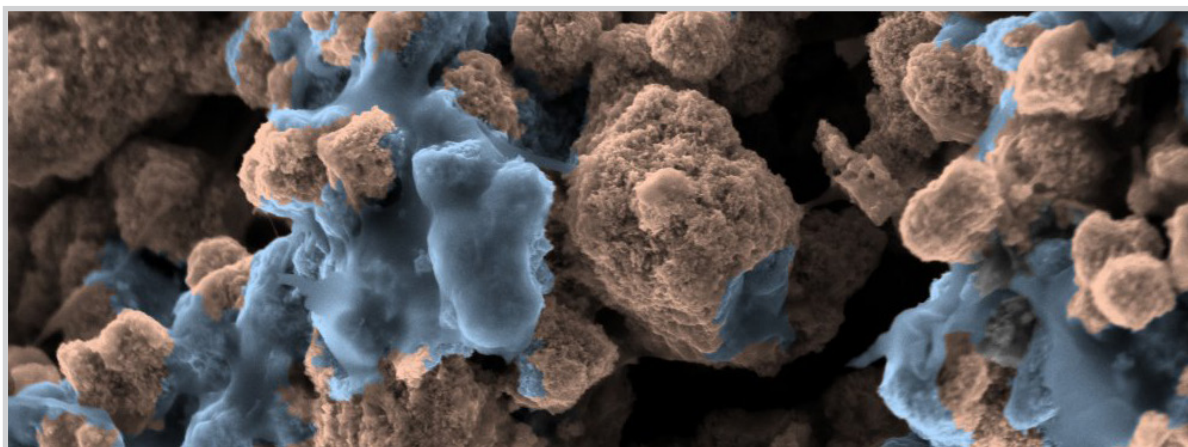


PAUL SCHERRER INSTITUT



# Annual Report 2023

Electrochemistry Laboratory



### **Cover**

*SEM image of an anode catalyst layer for a polymer electrolyte water electrolyzer cell (catalyst brown and ionomer blue).*

PAUL SCHERRER INSTITUT



# Annual Report 2023

Electrochemistry Laboratory

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# CONTENTS

<b>Editorial</b>	<b>3</b>
The Electrochemistry Laboratory at a Glance	4
<b>CURRENT SCIENTIFIC TOPICS</b>	<b>7</b>
SCIENTIFIC HIGHLIGHTS	
1 Updated Electrochemical Impedance Model for Understanding the Interface of Metallic Lithium	8
2 Integration of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Crystalline Films on Silicon Towards High-rate Performance Lithionic Devices	11
3 Towards Next Generation Membranes for Polymer Electrolyte Water Electrolysis	14
4 The Evolution of $\text{O}_2$ on Ir-based Catalysts Requires the Complete Oxidation of their Surface to $\text{Ir}^{+5}$	17
5 Polymer Electrolyte Water Electrolysis: Understanding the Microstructure of a Core-shell Based Anode Catalyst Layer	19
6 Importance of Identifying Key Experimental Parameters for the Li-ion Battery Performance Testing	21
7 Improving the Oxygen Evolution Reaction Activity of Co-based Oxides by Phosphate Functionalization	24
8 Insights into Radical Induced Degradation of Anion Exchange Membrane Constituents	26
9 Understanding the (De-)Lithiation Mechanism of Nano-sized $\text{LiMn}_2\text{O}_4$ Allows Achieving Long-term Cycling Stability	29
10 Quantification of PEFC Catalyst Layer Saturation via Small-Angle X-ray Scattering	32

## DISSERTATIONS

1	Fundamental Understanding of Critical Parameters Enabling Lithium Metal Batteries	36
2	Antioxidant Strategies for Non-Fluorinated Aromatic Proton Exchange Membranes for Hydrogen Fuel Cells	38
3	Fuel Cell Performance of a Carbon-Free Pt-Ni Aerogel Catalyst Layer under Automotive-Relevant Conditions	40
4	Gas Diffusion Layers to Enhance Cold-start Capability and Mitigate Freezing Damage in Fuel Cells	42
5	Development and Application of Spectroscopic Neutron Imaging: Advanced Characterization in Li-ion Battery Materials	44
6	Bifunctional Perovskite Oxide Electrocatalysts for the Oxygen Reduction and Oxygen Evolution Reactions	46
7	Flame-Spray Synthesized Electrocatalysts for Oxygen Evolution Reaction in Alkaline Environment	48
8	Quantification of Liquid Water in Polymer Electrolyte Fuel Cell Catalyst Layers via <i>Operando</i> Scanning Small-Angle X-ray Scattering	50
9	Synergizing the Porous Transport and Catalyst Layers in Polymer Electrolyte Water Electrolysis	52

## THE ELECTROCHEMISTRY LABORATORY 55

### FACTS & FIGURES

Structure 2023	56
Personnel 2023	57
Awards	60
Bachelor and Master Students	61
Conferences – Symposia	63
Documentation	64

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.

In 2023, the Lab has achieved significant scientific advancements. This Annual Report 2023 highlights 10 outstanding results from our Lab, addressing major challenges in electrochemical energy storage and conversion. Additionally, the report presents key facts and figures for 2023, including a comprehensive list of our 35 peer-reviewed publications and numerous presentations. These accomplishments underscore the leading role of PSI's Electrochemistry Laboratory on both national and international stages.

The 39<sup>th</sup> annual Swiss Electrochemistry Symposium, titled «Future Materials in Electrochemical Energy Systems», was successfully held in May at the Kultur & Kongresshaus in Aarau. The event featured world-class scientists and engineers as speakers and attracted an audience of over 100 participants. You can find more details about this event on page 63 of this annual report.

2023 was also a successful year for 9 of our PhD students who successfully defended their theses. An overview of their PhD work is provided in this report. Most of the new PhDs continued their careers in either academic or industrial environments.

However, 2023 also brought changes and challenges for the Lab. Firstly, Dr. Juan Herranz was elected as the new head of the Fuel Cell Systems and Diagnostics group. My heartfelt



congratulations to him! Secondly, due to my unexpected health problems in September, Mrs. Denise Verhoeven, the head of staff of the ENE Department, graciously took over the Lab head duties. My sincere thanks to her! In 2024, she will formally assume the Lab head position, and I wish her all the best for this challenge, which I have enjoyed immensely over the past 6 years.

At this point, in my last Editorial for this Yearly Report, I would like to thank the dedication and passion of all collaborators in the Lab, which I gratefully acknowledge. Also, we would not have been able to perform much of our work 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 is

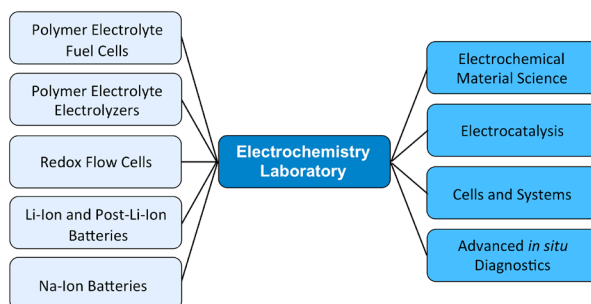
- to develop novel materials, cells & devices relevant for the Energy Transition;
- to use advanced insight-providing methods;
- to perform fundamental, applied & industry-oriented research;
- to educate highly skilled people.

PSI's Electrochemistry Laboratory is Switzerland's largest Center for Electrochemical Research with about 60 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. Additionally, the utilization of carbon dioxide for fuels or chemicals is an important aspect of a future non-fossil society. The Laboratory's R&D is hence focused on secondary batteries – specifically Li- and Na-based systems as well as polymer electrolyte fuel cells and electrolyzers to produce hydrogen and reduce CO<sub>2</sub>.

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, but also in the applied development of technical cells and device implementation.

