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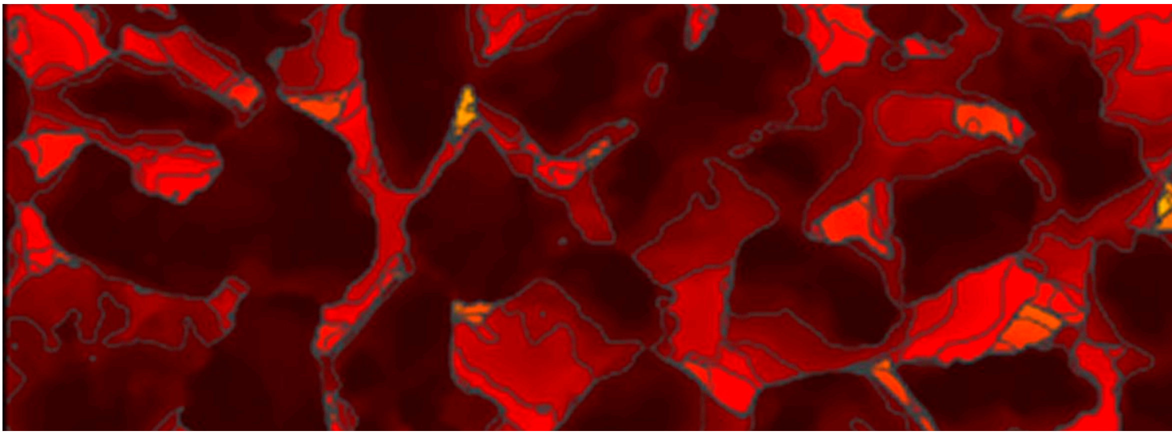

Annual Report 2022

Electrochemistry Laboratory

Cover
Surface profile of a porous Ti-based transport layer for polymer electrolyte water electrolyzer, obtained from X-ray tomography data.

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Annual Report 2022

Electrochemistry Laboratory

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CONTENTS

Editorial 3

The Electrochemistry Laboratory at a Glance 4

CURRENT SCIENTIFIC TOPICS 7

SCIENTIFIC HIGHLIGHTS

1 **Direct Evidence of *in situ* Co-Oxyhydroxide Formation on the Surface of $La_{0.2}Sr_{0.8}CoO_{3-\delta}$ Water Splitting Catalyst** 8

2 ***Operando* X-ray Tomographic Microscopy of Polymer Electrolyte Fuel Cell Freeze Start** 11

3 **Enabling the use of Thin Membranes in Water Electrolyzers using a Recombination Catalyst** 13

4 ***In situ* Spectroscopy Unveils the Structural Changes of the Sites in Single Atom Catalysts** 16

5 **Stable Performance of High Capacity Cobalt-Free Li-ion Battery** 18

6 **High Performance Doped Li-rich $Li_{1+x}Mn_{2-x}O_4$ Cathode Nanoparticles Synthesized by Facile, Fast and Efficient Microwave-assisted Hydrothermal Route** 21

7 **High Performance Gas Diffusion Layers with Added Deterministic Structures** 24

8 **The Effects of Hydrophobicity Treatment of Gas Diffusion Layer on Ice Crystallization in PEFCs** 27

9 **Damage-Repair Cycle in Hydrocarbon Based Membranes for Fuel Cells** 30

10 **Li-ion Solvation in TFSI- and FSI-based Ionic Liquid Electrolytes Probed by X-ray Photoelectron Spectroscopy** 33

11 **Versatile and Fast Methodology for Evaluation of Metallic Lithium Negative Battery Electrodes** 36

12 **Prevention of Freezing Propagation in Fuel Cells Using Segmentation** 39

DISSERTATIONS

1 **Evaporative Cooling for Polymer Electrolyte Fuel Cells – A Combined Numerical and Experimental Analysis** 43

2 **Investigation of the CO_2 Electroreduction Selectivity Determining Factors on Palladium Nanostructures** 45

3 **Ir Oxide Based Electrocatalysts for Water Splitting: Artifact-free Advanced *Operando* Spectroscopic Characterization** 47

4 **Non-invasive and Local Impedance Diagnostics for Polymer Electrolyte Fuel Cell Stacks** 49

5 **Characterizing Water Transport in the Microporous Layers of Polymer Electrolyte Fuel Cells** 51

6 **Electrochemical CO_2-Reduction on Au and Au-Cu Aerogels: From Selectivity Trends to Interfacial Effects** 53

7 **Design of Non-noble Metal Catalyst Layers for PEM Fuel Cells: Performance & Stability** 55

THE ELECTROCHEMISTRY LABORATORY **57**

FACTS & FIGURES

Structure 2022 58

Personnel 2022 59

Awards 62

Bachelor and Master Students 65

Conferences – Symposia 68

Documentation 70

EDITORIAL

PSI's Electrochemistry Laboratory is the leading center for research in 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.

With minor implications of the pandemic in 2022, the Lab has produced a strong scientific output. In this Annual Report 2022, you find 12 highlights on outstanding results of the Lab, contributing to the grand challenges of electrochemical energy storage and conversion. Further the Laboratories key facts and figures for 2022 are given, including a full list of our 44 peer reviewed publications and numerous talks demonstrating the leading role of PSI's Electrochemistry Laboratory on the national and international level.

After two years of on-line events in 2020/21 the annual 38th Swiss Electrochemistry Symposium «Electrochemical Valorization of Carbon Dioxide» was held successfully in May, back in the Kultur & Kongresshaus in Aarau, with world-class scientists and engineers as speakers, attracting an audience of more than 100 participants. Details of this event you will find also in this annual report on page 68.

2022 was also a successful year for 7 of our PhD students who successfully defended their theses. An overview on their PhD work is given in this report. The new PhDs mostly continued their careers directly 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 dedication and passion of all collaborators in the Lab, which I gratefully acknowledge, neither without the funding we received 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.

Felix N. Büchi

THE ELECTROCHEMISTRY LABORATORY AT A GLANCE

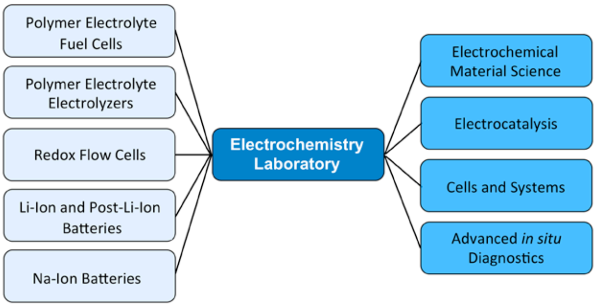
Our Mission

Advancing electrochemical energy storage and conversion by
- **developing novel electrochemical materials, cells and devices;**
- **using novel, advanced *in situ* and *operando* methods;**
- **performing fundamental, applied and industry-oriented research.**

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 and implementation of electrochemical energy storage and conversion, specifically in the context of a sustainable energy system. This requires renewable energy to be stored in secondary batteries or chemicals such as hydrogen and be (re-)converted into electricity. The Laboratory's R & D, is hence focused on secondary batteries – specifically Li-based systems as well as polymer electrolyte fuel cells and electrolyzers to produce hydrogen and reduce CO_2.

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 implementation.

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, making intensive use of PSI's unique large scale facilities such as the Swiss Light Source (SLS) and the Swiss Neutron Spallation Source (SINQ).



Topics of Electrochemistry Laboratory.

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 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.

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*.

Postdoc Dr. Valerie Siller and PhD student Samuel Gatti assemble air-sensitive Li-ion and Na-ion test cells with solid and liquid electrolytes.

Electrochemical Energy Conversion

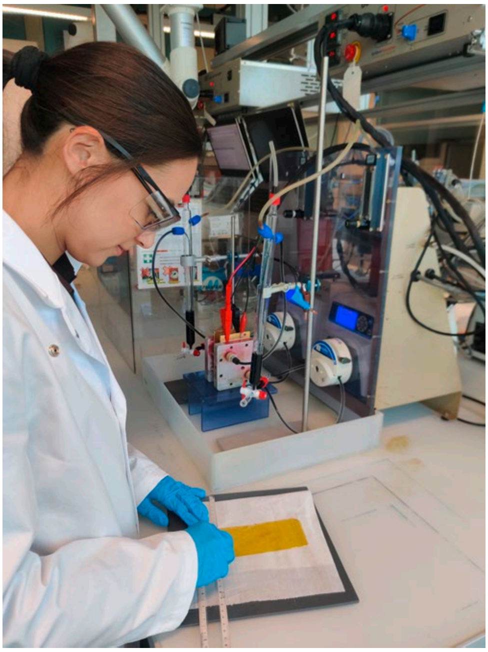
The Electrochemical Energy Conversion focuses on the development and in-depth understanding of materials, processes and devices for the conversion of renewable power to hydrogen (or syngas through the electrochemical reduction of carbon dioxide) and back to power. Especially in the context of a sustainable 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) with strong use of the large installations at PSI (Swiss Light Source and Neutron Spallation Source);
- research in electrocatalysis and the reaction kinetics of the relevant reactions (e.g., the oxygen electrode reactions) for developing new electrocatalysts and improved understanding of intrinsically limiting factors;
- development of new porous materials for PEFC and PEWE;
- membrane development based on functionalized commercial polymeric materials;
- system, stack and cell testing.

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.



Postdoctoral Researcher Elizabeth Hampson preparing membrane samples in front of the redox flow battery test station.

CURRENT SCIENTIFIC TOPICS

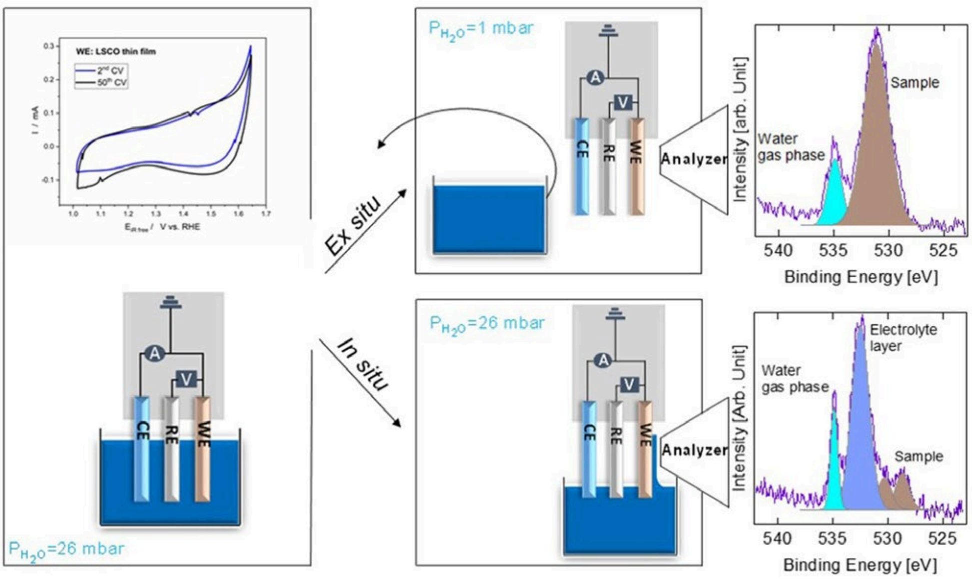
SCIENTIFIC HIGHLIGHTS

Direct Evidence of *in situ* Co-Oxyhydroxide Formation on the Surface of $La_{0.2}Sr_{0.8}CoO_{3-\delta}$ Water Splitting Catalyst

We carried out *in situ* and *ex situ* ambient pressure X-ray photoelectron spectroscopy (APXPS) experiments on a $La_{0.2}Sr_{0.8}CoO_{3-\delta}$ perovskite oxygen evolution reaction (OER) catalyst. The study shows that Sr is leached into the electrolyte after immersion, leading to surface Co active site enrichment. Such a Co-enriched surface evolves into a new phase during operation. With the help of theoretical simulations, such a species is assigned to Co-oxyhydroxide, providing direct evidence of its formation during the OER.

Understanding the mechanism of the oxygen evolution reaction (OER) on perovskite materials is of great interest for the development of more active catalysts. The complexity of catalytic systems and scarce *in situ* and *operando* surface sensitive spectroscopic tools render the detection of active sites and the understanding of reaction mechanisms challenging.

Recent progress in ambient pressure X-ray photoelectron spectroscopy (APXPS) allows the *in situ* surface investigation of OER catalysts. Particularly, by means of the «dip and pull» method, which makes use of a standard electrochemical three electrode setup, it is possible to simultaneously perform electrochemical and XPS characterizations. In the



«dip and pull» method, a thin liquid electrolyte layer (10–30 nm thickness) is stabilized at the sample surface. This provides potential control of the working electrode while performing XPS measurements.

However, in order to probe the buried interface of the electrode, it is necessary to generate photoelectrons with high kinetic energies, which can travel through the thin electrolyte layer and a vapor ambient pressure of 30 mbar. For this reason, tender X-rays (3000–10 000 eV) are typically used. Under OER conditions, OH ions in the thin electrolyte layer are quickly consumed and diffusion limitations from the bulk solution can lead to their depletion. This creates a high ohmic resistance that makes real *operando* measurements challenging. A second possibility for investigating catalyst surface changes induced by the OER is by performing XPS measurements *ex situ* directly after electrochemical measurements. In this case, XPS is not performed while a potential is applied to the working electrode. This *ex situ* approach overcomes drawbacks associated with the thin electrolyte meniscus, required for «dip and pull» measurements. Soft X-rays (< 2000 eV) can be utilized and their energy can be tuned to be sensitive to the topmost layers of the electrode, where active species form. In the present study, we have compared the results obtained by *in situ* and *ex situ* AP-XPS measurements on a $La_{0.2}Sr_{0.8}CoO_{3-\delta}$ (LSCO) thin film perovskite electrode. LSCO is known to be a highly OER-active catalyst.

Figure 1

Schematics of the experiment. Initially, the cyclic voltammograms of LSCO are measured in a three-electrode cell. In the case of in situ experiments (tender X-rays) the sample is pulled in the measurement position while holding the potential at 1.6 VRHE and XPS spectra are measured through the thin electrolyte. In the case of the ex situ experiments (soft X-rays), the sample is pulled out and measured by XPS outside the electrolyte under a partial pressure of 1 mbar. On the right, measured O 1s spectra are reported.

The different experimental approaches provide complementary information that allow a complete characterization of the surface during and after the OER. Immersion of LSCO in the electrolyte solution leads to the leaching of surface segregated strontium species, leaving cobalt active sites exposed. Thanks to *in situ* and *ex situ* photoemission of O 1s performed during and after the OER, respectively, a new phase has been detected and assigned to surface cobalt oxyhydroxide. Such results have been confirmed by means of theoretical calculations of core electron binding energies. The direct observation of perovskite surface reconstruction during the OER, and the clear detection of a spectroscopic signature, undoubtedly indicate that the real active site for the perovskite OER activity is a Co-based oxyhydroxide layer. However, the perovskite structure is still visible underneath Co-oxyhydroxide, suggesting an equilibrium between the two under the present experimental conditions.

This study represents a clear example of *in situ* and *ex situ* surface sensitive measurements combined to detect active species formed during a reaction.

Acknowledgement

The post-doc position of AB was funded by the Energy and Environment division of the Paul Scherrer Institute. ZN, NC and JTD acknowledge Swiss National Science Foundation for project grant 200020_172641. JTD additionally acknowledges the support from European Union's Horizon 2020 program (FPRESOMUS – MSCA 801459). This work was performed at the *PHOENIX I* (X07MB) beamline and *In situ Spectroscopy* (X07DB) beamline of the Swiss Light Source, Paul Scherrer Institut.

Publication

Direct Evidence of Cobalt Oxyhydroxide Formation on a $La_{0.2}Sr_{0.8}CoO_3$ Perovskite Water Splitting Catalyst.
Anthony Boucly, Luca Artiglia, Emiliana Fabbri, Dennis Palagin, Dino Aegerter, Daniele Pergolesi, Zbynek Novotny, Nicolo Comini, J. Trey Diulus, Thomas Huthwelker, Markus Ammann, Thomas J. Schmidt.
Journal of Materials Chemistry A ***10****, 2434 (2022).*
DOI: 10.1039/d1ta04957g

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Operando X-ray Tomographic Microscopy of Polymer Electrolyte Fuel Cell Freeze Start

Understanding the water management in polymer electrolyte fuel cells (PEFCs) during sub-zero operation is crucial for designing effective freeze start strategies. In collaboration with Toyota Motor Europe sub-second X-ray tomographic microscopy was used to study the water distributions in the gas diffusion layer (GDL) of PEFCs during dynamic freeze starts from –30°C that mimic automotive freeze start conditions at different pre-drying levels and varying the feed gas humidity.

Proper drying of PEFCs before shutdown and freeze has significant influence on freeze start performance.

The *operando* tomographic imaging at the TOMCAT beamline of the Swiss Light Source (SLS) at PSI revealed that no additional water formed in the GDL between –30°C and 0°C independent of the of the pre-drying level. Mechanical machining of the microporous layer (MPL) enabled to verify the existence of super-cooled liquid water at the interface between the catalyst layer and the MPL/GDL at intermediate humidity conditions, which cannot drain into the GDL due to the high capillary pressure barrier of the hydrophobic MPL with sub-micrometer pores. The formation of temporary gaps between the catalyst layer and the MPL was observed between –20 to 18°C due to the hygro-mechanical stresses caused by water uptake in the

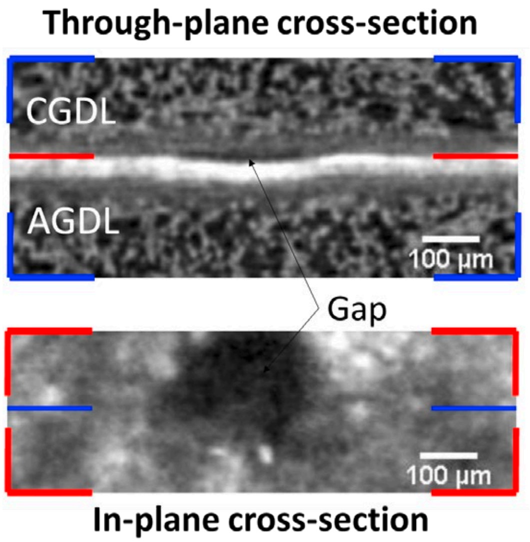

Figure 2
Gap between the cathode GDL & MPL (CGDL) and the membrane (white) in a polymer electrolyte fuel cell imaged by X-ray tomographic microscopy during transient freeze start at –3°C visualized in two perpendicular cross-sections.

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cell's membrane during the sub-zero operation and helps to explain fuel cell degradation during freeze-thaw-cycles (see Figure 2).

Overall, the insights will guide material development to reduce water saturation in the CL for improved freeze-start performance and to increase lifetime of PEFCs.

Publications

Investigation of the Transient Freeze Start Behavior of Polymer Electrolyte Fuel Cells.
Mayank Sabharwal, Felix N. Büchi,
Shinya Nagashima, Federica Marone, Jens Eller.
Journal of Power Sources ***489****, 229447 (2021).*
DOI: 10.1016/j.jpowsour.2020.229447

Understanding the Effect of Feed Gas Humidity on the Freeze Start Behavior of Polymer Electrolyte Fuel Cells.
Mayank Sabharwal, Margarita Charalambous,
Tim Dörenkamp, Shinya Nagashima,
Federica Marone, Felix N. Büchi, Jens Eller.
Journal of The Electrochemical Society ***168****, 114512 (2021).*
DOI: 10.1149/1945-7111/ac37ed

Acknowledgement

Part of this work was performed at the Surfaces/Interfaces Microscopy (SIM) beamline of the Swiss Light Source (SLS), Paul Scherrer Institut (PSI), Villigen Switzerland.

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Enabling the use of Thin Membranes in Water Electrolyzers using a Recombination Catalyst

The conversion efficiency for green hydrogen production in a polymer electrolyte water electrolyzer (PEWE) is strongly influenced by the ohmic cell resistance and therefore the thickness of the membrane used. The use of thin membranes (~50 micron or below) is limited by gas crossover of H_2 and O_2, which can lead to the formation of explosive gas mixtures. The incorporation of a recombination catalyst provides remedy and allows a more dynamic operating mode.

