Büchi	*Morphological and Topological Characterization of Porous Transport Layers for Proton Exchange Water Electrolysis* ModVal 2018 – 15th Symposium on «Modeling and Experimental Validation of Electrochemical Energy Devices», Aarau, Switzerland, April 12–13, 2018.
Y. Surace, T. Schott, S. Zürcher, M.E. Spahr, P. Novák, S. Trabesinger	*Development of SnO_2-Graphite Electrodes with Long-Term Cycling Stability* 1st Swiss and Surrounding Battery Days, Baden, Switzerland, May 23–25, 2018.
Y. Surace, T. Schott, S. Zürcher, M.E. Spahr, P. Novák, S. Trabesinger	*Development of SnO_2-Upgraded Graphite Electrodes with Excellent Cycling Stability* 19th International Meeting on Lithium Batteries, Kyoto, Japan, June 17–22, 2018.

A.O. Tezel, S. Sunde, D.K. Streich, A. Guéguen, J.L. Gómez-Cámer, M. Hahlin, K. Edström, P. Novák	*Boron Based Anion Receptor as Electrolyte Additive for Li Ion Batteries* 19th International Meeting on Lithium Batteries, Kyoto, Japan, June 17–22, 2018.
X. Wu, C. Villevieille, P. Novák, M. El Kazzi	*Operando X-ray Photoelectron Spectroscopy Monitoring Electrolyte – Electrode Interfaces in All-Solid-State Batteries* 34th PSI Electrochemistry Symposium, Paul Scherrer Institut, Villigen, Switzerland, April 25, 2018.
X. Wu, C. Villevieille, P. Novák, M. El Kazzi	*Operando X-ray Photoelectron Spectroscopy Monitoring Electrolyte – Electrode Interfaces in All-Solid-State Batteries* 1st International Symposium on Solid-State Batteries, Dübendorf, Switzerland, May 28–29, 2018.
H. Xu, M. Bührer, F. Marone, F.N. Büchi, T.J. Schmidt, J. Eller	*Studies of Water Distribution in the Gas Diffusion Layer of Polymer Electrolyte Fuel Cells using X-ray Tomographic Microscopy* ModVal 2018 – 15th Symposium on «Modeling and Experimental Validation of Electrochemical Energy Devices», Aarau, Switzerland, April 13, 2018.
H. Xu, M. Bührer, F. Marone, F.N. Büchi, T.J. Schmidt, J. Eller	*Quantification of GDL water feature detectability for operando subsecond X-ray tomographic microscopy imaging of PEFCs* 69th Annual Meeting of the International Society of Electrochemistry, Bologna, Italy, September 4, 2018.
M. Zlobinski, P. Boillat	*Water and Gas Distribution in Porous Transport Layers of Proton Exchange Membrane Water Electrolyzer* ModVal 2018 – 15th Symposium on «Modeling and Experimental Validation of Electrochemical Energy Devices», Aarau, Switzerland, April 12–13, 2018.

Conferences & Workshops Organizations

F.N. Büchi, E.J. Berg, J. Eller, L. Gubler	*17th Symposium on Polymer Electrolyte Fuel Cells PEFC 17* ModVal 2018 – 15th Symposium on «Model and Experimental Validation of Electrochemical Energy Devices», Aarau, Switzerland, April 12 – 13, 2018. Members of Organizing committee
F.N. Büchi	*34th PSI Electrochemistry Symposium: Pushing the Limits of Characterization in Electrochemistry* Paul Scherrer Institut, Villigen, Switzerland, April 25, 2018.
F.N. Büchi, T.J. Schmidt	*18th Symposium on Polymer Electrolyte Fuel Cells & Eletrolysis PEFC & EC18* 234th ECS Fall Meeting, Cancun, Mexico, September 30 – October 4, 2018. Members of Organizing committee
C. Villevieille, C. Marino	*1st Swiss and Surrounding Battery Days* Baden, Switzerland, May 23–25, 2018. Organizing committee

Editorial Work

F.N. Büchi, T.J. Schmidt (Co-Editors)	*Polymer Electrolyte Fuel Cells & Electrolysis 18 (PEFC & EC 18)* ECS Transactions **86** (13), The Electrochemical Society, Pennington, NJ, USA (2018).
C. Gloor, P. Lutz, F.N. Büchi, L. Gubler, T.J. Schmidt, C. Villevieille	*PSI Electrochemistry Laboratory Annual Report 2017* doi: 10.3929/ethz-a-007047464, ISSN 1661–5379

Paul Scherrer Institut :: 5232 Villigen PSI :: Switzerland :: Tel. +41 56 310 21 11 :: Fax +41 56 310 21 99 :: www.psi.ch