On many technical complexity levels, we are developing and utilizing advanced *in situ* and *operando* diagnostic tools to gain insights into 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 lifetime 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 electrochemi-

cal properties of insertion and conversion materials and electrochemical interfaces *in situ*. Also, we conduct electrochemical engineering work on three-dimensional electrodes and characterize industrial batteries



Hari Vignesh Ramasamy (left), Postdoc, and Efthymiadou Anastasia (right), Ph. D student, assembling the solid-state cell developed at PSI.

## 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<sub>2</sub> and water, respectively. In addition, work is devoted to the materials development for Redox Flow Cell systems.

The R&D strategy involves activities on four pathways:

- membrane development based on functionalized commercial polymeric materials;
  - system, stack and cell testing.
- On the level of technology demonstration, we have designed, developed and operated the so-called hydrogen path on PSI's Energy System Integration (ESI) Platform at the 100 kW level, *i.e.*, operate a technical scale PEWE System including product gas clean-up and a H<sub>2</sub>-O<sub>2</sub> PEFC reconversion system.
- 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;



Master student Masis Sirim is assembling a proton exchange membrane fuel cell.

# CURRENT SCIENTIFIC TOPICS

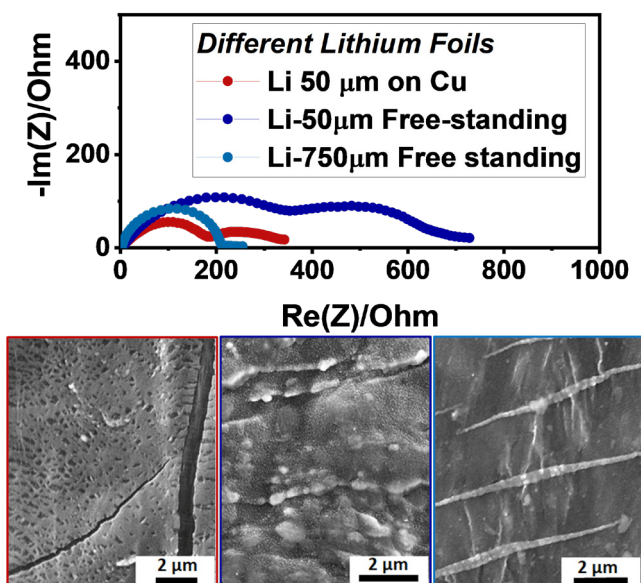
## SCIENTIFIC HIGHLIGHTS

## Updated Electrochemical Impedance Model for Understanding the Interface of Metallic Lithium

Lithium metal negative electrodes are often used as counter electrodes while testing other electrochemically active materials, and are considered to be equivalent, independently of their thickness, supplier and production processes used. Here, we clearly demonstrate, using Electrochemical Impedance Spectroscopy (EIS) that this is not the case, as well as the often-used symmetric cells are actually not so symmetric, when EIS spectra are disentangled using three-electrode cells.

High energy density rechargeable lithium metal battery technology is expected to dominate the next generation of rechargeable batteries, provided that the safety issues will be rectified. Its rise is predicted due to the demand for higher energy density from the electrification of vehicles and ever more powerful mobile electronic devices. As the achievable energy density by optimizing conventional lithium ion batteries, based on graphite negative and

transition metal positive electrodes, is reaching its limits, new solutions are needed. Since no truly new chemistries are emerging to enable significant increase of energy density of the battery, scientists have recently turned back to metallic lithium, which was discarded after discovery of lithium ion battery based on graphite intercalation, due to the safety concerns. Metallic lithium has highly negative potential ( $-3.04$  V vs. SHE) as well as high



*Figure 1*  
Electrochemical impedance spectroscopy spectra and scanning electron microscopy images of three different types of metallic lithium.

specific capacity ( $3860 \text{ mAh g}^{-1}$ ), both of which can potentially double the energy density of existing Li-ion batteries.

Progress in implementing metallic lithium technology is impeded by safety issues related to dendrite growth; limited cycle-life due to the high reactivity of metallic lithium toward the conventional organic liquid electrolytes, where the generated unstable solid electrolyte interphase (SEI) and dead lithium formed during cycling lead to continuous and irreversible lithium consumption; and large volume changes during lithium plating and stripping. All three aspects are related to the metallic lithium interface and therefore electrochemical impedance spectroscopy (EIS) is an important tool to obtain physical and chemical information. However, it is complex technique, requiring data post-treatment by applying fitting models in order to extract numerical values of different parameters, which allow comparison and correlation between different samples.

Most of the EIS studies, reported in literature, have been performed using thick lithium foil, and therefore, severely simplified equivalent Randles circuit has been used. However, the thin lithium of  $50 \mu\text{m}$  in thickness has shown

two semicircles, instead of one, as is usual in EIS spectra of thick ( $> 500 \mu\text{m}$ ) lithium. Therefore, we have updated the EIS model to enable studying more complex metallic lithium impedance spectra and taking into consideration both the lithium ion migration and the charge-transfer processes that occur at the Li interface, but still allowing to use standard software, coming with commercial potentiostats, instead of using much more complex transmission-line model, which requires dedicated scripts. Further investigation identified that all three commercially-available lithium foils give distinctly different EIS spectra, even if the thickness of two (of the three) is the same. Based on this, we have designed the experiments and proved that the resulting differences in EIS spectra are determined by native lithium passivation layer, which most likely comes either from the lithium foil production specificities or from lithium foil storage after production. A three-electrode set-up allowed us also to separate contributions of both working and counter electrodes during rest and cycling. As a result, a direct correlation of the observed overpotential during cycling of in symmetric cells and the corresponding impedance was demonstrated, clarifying working and counter electrode contributions to the overall cell impedance spectra.

Surprisingly, we have found that the impedance, generated at each side of the cell during cycling of symmetric cells, is not identical and should not be treated as such. We confirmed the continuous localized self-repairing re-passivation process, taking place after exposing freshly deposited lithium to the electrolyte, and demonstrated that it is time and electrolyte dependent. In conclusion, this work demonstrates that EIS can be used as a powerful technique, providing crucial information regarding the interfacial reactivity of the lithium metal anode at rest and during cycling. The proposed updated model has been validated in various conditions and is shown to be reliable for fitting EIS spectra of lithium metal anodes, regardless of the type of lithium used.

## Acknowledgement

Financial support from Innosuisse (Project 49354) is acknowledged.

## Publication

### **Insights into the Importance of Native Passivation Layer and Interface Reactivity of Metallic Lithium by Electrochemical Impedance Spectroscopy.**

Mohammed Srout, Marco Carboni, Jose-Antonio Gonzales, Sigita Trabesinger.

*Small*, 2206252 (2022).

DOI: 10.1002/sml.202206252

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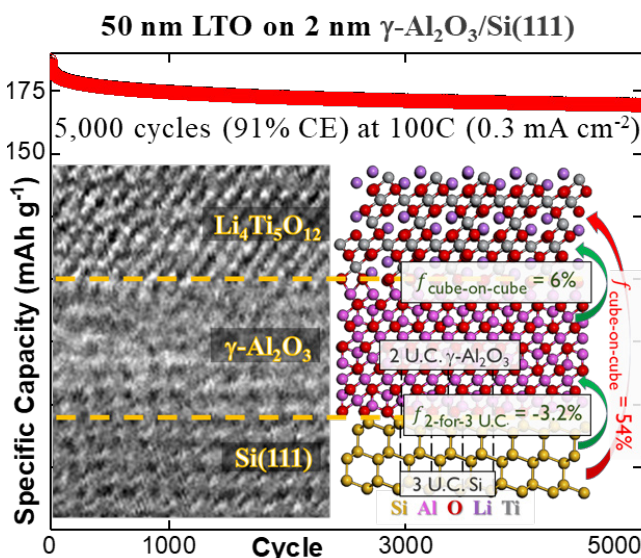
## Integration of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Crystalline Films on Silicon Towards High-rate Performance Lithionic Devices

The growth of crystalline Li-based oxide thin films on silicon substrates is essential for the integration of next-generation solid-state lithionic and electronic devices. In this work, we employ a 2 nm  $\gamma\text{-Al}_2\text{O}_3$  buffer layer on Si substrates in order to grow high quality crystalline thin films of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO). Long-term galvanostatic cycling of 50 nm LTO demonstrates exceptional electrochemical performance, with a specific capacity of  $175 \text{ mAh g}^{-1}$  and  $56 \text{ mAh g}^{-1}$  at 100 C and 5000 C respectively, with a capacity retention of 91% after 5000 cycles.