State of the art polymer electrolyte water electrolyzers typically use a perfluorinated proton exchange membrane of the Nafion type with a thickness of 150 to 200 micron. Such thick membranes lead to a large ohmic drop in the cell, limiting the conversion efficiency for hydrogen production. The ohmic resistance can be significantly reduced with the use of thinner membranes, such as Nafion 212 with a dry thickness of 60 micron. This, however, leads to an increase in the H_2 and O_2 crossover through the membrane. In particular, H_2 has a high diffusivity in Nafion, and the accumulation of hydrogen in the oxygen product stream can lead to the formation of an explosive gas mixture (the safety limit of H_2 in O_2 is 2 %). An approach to mitigate gas crossover to the opposite compartment of the cell is to introduce a so-called recombination catalyst into the membrane. These are platinum (or palladium) nanoparticles, which are deposited in the membrane. The dissolved H_2 and O_2 in the membrane react (‹recombine›) on the surface of the Pt-catalyst to water, thereby reducing the rate of gas crossover. In Figure 3a, the content of H_2 in O_2, measured at the gas outlet, is shown as a function of current density for an unmodified (pristine) membrane and a Pt-doped membrane during

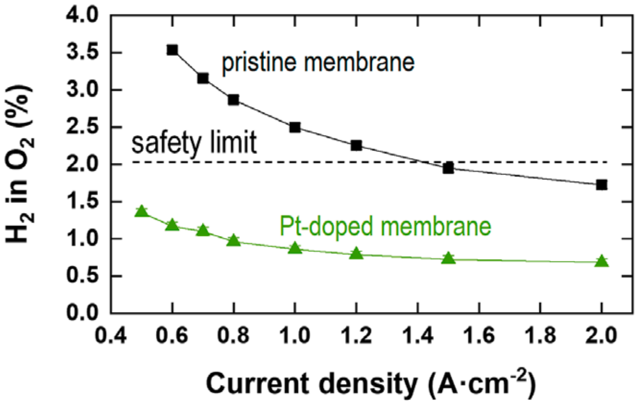
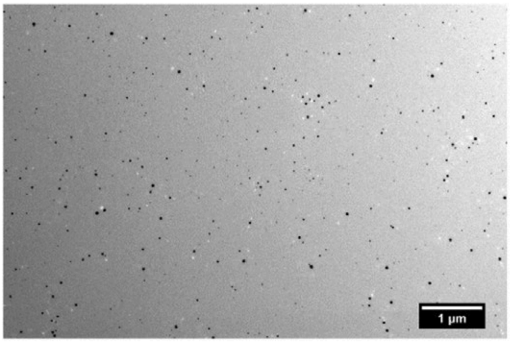


Figure 3 a
Concentration of hydrogen in the oxygen product stream of a single cell water electrolyzer with an active area of 25 cm^2 as a function of operating current density. Pristine membrane: Nafion™ 212 (thickness: 60 micron). The Pt-doped Nafion™ 212 membrane has a Pt loading of 0.1 mg/cm^2. Cell temperature: 60°C, cathode pressure: 10 bar, anode pressure: ambient.



Pt doped membrane (TEM image)

Figure 3 b
TEM image of Pt-doped membrane (acceleration voltage: 200 kV).

cell operation. With the pristine membrane, the safety limit of 2 % is exceeded at a current density below 1.4 A/cm^2. Above that, the produced O_2 provides sufficient dilution of the crossover H_2 for the concentration to be below 2 %. With the Pt-doped membrane the H_2 crossover is much lower and the cell can be operated down to low current densities, which greatly enhances the dynamic operation required if the electrolyzer is connected to a dynamic power supply. The operating current range is of particular importance if the electrolysis system is used for grid stabilization services. The cell performance is not significantly affected by the presence of the Pt-nanoparticles in the membrane, the cell voltage is only 32 mV higher at 2 A/cm^2 for the Pt-doped membrane compared to the pristine membrane. We investigated different methods of Pt-doping of membranes. Initially, $Pt[(NH_3)_4]^{2+}$ was introduced into the Nafion membrane by partial ion-exchange. Then, in a method adopted from the literature, the Pt(II) doped membrane was immersed into N_2H_4 solution to reduce the Pt-ions to metallic Pt clusters. In a novel approach (Patent application EP19175071.0,2019) hydrogen was used as a reducing agent, which led to a homogeneous dispersion of Pt-particles in the membrane with a size in the range of a few tens of nanometers (Figure 3b).

Publications

Communication – Pt-Doped Thin Membranes for Gas Crossover Suppression in Polymer Electrolyte Water Electrolysis.
Steffen Garbe, Ugljesa Babic, Elisabeth Nilsson, Thomas J. Schmidt, Lorenz Gubler.
J. Electrochem. Soc. ***166*** *(13), F873–F875 (2019).*
DOI: 10.1149/2.0111913jes

Comparison of Pt-Doped Membranes for Gas Crossover Suppression in Polymer Electrolyte Water Electrolysis.
Steffen Garbe, Erik Samuelsson, Thomas J. Schmidt, Lorenz Gubler .
J. Electrochem. Soc. ***168****, 104502 (2021).*
DOI: 10.1149/1945-7111/ac2925

Patent

Method for Preparing a Polymer Membrane for a Polymer Electrolyte Water Electrolyser
Steffen Garbe, Ugljesa Babic, Lorenz Gubler, Thomas J. Schmidt
European Patent Application EP19175071.0 (2019).

Acknowledgement

Swiss Federal Office of Energy (grant number SI/501603).

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Scientific Highlight

4

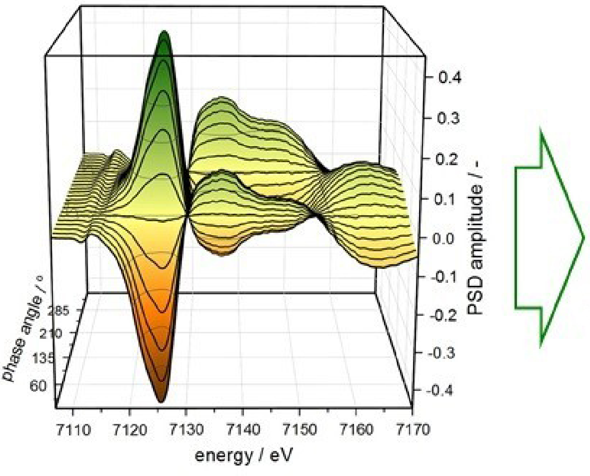
In situ Spectroscopy Unveils the Structural Changes of the Sites in Single Atom Catalysts

To improve the performance of single atom catalysts (SACs), the structure of their active sites under operative conditions needs to be better understood. For this, we performed *in situ* X-ray absorption spectroscopy measurements using a *modulation excitation* approach selectively sensitive to the species involved in the electrochemical reactions. This allowed to study the structural changes undergone by two types of SACs, and to tie the observed differences to their catalytic activities.

The commercialization of electrochemical energy conversion technologies requires inexpensive catalysts for the reactions taking place in their electrodes, like O_2- or CO_2-electroreduction. Single atom catalysts (SACs) based on abundant elements like iron show a promising performance for these reactions, but their activity, stability and selectivity need to be further improved in order to implement them in commercial devices. This calls for a better understanding of the ways in which the structure of these SACs' active sites change during operation.

With this motivation, PSI researchers performed X-ray absorption spectroscopy (XAS) measurements at the Swiss Light Source to study how the electrochemical potential affects the structure of the sites in two types of SACs. Unlike in previous XAS studies, the PSI team applied a modulation excitation approach that yields results that are only sensitive to the sites that participate in the electrochemical reactions of interest. In doing so, they discovered that the sites in both SACs transform from a 5- to a 4-fold coordination when the potential is

Figure 4
Example of a modulation excitation X-ray absorption spectrum (left hand panel) and schematic representation of the structural site changes derived from this work (right hand panel). Type 1 sites are more abundant in the less active catalyst, and undergo a change from 5- to 4-fold coordination upon decreasing the potential from 0.9 to 0.2 V. This change also affects the type 2 sites that are prevalent in the more active catalyst, but these sites get further transformed at 0.2 V.



decreased from 0.9 to 0.5 V. In the case of the most active catalyst, though, further reducing the potential to 0.2 V leads to a displacement of the iron above the plane of its coordination environment that is not observed for the least active material. On top of this, the researchers found significant differences between the rates at which these structural changes take place in each catalyst. Specifically, the oxidation of the active sites is faster for the most active SAC, suggesting that the structural changes associated to this oxidation are tied to the slowest step in the complex mechanisms of these reactions. As a result, this study has unveiled a new parameter determining the catalytic performance of this kind of catalysts.

Publication

Time-Resolved Potential-Induced Changes in Fe/N/C Catalysts Studied by *In Situ* Modulation Excitation X-Ray Absorption Spectroscopy.
Kathrin Ebner, Adam H. Clark, Viktoriia A. Saveleva, Grigory Smolentsev, Jingfeng Chen, Lingmei Ni, Jingkun Li, Andrea Zitolo, Frédéric Jaouen, Ulrike I. Kramm, Thomas J. Schmidt, Juan Herranz.
Advanced Energy Materials ***12****, 2103699 (2022).*
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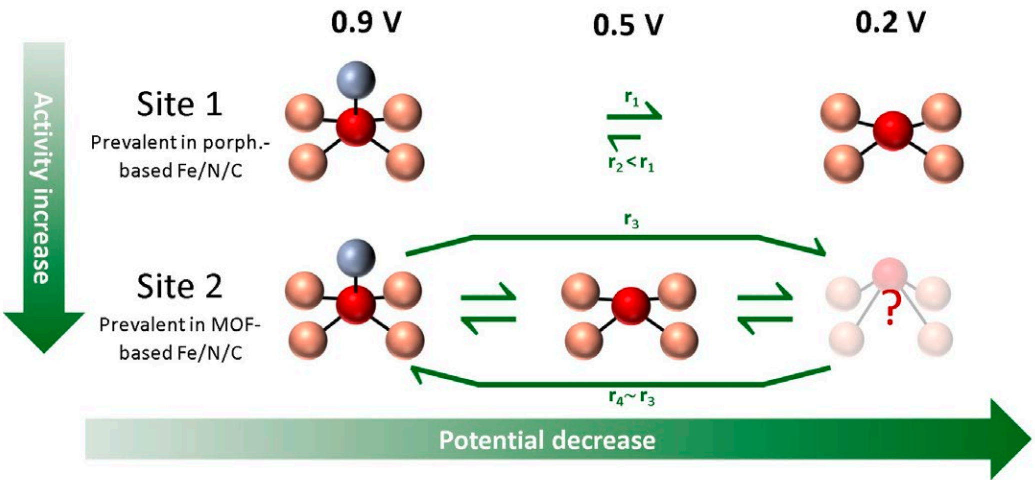


Scientific Highlight

5

Stable Performance of High Capacity Cobalt-Free Li-ion Battery

Lithium-rich layered oxides, containing cobalt, despite being promising high-capacity cathode materials, need alternatives to eliminate toxic and geopolitically restricted cobalt. An ongoing search for low-cost, Co-free Li-rich cathode materials with a better structural stability lead to investigation of $Li_{1.16}Ni_{0.19}Fe_{0.18}Mn_{0.46}O_2$ (LNFM), where cobalt is replaced by abundant iron. Our LNFM not only delivered a high capacity of 229 mAh/g but also has a stable average discharge voltage when cycled to upper cutoff potential of 4.8 V in additive-free electrolyte.

High-energy-density lithium-ion batteries are in demand due to ongoing mass electrification of the transport sector. As battery cathode materials play a vital role boosting the energy density of Li-ion cells, Li-rich layered oxides $xLi_2MnO_3{\cdot}(1-x)LiNi_{1-y-z}Co_yMn_zO_2$ (LR-NCMs) have received a lot of attention due to their high specific capacity and high energy density (up to 250 mAh/g and 900 Wh/kg on material level), when charged to above 4.6 V vs. Li^+/Li. During the initial charge, the LR-NCM cathodes show a plateau region at ≈ 4.5 V in their voltage profile, corresponding to an irreversible oxidation of the lattice oxygen. Such oxygen redox reactions result in a lower average oxidation state of the TMs at the end of the first discharge, facilitating a higher reversible capacity in the following cycles beyond the theoretical one.

However, although LR-NCM cathodes can deliver extra capacity via oxygen redox, at the same time, these reactions can induce irreversible capacity loss and oxygen evolution, causing structural degradation upon long-term cycling. In addition, the practical applications of the LR-NCM cathode materials are hindered by toxic nature of Co with its geopolitical restrictions and related high-cost. Several strategies have been developed to improve the electrochemical performance of LR-NCM, which are, for example, surface coating, doping by small fraction of atoms, various electrolyte additives, etc. However, these did not resolve capacity and

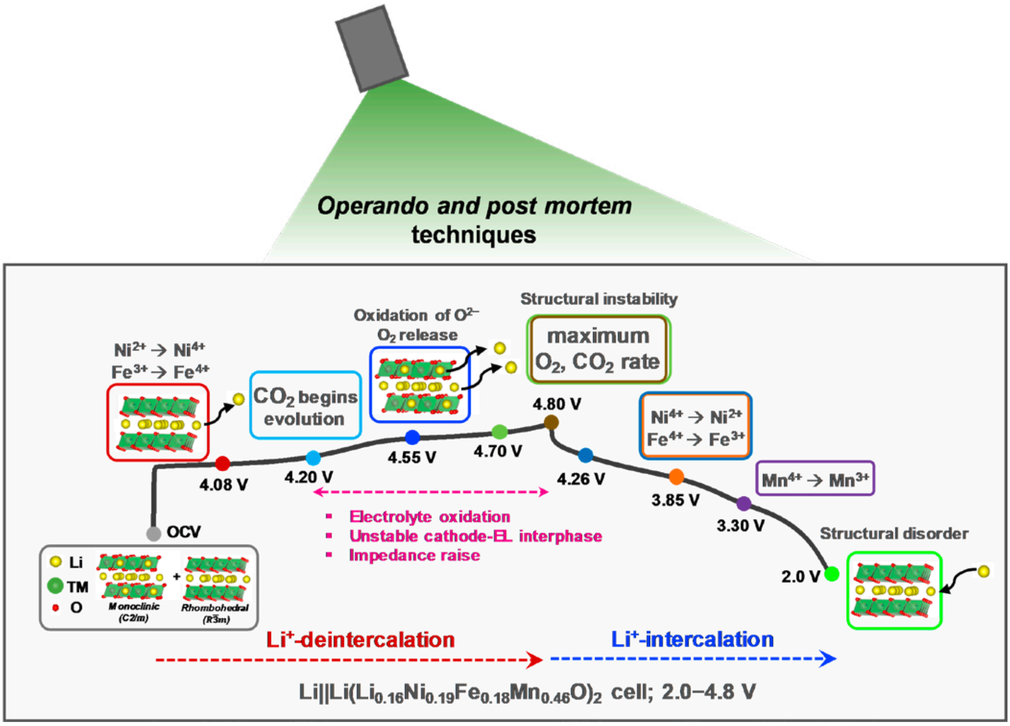
Figure 5

Proposed mechanism for structure and gas evolution and cathode-electrolyte interfacial reactions during the initial charge-discharge processes of Li||LNFM half-cell.

voltage fade upon long-term cycling, especially with high cut-off potential. All this has motivated the search for alternative high-capacity Co-free cathode materials with lower cost, better environmental friendliness, and without severe capacity and voltage fade.

In this regard, Co-free Fe–Mn based Li-rich cathodes (LNFM) are considered promising materials in the aspects of performance and cost, mainly due to the abundance, cheapness and environmental friendliness of Fe. So far, various LNFM cathode materials have been prepared using different synthesis methods, and the effect of Fe for improvement of the electrochemical performance was primarily studied. Therefore, we concluded that there is a need to understand the mechanism of oxygen redox reactions and their effects on the interfacial structure of LNFM, as well as to establish how these correlate to the cycling performance of in Co-free cathodes. Therefore, in this study, we have synthesized Co-free Fe–Mn-based Li-rich cathode material $Li_{1.16}Ni_{0.19}Fe_{0.18}Mn_{0.46}O_2$ (LNFM) by a simple co-precipitation method.

The identification of initial structural changes, gas evolution and oxygen redox, as well as



cathode–electrolyte interfacial reactions and their correlation to improved electrochemical performance led to mechanistic understanding of LNFM cathode material. By using *operando / ex situ* and *in situ* both XRD and Raman techniques, it is concluded that, upon Li^+-de(intercalation), LNFM layered structure remains dominant and there is no significant spinel formation during the initial cycles, as well as upon long-term cycling. The combination of *operando* OEMS and *in situ* EIS experiments allowed to identify both CO_2, O_2 and POF_3 gases and corresponding interfacial reactions at the cathode–electrolyte interface during the initial cycling of LNFM cathode. These results show that the weaker oxygen evolution lowers the conversion rate of LNFM layered structure to the spinel-like phase, alleviating voltage and capacity fade during cycling. Such structural stability along with sufficient interfacial stability lead to the improved electrochemical performance in half-cells. To further highlight the advantages offered by the LNFM cathode material, a full-cell comprising high-capacity LNFM cathode and graphite anode was electrochemically tested. Our LNFM not only delivered a high capacity of 229 mAh/g but also has a stable average discharge voltage when cycled to upper cutoff potential of 4.8 V in additive-free electrolyte. We believe that this work provides new insights into the available high performance Co-free LNFM cathode materials with simple synthesis procedure and already excellent performance even without electrolyte optimization.

Publication

Correlating the Initial Gas Evolution and Structural Changes to Cycling Performance of Co-free Li-rich Layered Oxide Cathode.
Hieu Quang Pham, Łukasz Kondracki,
Mohamed Tarik, Sigita Trabesinger.
Journal of Power Sources ***527****, 231181 (2022).*
DOI: 10.1016/j.jpowsour.2022.231181

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High Performance Doped Li-rich $Li_{1+x}Mn_{2-x}O_4$ Cathode Nanoparticles Synthesized by Facile, Fast and Efficient Microwave-assisted Hydrothermal Route

Li-rich nanoparticles of $Li_{1+x}Mn_{2-x}O_4$ doped with Al, Co or Ni are successfully synthesized using a facile, fast and efficient microwave-assisted hydrothermal route. In this study, we demonstrate that nanocrystallinity and cationic doping play an important role in improving the electrochemical performance with respect to $LiMn_2O_4$ microparticles. They significantly reduce the charge-transfer resistance, lower the 1st cycle irreversible capacity to 6 %, and achieve a capacity retention between 85 and 90 % after 380 cycles, with excellent coulumbic efficiency close to 99 %.

The most common commercial high voltage cathode materials for lithium-ion batteries (LIB) storage devices are layered oxides based on Ni and Co, frequently denoted as $LiNi_xCo_yMn_zO_2$ (NCM) and $LiNi_xCo_yAl_zO_2$ (NCA) families.

However, due to the high cost of Ni and Co, research on battery materials has changed focus towards the development of new cathode materials, based on safety, low cost and being abundant non-toxic elements. In this context, spinel $LiMn_2O_4$ as green and more sustainable batteries materials has shown great potential for LIB applications but still suffer from degradation mechanisms during cycling causing an irreversible loss of capacity which are related to

1) the slow dissolution of manganese at the electrode–electrolyte interface and
2) the strong presence of the irreversible Jahn-Teller distortion in its structure.

In order to mitigate the capacity fading and improve the cycling performance of $LiMn_2O_4$, we decided in our study to

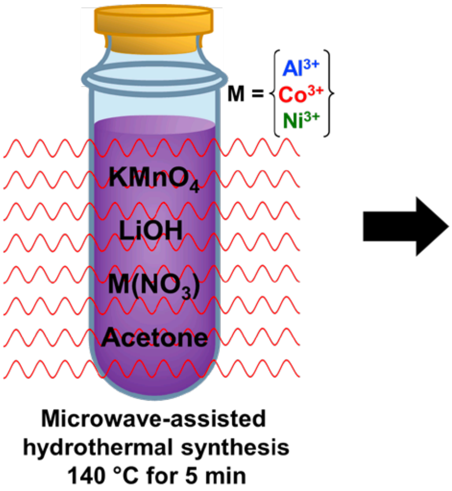
1) reducing the particle size to the nanoscale,
2) enrich $LiMn_2O_4$ with excess of lithium and
3) partially substitute (1 to 3 %) the Mn^{3+} by Al, Co or Ni cations.

The synthesis of the $LiMn_2O_4$ is carried out by a facile, fast and efficient microwave-assisted hydrothermal route at a low temperature of 140°C for a short time of 5 min from aqueous based-solutions.