In an ever-growing autonomous world, further technological developments within the internet-of-things (IoT) rely on monolithic integration and miniaturization of functional devices on-chip such as microbatteries, memristive neuromorphic architectures, and gas sensors. Solid-state lithionic devices, formed by integrating oxide-based Li-ion conducting thin films on silicon substrates, offer a very promising

solution for the aforementioned applications especially when combined with thin film solid electrolytes. The Li-ion migration mechanism within such lithionic devices enables operation over a multitude of applications:

- For energy storage, especially by employing three dimensional solid-state microbattery architectures to achieve high energy and power capability;



**Figure 2**  
High quality 90 nm and 50 nm  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  films integrated on silicon substrates with sharp interface by applying an ultrathin (2 nm)  $\gamma\text{-Al}_2\text{O}_3$  buffer layer. Exceptional electrochemical performance is archived, with a specific capacity of  $175 \text{ mAh g}^{-1}$  at 100 C, with a capacity retention of 91% after 5000 cycles.

- For resistive memory such as two-terminal or three-terminal memristive devices, where fast and low-energy operation (i.e. nonvolatile resistant switching) can be achieved between multilevel analog states;
- For electrochemical gas sensing and environmental monitoring/tracking devices, with enhanced stability and selectivity towards gaseous species. Accordingly, the use of Li-containing ceramics offers a path towards on-chip multipurpose (energy and memory) storage and sensing devices.

In order to achieve optimal performance of the aforementioned lithionic devices, the grown oxide-based thin films (i.e. Li-ion conductors including solid electrolytes) must exhibit excellent Li-ion conductivity as well as structural, mechanical, and (electro-)chemical stability under applied bias. Moreover, achieving the desired Li stoichiometry, the purest phase, a high degree of crystallinity, and sharp/stable interfaces will facilitate rapid Li-ion transport throughout the bulk and across the interfaces leading to a device with superior rate performance. However, integrating crystalline films of functional Li-based oxides directly onto technologically relevant silicon substrates, which is a standard within the electronics manufacturing industry, remains a challenging task due to the

large lattice mismatch between these materials as well as substrate reactivity at elevated deposition temperatures and high oxygen partial pressures. Such unwanted oxygen-containing species formed at the interface between the Si substrate and the Li ceramic compromise the growth quality while building up interfacial resistance, which could reduce overall device performance.

In summary, high-quality 90 nm and 50 nm  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO) films can be grown on silicon substrates by applying an ultrathin (2 nm)  $\gamma\text{-Al}_2\text{O}_3$  buffer layer. This alumina layer enables crystalline LTO films to be deposited by PLD at low temperature (500°C) while mitigating the formation of undesirable species such as silicates and  $\text{SiO}_2$  on the surface of the silicon substrate. From in-depth structural characterization, the PLD process results in columnar growth of LTO(111) bidomains with two grain orientations rotated by 180° along the [111] growth axis. HRTEM and elemental maps confirmed the sharp interfaces between Si/ $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ /LTO.

The electrochemical performance of the LTO thin films was verified in liquid-based half-cells using the surface-modified  $\gamma\text{-Al}_2\text{O}_3$ /Si(111) substrate directly as a current collector. Long-term



galvanostatic cycling measurements of 90 nm and 50 nm LTO films were conducted at 3 C with 97% capacity retention after 1000 cycles and at 100 C with 91% capacity retention after 5000 cycles, respectively. A multitude of rate capability tests were performed using different voltage ranges (1.4–1.7 V vs. 1–2.5 V vs. Li<sup>+</sup>/Li) and special conditions such as 10 C lithiation steps while varying the delithiation C-rates up to 5000 C. For the latter test, the 50 nm LTO/Al<sub>2</sub>O<sub>3</sub>/Si heterostructure cycled with a charge capacity of 56 mAh g<sup>-1</sup> at an extreme rate of 5000 C. Additionally, the thin film retained more than 80% of LTO's theoretical capacity up to a C-rate of 350 C. Furthermore, to showcase rapid Li-ion (de)intercalation of the LTO thin film, sub-millisecond current pulses (0.2 ms pulse at 1000 C or 3 mA cm<sup>-2</sup>) were successfully applied to the 50 nm LTO/Al<sub>2</sub>O<sub>3</sub>/Si heterostructure, which is promising for resistive memory devices with fast switching timescales.

This work highlights the feasibility of integrating oxide-based Li-ion conducting thin films on Si-based chips through interface engineering via a 2 nm alumina buffer layer to promote further developments in solid-state lithionic devices such as microbatteries, memristive memories or gas sensor technologies.

## Publications

### Integration of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> crystalline films on silicon towards high-rate performance lithionic devices.

Steven D. Lacey, Elisa Gilardi, Elisabeth Müller, Clement Merckling, Guillaume Saint-Girons, Claude Botella, Romain Bachelet, Daniele Pergolesi, Mario El Kazzi.

*ACS Appl. Mater. Interfaces* (2023).

DOI: 10.1021/acsami.2c17073

## Acknowledgement

S.D.L., E.G., and D.P. acknowledge support by the Swiss National Science Foundation (SNF) through the MARVEL NCCR. SNF is also kindly acknowledged for co-funding the electron microscope (R'Equip Project 206021\_177020) used herein.

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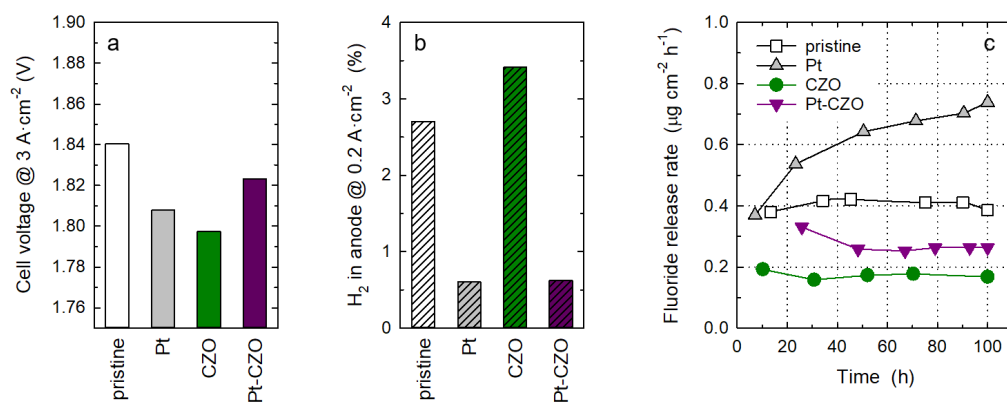
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## Towards Next Generation Membranes for Polymer Electrolyte Water Electrolysis

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. The use of thin membranes ( $\sim 50$  micron or below) is limited by gas crossover of  $H_2$  and  $O_2$ , which can lead to the formation of an explosive gas mixture. The incorporation of a Pt recombination catalyst provides remedy and allows a more dynamic operating mode (cf. Highlight 03/2022). However, the presence of Pt nanoparticles leads to an increase in the rate of membrane degradation. Therefore, we have additionally doped the membrane with cerium-zirconium-oxide (CZO) nanoparticles, which act as radical scavenger. The rate of membrane degradation can thus be reduced.

The use of thin membranes with a thickness of  $50 \mu\text{m}$  or below leads to a reduction of the ohmic loss of the polymer electrolyte water electrolyzer compared to membranes with a more traditional thickness of between 150 and 200 microns. The produced  $H_2$  and  $O_2$ , however, pass more easily through a thin membrane, which can lead to the formation of an explosive gas mixture. The situation is particularly critical on the anode side of the cell, where  $O_2$  is elec-

trochemically produced, since the diffusivity of  $H_2$  through the membrane is higher than that of  $O_2$  and the rate of  $O_2$  production is only half that of  $H_2$ . The flammability limit is 4%  $H_2$  in  $O_2$ , and a safety limit of 2%  $H_2$  in  $O_2$  is typically used. To mitigate the formation of an explosive gas mixture, a gas recombination catalyst, in the form of Pt nanoparticles, can be incorporated into the membrane. Crossover  $H_2$  and  $O_2$  will react to  $H_2O$  on its surface (hence 'recombination catalyst'),



thus the amount of gas reaching the opposite side is reduced.

During the reaction of  $H_2$  and  $O_2$  on the Pt surface OH-radicals are formed as intermediates, which have a high oxidative strength and attack the membrane polymer, leading to chain breakdown, which will eventually trigger membrane failure. Commercial perfluorinated membranes used in fuel cells contain radical scavengers, such as Ce(III) ions or cerium oxide ('ceria') nanoparticles, which quench the radicals according to the reaction  $\cdot OH + Ce(III) + H^+ \rightarrow H_2O + Ce(IV)$ , thus protecting the ionomer against radi-

cal attack. Ceria is preferred over cerium-ions as radical scavenger, because i) it does not displace protons from the membrane, and ii) it does not migrate under the influence of the electric field, unlike cerium-ions. However, ceria ( $CeO_{2-6}$ ) is thermodynamically unstable at low pH and the potentials prevalent in an electrolyzer. Therefore, in the presented approach, we used a mixed oxide, cerium-zirconium oxide (CZO), as a membrane dopant and radical scavenger.

Membranes were prepared by solution casting of Nafion™ dispersion onto a glass plate, followed by drying and curing, to obtain a membrane thickness of around 60 micron. In addition to a pristine, undoped membrane, a membrane containing Pt-black nanoparticles as recombination catalyst with a loading of  $0.04 \text{ mg}_{Pt}\cdot\text{cm}^{-2}$  was prepared. Another series of membranes was prepared that contained commercial CZO nanoparticles as a radical scavenger with up to a content of 10 wt %. At a dopant level of 5 wt % and above, an impact on cell performance was observed, therefore subsequent experiments were performed with a CZO content of 1 wt %. Finally, a membrane co-doped with Pt at a loading of  $0.04 \text{ mgPt}\cdot\text{cm}^{-2}$  and 1 wt % CZO was prepared. The membranes were coated with a Pt-based cathode catalyst

### Figure 3

(a) Cell performance, (b)  $H_2$  crossover, and (c) fluoride release rate measured in the single cell water electrolyzer using solution cast Nafion™ membranes (thickness ~ 60 micron) with and without Pt gas recombination catalyst ( $0.04 \text{ mg}_{Pt}\cdot\text{cm}^{-2}$ ) and cerium-zirconium oxide (CZO) radical scavenger (1 wt %). Cell temperature: 80°C, cathode pressure: 3 bar, anode pressure: ambient. Current density during 100 h test:  $2 \text{ A}\cdot\text{cm}^{-2}$ .

layer and a IrTiO<sub>x</sub>-based anode catalyst layer to obtain catalyst coated membranes (CCMs) with an active area of 25 cm<sup>2</sup>. CCMs were assembled into single cells, using a sintered titanium porous transport layer (PTL) on the anode and a carbon based gas diffusion electrode (GDL) on the cathode. Cell tests were performed at a temperature of 80°C. Polarization curves were recorded after conditioning, from which the cell voltage values at a current density of 3 A·cm<sup>-2</sup> were extracted (see Figure 3, Panel a). The doped membranes did not have an adverse effect on cell performance. However, the gas crossover was significantly reduced in the presence of the Pt recombination catalyst (Panel b). In extended cell operation over 100 h at a constant current density of 2 A·cm<sup>-2</sup>, the rate of membrane degradation was assessed by measuring the fluoride release rate (FRR), as radical attack of Nafion™ leads to the emission of fluoride ions. As explained above, the incorporation of the Pt recombination catalyst leads to an enhanced rate of membrane degradation, which moreover appears to increase over time. Doping of membranes with CZO reduces membrane degradation through radical scavenging. Although the FRR of the Pt-CZO co-doped membrane is higher than that of the CZO-only doped membrane, the values are still lower than those of the pristine Nafion™ membrane. This indicates that co-doping of membranes with a recombi-

nation catalyst and a radical scavenger improves membrane functionality for water electrolyzer applications, highlighting potential design strategies for next-generation membranes.

## Publications

### Platinum and Cerium-Zirconium Oxide Co-Doped Membrane for Mitigated H<sub>2</sub> Crossover and Ionomer Degradation in PEWE.

Zheyu Zhang, Zongyi Han, Andrea Testino, Lorenz Gubler.

*Journal of The Electrochemical Society* 169, 104501 (2022).

DOI: 10.1149/1945-7111/ac94a3

## Acknowledgement

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## The Evolution of O<sub>2</sub> on Ir-based Catalysts Requires the Complete Oxidation of their Surface to Ir<sup>+5</sup>

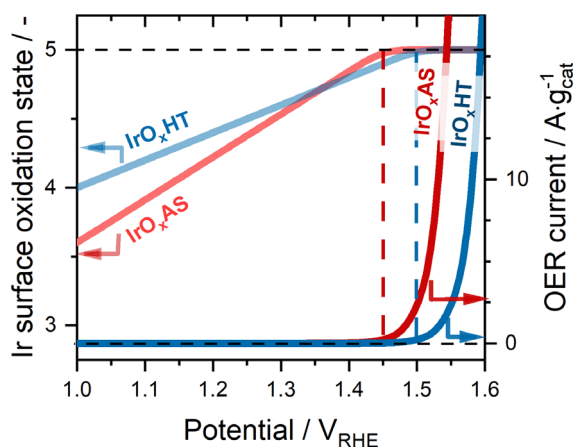
The evolution of O<sub>2</sub> occurring in polymer electrolyte water electrolyzer anodes is a very slow reaction that must be catalyzed using iridium (Ir-) based materials. However, Ir is an extremely scarce metal, and thus the extended commercialization of these electrolyzers will only be possible if the amount of Ir implemented in their anodes is drastically reduced. This requires an improved understanding of the individual steps through which these Ir-based materials catalyze the evolution of O<sub>2</sub>. To shed light on this matter, in this work we studied four different Ir-based catalysts under operative conditions using time resolved X-ray absorption spectroscopy. Our results show for the first time that, despite the differences between these materials, their surfaces must systematically be completely oxidized to a +5 state in order for the evolution of O<sub>2</sub> to proceed on them.

Polymer electrolyte water electrolyzers (PEWEs) are very well suited for the production of hydrogen using renewable electricity. However, PEWE-commercialization could be severely limited due to the reliance of this technology on scarce and expensive Ir-based materials to catalyze the evolution of O<sub>2</sub> in PEWE-anodes. This translates in the need for a significant decrease

of the amount of Ir used in these electrolyzers, which will in turn be possible by improving our understanding of how these materials catalyze the evolution of O<sub>2</sub> (i.e., of the so-called reaction mechanism). In this context, there is a vivid debate regarding the changes in oxidation state undergone by the surface of the Ir-based catalysts during the O<sub>2</sub>-evolution reaction (OER).