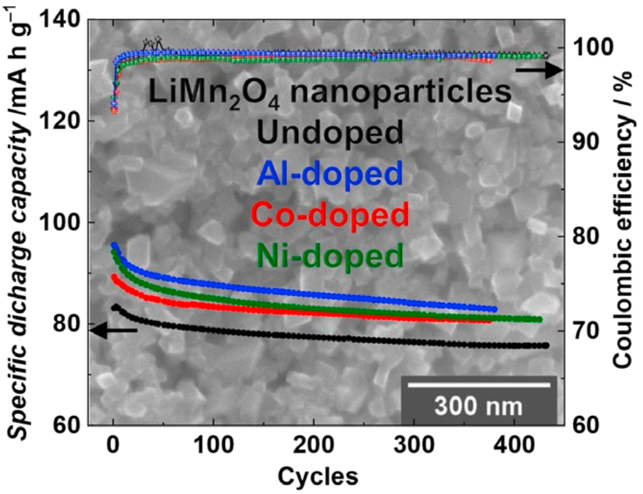
SAXS and SEM confirmed the average size of the particles between (60 to 100 nm) and synchrotron X-ray diffraction validated the formation of highly crystalline Li-rich $Li_{1+x}Mn_{2-x}O_4$ cubic spinel phase. X-ray absorption spectroscopy analysis at the Co and Ni K- and L-edges verify that the dopants are within the $Li_{1+x}Mn_{2-x}O_4$ spinel structure and are inactive during cycling in the bulk and at the surface. From the XANES at Mn K-edge it was possible to monitor the Mn oxidation state in the bulk of the nanoparticles,

Figure 6

Li-rich nanoparticles of $Li_{1+x}Mn_{2-x}O_4$ *doped with Al, Co or Ni synthesized by a facile, fast and efficient microwave-assisted hydrothermal route. Their capacity retention is greater than 86 % with the best result of 91% for the undoped nano-sized* $Li_{1+x}Mn_{2-x}O_4$*, presenting an excellent long-term stability. In terms of specific discharge capacity, the Al-doped nano-sized* $Li_{1+x}Mn_{2-x}O_4$ *delivered the highest value of 99 mA h* g^{-1}.



and it was suggested that the insertion of the Li^+ ions is much easier in the nano-sized particles compared to the micron-sized, supported also by the higher coulumbic efficiency of 94 % during the 1st cycle. Mn L-edge spectra show that after long cycling the Mn oxidation state in the bulk differs from the one on the surface proposed to be caused by the surface Mn disproportion reaction. The cationic doping helps to mitigate the Mn dissolution with respect to the undoped nano-sized spinels as shown by the ICP measurements.



Publication

High Performance Doped Li-rich Li$_{1+x}$Mn$_{2-x}$O$_4$ Cathodes Nanoparticles Synthesized by Facile, Fast and Efficient Microwave-assisted Hydrothermal Route.
Juliana B. Falqueto, Adam H. Clark, Aleš Štefančič, Glen J. Smales, Carlos A.F. Vaz, Albert J. Schuler, Nerilso Bocchi, Mario El Kazzi.
ACS Applied Energy Materials ***5****, 8357–8370 (2022).*
DOI: 10.1021/acsaem.2c00902

Acknowledgement

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High Performance Gas Diffusion Layers with Added Deterministic Structures

Hydrogen will play an important role in a future energy system based on renewable sources, providing energy storage, being a base material for industry and an energy carrier in transport applications. For the efficient electrification of hydrogen, polymer electrolyte fuel cell technology is developed and applied today in trucks, passenger cars and stationary applications. It is envisaged that even more demanding applications such as airplanes may follow. For road transport applications an increase in power density is required to further reduce cost and future applications may need these advances to be technically competitive. In this work we describe a novel concept for gas diffusion layers, highly important for achieving high fuel cell power densities.

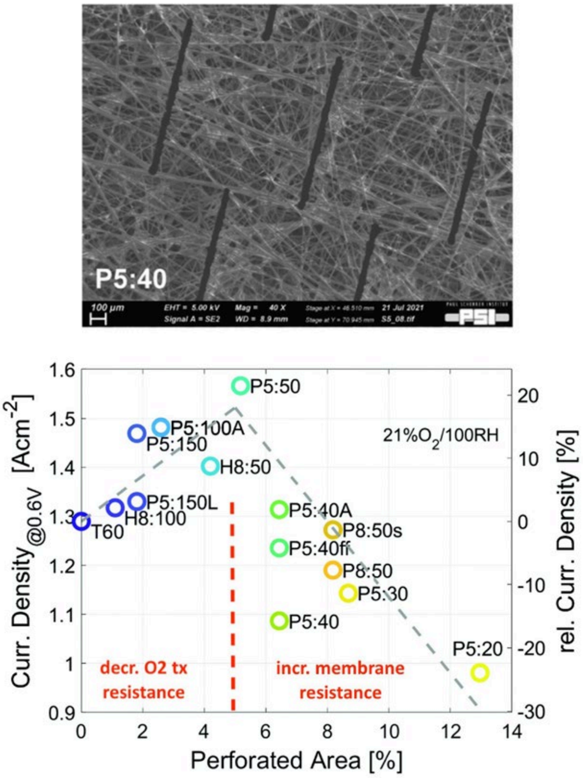

Figure 7
Top: SEM image of Toray GDL with laser structured lines.
Bottom: Volcano-like plot of the cell performance (current density at 0.6 V) with different perforated GDL's under wet conditions (80 % RHA/100 % RHC) with H_2/air at 150 kPa.

Future high power density fuel cells will operate at higher current densities and thus will have to cope with increased water production rates. In this study we show that the addition of deterministic structures to GDLs with a stochastic pore size distribution improves water and gas transport. A series of 16 laser-perforated patterns, with a systematic variation of perforation width, length and density was designed and characterized to identify the optimum modification pattern. Other than in previous work, where laser-perforated holes were added to already hydrophobized GDLs, here the materials were hydrophobized after laser treatment, to render also perforations and their vicinity hydrophobic. The perforated area was used as a descriptor to compare the wide variety of patterns.

The structure and transport properties of the GDL materials are described and their performance is characterized under different operating conditions to probe the impact of the deterministic modifications. Under H_2/air operation and wet conditions (80 % RHA/100 % HC), with the best perforation patterns, cell performance increased at 0.6 V by up to +20 %. When simulating future very high current density operation by using 100 % O_2 as the cathode feed, and the corresponding high water production, the same current density increase at 0.6 V of 20 %, was observed. Oxygen transport resistances, obtained from limiting current analysis, showed a 40 % to 60 % reduction at current densities of 3 A cm^{-2} under the wet operating conditions, supporting the hypothesis of improved water transport away from the CL to the gas channels.

The improvement of water management with increasing perforation density is limited at about 5 % perforated GDL area by increasing membrane resistance. Above this threshold, ohmic losses limit the performance gain for more open patterns. The membrane drying effect is more dominant at the anode and can be reduced by an asymmetric GDL combination with a denser GDL at the anode (no or lower perforation) than the cathode (higher perforation). As observed in earlier work, hole patterns show unstable performance, underlining the importance of the slit geometry connecting flow-field channels and lands, being not just a change in pore size distribution. Further improvements still seem possible by optimization of the anode/cathode asymmetric GDL combinations or in combination with specialized MPLs or adapted flow field geometries.

The presented simple, but powerful modification technique with perforation of conventional, commercial GDLs presents a way forward for changing and improving the water management by introducing rational, deterministic structures into the stochastic, random GDL pore space. Laser processing or other means of mechanical modifications such as punching, are commonly used in industrial manufacturing. Thus, these mechanical modifications seem suitable for scalable production.

In summary, the presented development, with the perforated area as the main descriptor shows the potential of rationally structured GDL, enabling higher current density operation for future fuel cell systems. The generic findings founded on a large number of investigated patterns and thorough scientific analysis, make us confident that this approach can be extended to other types of stochastic, carbon fiber based GDLs to improve water management and fuel cell performance.

Publications

High performance gas diffusion layers with added deterministic structures.
Christoph Csoklich, Thomas J. Schmidt,
Felix N. Büchi.
*Energy & Environmental Science **15**, 1293–1306 (2022).*
DOI: 10.1039/D1EE03246A

Gas Diffusion Layers with Deterministic Structure for High Performance Polymer Electrolyte Fuel Cells
Christoph Csoklich, Roland Steim, Federica Marone, Thomas J. Schmidt, Felix N. Büchi.
*ACS Applied Materials & Interfaces **13**, 9908–9918 (2021).*
DOI: 10.1021/acsami.0c20896

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The Effects of Hydrophobicity Treatment of Gas Diffusion Layer on Ice Crystallization in PEFCs

Water management is crucial to the successful cold-start in polymer electrolyte fuel cells (PEFCs). The sudden freeze of supercooled water blocks the reactant gas in the cathode and causes rapid voltage failure. In this work, we statistically evaluated the effects of the gas diffusion layer (GDL) substrate, size, saturation, and the coating loads and methods of hydrophobic polymer on the freezing probability of supercooled water by differential scanning calorimetry (DSC).

Pure water remains as supercooled liquid, until it encounters nucleation seeds or the temperature reaches below the onset freezing point, T_onset. Ice forms on nuclei, grows, and eventually spreads rapidly throughout the GDL.

Statistical DSC ramping measurements were performed at a sweeping rate of 5 K/min between −35°C and 10°C. Fluorinated ethylene propylene (FEP) coating was applied to untreated Toray and Freudenberg GDLs with loadings from 10 to 70 wt.% by dip-coating (DC) and vacuum-coating (VC). Samples were then punched to 6 mm in diameter and saturated with ultrapure water ($R > 18.8\ M\Omega$) in the vacuum chamber (20 mbar).

The probability of freezing increased marginally with sample size, while it was not affected noticeably by the saturation level. T_onset distributions were achieved by 5–10 samples with 20 repetitions, as shown in Figure 8. Regardless of porosity, pore size distribution, and fiber structure, plain Toray and Freudenberg showed comparable T_onset distributions, with the median T_onset and relative frequency peaking at −15°C (Figure 8 a and b).

We observed similar or higher freezing probability for the samples with hydrophobic coatings (dip-coated, 10–70 wt.%). This was due to the uneven distribution of coating, resulting in a partial surface coverage and isolation of ice nucleation seeds from the supercooled water.

With the FEP distribution improved by vacuum coating, the probability of freezing was noticeably decreased with 15 % FEP loading, and one freezing event occurred below −20°C. This late crystallization phenomenon was consistently observed in one of the Toray-50% FEP-VC samples over 20 cycles, with T_onset distributed between −20°C and −22°C. This suggests that crystallization can be inhibited, given that hydrophobic coating effectively covers the GDL fibers. However, morphological features of the coating, such as roughness and defects, can also be ice nucleation seeds, increasing the chances of freezing, as seen from the T_onset distributions of Toray and Freudenberg with 70 % FEP coating (Figure 8 c).

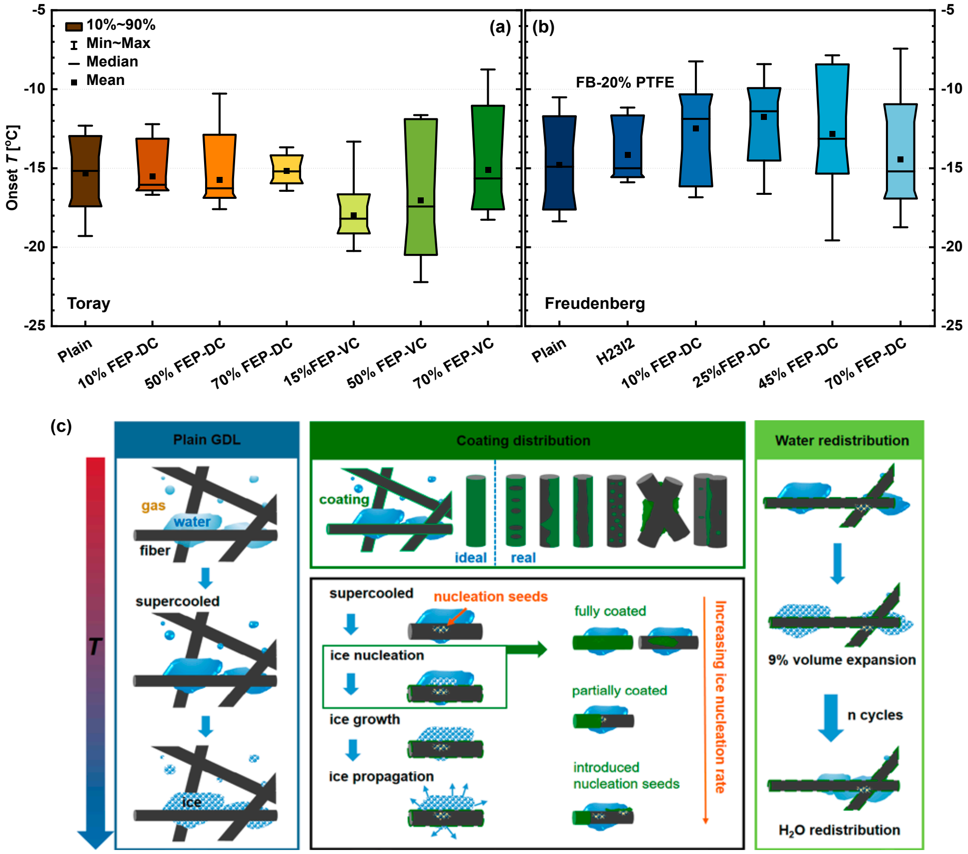
Inter-sample variation was more pronounced than the inter-cycle variation because of the small sample size used in this work and distribution/redistribution of water during cycling,

Figure 8

(a) The T_onset distributions of plain and FEP-coated Toray;

(b) The T_onset distributions of plain and FEP-coated Freudenberg;

(c) The phase transition of supercooled water to ice as a result of coating distribution and water redistribution in GDL.



which was promoted by the volume expansion of the ice (9 %) and the hydrophobicity of the GDL (Figure 8 c). This helps to understand the *in situ* cold start of PEFC, since water is continuously generated in the CL and redistributed in the GDL. Therefore, for cold starts, even the T_onset for a given cycle may be random; given that the numbers of samples and cycles are representative, the probability of freezing is predictable from the T_onset distribution obtained from statistical *ex situ* DSC measurements.

GDL surface can be modified by direct fluorination and electro-grafting to improve the cold start capability of PEFC, as these surface treatments enable a homogeneous coating of the carbon fibers without compromising porosity or introducing seeds. Another strategy is to prevent the ice propagation chemically or mechanically, which facilitates diffusion of reactant gas in the unfrozen regions in GDL, given that some regions are blocked by ice.

Publication

The Effects of Hydrophobicity Treatment of Gas Diffusion Layers on Ice Crystallization in Polymer Electrolyte Fuel Cells.
W. Liu, J. Lee, V. Manzi-Orezzoli, M. Ntalis,
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ACS Applied Materials & Interfaces (submitted).

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Scientific Highlight

9

Damage-Repair Cycle in Hydrocarbon Based Membranes for Fuel Cells

The development of next generation fuel cell membranes based on aromatic hydrocarbon chemistry calls for a new antioxidant strategy to tackle radical induced membrane degradation. Although damage by radicals cannot be prevented, the formed aromatic intermediates can be repaired by a suitable additive. Fuel cell experiments demonstrate that the approach is viable on the device level and that repair is a catalytic mechanism.

Today's polymer electrolyte fuel cells (PEFCs), used for example in the Toyota Mirai, contain perfluoroalkylsulfonic acid (PFSA) membranes, which show high chemical stability and proton conductivity. These fluorinated materials have been around for over 50 years and have seen many technological advances, such as thin reinforced membranes, end-group stabilization, short side-chain, and the addition of radical scavengers. Nevertheless, PFSA membranes have some inherent disadvantages in fuel cell applications, in particular a low glass transition temperature of ~110°C, which limits higher temperature operation, and high gas permeability.

Hydrocarbon-based polyaromatic ionomers are therefore of interest for next-generation proton conducting membranes in the PEFC. Their most critical shortcoming is the presence of aromatic groups contained within the polymer, which make these materials susceptible

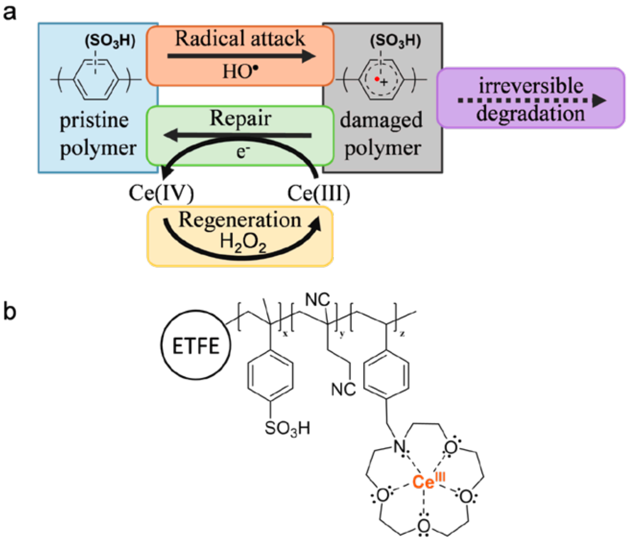
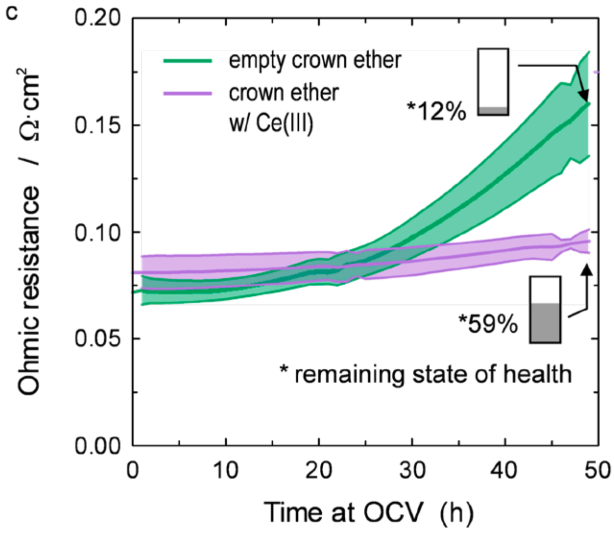


Figure 9

- a) *Schematic representation of the catalytic damage-repair cycle of aromatic polymers to mitigate irreversible degradation.*
- b) *Chemical structure of radiation grafted membrane (base film: 25 micron ETFE film), containing crown ether with complexed Ce(III).*
- c) *Ohmic resistance of single fuel cell during an accelerated stress test. Ion exchange capacity at the end of test is measured to represent remaining state of health. Conditions: open circuit voltage (OCV) under 200 mln/min H_2/O_2, 80°C, 2.5 bara, and 100 % R.H.*

to $HO^{\cdot}$ radical induced degradation reactions. In PFSA membranes, the lifetime of $HO^{\cdot}$ is in the range of microseconds, which allows the use of radical scavengers to mitigate $HO^{\cdot}$ attack on the polymer and subsequent degradation. Owing to the much faster rate of reaction of $HO^{\cdot}$ with aromatic compounds, Ar, radical scavenging is ineffective and $HO^{\cdot}$ attack is virtually unavoidable. It is, however, conceivable that the intermediates formed upon radical attack are sufficiently long-lived to allow repair by a suitable antioxidant. In particular, cation radicals, $Ar^{\cdot+}$, have shown to be such intermediates. In pulse radiolysis studies, we have shown that they can be repaired by Ce(III) ions to restore the parent compound, Ar. The formed Ce(IV) reacts with H_2O_2 present in the fuel cell in the concentration range of millimolar, whereby Ce(III) is restored. Therefore, the repair of cation radicals by Ce(III) may be a catalytic reaction. Consequently, the rate of irreversible degradation of the membrane is significantly reduced (Figure 9 a).

The concept of membrane stabilization by addition of Ce(III) was subsequently investigated in the fuel cell. We prepared radiation grafted membranes containing a crown ether pendant group (Figure 9 b), which served to complex the Ce(III) ions to prevent their loss by leaching. An accelerated stress test was used to assess the rate of chemical membrane degradation in the cell, with and without complexed cerium. The measured ohmic resistance of the cell (Figure 9 c) is an indication of the state of health of the membrane. The much lower increase in the presence of cerium suggests that chemical degradation is mitigated, which is confirmed by the remaining ion exchange capacity (IEC)



at the end of test after 50 h. From the chemical degradation studies of PFSA membranes, Ce(III) is known to act as a radical scavenger. However, in the presence of aromatic polymer constituents, the reaction of Ce(III) with $HO^{\cdot}$ is too slow to have a notable scavenging yield. Therefore, it is likely that Ce(III) serves as a repair agent, which acts on intermediates with a lifetime in the range of microseconds, to reduce irreversible polymer chain breakdown. Based on post-test analysis of membranes, we estimated that each cerium-ion was involved in ~25 repair reactions, which supports the notion of a catalytic repair mechanism.