**Figure 4**

Schematic representation of the processes triggering the evolution of O<sub>2</sub> on Ir-based catalysts, as inferred from our time-resolved XAS-measurements under operative conditions. As the potential increases from 1.0 V vs. the reversible hydrogen electrode (VRHE, X-axis), the surface oxidation state of two different Ir-oxides with their surfaces in an Ir<sup>+4</sup> or a mixed Ir<sup>+3</sup>/Ir<sup>+4</sup> oxidation states (IrO<sub>x</sub>HT vs. IrO<sub>x</sub>AS, respectively) linearly increases (see left-hand Y-axis), while the OER-current remains negligible (right-hand Y-axis). This surface oxidation process reaches a plateau once a value of +5 is reached, which in turn overlaps with the O<sub>2</sub>-evolution onset for each catalyst.



To get a better understanding of this question, in this work we selected four Ir-based catalysts with very different surface areas, initial oxidation states and O<sub>2</sub>-evolution activities, and studied them under operative conditions using X-ray absorption spectroscopy (XAS). We performed these measurements using a setup available at the SuperXAS beamline of the Swiss Light Source that allowed us to continuously record X-ray absorption spectra with an acquisition frequency of one spectrum per second. The analysis of these time-resolved data showed that the surface of all catalysts becomes linearly more and more oxidized as the applied potential increases. Most importantly, this oxidation process systematically reaches a plateau at a potential specific to each catalyst, but that systematically coincides with the onset of O<sub>2</sub>-evolution on its surface. Finally, we compared these spectra acquired under operative conditions with others recorded on reference Ir-compounds with well-defined oxidation states; this allowed us to conclude that for all catalysts the surface oxidation state triggering O<sub>2</sub>-evolution corresponds to Ir<sup>+5</sup>. As such, our results discard previous reaction mechanisms that postulated that in order to catalyze the OER, Ir-based surfaces only reach oxidation states < +5.

## Publication

### Surface Ir<sup>+5</sup> formation as a universal prerequisite for O<sub>2</sub>-evolution on Ir-oxides.

Nataša Diklić, Adam H. Clark, Juan Herranz, Dino Aegerter, Justus S. Diercks, Alexandra Beard, Viktoriia A. Saveleva, Piyush Chauhan, Maarten Nachtegaal, Thomas Huthwelker, Dmitry Lebedev, Paula Kayser, José Antonio Alonso, Christophe Copéret, Thomas J. Schmidt.

*ACS Catalysis*, **13**(16), 11069–11079 (2023).

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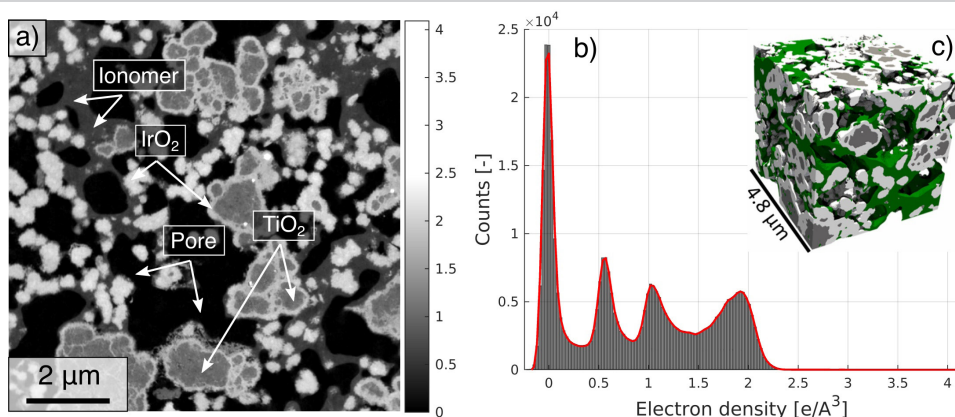
## Polymer Electrolyte Water Electrolysis: Understanding the Microstructure of a Core-shell Based Anode Catalyst Layer

Reducing precious metal loading in the anodic catalyst layer (CL) is indispensable for lowering capital costs and enabling the widespread adoption of polymer electrolyte water electrolysis (PEWE). This work presents the first three-dimensional reconstruction of a  $\text{TiO}_2$ -supported  $\text{IrO}_2$  based core shell catalyst layer, using high-resolution X-ray ptychographic tomography at cryogenic temperature of 90 K. The high data quality and phase sensitivity of the technique have allowed the reconstruction of all four phases namely pore space,  $\text{IrO}_2$ ,  $\text{TiO}_2$  support matrix and the ionomer network, the latter of which has proven to be a challenge in the past.

The analyzed volume of  $9 \times 9 \times 7 \mu\text{m}^3$  is proved to be representative for all phases. The phase fraction calculations show a discrepancy compared to the expected values derived from the catalyst layer ink composition. The overestimation of segmented  $\text{IrO}_2$  volume fraction is caused by the presence of nanoporous  $\text{IrO}_2$  as confirmed by

SEM images. The analysis of the continuous pore and particle size distribution reveals that the void phase presents a broader size distribution compared to the other phases.

Results show that the pore phase has the least tortuosity while the ionomer with a value



**Figure 5**

Two-dimensional slice obtained from the entire tomogram showing all phases present in the electrode.

a) The grayscale values represent the electron density expressed in  $\text{e}/\text{\AA}^3$ ;

b) Electron density histogram calculated over the entire volume;

c) Three-dimensional rendering of a subvolume extracted from the full segmented dataset. In c), the white phase is the  $\text{IrO}_2$ , the gray phase is the  $\text{TiO}_2$ , the green phase is the ionomer and the porosity is transparent.

of 7.1 presents the highest values. The effective conductivities computed from the tomographic data are comparable to previous experimentally reported values and indicate that, in the structure with a non-swollen ionomer, the ionic conductivity is the limiting component, even if the ionomer is in a well-conducting state.

The analysis of the CL ionic and electronic conductivity shows that for a dry CL, the ionic conductivity is orders of magnitudes lower than the electronic conductivity. Varying the electronic conductivity of the support phase by simulations, reveals that the conductivity of the support does not have a considerable impact on the overall CL electrical conductivity.

This study provides not only insights into state-of-the-art catalyst layers via synchrotron-based PXCT and guidance on rational catalyst layer design but also provides a novel tool for analysis of future generation low-loaded CL microstructures.

## Publication

### **Understanding the microstructure of a core-shell based anode catalyst layer for polymer electrolyte water electrolysis.**

Salvatore De Angelis, Tobias Schuler, Mayank Sabharwal, Mirko Holler, Manuel Guizar-Sicairos, Elisabeth Müller, Felix N. Büchi.

*Scientific Reports* 13, 4280 (2023).

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## Acknowledgement

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## Importance of Identifying Key Experimental Parameters for the Li-ion Battery Performance Testing

The mass loading of Si-graphite electrodes is often considered as a parameter of secondary importance when testing their performance. However, if a sacrificial additive is present in the electrolyte, the electrode loading becomes the battery cycle-life-determining factor. A lower loading was obtained by keeping slurry preparation steps unchanged from binder to binder and resulted in a longer lifetime for some of the binders. When the final loading was kept constant instead, the performance became independent of the binder used.

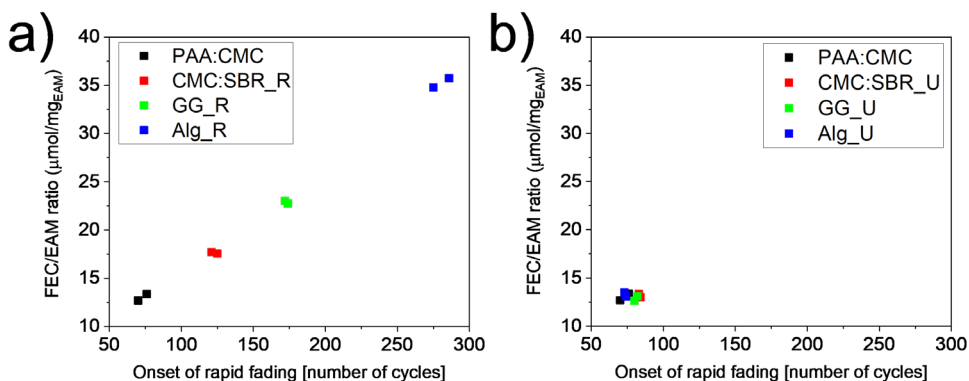
The increasing market demand for high energy density batteries urges scientists to develop simple but feasible approaches to improve gravimetric and volumetric energy of commercial cells. This can be achieved either by increasing the cell's voltage or its capacity. One of the approaches is to increase the capacity of the anode, as the capacity of cathodes is fundamentally more limited. The simplest method to do so is to mix graphite with a capacity of 372 mAh/g, with a specific charge-enhancing component (an element or compound possessing a significantly higher capacity than graphite), such as silicon with a capacity of 3572 mAh/g, i.e. a capacity about ten times higher than that of graphite.

However, an increasing fraction of silicon also renders cell cycling less stable, and different electrode engineering approaches are used to improve their cycling stability. One of the remedies often discussed in literature is functional binders, such as polyacrylic acid (PAA), sodium carboxymethyl cellulose (Na-CMC), and Na-alginate, because they are able to partially buffer Si volume expansion thanks to the formation of a cross-linking network and a strong interaction

with Si particles. Another often-used remedy is electrolyte additives, significantly improving the cycle life of silicon-containing electrodes, where the most used is fluoroethylene carbonate (FEC).

The long-term cycling stability of silicon-graphite electrodes in presence of additives indirectly depends on another important parameter: the electrode mass loading. Because the additives are often of the sacrificial character and are consumed during cycling, it has been proven that the lifetime of a cell, containing silicon electrodes, is linearly dependent on the ratio between the additive and active material loading. This means that a larger amount of additive or lower mass loading will result in a longer lifetime of the cell with the same amount of electrolyte. However, the electrode loading is a parameter often unreported in many scientific publications. Therefore, we performed a systematic study to show the importance of these experimental parameters once and for all.

There are two approaches how to perform comparable experiments: either keep the procedure constant or keep the final testing set up con-



stant – in this case, either the slurry recipe or the mass loading of final electrode. An alternative approach would be to adjust the electrolyte and additive amount to the loading, in which case experiment reliability is less robust. Therefore, the goal of our study was to demonstrate the interrelation between electrolyte additive, electrode loading, and type of binder, and how these parameters influence the cycling stability of silicon–graphite electrodes.

The results of this study showed that in the presence of a constant amount of electrolyte additive, the loading plays a major role in determining the cell cycle-life, and therefore more attention has to be paid to this parameter in order to provide truthful results to the scientific and industrial communities. Electrodes with various mass loadings and different types of binder were fading after a number of cycles, the onset of which linearly correlated to additive/loading ratio and, contrary to the expectations,

the battery cycle life did not depend on the type of binder. In cases where electrodes were prepared with different binder types but with very close values for active materials loading, the differences in cycle life were minor, which leads to the conclusion that the FEC consumption per amount of active material per cycle is the same, independently of the binder used.

This means that when revisiting past results, where binder properties are considered as performance-enhancing factors using sacrificial additives, careful scrutiny of experimental conditions and especially differences in electrode loading and electrolyte (additive) to active materials ratio should be done. Our results also show that in order to test the effects of electrode composition changes (such as the binder in our case), the same active material loading should be the guiding parameter and not the same electrode preparation conditions.

### Figure 6

a) Linear dependency of cycle number on electrolyte to electroactive material loading.

b) Identical performance of the cells when electroactive materials loading is unified and the only difference between cells is the nature of the binder.

## Publication

### Performance-Determining Factors for Si–Graphite Electrode Evaluation: the Role of Mass Loading and Amount of Electrolyte Additive.

Yuri Surace, Fabian Jeschull, Petr Novák, Sigita Trabesinger.

*Journal of The Electrochemical Society* **170**(2), 020510 (2023).

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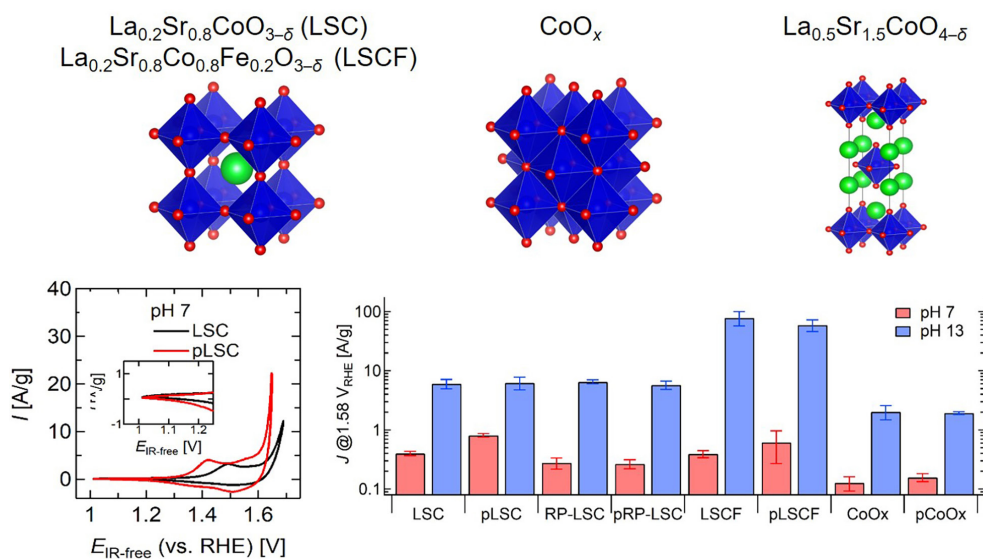
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# Improving the Oxygen Evolution Reaction Activity of Co-based Oxides by Phosphate Functionalization

Our findings disclose that P-functionalization successfully enhances the oxygen evolution reaction (OER) activity of different cobalt-based catalysts (namely,  $\text{La}_{0.2}\text{Sr}_{0.8}\text{CoO}_{3-\delta}$ ,  $\text{La}_{0.2}\text{Sr}_{0.8}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ , and  $\text{CoO}_x$ ) at near-neutral pHs and that both phosphate ion assistance in the OER mechanism and catalyst Co oxidation state can play a role in the enhanced OER activity.

Alkaline exchange membrane water electrolyzers (AEMWE) are a promising electrochemical energy conversion device to produce green hydrogen from intermittent renewable energies. The electrochemical reaction that suffers most from high overpotentials is the oxygen evolution reaction (OER). Transition metal oxide catalysts can exhibit relatively high OER activity and stability at high basicity ( $> \text{pH } 13$ ), but their electrochemical properties degrade in near-neutral pH (7–10) environments.