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Publications

Chemical Stability Enhancement of Aromatic Proton Exchange Membranes Using a Damage Repair Mechanism.
Tym de Wild, Tamas Nemeth, Thomas Nauser, Thomas J. Schmidt, Lorenz Gubler.
ECS Transactions ***109****(9), 317–325 (2022).*
DOI: 10.1149/10909.0317ecst

Repair of Aromatic Hydrocarbon-Based Membranes Tested Under Accelerated Fuel Cell Conditions.
Tym de Wild, Tamas Nemeth, Pascal Becker, Detlef Günther, Thomas Nauser, Thomas J. Schmidt, Lorenz Gubler.
J. Power Sources ***560****, 232525 (2023)).*
DOI: 10.1016/j.jpowsour.2022.232525

Moderation of Oxidative Damage on Aromatic Hydrocarbon-Based Polymers.
Tamas Nemeth, Tym de Wild, Lorenz Gubler, Thomas Nauserr.
J. Electrochem. Soc. ***169****, 054529 (2022).*
DOI: 10.1149/1945-7111/ac6f85

Impact of Substitution on Reactions and Stability of One-Electron Oxidised Phenyl Sulfonates in Aqueous Solution.
Tamas Nemeth, Tym de Wild, Lorenz Gubler, Thomas Nauser.
Phys. Chem. Chem. Phys. ***24****, 895–901 (2022).*
DOI: 10.1039/d1cp04518k

Possible Repair Mechanism for Hydrocarbon-Based Ionomers Following Damage by Radical Attack.
Tym de Wild, Tamas Nemeth, Tom M. Nolte, Thomas J. Schmidt, Thomas Nauser, Lorenz Gubler.
J. Electrochem. Soc. ***168****, 054514 (2021).*
DOI:10.1149/1945-7111/abf9be

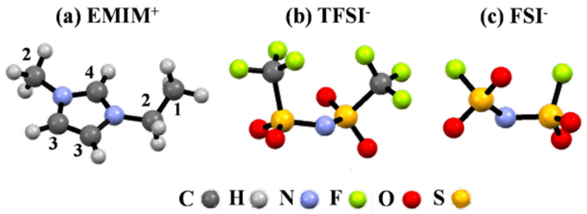
Li-ion Solvation in TFSI- and FSI-based Ionic Liquid Electrolytes Probed by X-ray Photoelectron Spectroscopy

We demonstrate the capability of conventional laboratory XPS to determine the anion solvation shell of Li^+ cations within 1M of LiTFSI and 1M of LiFSI salts dissolved in ($EMIM^+$-FSI^-) and ($EMIM^+$-$TFSI^-$) ionic liquids. The binding energy difference between the N1s components originating from the $EMIM^+$ cation and from $TFSI^-$ or FSI^- anions, solvating the Li^+, confirms that both $TFSI^-$ and FSI^- contribute simultaneously to the Li^+ solvation. Additionally, the degradation of the TFSI- and FSI-based electrolytes under X-ray exposure is proved.

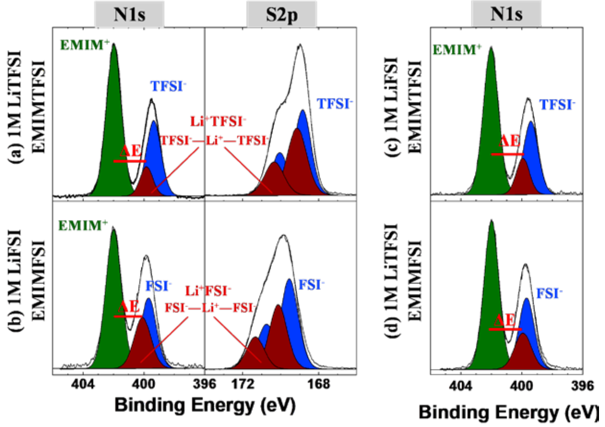
The continuous need for increasing the energy density, safety and electrochemical performance of Li-ion batteries (LiBs) requires an incessant development of characterization techniques capable of providing better insights into the physics and chemistry of the various parts in a battery.

When explicitly investigating surface/interface modifications, X-ray photoelectron spectroscopy (XPS) is routinely employed. For LiBs, it is considered to be one of the suitable characterization techniques allowing to study the interface evolution occurring on cycled electrodes. The advantage of the XPS is the surface

Figure 10



Structural formula of (a) $EMIM^+$ cation, (b) $TFSI^-$ and (c) FSI^- anions.



N1s and S2p XPS core levels acquired on (a) 1M LiTFSI in [$EMIM^+$-$TFSI^-$] and (b) 1M LiFSI in [$EMIM^+$-FSI^-].

N1s acquired on (c) 1M LiFSI in [$EMIM^+$-$TFSI^-$] and (d) 1M LiTFSI in [$EMIM^+$-FSI^-].

The binding energy difference [ΔE=N1s(EMIM)-N1s(solvated Li)] between the N1s components originating from the $EMIM^+$ cation and from $TFSI^-$ or FSI^- anions allows to determine the solvation shell of the Li^+ cation.

sensitivity providing direct information of e.g. the by-product species related to the electrolyte stability, in both liquid- and solid-based electrolytes. XPS in LiBs is not limited to study the electrolyte/electrode interface chemistry, it can also be carried out to probe just the liquid electrolyte and investigate the Li-ion solvation for example in carbonate-based electrolytes as already demonstrated by our group using near ambient pressure photoemission (NAP) combined with a liquid jet. Such experiment and information are very precious, as the Li-ion solvation in the LiBs' electrolyte play an important role in improving the cycling performance, by directly affecting the ionic conductivity, the stability at high or low potential and temperature, as well as the property of the solid electrolyte interphase (SEI).

In this work, conventional XPS using Al Kα X-ray source is employed to investigate the cation and anion electronic structure and to monitor the Li-ion solvation within droplets of low vapor pressure and vacuum compatible ionic liquid electrolytes. Ionic liquid-based electrolytes are considered as promising alternative for next generation high energy density LiBs owing to their low vapor pressure and high thermal as well as electrochemical stability.

However, not all ionic liquid-based electrolytes can successfully be deployed in LiBs. For example, stable electrochemical cycling of graphite in ionic liquid electrolytes can be achieved in presence of FSI^- anion originating either from the LiFSI salt or as an anion from the ionic liquid. On the contrary, graphite cannot be cycled when $TFSI^-$ anion is used, unless FSI^- is added in the electrolyte, despite the structural similarity between the anions.

Intrigued about this phenomenon, we examined in this study the Li-ion solvation when both $TFSI^-$ and FSI^- are present simultaneously in the electrolyte, as a salt or as anion in the ionic liquid. 1M of LiTFSI and 1M of LiFSI salts dissolved in ($EMIM^+$- FSI^-) and ($EMIM^+$- $TFSI^-$) ionic liquids, respectively, are investigated by acquiring the F1s, N1s, C1s, S2p and Li1s core levels. The abbreviations of EMIM, TFSI and FSI stand for 1-ethyl-3-methylimidazolium, bis(trifluormethanesulfonyl) imide and bis(fluorosulfonyl) imide, respectively.

The measurements of the binding energy difference [ΔE=N1s(EMIM)-N1s(solvated Li)] between the N1s component originating from the $EMIM^+$ cation and the N1s component originating from $TFSI^-$ or FSI^- anions, solvating the Li^+, confirm that both $TFSI^-$ and FSI^- contribute simultaneously to the Li^+ solvation. This result can partially explain why adding FSI^- in the electrolyte prevents the $EMIM^+$ co-intercalation in the graphite by forming a favorable SEI during the first reduction. Moreover, this study sheds light on the stability of the ionic liquid electrolyte under the X-ray source, investigated by acquiring the F1s core level. It is worth mentioning that the measured pure ionic liquids EMIM$^+$-TFSI$^-$ or EMIM$^+$-FSI$^-$ without the salts show good stability under X-ray. No sign of any ionic liquid degradation by-product is detected and no change in the XPS core levels is observed even after long exposure time beyond 2 hours. However, as soon as the salts are added in the ionic liquid, then LiF component is detected as a by-product of the electrolyte degradation under the X-ray. This result limits our ambition in performing *operando* XPS measurements at the interface of ionic liquid electrolytes versus any working electrodes, where alternative solutions need to be invented for such an issue, like the use of liquid jet where fresh electrolyte is continuously measured.

Publication

Li-ion Solvation in TFSI and FSI-based Ionic Liquid Electrolytes Probed by X-ray Photoelectron Spectroscopy.
Mario El Kazzi.
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DOI: 10.1051/epjconf/202227301001

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Versatile and Fast Methodology for Evaluation of Metallic Lithium Negative Battery Electrodes

Evaluating potential electrolyte candidates is typically a lengthy procedure requiring long-term cycling experiments. To speed this process up, we have investigated potentiostatic lithium plating as a potential method for fast electrolyte suitability investigation. The applications of this methodology is not limited to liquid electrolytes – effects of solid-state electrolytes, coatings, and other modifications can be readily assessed.

In many applications, lithium-ion batteries are currently a preferred choice due to their high energy density, high round-trip efficiency and reasonable cycle lifetimes. The next step to higher energy density will not be achieved by optimizing conventional LIB designs based on graphite negative and transition metal positive electrodes, and therefore new solution are needed. One of the «new» materials, able to significantly increase energy density of the battery is metallic lithium, considered as the ‹holy grails› in the battery field due to its highly negative potential (—3.04 V vs. SHE) as well as high specific capacity (3860 mAh g^{-1}), both of which can potentially double the energy density of already-existing Li-ion batteries.

There are numerous approaches to improve metallic lithium reversibility, where modification of the electrolyte composition is one of the most studied: without an adequate additive, existing carbonate-based chemistries rather accelerate degradation processes and dendritic deposition than prevent it. On the other hand, ether-based systems allow for higher cycling stability, but their limited electrochemical stability window hinders using standard cathode materials as positive electrodes and because of that prevents achieving high energy density. Therefore, finding a fully compatible electrolyte for LMBs is considered one of the main challenges.

Nonetheless, the development of lithium-metal-compatible electrolytes is not a trivial process. A complete evaluation of the suitability of a single electrolyte typically requires multiple methods and methodologies, such as electrochemical stability tests, long-term cycling, impedance measurements, surface analysis, and computational studies. This can make screening of electrolytes, while varying their composition, a complex and time-consuming process, essentially forming a bottleneck for advancements in the field. This gave us the idea to start looking at potential methodologies that would allow to screen an electrolyte and obtain information about its impact on the kinetics of lithium plating within a matter of hours.

In an unusual approach, we let ourselves inspire from the so-called ‹electrochemical hydrogen pumping› experiment, which is commonly applied in the field of fuel cells. While in the vast majority of experiments on lithium metal anodes, standard galvanostatic plating is being employed; in electrochemical hydrogen pumping, the driving force of reactions is the potential. While the idea of potentiostatic pulse plating is

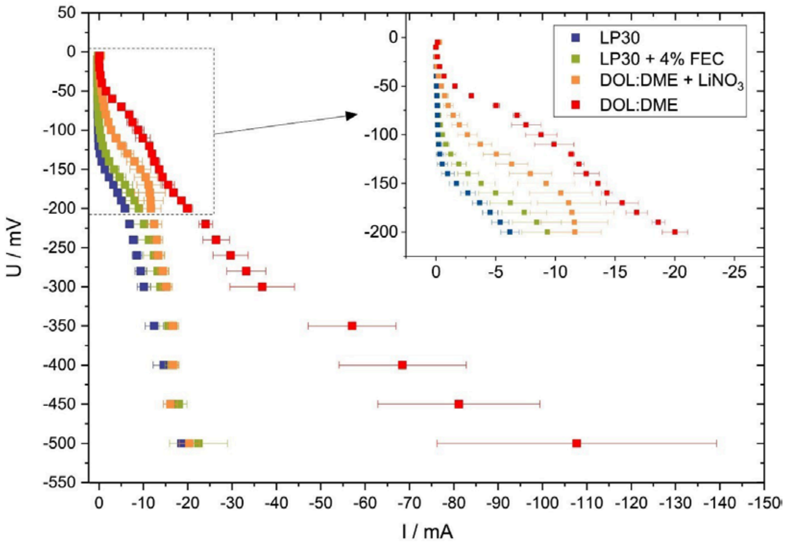

Figure 11
Electrolyte-dependent differences in current response to applied potential.

not completely new, we are taking a more holistic look by not just looking at ultrafast kinetics, but instead seek to characterise different electrolytes. This we have achieved by applying a fixed, incrementally increasing potential to coin-type cells, while letting the current flow freely during this process. The resulting potential-versus-current curve, which closely resembles a typical cell polarisation curve, helps to obtain information about the lithium deposition kinetics in the electrolytes under evaluation.

In a short experiment, valuable information on the kinetics of Li deposition, such as activation barrier and overpotential, as well as exchange currents, could be obtained. Repeated cycling also showed that there is a close correlation between stepwise deposition of fresh Li layers on cycled electrodes with inactive, so called ‹dead›, lithium, and the measured current response curve. In already cycled electrodes, additional activation barriers – as compared to pristine current collector – were observed, each corresponding to the nucleation of a new, island-like metal layer on top of ‹dead› Li. In addition, when looking at a benchmark of several ether and carbonate electrolytes, electrolyte-specific current responses were observed.

In addition to tracking the progress of Li deposition, potentiostatic plating is a helpful tool for comparative experiments, especially due to the close relation between the onset potential of nucleation and the self-diffusion coefficient of Li. Hereby, high self-diffusion corresponded to early deposition of the metal. Lastly, it was also found that addition of 4 wt.% fluoroethylene carbonate additive to commercial carbonate electrolyte brings its kinetic properties much closer to the well-behaved ether electrolytes, which are generally considered a better choice for metallic Li cycling.

The application of this methodology is not limited to liquid electrolytes – effects of solid-state electrolytes, coatings, and other modifications can be readily assessed.

Publication

Potentiostatic Lithium Plating as a Fast Method for Electrolyte Evaluation in Lithium Metal Batteries.
Eric Winter, Thomas J. Schmidt, Sigita Trabesinger.
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Prevention of Freezing Propagation in Fuel Cells Using Segmentation

The ability to start-up in extreme environmental conditions, including sub-freezing temperatures, is essential to the deployment of the fuel cell technology. Water produced in fuel cells at these temperatures can be in the super-cooled state, and freezing can lead to a rapid shutdown, as water cannot be removed anymore as a liquid. By segmenting a fuel cell, it is possible to prevent the propagation of freezing, which enables the cell operation even after the first freezing event occurred.

Freezing in super-cooled water is a stochastic event, the probability of which depends on the degree of super-cooling. Once freezing occurs in a particular location, it rapidly propagates to the whole volume of water connected to this location. Fuel cells of larger dimensions result in a higher probability of freezing in a given amount of time compared to smaller cells, because the volume of accumulated water is greater. The segmentation of water into distinct clusters has, therefore, the potential of extending the operation time of fuel cells at low temperature. Even when the first freezing occurs, ice propagation is limited within one segment, and the rest of the segments can further operate.

To evaluate the feasibility of this approach, a cell with an active area of 8 cm^2 was physically segmented into 8 separate regions. The segmentation was done on the catalyst layer by laser ablation and on the gas diffusion layer by mechanical cutting, while the membrane and flow fields were not segmented. The fuel cell was started and operated at constant temperatures of –5°C and –7.5°C, using either air or pure oxygen as cathode gas. Several methods were used to analyze the freezing events during cell operation. Heat flux sensors were able to detect the exothermal peaks corresponding to freezing with a high temporal precision, but without a precise identification of the freezing location. The water distribution measured by neutron imaging allowed indirectly to identify the location of frozen sections, as the absence of electrochemical reaction was evidenced by the fact that no more water was produced.

The possibilities and challenges of the segmentation approach are illustrated in 3 start-up experiments as shown in Figure 12. In the first experiment, the cell was started and operated at a temperature of –5°C using air at the cathode. The first freezing occurs (as evidenced by the exothermal peak) after 350 s, but the cell could further be operated. As shown from the subsequent water distribution images (Figure 12 c–e), water was only produced in the upper section of the cell, indicating that the lower segments were frozen. Starting at approximately 800 s, the cell voltage gradually degraded, and the cell finally reached shutdown. In this case, the shutdown was not attributed to a further freezing, but to the fact that when the water produced in the upper segments reached the flow channels, the gas flow was impeded and tended to redistribute

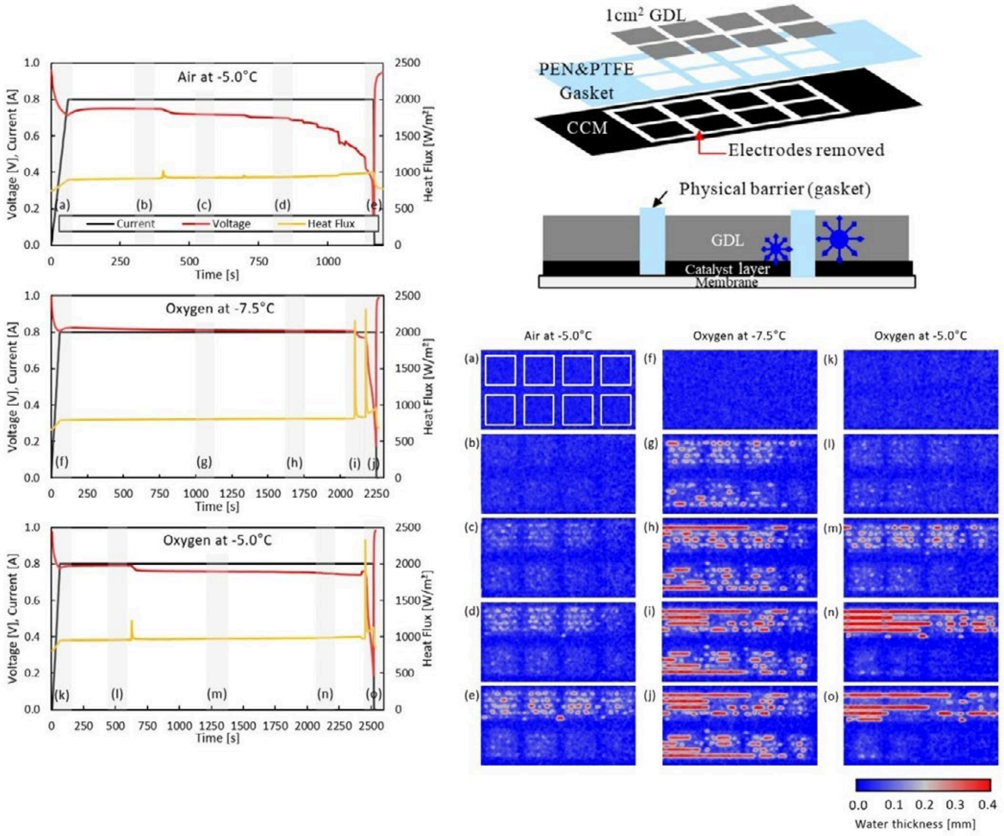

Figure 12

Top right: Illustration of the cell segmentation.

Left: Voltage, current and heat flux of the fuel cell during startup in 3 different experiments (air at –5°C, pure O_2 at –7.5°C, pure O_2 at –5°C).

Bottom right: Corresponding water distribution at selected moments.

towards the lower section of the cell. Eventually, this resulted in severe mass transport losses leading the shutdown.

To support this hypothesis, startups were analyzed using pure oxygen in the cathode, in which case mass transport was not impeded even when the gas flow suffered from an important imbalance between the upper and lower segments. The experiments using pure oxygen did not exhibit the gradual decrease of voltage seen with air. In both experiments with pure oxygen, two different freezing events were observed, the second leading to a rapid shutdown of the cell.

Our study demonstrates that segmentation of the electrodes and GDL can extend the operation time of fuel cells under sub-zero temperature, which could allow non-assisted start-ups from extreme temperatures. However, in all experiments performed, the segmentation was only effective between the upper and lower sections of the cell. Furthermore, in the case where water reached the gas flow channels, the impact of water accumulation on gas flow distribution led to sever mass transport issues. This limited the duration of cell operation, but overall the prolonged operation time was confirmed thanks to segmentation that could contribute to a successful start-up.