However, near-neutral pHs are highly relevant in practical applications. Using KOH electrolytes in AEMWE creates vulnerability to carbonation during operation, lowering the initially high pH level toward near-neutral pHs. Carbonation is a significant problem in recently established AEMWE systems using a carbonate membrane that operates as a co-electrolysis cell by replacing the cathodic hydrogen evolution reaction with carbon oxide reduction



This study has investigated a dry phosphate ion treatment to functionalize nano-sized cobalt-based oxygen evolution reaction (OER) catalysts ( $\text{La}_{0.2}\text{Sr}_{0.8}\text{CoO}_{3-\delta}$ ,  $\text{La}_{0.2}\text{Sr}_{0.8}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ ,  $\text{La}_{0.5}\text{Sr}_{1.5}\text{CoO}_{4-\delta}$ , and  $\text{CoO}_x$ ) at near-neutral pHs. We proved that a dry treatment process using  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  as P source is effective for catalyst surface functionalization, especially for nano-sized catalysts. Electrochemical evaluations revealed that phosphate ion functionalized cobalt-based oxides, except for  $\text{La}_{0.5}\text{Sr}_{1.5}\text{CoO}_{4-\delta}$ , exhibited higher OER activity at neutral pH than the as-synthesized catalysts. The mechanism of deteriorated OER performance in  $\text{La}_{0.5}\text{Sr}_{1.5}\text{CoO}_{4-\delta}$  at neutral pH was successfully explained by surface-sensitive soft X-ray absorption and X-ray photoelectron spectroscopy measurements. Electrochemically inert SrO-based surface segregations likely inhibit the phosphate ion functionalization on the active cobalt layer of  $\text{La}_{0.5}\text{Sr}_{1.5}\text{CoO}_{4-\delta}$  and reduce OER activity, especially at near-neutral pHs. Differently, phosphate functionalization seems to be beneficial for

$\text{CoO}_x$ ,  $\text{La}_{0.2}\text{Sr}_{0.8}\text{CoO}_{3-\delta}$ , and  $\text{La}_{0.2}\text{Sr}_{0.8}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ , and particularly for the  $\text{La}_{0.2}\text{Sr}_{0.8}\text{CoO}_{3-\delta}$  catalyst. It is hypothesized that phosphate ion groups could assist the deprotonation step of the OER mechanism in electrolytes with low OH<sup>-</sup> concentration. In addition, we unveiled that P-treatment led to a reduced cobalt oxidation state in  $\text{La}_{0.2}\text{Sr}_{0.8}\text{CoO}_{3-\delta}$ , which could also boost its OER activity at neutral pH. Thus, it would be important in the future to decouple the effect of phosphate functionalization on the physicochemical properties of the catalysts from the phosphate ion role in the OER mechanism and kinetics. Additionally, optimization of the P functionalization process could result in a further improvement of OER activity at neutral pHs.

## Publications

### The Role of Phosphate Functionalization on the Oxygen Evolution Reaction Activity of Cobalt-Based Oxides at Different pH Values.

Wataru Yoshimune, Juliana B. Falqueto, Adam H. Clark, Nur Sena Yüzbaşı, Thomas Graule, Dominika Baster, Mario El Kazzi, Thomas J. Schmidt, Emiliana Fabbri.

*Small Structures* 4(12), 2300106 (2023).

DOI: 10.1002/ssstr.202300106

## Acknowledgement

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### Figure 7

Top: Crystal structure of the investigated cobalt-based oxides.

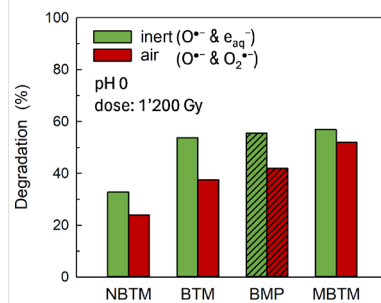
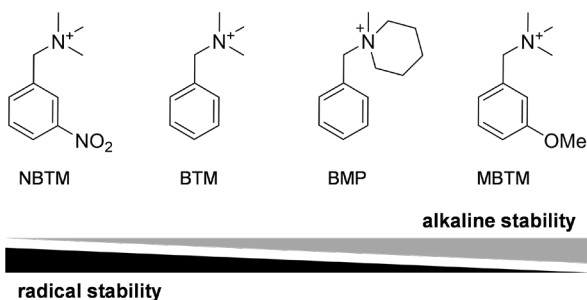
Bottom: Cyclic voltammograms (25<sup>th</sup> cycle at 10 mV s<sup>-1</sup>) of the as-synthesized (LSC) and phosphate-treated (p-LSC)  $\text{La}_{0.2}\text{Sr}_{0.8}\text{CoO}_{3-\delta}$  catalyst at pH 7 (left) and OER activity at 1.58 VRHE for each catalyst at pH 13 and 7 (right).

## Insights into Radical Induced Degradation of Anion Exchange Membrane Constituents

Electrochemical energy conversion devices, such as fuel cells and electrolyzers, using an anion exchange membrane (AEM) operating in the alkaline regime offer the prospect of the use of non-noble metal electrocatalysts and lower-cost cell construction materials. The widespread application of electrochemical cells with AEMs has been largely limited by the low chemical stability of the material. AEM degradation is triggered by i) nucleophilic attack by  $\text{OH}^-$ , and ii) by reaction with free radicals formed during cell operation. Whereas the alkaline stability of AEMs has been greatly increased over the last 10 years, the understanding of mechanisms of radical induced degradation is limited. In this study, we have addressed this topic for the first time.

Electrochemical cells using membrane electrolytes and a zero-gap configuration have a low ohmic resistance, thus enabling operation at high current density (in the range of  $\text{A}/\text{cm}^2$ ), and allow a compact stack design with high power density. Proton exchange membranes (PEMs) have been used successfully in fuel cells and water electrolyzers for decades and reached a high level of technical maturity. The acidic environment in the cell, however, necessitates the use of noble metal electrocatalysts, for reasons of activity and stability, for the hydrogen and oxygen half-cell reactions. Alkaline conditions allow the use of non-noble metal catalysts and cheaper cell build materials (such

as nickel instead of titanium), thus reducing cost and the use of critical raw materials. AEMs operating under alkaline conditions are susceptible to nucleophilic attack by  $\text{OH}^-$ , yet significant improvements have been made over the past  $\sim 10$  years. Today, several suppliers (e.g., Dioxide Materials, Versogen, Orion Polymer, Xergy, Ionomr) offer AEMs for fuel cells and electrolysis cells. It has been known for a long time that the chemical durability of PEMs is limited by radical induced degradation. The radical induced aging of AEMs, however, has received little attention. The increase in alkaline stability of AEMs increases the importance



of studying and improving stability of AEMs against radical induced polymer breakdown.

The presence of radicals in AEM fuel cells during operation has been confirmed experimentally and reported in the literature. Radicals form as a result of the interaction of  $H_2$ ,  $O_2$  and the electrocatalyst. The type of prevalent radical species depends strongly on the local pH in the cells. The pKa of radicals are 4.8 for  $HOO^\cdot$ , 9.1 for  $H^\cdot$ , and 11.9 for  $HO^\cdot$ . This means that the dominant radicals at alkaline pH of  $> 12$  are  $O_2^{\cdot-}$ ,  $eaq^-$ , and  $O^{\cdot-}$ . We studied the reaction of radicals in an aqueous solution with selected aromatic quaternary ammonium compounds, mimicking different AEM exchange groups, namely benzyl-trimethylammonium (BTM), N-benzyl-N-methyl-piperidinium (BMP), 3-methoxy-

benzyltrimethylammonium (MBTM), and 3-nitro-benzyltrimethylammonium (NBTM). We used pulse radiolysis at ETH Zürich with time-resolved transient spectroscopy to study the kinetics of radical reactions, and performed degradation studies where radicals are produced continuously at low dose rate using a  $^{60}Co$  gamma source at PSI.