Publication

Preventing ice propagation in fuel cells by segmentation.
Jongmin Lee, Muriel Siegwart,
Ricardo Carreon-Ruiz, Pierre Boillat
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(target: Journal of The Electrochemical Society).

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DISSERTATIONS 2022

Evaporative Cooling for Polymer Electrolyte Fuel Cells – A Combined Numerical and Experimental Analysis

Michael Striednig

Ph.D. Thesis No. 28192, ETH Zürich, February 2022.

Examiners:
Prof. Dr. Thomas J. Schmidt, PSI Villigen / ETH Zürich
Prof. Dr. Dimos Poulikakos, ETH Zürich
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Abstract

Fuel cell electric vehicles (FCEV) are a promising alternative to conventional as well as battery electric vehicles (BEV). Hydrogen-based powertrains are especially competitive in heavy-duty transport applications, such as trucks, buses, coaches or trains, since they allow high mileages and short refueling times. Polymer electrolyte fuel cells (PEFC) are the most suitable fuel cell technology for automotive applications since they show high power densities and system efficiencies, a fast dynamic response and decent freeze-start capabilities. However, to achieve a significant market penetration, fuel cell costs have to be further reduced.

The cooling system of polymer electrolyte fuel cells contributes significantly to system volume, mass and cost. On the one hand, conventional liquid cooling requires a complex, multi-layered design of bipolar plates and on the other hand, an increased operating temperature is necessary to reject the entire waste heat to the environment. To ensure a suitable ionic conductivity of the polymer electrolyte membrane at elevated temperatures, an external humidifier is considered in many system architectures. This, however, leads to additionally system volume, mass and costs.

Evaporative cooling is a combined cooling and humidification concept, which allows to overcome these hurdles. It reduces the complexity of the bipolar plates and eliminates the need for external humidification. However, the interactions between operating conditions and the fuel cell performance, cooling power and humidification are complex and have not been investigated in detail yet.

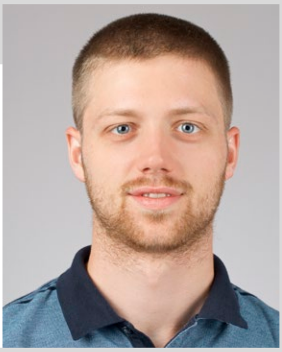
Therefore, a combined numerical and experimental analysis of evaporative cooling for PEFC is conducted in this work and the concept is evaluated on different scales from cell to stack and system levels. Isothermal *in situ* and *operando* measurements are performed under technical cell boundary conditions to analyze the

evaporation behavior, cooling power, internal humidification, electrochemical performance and stability of an evaporatively cooled fuel cell. Additionally, a zero dimensional fuel cell system model is developed to analyze optimal stack operating conditions and to investigate the interactions between the fuel cell stack and balance of plant.

Results show the viability of evaporative cooling over a broad range of operating conditions. The entire waste heat is effectively removed and a sufficient membrane humidification is achieved. The optimum system power and highest system efficiency are achieved at high temperatures (80 to 90°C), low gas pressures (125 to 150 kPa) and a corresponding cathode stoichiometry between 1.5 and 3. Under these conditions, sufficient water can be retrieved from the exhaust gas to ensure a closed water loop. Therefore, filling and storage of liquid water is not required. However, the performance as well as the pressure drop of the exhaust gas condenser is key to an efficient operation. The experimentally observed electrochemical performance is comparable to conventional cooling with humidified gases at the inlet, center and outlet of the cell. An insignificant reduction in electrochemical performance is offset by the volume and weight saving potential of up to 30% and thus considerably reduced cost. In conclusion, this work provides a principal proof of concept for the evaporative cooling approach.

Investigation of the CO_2 Electroreduction Selectivity Determining Factors on Palladium Nanostructures

Justus Sebastian Diercks



Ph.D. Thesis No. 28461, ETH Zürich, July 2022.

Examiners:
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Dr. Juan Herranz, PSI Villigen
Prof. Dr. Maksym Kovalenko, ETH Zürich

Abstract

The capture and subsequent utilization of CO_2 is generally viewed as a vital part of a future carbon-neutral energy society and likely a necessity to reach the mid-century climate goals. In this context, the electrochemical conversion of CO_2 to value-added products has gained increasing attention due to the potential to convert captured CO_2 to fuels or reactants for the chemical industry using renewable energy.

While many catalysts have been previously tested for this reaction, current challenges still include increasing the selectivity and activity toward cost-competitive products, improving catalyst testing procedures as well as further understanding the reaction mechanisms to guide the design of better catalysts for this reaction. Particularly for palladium-based catalysts, their unique, potential-dependent selectivity toward CO or formate at high vs. low overpotential, respectively, remains poorly understood.

With this motivation, in this work, firstly an electrochemical cell setup for selectivity tests employing online gas chromatography for the detection of gaseous products and liquid product detection from the electrolyte was designed. The cell setup was validated using the hydrogen evolution reaction and its capabilities for CO_2 electroreduction selectivity measurement were shown on a commercial Pd/C catalyst. This setup was thereafter used to systematically study the CO_2-reduction performance of several unsupported PdPt alloy aerogels that had been identified as promising CO_2 electroreduction catalysts due to their unsupported nature (which should suppress hydrogen evolution) and previous works that had found Pd-rich PdPt alloys to selectively yield formate as a product. These selectivity measurements were accompanied by an extensive characterization of the aerogels using microscopic, spectroscopic, and electrochemical methods that enabled the correlation of selectivity trends to the aerogels'

material properties, specifically its alloy homogeneity and surface composition.

Furthermore, in an effort to improve the understanding of the switchable selectivity of Pd-electrocatalysts for CO_2 electroreduction, the formation of Pd hydride (PdH) and surface-adsorbed CO under CO_2 electroreduction conditions was studied. Here, the Pd aerogels were employed in time-resolved X-ray absorption spectroscopy measurements to track the formation of PdH throughout a potential hold. These measurements were combined with cyclic voltammetry measurements in a rotating disk electrode setup from which the CO surface coverage and PdH-stoichiometry (PdH_X) were extracted. This, in combination with experiments aiming to carefully reconstruct PdH_X- and CO-formation using electrochemical model experiments, enabled the detailed analysis of the interplay of the CO monolayer and the Pd hydride phase formation during CO_2 electroreduction potential holds.

Lastly, the formation of Pd hydride in a carbon-free electrolyte was used as a model reaction to investigate layer thickness effects caused by the requirement of high electrode loadings in transmission X-ray absorption spectroscopy studies. Therein, the Pd aerogel and a Pd/C catalyst were studied at different loadings in a rotating disk electrode setup in which the time and potential dependence of PdH_X-formation were investigated. Hence, the influence of the layer thickness, the catalyst's morphology, and the presence of the voluminous carbon support on this supposedly fast absorption reaction could be disentangled.

Therewith, the results presented in this thesis entail an improved definition of the testing procedures employed for quantifying the CO_2 electroreduction selectivity of Pd-based electrocatalysts. Combined with the investigations on the influence of surface-adsorbed CO on the formation of PdH_X under CO_2 electroreduction conditions these findings significantly contribute to the understanding of the selectivity determining factors on Pd and PdPt electrocatalysts. Furthermore, these studies' results regarding the effects of the electrode thickness on *in situ* spectroscopic measurements relevant for a large variety of electrochemical reactions are analyzed in detail. Hence, this work contributes to the advancement of two frequently applied measurement methods and the understanding of the CO_2 electroreduction on Pd-based materials essential for future catalyst design and performance improvements.

Ir Oxide Based Electrocatalysts for Water Splitting: Artifact-free Advanced *Operando* Spectroscopic Characterization

Nataša Diklić

Ph.D. Thesis No. 28548, ETH Zürich, July 2022.

Examiners:
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Prof. Dr. Christophe Copéret, ETH Zürich
Dr. Juan Herranz, PSI Villigen

Abstract

The alarming levels of current anthropogenic CO_2 emissions call for the urgent replacement of primary energy sources based on fossil fuels with renewable energy. The large-scale installation of the latter «green» technologies in the last decade has led to a remarkable decrease in the costs of renewable electricity that confirms their capability to reduce CO_2 emissions while highlighting the need for energy storage solutions for those times in which renewable electricity production exceeds demand.

In this context, hydrogen produced by water electrolysis represents one plausible solution, as H_2 can be stored, transported and used as a fuel when needed. Additionally, hydrogen is an important feedstock for the chemical industry, but its production from natural gas remains carbon intensive and therefore implies additional CO_2 emissions. In this respect, polymer electrolyte membrane water electrolyzers (PEMWEs) can help to decarbonize H_2 production and the concomitant, seasonal storage of renewable energy. Although polymer electrolyte membrane water electrolysis is a mature technology, its deployment at a large scale is hindered by its high price, whereby at the MW scale, the Ir-based catalysts used to catalyze the oxygen evolution reaction in PEMWE-anodes account for a considerable portion of the electrolyzer's costs. Moreover, the use of high Ir loadings (i.e., ≈ 2 mgIr·cm^{-2}) further restricts the installation capacity due to limited Ir resources. Therefore, the development of new catalysts allowing considerably lower Ir loadings is essential for the commercial success of this technology. This in turn translates in the need to understand the catalyst properties that dictate its activity and stability under operative conditions.

With this motivation, the first part of this thesis primarily focuses on investigating the stability of a series of supported Ir oxide catalysts provided by an industry collaborator, Umicore AG & Co. KG. The choice of Nb_2O_5 as a support for IrO_2 was motivated by predictions regarding this

support's stability inferred from Pourbaix diagrams that suggested that this materials combination could be used as an oxygen evolution reaction catalyst even in fuel cell anodes during cell reversal events. Two IrO_2/Nb_2O_5 catalysts with ≈ 75 wt.% of Ir were evaluated and they exhibited improved stabilities compared to an unsupported IrO_2 catalyst. Nevertheless, even if more stable, these catalysts exhibited considerable OER current losses at the end of the stability protocol, and thus a systematic study was carried out in order to pinpoint and decouple specific degradation mechanisms affecting these catalysts. The obtained results suggested that processes other than intrinsic catalyst degradation are responsible for the observed current losses. For this reason, experimental artifacts related to the measurement setup were additionally investigated, and were complemented with stability measurements in a single PEMWE cell. Furthermore, the effect of decreasing the Ir loading in these Nb_2O_5 supported materials was investigated, with respect to both mass specific OER activity and catalyst stability.

Subsequently, in the second part of the thesis advanced operando X-ray absorption spectroscopy was applied to four Ir oxide materials with different surface speciations with the goal to unveil the oxidation state of Ir under reaction conditions, that remains a matter of vivid debate in the literature. To this end, possible artifacts related to such operando measurements were first identified in order to establish the best experimental practices and to avoid the misinterpretation of the collected data. On this foundation, artifact-free operando X-ray absorption measurements were then performed on the above-cited Ir oxide catalysts, and the combination of this spectroscopic approach with multivariate curve resolution revealed the potential dependent distribution of oxidized and reduced Ir species in each catalyst. Moreover, modulation excitation measurements shed light on the exact Ir oxidation state under reaction conditions, which was shown to be the same (and equal to $+5$) for all the Ir oxides employed in the study.

In summary, this thesis addressed important questions related to the development of anode catalysts in PEMWEs. Particularly, lowering the Ir-loading by using Nb_2O_5 as a support for IrO_2 was investigated, with respect to both mass specific OER activity and catalyst stability. Additionally, the findings from operando XAS studies on state-of-the-art Ir oxides provide novel and generalized insight on the electronic structure of Ir under reaction conditions.

Non-invasive and Local Impedance Diagnostics for Polymer Electrolyte Fuel Cell Stacks

Arnaud Schuller

Ph.D. Thesis No. 28836, ETH Zürich, November 2022.

Examiners:
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Abstract

Polymer electrolyte fuel cells (PEFCs) stacks with power in the kW-range are having gradients in gas composition and humidity which can’t be avoided and complicate the water management of the cells. Diagnostic tools able to provide local and spatial resolved information are needed to study these inhomogeneities and to improve cell performance. Most of these methods are however invasive and not suitable for application outside of laboratory setups.

In this thesis, the foundation is laid for a new non-invasive and local diagnostic tool for PEFCs: Electrical Impedance Tomography (EIT). It is an already established method in different fields such as medicine, geology and different industrial processes and its principles are applied the first time to PEFCs. It is based on the relationship that exists between the conductivity inside an object and the boundary voltages existing when an AC current is supplied to the object. The reconstruction process to retrieve the conductivity distribution from the boundary voltages, however, is very challenging.

In order to assess the feasibility of the method on a fuel cell, a numerical feasibility study was performed. It showed that for the method to work, a very high level of accuracy was needed between the model and the experiments. If this accuracy was reached, different conductivity distribution typical of fuel cell operation could be reconstructed even though the center of the active area was not probed. A dedicated measurement system with the best possible accuracy was then designed, installed and programmed. Different experimental tests of increasing complexity were performed to investigate if the required accuracy between the model and the experiments could indeed be reached. These tests uncovered severe challenges for fuel cell application even though the model was able to predict the boundary voltages with an accuracy of about 15 %.

A different way to retrieve local information from local measurements was investigated as an alternative to the FEM based EIT reconstruction. It is based on the interpretation of local current supply and voltage measurements all around the cell. The ability to assign a zone of the active area to each stimulation, coupled with reference measurement at specific conditions allowed to study the conductivity distribution of an operating fuel cell stack. Different conditions were studied and compared well with literature. Time resolved measurements were also performed to highlight the transient capabilities of the method. Finally, extending the frequency range allowed to study the local influence of oxygen concentration and current density on the low frequency features of the impedance spectrum with non-invasive local electrochemical impedance spectroscopy.

Being able to non-invasively determine the impedance distribution in a fuel cell stack is a great asset, especially as it could also be easily and quickly adapted to different cell designs. The developed methodologies could be used to check the homogeneity of the conductivity distribution in a stack for research and development purposes but also in practical operation, to provide feedback to the control system.

Characterizing Water Transport in the Microporous Layers of Polymer Electrolyte Fuel Cells

Yen-Chun Chen

Ph.D. Thesis No. 28889, ETH Zürich, November 2022.

Examiners:
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Prof. Dr. Marco Stampanoni, co-examiner, PSI Villigen / ETH Zürich
Dr. Felix N. Büchi, PSI Villigen

Abstract

Microporous layers (MPLs) are an essential part of the gas diffusion layers (GDLs), which improve polymer electrolyte fuel cell (PEFC) performance, particularly at high current density and humid operating conditions. One of the ways to reach future PEFC performance and cost target is through better design and integration of this layer. To achieve this, understanding of the water transport in MPLs is important.

This thesis aims at obtaining insight to the morphology of and water transport in the MPLs by means of X-ray tomographic microscopy (XTM). The opening three chapters provide the general background of this thesis study. Chapter 1 lays out the motivation for this work. Chapter 2 gives a basic overview of PEFC thermodynamics, efficiency and major loss mechanisms. Chapter 3 summarizes the methods used in this thesis work, including XTM principles and fundamentals, illustration of the laboratory computed tomography (CT) and beamline XTM setups and the image processing steps.

First, MPL properties and water saturation within are characterized in an *ex situ* setup (Chapter 4 and Chapter 5). In Chapter 4, this work extends the use of polychromatic XTM for the quantitative determination of water saturation in MPLs through establishing a calibration relation between greyscale values and linear attenuation coefficients. From there on, MPL properties and porosity are characterized based on laboratory CT imaging. The results show that the porosity distribution of MPLs is not homogeneous and therefore, for accurate determination of the spatial water saturation distribution, porosity distribution must be obtained first. In Chapter 5, 15 commercially available MPL materials are characterized for their total porosity, the microporosity, the crack volume, thickness and porosity heterogeneity. Some of these properties (especially the porosity and its heterogeneity) were previously unknown. This provides a new insight to the properties of MPLs and reveals the diversity of commercial MPLs with respect to thickness, porosity and morphology, which

cannot be summarized in a single morphological category as previously often done.

Moving on, operando water transport in MPLs and GDLs is characterized in Chapter 6 and Chapter 7. In Chapter 6, high porosity MPLs with different pore size distribution (PSD) are investigated, and the work is focused on the first minute fuel cell operation from dry state as this allows for easier characterization of the water transport modes. Data show that the addition of both kind of high porosity MPLs (with different PSD) resulted in enhanced vapor transport at the beginning of fuel cell operation. Therefore, it was hypothesized that the (low) thermal conductivity of MPLs is one of the important properties determining water transport mechanisms. In Chapter 7, water transport in MPLs of the same material but with different morphology (flat and intruding) is investigated. Here, results show that an intruding MPL morphology leads to lower liquid water saturation in the GDL, especially the MPL/GDL mixed region. This is proposed to be the reason for the better performance of the PEFC with at highly humid and high current density conditions.

Chapter 8 summarizes the results and conclusions from this work and motivates further XTM studies for water transport characterization in PEFCs, operated at even more realistic operating conditions with further developed MPLs and GDLs.

Electrochemical CO_2-Reduction on Au and Au-Cu Aerogels: From Selectivity Trends to Interfacial Effects

Piyush Chauhan

Ph.D. Thesis No. 28976, ETH Zürich, December 2022.

Examiners:
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Abstract

The fossil fuel-driven global economy has triggered a sharp rise in the levels of anthropogenic CO_2 emissions in the last few decades, necessitating a move towards renewable energy sources in a bid to fulfil the ambitious targets from the UN Climate Change Conference for limiting the effects of climate change.

The electrochemical CO_2-reduction reaction (CO_2RR) to produce value-added chemicals has become increasingly crucial in the context of this energy transition, as it presents us with the dual benefits of utilizing CO_2 to produce carbon-based fuels, which in turn provides a pathway facilitating long-term energy storage. While the electroreduction of CO_2 has been researched for decades, challenges such as the poor activity and selectivity exhibited by present-day catalysts towards industrially-relevant products, a lack of understanding of reaction mechanisms, and of the role of the catalytic microenvironment therein still exist. In this context, there is an urgent need for novel CO_2RR-electrocatalysts displaying high activity and selectivity for economically-desirable products and to investigate how the kinetics and product distribution of these catalysts are affected by the parameters of their local environment.

Motivated by this, the first part of this work explores the use of novel, unsupported aerogel electrocatalysts for the CO_2-reduction reaction, where the absence of carbon-based support materials improves the possibility of suppressing the competing H_2 evolution reaction. Firstly, a monometallic Au aerogel is characterized for its electrochemically-available surface area, CO_2RR-performance and structural stability using electrochemical and microscopic techniques, and is compared to a similar commercially-employed carbon-supported Au catalyst. These measurements sought to establish a benchmark for CO-specific activity and selectivity achieved by a pure Au aerogel in an

electrochemical setup with online gas chromatography, with the objective of extending this established methodology to bimetallic Au_3Cu and AuCu aerogels under the context of a possible, favourable-tuning of the CO-binding energy. Additionally, the surface composition of these alloy aerogels was systematically tuned using electrochemical methods and its effect on the surface areas and CO_2RR-performance was assessed. Further, a comparison of the CO-specific Au-mass activity of the Au, Au_3Cu and AuCu aerogel catalysts was performed in order to analyze the noble metal utilization capability.

The second part of this work focused on quantifying the pH on Au surfaces during CO_2-reduction reaction in a well-defined hydrodynamic system in order to obtain a deeper understanding of the changes occurring in the catalyst microenvironment. This electrochemical investigation was facilitated by performing the CO_2-reduction reaction on a polycrystalline Au and a Au aerogel catalyst in a rotating ring-disk electrode (RRDE) configuration, which enabled the detection of the CO_2RR-products as well as the quantification of the changing interfacial pH. The experimental findings were corroborated by the results of a mathematical model that allowed the quantification of shifts in pH and potential scales occurring at the electrode surface during CO_2RR. Finally, the RRDE methodology of product detection and pH quantification was extended to examine the effect of ionomer thin-films deposited on a catalyst surface on product selectivity and surface pH during the CO_2RR. More precisely, a cation-exchange and an anion-exchange ionomer were chosen to produce thin-films on a polycrystalline Au electrode and the possible effects of the nature of hydrophobic backbones and functional moieties employed on the CO-selectivity and local pH changes were investigated.

In summary, the research presented in this thesis contributes an extensive and systematic electrochemical assessment of Au and Au_xCu_y alloy aerogels in the context of electrochemical CO_2-reduction, which enhances the existing knowledge pool of Au- and AuCu-based electrocatalysis while providing a platform to allow benchmarking of future investigations involving aerogel-like unsupported electrocatalysts. Specifically, the electrochemical surface area measurements discussed in this work bring to light the inaccurate methodologies widely employed in the literature and the need for the implementation of this parameter for the unambiguous determination of an electrocatalyst's CO_2RR-performance. Furthermore, the rotating ring-disk electrode studies for interfacial pH measurements provide a reliable methodology for assessing the changes occurring at the electrode-electrolyte surface during the CO_2RR and emphasize the extent of deviation in the interfacial potential. Finally, the employment of ionomer-films in an RRDE setup to further investigate the changes in the catalyst microenvironment represents a first such study reported in this domain and would contribute considerably to the future strategies for catalyst designs and CO_2RR-performance tuning.

Design of Non-noble Metal Catalyst Layers for PEM Fuel Cells: Performance & Stability

Seçil Ünsal Dayanık

Ph.D. Thesis No. 28945, ETH Zürich, December 2022.

Examiners:
Prof. Dr. Thomas J. Schmidt, PSI Villigen / ETH Zürich
Prof. Dr. Victor Mougel, ETH Zürich
Dr. Juan Herranz, PSI Villigen

Abstract

The severe environmental consequences of the extensive use of fossil fuels as a primary energy source can only be reversed through their substitution with renewable energies. Within this prospect, hydrogen is systematically regarded as a key energy carrier excellently suited to store excess renewable electricity, and its re-electrification in fuel cells is also expected to play a crucial role in the transportation sector. Specifically, proton exchange membrane fuel cells (PEMFCs) are very promising to be implemented in environmentally friendly transportation applications, but the high Pt-loadings required in their cathodes to catalyze the sluggish oxygen reduction reaction (ORR) inhibit their widespread commercialization. In order to address this issue, tremendous efforts are being devoted to develop inexpensive, non-noble metal catalysts (NNMCs). Novel syntheses established in recent years have led to NNMCs with initial ORR-activities comparable to those of Pt-based materials. However, NNMC cathode loadings need to be much higher (≈ 4 mgNNMC·cm^{-2}) than those of Pt-based catalyst layers (CLs, with loadings ≤ 0.3 mgPt·cm^{-2}) to compensate for their intrinsically lower ORR-activity compared to Pt. Therefore, the resulting, thick NNMC layers (up to ≈ 100 µm) suffer from severe mass transport issues which prevent them from reaching the high current densities at high potentials required for automotive applications.

The large diversity of NNMC synthesis approaches reported in the literature results in materials featuring a wide variety of particle sizes and morphologies, and the effect of these properties on these thick catalysts layers' PEMFC performance remains poorly understood. Moreover, these materials show a remarkably poor durability in PEMFC tests, and several degradation mechanisms have been postulated to explain this fast performance decay. However, very little is known regarding the relative contributions of these mechanisms to the overall PEMFC-perfor-

mance loss and as a function of the operative conditions.

To shed light on these matters, the first part of this thesis presents the physical and electrochemical properties of NNMC layers prepared from materials featuring broadly different aggregate sizes, whereby this property was tuned by ball milling (BM) the precursors used in the NNMCs' synthesis in the absence vs. presence of a solvent (i.e., using dry- vs. wet-milling, respectively). This led to two NNMCs featuring similar Fe-speciations and ORR-activities, but with vastly different aggregate sizes of > 5 µm vs. ≈ 100 nm, respectively. Following the extensive characterization of these materials' CLs, PEMFC tests unveiled that the smaller aggregate size of the wet-milled sample resulted in a significant improvement of its mass transport properties (and corresponding high current density performance) over the dry-milled material (i.e., the one featuring a larger aggregate size). Additionally, for the catalyst featuring a small aggregate size, the mass transport improved with the loading up to a certain thickness due to a hypothetical, positive impact of the number of active sites on the mass transport properties; by comparison, the performance at high currents worsened at very high loadings due to the excessive thickness of the resulting CL, which limits the mass transport.

Subsequently, an extensive rotating ring disk electrode (RRDE) study was carried out to assess the effect of film thickness and quality on the electrochemical behavior (i.e., ORR-activity and H_2O vs. H_2O_2 selectivity) of the above NNMCs featuring different aggregate sizes. The RRDE-results displayed a significant enhancement in the ORR limiting current of the NNMC with a smaller particle size that we tied to the improved mass transport properties of its RRDE thin-film layer. Moreover, improving the thin film quality led to a ≈ 2-fold enhancement of the H_2O_2-yield (vs. a similarly loaded, yet non-homogeneous NNMC-film) that demonstrates the importance of this parameter for the ORR-selectivity trends inferred from these RRDE measurements.

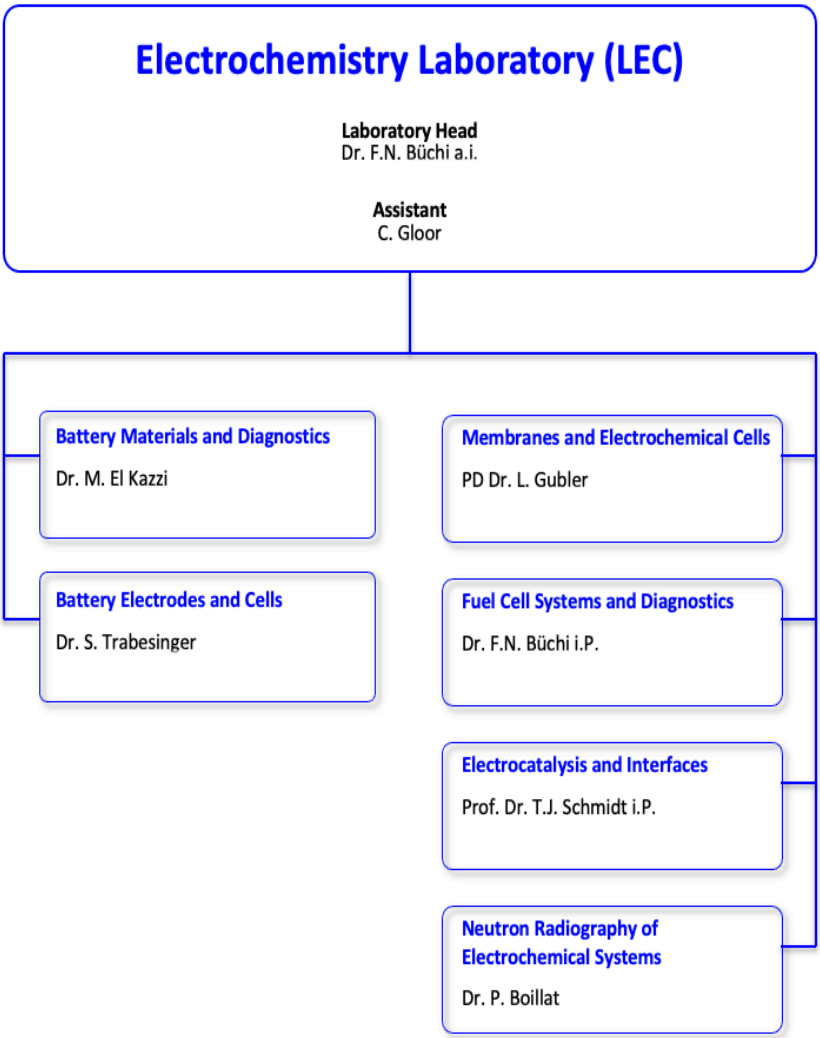
Finally, the last part of this thesis addresses the instability of NNMC cathodes. Four degradation protocols including different cathode gas feeds (i.e., air vs. N_2) and potential hold durations were designed in order to decouple the relative contribution of the three main deactivation paths proposed in the literature (i.e., demetallation, electrochemical carbon oxidation, and H_2O_2-related effects) to the overall PEMFC-performance loss. The results indicated that H_2O_2-effects on the catalytic activity appear to depend only on the ORR-charge, and not on the potential. Moreover, it was found that carbon electro-oxidation contributes to the activity loss in PEMFCs much more than the demetallation mechanism.

Overall, the results presented in this thesis provide valuable contributions to NNMC research which shall aid to achieve the performance and stability targets set for the successful application of these materials in commercial PEMFC cathodes.

THE ELECTROCHEMISTRY LABORATORY

FACTS & FIGURES

STRUCTURE 2022



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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 2022

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Dr. Emiliana FABBRI (Scientist)
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Dr. Davide MASIELLO (Postdoctoral Researcher))
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Tym DE WILD
Matthieu DESSIEX
Justus DIERCKS
Nataša DIKLIĆ
Tim DÖRENKAMP
Jacobus DUBURG
Meriem FIKRY
Samuel GATTI
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Jiyun KWEN
Barthélémy LELOTTE
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Wenmei LIU
Arnaud SCHULLER
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Eric WINTER
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Zheyu ZHANG

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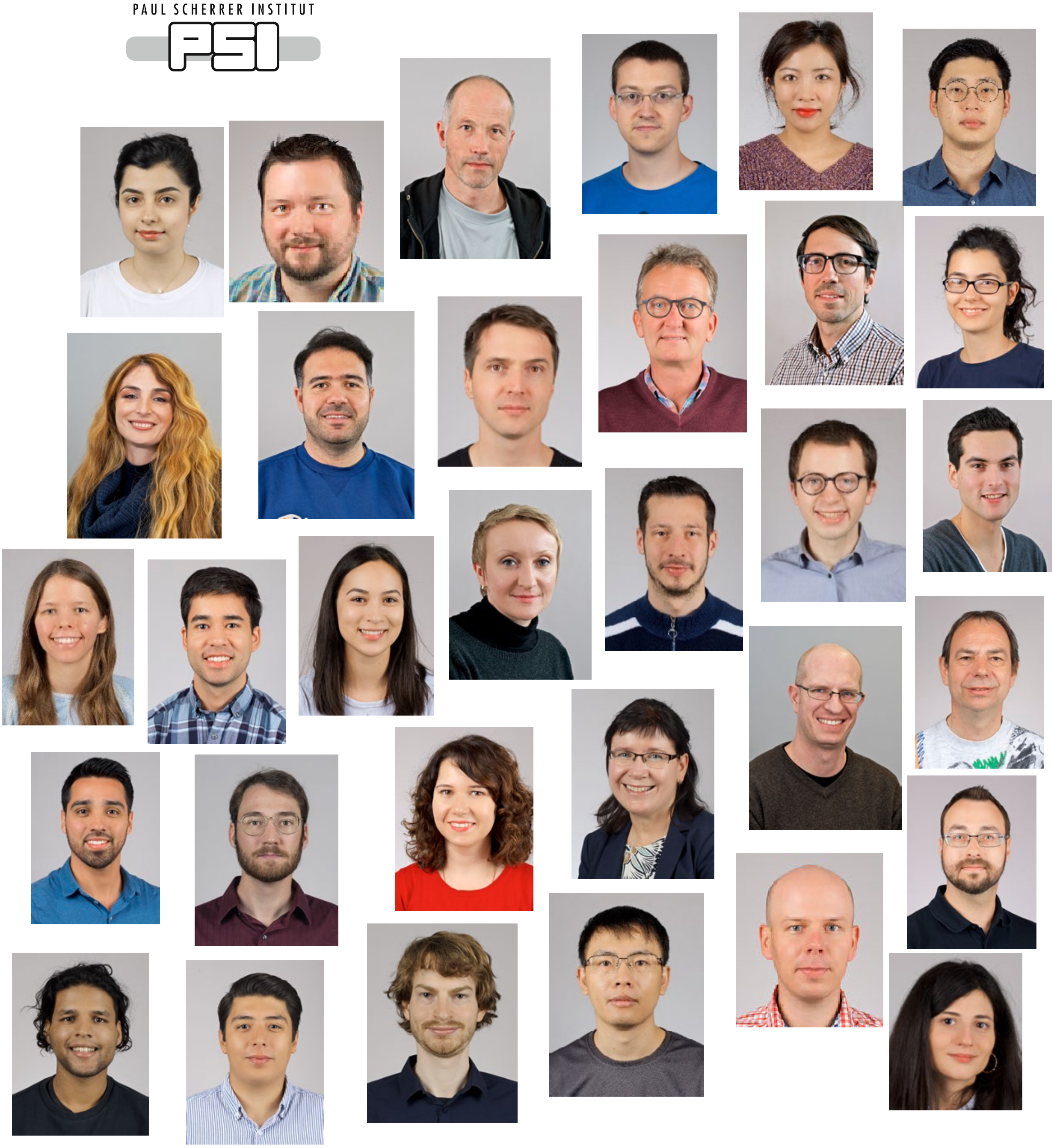


Members of the Electrochemistry Laboratory in 2022.

AWARDS 2022

T. de Wild, T. Nemeth, P. Becker, D. Günther, T. Nauser, T.J. Schmidt, L. Gubler

Best Poster Award

Poster: «Hydrocarbon-Membrane Degradation and Repair during Fuel Cell Operation».

Event: ACS conference: Polymers for Fuel Cells, Energy Storage, and Conversion
May 15–18, 2022
Napa, CA, USA

T. Dörenkamp, M. Sabharwal, F. Marone, J. Eller

2nd Prize Poster Award

Poster: «Investigation of Water Cluster and Droplet Interactions in PEFC using Operando XTM».

Event: ModVal-2022 – 18th Symposium on Modeling and Experimental Validation of Electrochemical Energy Technologies
March 14–16, 2022
Schloss Hohenkammer, Germany

J. Duburg

Swiss National Science Foundation Mobility Grant

Mobility Grant for research stay at the Simon Fraser University (Prof. S. Holdcroft), May – October 2022, Vancouver, BC, Canada.

T.J. Schmidt

Election into the Swiss Academy of Technical Sciences SATW

«Elected in recognition of his extraordinary achievements in the field of electrochemistry with important findings in the field of electrochemical materials, cells and devices for energy conversion and storage» (May 3, 2022).

E.R. Carreon Ruiz, J. Lee, M.-O. Ebert, J.I. Márquez Damián, M. Strobl, L. Gubler, P. Boillat

Poster Prize Winner (QENS 1st place)

Poster: «Discerning Hydrogen Dynamics in Li-Ion Battery Organic Solvents via Wavelength-Resolved Neutron Imaging».

Event: QENS/WINS 22 International Conference
May 23–27, 2022
San Sebastian, Spain

J. Linke, T. Rohrbach, A.H. Clark, M. Nachtegaal, M. Andrzejewski, N.P.M. Casati, T. Huthwelker, M. Ranocchiari, T.J. Schmidt, E. Fabbri

1st Poster Price

Poster: «Metal-Organic Framework based Catalysts for the Oxygen Evolution Reaction in Alkaline Electrolysis».

Event: 3rd International Conference on Electrolysis 2021
June 20–23, 2022
Golden, CO, USA

E.R. Carreon Ruiz , L. Gubler, P. Boillat

Best student talk / Presentation Award

Neutron imaging and its use in batteries.

Event: Summer School on Image Processing SSIP 2022
July 6–15, 2022
Szeged, Hungary

BACHELOR AND MASTER STUDENTS

Bowen Li ETH Zürich, Switzerland

Surface coatings for layered cathode materials for Na-ion batteries and Li-ion batteries in order to improve the stability towards electrolytes

October 2021 – January 2022 (Battery Materials and Diagnostics)

Michael Neuwirt ETH Zürich, Switzerland and
Korea Institute of Technology (KIST) (Prof. D. Henkensmeier)

Influence of process parameters on the properties of PBI membranes for use in redox flow batteries

November 2021 – January 2022 (Membranes and Electrochemical Cells)

Gian Müller ETH Zürich, Switzerland

ECSA estimation and CO_2 reduction on Au_3Cu and AuCu aerogels

September 2021 – January 2022 (Electrocatalysis and Interfaces)

Laura King University of Edinburgh, Edinburgh, United Kingdom

Enabling anode-free lithium metal cells for high energy density batteries

September 2021 – May 2022 (Battery Electrodes and Cells)

Simon Leisibach ETH Zürich, Switzerland

Performance Characterization of Pt_3Ni Aerogel Catalysts in Proton Exchange Membrane Fuel Cells at Low Temperatures and Low Relative Humidity

February – July 2022 (Electrocatalysis & Interfaces)

Lisa Morandi ETH Zürich, Switzerland,
Department of Automatic Control Laboratory

Identification and MPC control of a hydrogen energy storage system for peak shaving EV demand

March – September 2022 (Fuel Cell Systems and Diagnostics)

Adil Baiju ETH Zürich, Switzerland

Stabilizing thin metallic lithium anode by LiI passivation layer for high energy density Li-ion batteries

April – September 2022 (Battery Materials and Diagnostics)

Robin Wullich ETH Zürich, Switzerland

High Voltage Cathode Surface Modification for Stable Interface in All-Solid-State Batteries

July – November 2022 (Battery Materials and Diagnostics)

Ernesto Claure Ramirez

Friedrich-Alexander Universität
Erlangen-Nürnberg, Germany

Surface engineering of high-voltage cathode materials for Na-ion batteries for improved interfacial stability of cathode /electrolyte interface and long-term cycling stability

September 2022 – November 2022 (Battery Materials and Diagnostics)

Zongyi Han

ETH Zürich, Switzerland

Novel PVDF-based aromatic hydrocarbon grafted proton exchange membranes for fuel cells

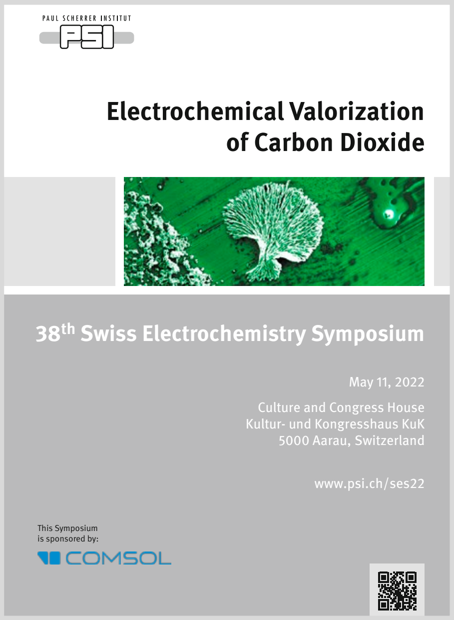
September 2022 – March 2023 (Membranes and Electrochemical Cells)

38th Swiss Electrochemistry Symposium

May 11, 2022
Culture & Congress House (KuK), Aarau

Electrochemical Valorization of Carbon Dioxide

Organizers	Felix N. Büchi, Cordelia Gloor, Lorenz Gubler, Juan Herranz, Sigita Trabesinger, (Electrochemistry Laboratory)
Contributions from (in order of appearance)	Paul J. Corbett, Shell Technology Center, Amsterdam, The Netherlands Ioannis Katsounaros, FZ Jülich / HelmholtzInstitut Erlangen-Nürnberg, Germany (Zoom) Corsin Battaglia, Empa, Dübendorf, Switzerland Viola Becattini, ETH Zürich, Switzerland Christian Bauer, Paul Scherrer Institut, Villigen, Switzerland Richard Masel, Dioxide Materials, Boca Raton, Florida, USA (Zoom) Curtis P. Berlinguette, The University of British Columbia, Vancouver, Canada (Zoom)



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Electrochemical Valorization
of Carbon Dioxide

38th Swiss Electrochemistry Symposium

May 11, 2022

Culture and Congress House
Kultur- und Kongresshaus KuK
5000 Aarau, Switzerland

www.psi.ch/ses22

This Symposium
is sponsored by:
COMSOL

Program

09:00 **Welcome Coffee**

09:30 **Felix N. Büchi, PSI Villigen**
Welcome & Introduction

09:40 **Paul J. Corbett, Shell Technology Center, Amsterdam, The Netherlands**
Carbon-Based Electrolysis and Industrial Applications

10:20 **Ioannis Katsounaros, FZ Jülich/Helmholtz-Institut Erlangen-Nürnberg, Germany**
Tracking products of CO_2 reduction in real time

11:00 **Coffee Break 30 Min.**

11:30 **Corsin Battaglia, Empa, Dübendorf, Switzerland**
Electrocatalytic reduction of CO_2 on fiber-based gas-diffusion electrodes

12:10 **Buffet-Lunch and Poster Session**

13:30 **Viola Becattini, ETH Zürich, Switzerland**
The role of CO_2 capture, utilization and storage to enable a net-zero-CO_2-emissions society

14:10 **Christian Bauer, Paul Scherrer Institut, Villigen, Switzerland**
Hydrogen-based e-fuels in climate change mitigation: the environmental and economic perspective

14:50 **Coffee Break 20 Min.**

15:10 **Richard Masel, Dioxide Materials, Boca Raton, Florida, USA (Zoom)**
Concentration and Impurity Effects on CO_2 electrolysis

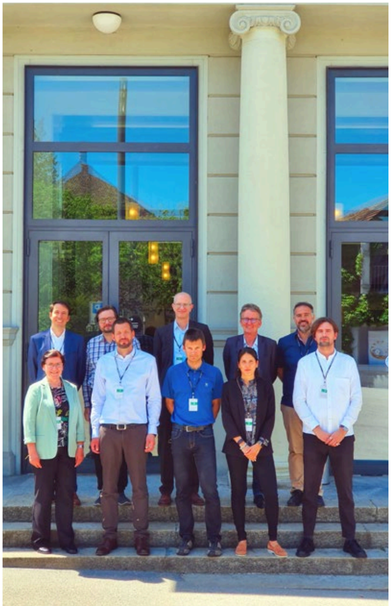
15:50 **Curtis P. Berlinguette, The University of British Columbia, Vancouver, Canada (Zoom)**
Direct Conversion of Carbon Capture Solutions into Products

16:30 **Felix N. Büchi, PSI Villigen**
Summary

16:40 **Networking and Farewell Coffee**

3

38th Swiss Electrochemistry Symposium
Electrochemical Valorization of Carbon Dioxide



Impressions from the 38th Swiss Electrochemistry Symposium.

Speakers and organizers.

Collaborations with Industrial Partners

The Electrochemistry Laboratory had the pleasure to collaborate with the following industrial partners during the year 2022:

anaxam
analytics for advanced manufacturing

BASF
The Chemical Company

BEKAERT
better together

BELENOS
Clean Power Holding Ltd

BMW

GORE

INNOLITH

JM Johnson Matthey
Inspiring science, enhancing life

Metrohm

TOYOTA

oerlikon

saft
a company of TOTAL

SIEMENS energy

umicore

Collaborations with External Partners

The Electrochemistry Laboratory had the pleasure to collaborate with the following external partners during the year 2022:

energieschweiz

Schweizerischer Nationalfonds

SNF Sinergia

Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Bundesamt für Energie BFE
Office fédéral de l'énergie OFEN

ETH zürich

BRIDGE

EPFL

Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Swiss Confederation

Innosuisse – Swiss Innovation Agency

Empa

zh aw School of Engineering

catCHy EUROPEAN TRAINING NETWORK
Novel catalysts for CO_2 Hydrogenation and Electro-reduction

FCH FUEL CELLS AND HYDROGEN JOINT UNDERTAKING

BEPA Batteries European Partnership Association

BATT4EU Batteries European Partnership

HIGHTECH ZENTRUM AARGAU

iBAT

SNI
Swiss Nanoscience Institute
Center of Excellence supported by the University of Basel and the Canton of Aargau

EFCF EUROPEAN FUEL CELL FORUM

European Commission
Marie Skłodowska-Curie Actions

HZDR
HELMHOLTZ ZENTRUM DRESDEN ROSSENDORF

Strategic Focus Area
Advanced Manufacturing

TECHNISCHE UNIVERSITÄT DARMSTADT

TECHNISCHE UNIVERSITÄT DRESDEN

TUM
Technische Universität München

Teaching Activities

Teaching

Dr. E. Fabbri, PD Dr. L. Gubler, Dr. J. Herranz	*Electrochemical Energy Conversion & Storage Technologies* ETH Zürich, FS 2022.
Dr. E. Fabbri, PD Dr. L. Gubler, Dr. J. Herranz, Dr. S. Trabesinger	*Hands-on Electrochemistry for Energy Storage and Conversion Applications* ETH Zürich, HS 2022.
Dr. E. Fabbri	*Electrochemistry: Basics and Practice (course number 64133-01)* University of Basel, FS 2022.
PD Dr. L. Gubler	*Electrochemistry: Fundamentals, Cells & Applications* ETH Zürich, HS 2022.
Prof. Dr. T.J. Schmidt	*Physical Electrochemistry & Electrocatalysis* ETH Zürich, FS 2022.

Contributions to Courses

PD Dr. L. Gubler	*Energy Storage Systems* Lucerne University of Applied Sciences and Arts, March 23, 2022.

Publications

Peer Reviewed Papers

E.B. Boz, P. Boillat, A. Forner-Cuenca	*Taurine Electrografting onto Porous Electrodes Improves Redox Flow Battery Performance* ACS Applied Materials & Interfaces **14**, 41883–41895 (2022). DOI: 10.1021/acsami.2c08211
M. Bozzetti, A. Berger, R. Girod, Y.-C. Chen, F.N. Büchi, H.A. Gasteiger, V. Tileli	*On the role of pore constrictions in gas diffusion electrodes* Chemical Communications **58**, 8854–8857 (2022). DOI: 10.1039/D2CC02844A
P. Chauhan, K. Hiekel, J.S. Diercks, J. Herranz, V.A. Saveleva, P. Khavlyuk, A. Eychmüller, T.J. Schmidt	*Electrochemical Surface Area Quantification, CO_2 Reduction Performance, and Stability Studies of Unsupported Three-Dimensional Au Aerogels versus Carbon-Supported Au Nanoparticles* ACS Materials Au **2**, 278–292 (2022). DOI: 10.1021/acsmaterialsau.1c00067
Y.-C. Chen, C. Karageorgiou, J. Eller, T.J. Schmidt, F.N. Büchi	*Determination of the porosity and its heterogeneity of fuel cell microporous layers by X-ray tomographic microscopy* Journal of Power Sources **539**, 231612 (2022). DOI: 10.1016/j.jpowsour.2022.231612
C. Csoklich, M. Sabharwal, T.J. Schmidt, F.N. Büchi	*Does the thermal conductivity of gas diffusion layer matter in polymer electrolyte fuel cells?* Journal of Power Sources **540**, 231539 (2022). DOI: 10.1016/j.jpowsour.2022.231539
C. Csoklich, T.J. Schmidt, F.N. Büchi	*High performance gas diffusion layers with added deterministic structures* Energy & Environmental Science **15**, 1293–1306 (2022). DOI: 10.1039/D1EE03246A

M. Dalkilic, A. Schmidt, T.D. Schladt, P. Axmann, J. DuMont, J. Travis, D. Lindblad, Ł. Kondracki, M. Wohlfahrt-Mehrens, S. Trabesinger, M. Lindén	*Tantalum Oxide Coating of Ni-Rich Cathode Active Material via Atomic Layer Deposition and its Influence on Gas Evolution and Electrochemical Performance in the Early and Advanced Stages of Degradation* Journal of The Electrochemical Society **169**, 110537 (2022). DOI: 10.1149/1945-7111/aca2e5
T. de Wild, T. Nemeth, T. Nauser, T.J. Schmidt, L. Gubler	*Chemical Stability Enhancement of Aromatic Proton Exchange Membranes using a Damage Repair Mechanism* ECS Trans. **109**, 317–325 (2022). DOI: 10.1149/10909.0317ecst
J.S. Diercks, M. Georgi, J. Herranz, N. Diklić, P. Chauhan, A.H. Clark, R. Hübner, A. Faisnel, Q. Chen, M. Nachtegaal, A. Eychmüller, T.J. Schmidt	*CO_2 Electroreduction on Unsupported PdPt Aerogels: Effects of Alloying and Surface Composition on Product Selectivity* ACS Applied Energy Materials **5**, 8460–8471 (2022). DOI: 10.1021/acsaem.2c00987
J.S. Diercks, J. Herranz, M. Georgi, N. Diklić, P. Chauhan, K. Ebner, A.H. Clark, M. Nachtegaal, A. Eychmüller, T.J. Schmidt	*Interplay between Surface-Adsorbed CO and Bulk Pd Hydride under CO_2-Electroreduction Conditions* ACS Catalysis **12**, 10727–10741 (2022). DOI: 10.1021/acscatal.2c02660
N. Diklić, A.H. Clark, J. Herranz, J.S. Diercks, D. Aegerter, M. Nachtegaal, A. Beard, T.J. Schmidt	*Potential Pitfalls in the Operando XAS Study of Oxygen Evolution Electrocatalysts* ACS Energy Letters **7**, 1735–1740 (2022). DOI: 10.1021/acsenergylett.2c00727

K. Ebner, A.H. Clark, V.A. Saveleva, G. Smolentsev, J. Chen, L. Ni, J. Li, A. Zitolo, F. Jaouen, U.I. Kramm, T.J. Schmidt, J. Herranz	*Time-Resolved Potential-Induced Changes in Fe/N/C-Catalysts Studied by In Situ Modulation Excitation X-Ray Absorption Spectroscopy* Advanced Energy Materials **12**, 2103699 (2022). DOI: 10.1002/aenm.202103699
M. El Kazzi	*Li-ion solvation in TFSI and FSI -based ionic liquid electrolytes probed by X-ray photoelectron spectroscopy* EPJ Web Conf. **273**, 01001 (2022). DOI: 10.1051/epjconf/202227301001
J.B. Falqueto, A.H. Clark, A. Štefančič, G.J. Smales, C.A.F. Vaz, A.J. Schuler, N. Bocchi, M. El Kazzi	*High Performance Doped Li-Rich* $Li_{1+x}Mn_{2-x}O_4$ *Cathodes Nanoparticles Synthesized by Facile, Fast, and Efficient Microwave-Assisted Hydrothermal Route* ACS Applied Energy Materials **5**, 8357–8370 (2022). DOI: 10.1021/acsaem.2c00902
R. Fischer, C.M. Schlepütz, J. Zhao, P. Boillat, D. Hegemann, R.M. Rossi, D. Derome, J. Carmeliet	*Wicking dynamics in yarns* Journal of Colloid and Interface Science **625**, 1–11 (2022). DOI: 10.1016/j.jcis.2022.04.060
A. Garcia, S. Biswas, D. McNulty, A. Roy, S. Raha, S. Trabesinger, V. Nicolosi, A. Singha, J.D. Holmes	*One-Step Grown Carbonaceous Germanium Nanowires and Their Application as Highly Efficient Lithium-Ion Battery Anodes* ACS Applied Energy Materials **5**, 1922–1932 (2022). DOI: 10.1021/acsaem.1c03404
L. Gubler	*Wire-free electrochemical* CO_2 *scrubbing* Nature Energy **7**, 216–2017 (2022). DOI: 10.1038/s41560-022-00983-1
S.D. Lacey, E. Gilardi, E. Müller, C. Merckling, G. Saint-Girons, C. Botella, R. Bachelet, D. Pergolesi, M. El Kazzi	*Integration of* $Li_4Ti_5O_{12}$ *Crystalline Films on Silicon Toward High-Rate Performance Lithionic Devices* ACS Applied Materials & Interfaces **15**, 1535–1544 (2022). DOI: 10.1021/acsami.2c17073

V. Mastronardi, J. Kim, M. Veronesi, T. Pomili, F. Berti, G. Udayan, R. Brescia, J.S. Diercks, J. Herranz, T. Bandiera, K.A. Fichthorn, P.P. Pompa, M. Moglianetti	*Green Chemistry and First-Principles Theory Enhance Catalysis: Synthesis and 6-Fold Catalytic Activity Increase of sub-5 nm Pd and Pt@Pd Nanocubes* Nanoscale **14**, 10155–10168 (2022). DOI: 10.1039/D2NR02278H
A.P. Muroyama, L. Gubler	*Carbonate Regeneration Using a Membrane Electrochemical Cell for Efficient CO_2 Capture* ACS Sustainable Chemistry & Engineering **10**, 16113–16117 (2022). DOI: 10.1021/acssuschemeng.2c04175
T. Nemeth, M. Agrachev, G. Jeschke, L. Gubler, T. Nauser	*EPR Study on the Oxidative Degradation of Phenyl Sulfonates, Constituents of Aromatic Hydrocarbon-Based Proton-Exchange Fuel Cell Membranes* The Journal of Physical Chemistry C **126**, 15606–15616 (2022). DOI: 10.1021/acs.jpcc.2c04566
T. Nemeth, T. de Wild, L. Gubler, T. Nauser	*Impact of substitution on reactions and stability of one-electron oxidised phenyl sulfonates in aqueous solution* Phys. Chem. Chem. Phys. **24**, 895–901 (2022). DOI: 10.1039/d1cp04518k
T. Nemeth, T. de Wild, L. Gubler, T. Nauser	*Moderation of Oxidative Damage on Aromatic Hydrocarbon-Based Polymers* Journal of The Electrochemical Society **169**, 054529 (2022). DOI: 10.1149/1945-7111/ac6f85
T. Nemeth, T. Nauser, L. Gubler	*On the Radical Induced Degradation of Quaternary Ammonium Cations for Alkaline Fuel Cell Membranes and Electrolyzers* ChemSusChem **15**, e202201571 (2022). DOI: 10.1002/cssc.202201571
C. Peter, E. Vrettos, F.N. Büchi	*Polymer electrolyte membrane electrolyzer and fuel cell system characterization for power system frequency control* International Journal of Electrical Power & Energy Systems **141**, 108121 (2022). DOI: 10.1016/j.ijepes.2022.108121

H.Q. Pham, Ł. Kondracki, M. Tarik, S. Trabesinger
Correlating the Initial Gas Evolution and Structural Changes to Cycling Performance of Co-Free Li-Rich Layered Oxide Cathode
Journal of Power Sources **527**, 231181 (2022).
DOI: 10.1016/j.jpowsour.2022.231181

A. Schuller, T.J. Schmidt, J. Eller
Noninvasive Measurement of Humidity Distribution in Polymer Electrolyte Fuel Cells (PEFCs). Part II: Operando Analysis of a Fuel Cell Stack
Journal of The Electrochemical Society **169**, 124512 (2022).
DOI: 10.1149/1945-7111/aca0e3

A. Schuller, T.J. Schmidt, J. Eller
Non-Invasive Measurement of Humidity Distribution in Polymer Electrolyte Fuel Cells (PEFCs): Part I. In Situ Proof of Concept
Journal of The Electrochemical Society **169**, 074504 (2022).
DOI: 10.1149/1945-7111/ac7a62

A. Schuller, T.J. Schmidt, J. Eller
Finite Element Model Based Determination of Local Membrane Conductivity of Polymer Electrolyte Fuel Cells
Journal of The Electrochemical Society **169**, 044525 (2022).
DOI: 10.1149/1945-7111/ac6390

L. Seidl, R. Grissa, L. Zhang, S. Trabesinger, C. Battaglia
Unraveling the Voltage-Dependent Oxidation Mechanisms of Poly(Ethylene Oxide)-Based Solid Electrolytes for Solid-State Batteries
Advanced Materials Interfaces **9**, 2100704 (2022).
DOI: 10.1002/admi.202100704

M. Srout, M. Carboni, J.-A. Gonzalez, S. Trabesinger
Insights into the Importance of Native Passivation Layer and Interface Reactivity of Metallic Lithium by Electrochemical Impedance Spectroscopy
Small, 2206252 (2022).
DOI: 10.1002/smll.202206252

M. Striednig, M. Cochet, P. Boillat, T.J. Schmidt, F.N. Büchi
A model based investigation of evaporative cooling for polymer electrolyte fuel cells – Stack level analysis
Journal of Power Sources **517**, 230706 (2022).
DOI: 10.1016/j.jpowsour.2021.230706

M. Striednig, T.J. Schmidt, F.N. Büchi
A model based investigation of evaporative cooling for polymer electrolyte fuel cells – System level analysis
Journal of Power Sources **542**, 231720 (2022).
DOI: 10.1016/j.jpowsour.2022.231720

Y. Surace, D. Leanza, M. Mirolo, Ł. Kondracki, C.A.F. Vaz, M. El Kazzi, P. Novák, S. Trabesinger	*Evidence for Stepwise Formation of Solid Electrolyte Interphase in a Li-Ion Battery* Energy Storage Materials **44**, 156–167 (2022). DOI: 10.1016/j.ensm.2021.10.013
K.M. Tenny, K.V. Greco, M. van der Heijden, T. Pini, A. Mularczyk, A.-P. Vasile, J. Eller, A. Forner-Cuenca, Y.-M. Chiang, F.R. Brushett	*A Comparative Study of Compressive Effects on the Morphology and Performance of Carbon Paper and Cloth Electrodes in Redox Flow Batteries* Energy Technology **10**, 2101162 (2022). DOI: 10.1002/ente.202101162
S. van Rooij, M. Magnini, A. Mularczyk, H. Xu, F.N. Büchi, S. Haussener	*Conductive Heat Transfer in Partially Saturated Gas Diffusion Layers with Evaporative Cooling* Journal of The Electrochemical Society **169**, 034515 (2022). DOI: 10.1149/1945-7111/ac4e5c
E. Winter, M. Briccola, T.J. Schmidt, S. Trabesinger	*Enabling $LiNO_3$ in Carbonate Electrolytes by Flame-Retardant Electrolyte Additive as a Cosolvent for Enhanced Performance of Lithium Metal Batteries* Applied Research, e202200096 (2022). DOI: 10.1002/appl.202200096
H. Xu, M. Bührer, F. Marone, T.J. Schmidt, F.N. Büchi, J. Eller	*Effects of Gas Diffusion Layer Substrates on PEFC Water Management: Part II. In Situ Liquid Water Removal via Evaporation* Journal of The Electrochemical Society **169**, 104503 (2022). DOI: 10.1149/1945-7111/ac94a2
L. Zhang, E.A. Müller Gubler, C.-W. Tai, Ł. Kondracki, H. Sommer, P. Novák, M. El Kazzi, S. Trabesinger	*Elucidating the Humidity-Induced Degradation of Ni-Rich Layered Cathodes for Li-Ion Batteries* ACS Applied Materials & Interfaces **14**, 13240–13249 (2022). DOI: 10.1021/acsami.1c23128
Z. Zhang, Z. Han, A. Testino, L. Gubler	*Platinum and Cerium-Zirconium Oxide Co-Doped Membrane for Mitigated H_2 Crossover and Ionomer Degradation in PEWE* Journal of The Electrochemical Society **169**, 104501 (2022). DOI: 10.1149/1945-7111/ac94a3

W. Zhao, L. Zou, L. Zhang, X. Fan, H. Zhang, F. Pagani, E. Brack, L. Seidl, X. Ou, K. Egorov, X. Guo, G. Hu, S. Trabesinger, C. Wang, C. Battaglia	*Assessing Long-Term Cycling Stability of Single-Crystal Versus Polycrystalline Nickel-Rich NCM in Pouch Cells with 6 mAh* cm^{-2} *Electrodes* Small **18**, 2107357 (2022). DOI: 10.1002/smll.202107357
Y. Zhao, T. Zhou, T. Ashirov, M.E. Kazzi, C. Cancellieri, L.P.H. Jeurgens, J.W. Choi, A. Coskun	*Fluorinated ether electrolyte with controlled solvation structure for high voltage lithium metal batteries* Nature Communications **13**, 2575 (2022). DOI: 10.1038/s41467-022-29199-3
Y. Zhao, T. Zhou, M. El Kazzi, A. Coskun	*Fluorinated Cyclic Ether Co-solvents for Ultra-high-Voltage Practical Lithium-Metal Batteries* ACS Applied Energy Materials **5**, 7784–7790 (2022). DOI: 10.1021/acsaem.2c01261
T. Zhou, Y. Zhao, M. El Kazzi, J.W. Choi, A. Coskun	*Integrated Ring-Chain Design of a New Fluorinated Ether Solvent for High-Voltage Lithium-Metal Batteries* Angewandte Chemie International Edition **61**, e202115884 (2022). DOI: 10.1002/anie.202115884

Talks

Invited Talks

P. Boillat	*Neutron Imaging in Electrochemistry* EMPA Topical Day – Imaging and Image Analysis XIII, Online, May 10, 2022.
P. Boillat	*Neutron imaging insights into electrochemical devices for the energy transition* 9th International Topical meeting on Neutron Radiography, Buenos Aires, Argentina, October 19, 2022.
F.N. Büchi	*Towards better understanding of the Transport- & Catalyst layer Interface* International Conference on Electrolysis, Golden, CO, USA, June 21, 2022.
F.N. Büchi	*Porous Material Development for FC and ELY* Departmental Seminar, ESIP, Renewable Energy National Laboratory, Golden, CO, USA, June 28, 2022.
F.N. Büchi	*Porous Material Development for FC and ELY* Departmental Seminar, Department of Chemical and Biomolecular engineering, University of California, Irvine, CA, USA, July 19, 2022.
F.N. Büchi	*From Stochastic to Deterministic Transport – Rethinking GDL Development* Fuel Cell Gordon Conference, Smithfield, RI, USA, July 28, 2022.
F.N. Büchi	*Porous Transport Layer Characterization & Development* Research Seminar, Plug Power, Concord, MA, USA, August 1, 2022.
F.N. Büchi	*From Stochastic to Deterministic Transport – Advancing GDL Materials for Polymer Electrolyte Fuel Cells* 9th International Fuel Cell Workshop IFCW, Kofu, Japan (Online), November 15, 2022.

F.N. Büchi	*Polymer Electrolyte Water Electrolysis: Better Understanding of the Transport-/Catalyst Layer Interface* Grand Renewable Energy 2022, International Conference (Grand Re 2021), Japan (Online), December 12, 2022.
K. Ebner	*Fe-N-C Catalytic Activity Towards the Oxygen Reduction Reaction… and What It's Got to Do With Spin and Geometry* GDCh Lunch Talk Electrochemistry #6, Online, November 30, 2022.
M. El Kazzi	*Propriétés (electro-)chimiques et électroniques de l'interface* $LiCoO_2$-Li_3PS_4 *examiné par operando XPS dans une batterie tout-solide* Journées Nationales des Spectroscopies de PhotoEmission (JNSPE) Dijon, France, May 16–18, 2022.
M. El Kazzi	*Insight into the Reactivity and Potential Profile across the Electrified Interface in All-Solid-State Batteries Enabled by Operando X-Ray Photoelectron/Absorption Spectroscopy* CIMTEC 2022 – Conference, Perugia, Italy, June 20–24, 2022.
M. El Kazzi	*Operando X-Ray Photoelectron/Absorption Spectroscopy to Probe the (Electro-)Chemical and Electronic Interface properties in All-Solid-State Batteries* ISE-2022 – 73rd Annual Meeting of the International Society of Electrochemistry, Online, September 12–16, 2022.
L. Gubler	*Functionalized PBI Membranes for High-Performance Vanadium Redox Flow Batteries* ACS Conference «Polymers for Fuel Cells, Energy Storage, and Conversion», Napa, CA, USA, May 15–18, 2022.
L. Gubler	*Tethered Antioxidant for Improved Chemical Stability of Sulfonated Hydrocarbon-based Fuel Cell Membranes* EMEA-2022 – Workshop on Ion Exchange Membranes for Energy Applications, Bad Zwischenahn, Germany, June 20–22, 2022.
J. Herranz	*Fuel Cell Research Activities at PSI's Electrochemistry Laboratory* Imerys Graphite and Carbon Innovation Day MOBILE ENERGY, Bironico, Switzerland, July 5, 2022.

J. Herranz	*Possible Pitfalls in Operando XAS Electrochemical Measurements* Sinergia Project Meeting @ EPFL, Lausanne, Switzerland, September 30, 2022.
J. Herranz	*Decoupling the Contributions of Different Instability Mechanisms to the PEFC Performance Decay of Fe-Based O_2-Reduction Catalysts* ECS-2022 – 242nd The Electrochemical Society Meeting, Atlanta, USA (Online), October 9–13, 2022.
T.J. Schmidt	*Hydrogen and Power-to-X* Swiss-Canadian Innovation Summit, Online, March 16, 2022.
T.J. Schmidt	*Energy Storage Using Power-to-X: A Critical Player for the Net-Zero Society* Symposium on Energy Storage, The Royal Swedish Academy of Science, Stockholm, Sweden, June 08, 2022.
T.J. Schmidt	*Energiespeicher als Schlüssel für das Energiesystem 2050* Ringvorlesung Interface, FHNW, Windisch, Switzerland, September 26, 2022.
S. Trabesinger	*Cross-talk Suppressing Multifunctional Electrolyte Additives for Enhanced Interfacial Stability of Ni-rich NCMs* CIMTEC 2022 – Conference, Perugia, Italy, June 20–24, 2022.
S. Trabesinger	*Importance of Advanced Analytics for Battery Development* Imerys Graphite and Carbon Innovation Day MOBILE ENERGY, Bironico, Switzerland, July 5, 2022.
S. Trabesinger	*Deciphering the Mechanism of FEC-induced SEI Formation in Li-ion Batteries* INESS 2022 – Nur-Sultan, Kazakhstan, August 5–6, 2022.
S. Trabesinger	*Towards High Energy Density Batteries* Electrosuisse e-mobile Online Forum «Future of batteries», Online, October 19, 2022.
S. Trabesinger	*Battery Technology: Status and Outlook* Energiezukunft: Herausforderungen und Lösungen, Hightech Zentrum Aargau, Brugg, Switzerland, October 25, 2022.

Contributed Talks

K. Aliyah, C. Appel, C. Prehal, M. Guizar-Sicairos, L. Gubler, J. Eller	*Representative Morphology Model for PEFC Catalyst Layer: Operando Water Saturation Determined via Small-Angle X-ray Scattering* ModVal-2022 – 18th Symposium on Modeling and Experimental Validation of Electrochemical Energy Technologies, Schloss Hohenkammer, Germany, March 14–16, 2022.
K. Aliyah, C. Appel, C. Prehal, M. Guizar-Sicairos, L. Gubler, J. Eller	*Operando Determination of Pore-filling Mechanism and Saturation of PEFC Catalyst Layer using Small-Angle X-ray Scattering* InterPore2022, Abu Dhabi, Dubai (Online), May 30 – June 2, 2022.
K. Aliyah, C. Appel, C. Prehal, M. Guizar-Sicairos, L. Gubler, J. Eller	*Mechanistic Insights into Liquid Water Saturation in Fuel Cell Catalyst Layers using Operando Small Angle X-ray Scattering* XVIII International Small-Angle Scattering Conference 2022, Campinas, Brazil, September 11–16, 2022.
K. Aliyah, C. Appel, C. Prehal, M. Guizar-Sicairos, L. Gubler, J. Eller	*Operando Liquid Water Saturation in PEFC Catalyst Layers Determined Via Small Angle X-Ray Scattering* ECS-2022 – 242nd The Electrochemical Society Meeting, Atlanta, USA (Online), October 9–13, 2022.
K. Azizi, H.A. Hjuler, L.N. Cleemann, D. Henkensmeier, J.C. Duburg, L. Gubler	*Polybenzimidazole Membrane for Vanadium Flow Battery Applications* ECS-2022 – 242nd The Electrochemical Society Meeting, Atlanta, Georgia, USA, October 9–13, 2022.
D. Baster, C.A.F. Vaz, A.H. Clark, M. El Kazzi	*The Role of Surface Degradation in the Capacity Fading Mechanism of Layered Oxide Cathode Materials for Sodium-ion Batteries* ISE-2022 – 73rd Annual Meeting of the International Society of Electrochemistry, online, September 12–16, 2022.
P. Chauhan, K. Hiekel, M. Georgi, G. Muller, J. Diercks, J. Herranz, A. Eychmuller, T.J. Schmidt	*ECSA Quantification, CO_2 Reduction Performance and Stability Studies of Unsupported Au and Au-Cu Aerogels* ECS-2022 – 241st The Electrochemical Society Meeting, Vancouver, BC, Canada, May 29 – June 2, 2022.

T. de Wild, T. Nemeth, T. Nauser, T.J. Schmidt, L. Gubler	*Chemical Stability Enhancement of Aromatic Proton Exchange Membranes Using a Damage Repair Mechanism* ECS-2022 – 242nd The Electrochemical Society Meeting, Atlanta, Georgia, USA, October 9–13, 2022.
J. Diercks, J. Herranz, M. Georgi, N. Diklić, P. Chauhan, A.H. Clark, M. Nachtegaal, A. Eychmuller, T.J. Schmidt	*Interplay Between Surface-Adsorbed CO and Bulk Pd-Hydride at CO_2 Electroreduction Conditions* ECS-2022 – 241st The Electrochemical Society Meeting, Vancouver, BC, Canada, May 29 – June 2, 2022.
N. Diklic, A.H. Clark, J. Herranz, D. Aegerter, A. Beard, T.J. Schmidt	*Oxygen Evolution Reaction on Ir-Oxide Based Materials Studied By Modulation Excitation X-Ray Absorption Spectroscopy* ECS-2022 – 241st The Electrochemical Society Meeting, Vancouver, BC, Canada, May 29 – June 2, 2022.
J.C. Duburg, L. Gubler, T.J. Schmidt	*The Influence of Non-Charged Sidechains on the Performance of Meta-Polybenzimidazole Membranes in Vanadium Redox Flow Batteries* ECS-2022 – 241st The Electrochemical Society Meeting, Vancouver, BC, Canada, May 29 – June 2, 2022.
B. Lelotte, C.A.F. Vaz, V. Pelé, C. Jordy, L. Gubler, M. El Kazzi	*Unveiling The (Electro-)Chemical Interface Degradation Upon Cycling Of NCM622/LPSCl Solid-State Batteries* E-MRS 2022 Spring Meeting – European Materials Research Society, Online, May 30 – June 3, 2022.
B. Lelotte, C.A.F. Vaz, C. Borca, T. Huthwelker, V. Pelé, C. Jordy, L. Gubler, M. El Kazzi	*Interface Evolution of the $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2/Li_6PS_5Cl$ Solid-State Battery Cathodes During Cycling* Solid-State Batteries V, Frankfurt am Main, Germany, November 22–24, 2022.
W. Liu, J. Lee, Y.-C. Chen, Y. Yao, S. Neuhaus, A. Goel, T.J. Schmidt, P. Boillat	*Advanced Water Management in Polymer Electrolyte Fuel Cells at Subzero Temperatures: Gas Diffusion Layer with Patterned Wettability* 2022 MRS Fall Meeting, Boston, USA (online talk), December 6, 2022.

A. Muroyama, L. Gubler	*Electrochemical Anion Exchange Membrane Recovery of CO_2 from Carbonate Solution* EMEA-2022 – Workshop on Ion Exchange Membranes for Energy Applications, Bad Zwischenahn, Germany, June 20–22, 2022.
T. Nemeth, T. de Wild, T. Nauser, L. Gubler	*Impact of Electron Density on Reactions and Stability of One-electron Oxidized Phenyl Sulfonates in Aqueous Solution* 19th Radiochemical Conference, Mariánské Lázně, Czeck Republic, May 15–20, 2022.
T. Nemeth, T. de Wild, T. Nauser, L. Gubler	*On the Radical-Induced Degradation of Anion Exchange Fuel Cell Membranes* EMEA-2022 – Workshop on Ion Exchange Membranes for Energy Applications, Bad Zwischenahn, Germany, June 20–22, 2022.
A. Schuller, T.J. Schmidt, J. Eller	*Noninvasive Determination of the local Impedance in Polymer Electrolyte Fuel Cells* 32nd Topical Meeting of the International Society of Electrochemistry, Stockholm, Sweden, June 19–22, 2022.
V. Siller, C.A.F. Vaz, C. Borca, T. Huthwelker, M. El Kazzi	*Elucidating the redox processes of lithium thiophosphate solid electrolytes by X-ray spectroscopic techniques* Solid-State Batteries V, Frankfurt am Main, Germany, November 24, 2022.
C.C. Weber, F.N. Büchi, S. De Angelis	*Two-Dimensional Model Porous Transport Layers for Interfacial Characterization in Polymer Electrolyte Water Electrolysis* ECS-2022 – 241st The Electrochemical Society Meeting, Vancouver, BC, Canada, May 29 – June 2, 2022.
C.C. Weber, M. Holler, L. Gubler, F.N. Büchi, S. De Angelis	*Three-Dimensional Analysis of Morphological Changes in Anodic PEMWE Catalyst Layers by X-ray Ptychographic Laminography* ICE Conference – 3rd International Conference on Electolysis, Golden, CO, USA, June 22, 2022.
E. Winter, T.J. Schmidt, S. Trabesinger	*Unravelling Lithium Nucleation and Dissolution in Lithium-Metal Batteries* Swiss Battery Days 2022, Dübendorf, Switzerland, August 29–31, 2022.

Z. Zhang, Z. Han, A. Testino, L. Gubler	*Suppressing Hydrogen Crossover and Scavenging Radicals By Incorporation of Pt and Cerium-Zirconium Oxide for Polymer Electrolyte Water Electrolyzers* ECS-2022 – 241st The Electrochemical Society Meeting, Vancouver, BC, Canada, May 29 – June 2, 2022.

Posters

A. Baiju, T. Liu, M. Carboni, J.-A. Gonzalez, M. El Kazzi	*Stabilizing Thin Metallic Lithium Anode by LiI Surface Passivation Layer for High Energy Density Li-Ion Batteries* Swiss Battery Days 2022, Dübendorf, Switzerland, August 29–31, 2022.
D. Baster, C.A.F. Vaz, A.H. Clark, M. El Kazzi	*Unveiling the Surface and Bulk Degradation of P2-type Sodium Layered Oxide Cathode Material Operating at High-Voltages* Swiss Battery Days 2022, Dübendorf, Switzerland, August 29–31, 2022.
D. Baster, C.A.F. Vaz, A.H. Clark, M. El Kazzi	*Investigations of The Structural Degradation and Surface Side Reactions of P2-Type Sodium Layered Oxide Cathode Material Operating at High-Voltages* Sodium (Na) Battery Symposium, Berlin, Germany, September 26–27, 2022.
E.R. Carreon Ruiz, J. Lee, M.-O. Ebert, J.I. Márquez Damián, M. Strobl, L. Gubler, P. Boillat	*Discerning Hydrogen Dynamics in Li-Ion Battery Organic Solvents via Wavelength-Resolved Neutron Imaging* IFBF International Flow Battery Forum, Brussels, Belgium, June 28–29, 2022.
J. Casella, E. Hampson, J.C. Duburg, L. Gubler	*Pretreated Meta-Polybenzimidazole (mPBI) Membranes for High Performance Vanadium Redox Flow Batteries* QENS/WINS 22 International Conference, San Sebastian, Spain, May 23–27, 2022.
P. Chauhan, M. Georgi, G. Muller, J. Diercks, J. Herranz, A. Eychmüller, T.J. Schmidt	*Effects of Electrochemical Conditioning on Electrochemical Surface Area, CO_2 Reduction Performance and Nanostructural Stability of Au-Cu Aerogels* Gordon Research Conference on Renewable Energy: Solar Fuels, Lucca (Barga), Italy, May 8–13, 2022.

M. Dessiex, S. Haussener, F.N. Büchi	*Water Management in Gas-Fed CO_2 Reduction Devices with Bipolar Membranes* ModVal-2022 – 18th Symposium on Modeling and Experimental Validation of Electrochemical Energy Technologies, Schloss Hohenkammer, Germany, March 14–16, 2022.
T. de Wild, T. Nemeth, P. Becker, D. Günther, T. Nauser, T.J. Schmidt, L. Gubler	*Hydrocarbon-Membrane Degradation and Repair during Fuel Cell Operation* ACS Conference «Polymers for Fuel Cells, Energy Storage, and Conversion», Napa, CA, USA, May 15–18, 2022.
T. Dörenkamp, M. Sabharwal, F. Marone, J. Eller	*Investigation of Water Cluster and Droplet Interactions in PEFC using Operando XTM* ModVal-2022 – 18th Symposium on Modeling and Experimental Validation of Electrochemical Energy Technologies, Munich, Germany, March 14–16, 2022.
T. Dörenkamp, M. Sabharwal, F. Marone, J. Eller	*Investigating Water Transport Phenomena by Point Injection in Polymer Electrolyte Fuel Cells using Operando X-Ray Tomographic Microscopy* Gordon Research Conference 2022 – Bryant University, Rhode Island, USA, July 23–29, 2022.
Ł. Kondracki, L. Skarjan, D. Wierzbicki, A. Wach, S. Trabesinger	*Influence of Li-substitution on Performance of Cobalt-free Materials for Na-ion Batteries* Swiss Battery Days 2022, Dübendorf, Switzerland, August 29–31, 2022.
Ł. Kondracki, J. Stropp, S. Steiner, D. Wierzbicki, A. Wach, S. Trabesinger	*Investigation of Charge Compensation Mechanism in Co-free Materials for Na-ion Batteries* IBA 2022 – International Battery Association Hybrid Conference, Bled, Slovenia, October 2–7, 2022.
J. Linke, T. Rohrbach, A.H. Clark, M. Nachtegaal, M. Andrzejewski, N.P.M. Casati, T. Huthwelker, M. Ranocchiari, T.J. Schmidt, E. Fabbri	*Metal-Organic Framework based Catalysts for the Oxygen Evolution Reaction in Alkaline Electrolysis* 3rd International Conference on Electrolysis 2021 (in June 2022), Golden, CO, USA, June 20–23, 2022.

T. Liu, M. Srout, C.A.F. Vaz, M. Carboni, J.-A. Gonzalez, S. Trabesinger, M. El Kazzi	*Regulating Uniform Li Plating/Stripping Via Li_2O/LiOH-Rich Passivation Layer for Long-Life Thin Li Metal Batteries* Swiss Battery Days 2022, Dübendorf, Switzerland, August 29–31, 2022.
T. Liu, M. Srout, C.A.F. Vaz, M. Carboni, J.-A. Gonzalez, S. Trabesinger, M. El Kazzi	*Enabling uniform Li plating/stripping for long-life thin Li metal batteries via Li_2O/LiOH-rich passivation layer* IBA-2022 – International Battery Association Meeting, Bled, Slovenia, October 2–7, 2022.
A. Muroyama, L. Gubler	*Electrochemical Regeneration of Carbonate Solution and CO_2 Enrichment of a H_2 Stream* 38th Swiss Electrochemistry Symposium, Aarau, Switzerland, May 11, 2022.
A. Ruffo, P. Boillat, M. Strobl, M. Kenzelmann	*Neutron nanomediators: towards in-situ measurements* Annual Meeting of the Swiss Nanoscience Institute, Lenzerheide, Switzerland, September 7, 2022.
S. Ünsal, M. Bozzetti, R. Girod, A. Berger, V. Tileli, H.A. Gasteiger, T.J. Schmidt, J. Herranz	*Aggregate Size Effect on the Mass Transport Properties of Non Noble Metal Catalyst Layers in PEMFC Cathodes* Gordon Research Conference on Fuel Cells, Smithfield, RI, USA, July 24–29, 2022.
E. Winter, T.J. Schmidt, S. Trabesinger	*Understanding electrolyte influence on lithium plating via potential-driven deposition* 38th Swiss Electrochemistry Symposium, Aarau, Switzerland, May 11, 2022.
E. Winter, T.J. Schmidt, S. Trabesinger	*Understanding electrolyte influence on lithium plating via potential-driven deposition* CIMTEC 2022 – Conference, Perugia, Italy, June 20–24, 2022.
L. Xu, B. Lelotte, L. Höltschi, J. Eller, T.J. Schmidt, M. El Kazzi	*Accurate Voltage Measurement in All-Solid-State Batteries Enabled by the Design of Three-Electrode Cells* Swiss Battery Days 2022, Dübendorf, Switzerland, August 29–31, 2022.

J. Zhang, T.J. Schmidt, M. El Kazzi	*The Impacts of Cell Physical Parameters on the Cycling Performance of Thin Metallic Lithium in Sulfide-Based All-Solid-State Batteries* Swiss Battery Days 2022, Dübendorf, Switzerland, August 29–31, 2022.
J. Zhang, T.J. Schmidt, M. El Kazzi	*The Impacts of Cell Physical Parameters on the Cycling Performance of Thin Metallic Lithium in Sulfide-Based All-Solid-State Batteries* IBA-2022 – International Battery Association Meeting, Bled, Slovenia, October 2–7, 2022.

Conference Organizations

F.N. Büchi, C. Gloor, L. Gubler, J. Herranz, S. Trabesinger (Organizers)	*38th Swiss Electrochemistry Symposium: Electrochemical Valorization of Carbon Dioxide.* Culture & Congress House (KuK), Aarau, Switzerland, May 11, 2022.
S. Trabesinger (vice Chair)	*Swiss Battery Days 2022* Empa Academy, Dübendorf, Switzerland, August 29–31, 2022.
E. Fabbri, J. Herranz, C. Gloor, (Organizers)	*1st PSI Electrochemistry Day* Paul Scherrer Institut, Villigen, Switzerland, September 13, 2022.

Editorial Work

T.J. Schmidt (Associate Editor)	Journal of the Electrochemical Society.
S. Trabesinger (Editorial Board)	Applied Research, Wiley.

Patent

A.P. Muroyama, L. Gubler	*A system for electrochemically releasing carbon dioxide being captured in an aqueous solution to a hydrogen gas stream.* EP22170163, filed April 27, 2022.

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