Pulse radiolysis studies indicate that the reaction of  $O^{\cdot-}$  with the benzyl-type quaternary ammonium (QA) compounds results in the formation of mainly reducing but also oxidizing species with a lifetime on the order of milliseconds. Steady-state gamma-radiolysis experiments show that the electron density of the aromatic ring critically influences the behavior of the compound. The presence of an electron-

### Figure 8

*Left: benzyl-type quaternary ammonium model compounds mimicking the chemistry of anion exchange membranes. All compounds contain perchlorate as counter anion. NBTM = 3-nitro-benzyltrimethylammonium, BTM = benzyltrimethylammonium, BMP = N-benzyl-N-methyl-piperidinium, MBTM = 3-methoxy-benzyltrimethylammonium. Degradation of compounds (1 mM)*

*after exposure in the  $^{60}Co$  gamma cell to a dose of 1'200 Gy, corresponding to 0.75 mM of radicals. Comparison between inert atmosphere and air, which leads to different mixtures of predominant radicals. The stability against radical induced degradation increases with decreasing ring electron density, whereas the opposite trend has been observed for alkaline stability.*

withdrawing group decreases alkaline stability by increasing the overall electrophilic character of the aromatic compound, thus rendering it more susceptible to nucleophilic attack by  $\text{OH}^-$ . Concomitantly, stability against radical induced degradation is increased because an electron poor character destabilizes intermediate radical species that form following radical attack.

Therefore, a careful balance needs to be established between alkaline and radical durability. Under neutral and acidic conditions,  $\text{HO}^\cdot$  is the radical with the highest oxidative strength and readily reacts by addition to the aromatic ring. Yet at high pH,  $\text{HO}^\cdot$  is deprotonated, and the formed  $\text{O}^{\cdot-}$  reacts with the substrate mainly by hydrogen atom abstraction or by dealkylation through reduction. In analogy, at high pH hydrogen radicals,  $\text{H}^\cdot$ , will deprotonate to the highly reducing hydrated electron,  $e_{\text{aq}}^-$ , and will readily attack the QA groups, which results in fragmentation of the compound.

A key finding of the study is the understanding of the influence of ring electron density on the susceptibility to degradation of benzyl-type QA compounds: electron-donating constituents promote radical induced degradation, while electron withdrawing ones improve stability.

Therefore, resistance against radical-induced degradation shows an opposite trend to alkaline stability, which is known to be decreased for electron-poor compounds due to their high reactivity towards the nucleophilic attack of  $\text{OH}^-$ .

## Publication

### On the Radical-Induced Degradation of Quaternary Ammonium Cations for Anion-Exchange Membrane Fuel Cells and Electrolyzers.

Tamas Nemeth, Thomas Nauser, Lorenz Gubler  
*ChemSusChem* **15**, e202201571 (2022).  
DOI: 10.1002/cssc.202201571

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## Understanding the (De-)Lithiation Mechanism of Nano-sized $\text{LiMn}_2\text{O}_4$ Allows Achieving Long-term Cycling Stability

We report an in-depth investigation of the local atomic geometry, electronic and crystallographic structure evolution of nano-sized  $\text{LiMn}_2\text{O}_4$  using operando XAS and XRD to shed light on (de-)lithiation mechanism when cycled in a wide voltage range of 2.0 to 4.3 V vs  $\text{Li}^+/\text{Li}$ . Leveraging these findings, a novel electrochemical cycling protocol, with periodic deep discharge, yields superior electrochemical performance cycled in the range of 3.3 to 4.3 V, exhibiting excellent structure cyclability and an unprecedented increase in the specific capacity upon long cycling.

Lithium-ion battery (LIB) remains the most widely used technology for portable electronic, electric vehicle and as backup power, connected to the grid when electricity is produced from renewable sources. Despite the substantial progress in this area over the last years, the development of advanced LIBs to meet safety, low cost, environmentally friendly with the desirable

stable power and energy densities is one of the most important challenges in modern electrochemistry today. In this context,  $\text{LiMn}_2\text{O}_4$  spinel-type has received continuous and considerable attention as cathode material for LIB applications. Besides its low-cost and being abundant non-toxic material,  $\text{LiMn}_2\text{O}_4$  is a high voltage cathode with the ability of accommodating

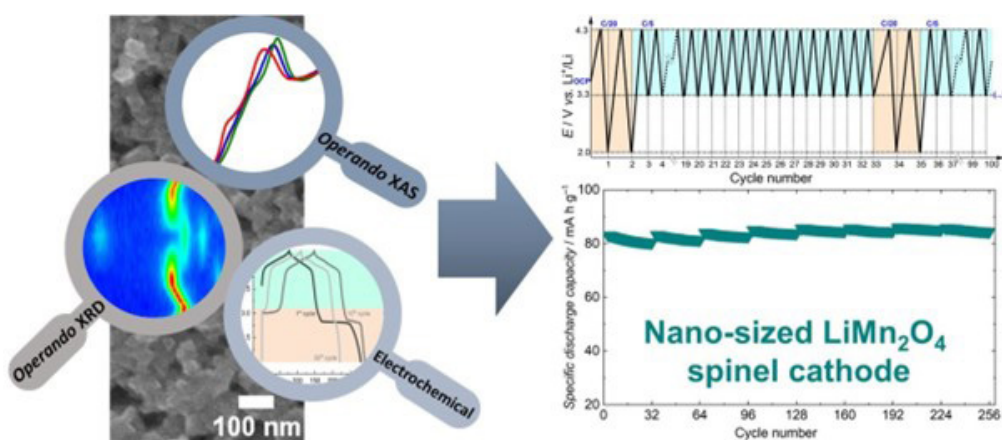


Figure 9

Operando XAS and XRD of nano-sized  $\text{LiMn}_2\text{O}_4$ , to shed light on (de-)lithiation mechanism and the role playing the Jahn-Teller distortion. Based on these findings, a novel electrochemical cycling protocol, with periodic deep discharge to 2 V, yields superior electrochemical performance when cycled in the 3.3 V to 4.3 V range exhibiting an excellent structure cyclability and an unprecedented increase in the specific capacity upon long cycling.

two  $\text{Li}^+$  per unit cell resulting in  $296 \text{ mAh g}^{-1}$  as theoretical specific capacity. Unfortunately,  $\text{LiMn}_2\text{O}_4$  and other transition metal cathode materials have been observed to suffer from irreversible phase transformations responsible for the capacity fading upon long cycling. Particularly, for the  $\text{LiMn}_2\text{O}_4$ , one of the causes of low cyclability is related to the presence of the Jahn-Teller distortion, which is a phase change from cubic to tetragonal when the second  $\text{Li}^+$  is intercalated. Such Jahn-Teller distortion destabilizes the host structure of cathode material, resulting in a large volume change.

The synthesis of nanostructured electrode materials represents one of the most attractive strategies to enhance battery performance, including cycling life and rate capability. In addition to the better  $\text{Li}^+$  diffusion resulting from the short diffusion pathway, nano-sized particles compared to micron-sized can better accommodate the strain caused by the volume change during cycling, which can cause cracking, fracture, and pulverization of the active particles during cycling and rapid fading of the cell.

In this study we exploited the capability of operando XAS and XRD to shed light on the (de-)lithiation processes within nano-sized

and micron-sized  $\text{LiMn}_2\text{O}_4$  spinel and to elucidate the mechanism and the role of the Jahn-Teller distortion in two different cycling voltage ranges. By monitoring the local atomic geometry change, the electronic and crystallographic structure evolution, we demonstrated the contrasting Li diffusivity of nano-sized and micron-sized spinels. In the case of nano-sized particles, we observed that it is easier to intercalate Li during discharge, while in the micron-sized particles, it is easier to de-intercalate  $\text{Li}^+$  upon charge. Furthermore, when the nano-sized spinel is cycled in the wide voltage range from 2.0 and 4.3 V, we observe clear evidence of a significant Jahn-Teller distortion occurring during deep discharge at low potential which is reversible during charging to 3.3 V. We additionally find that in the nano-sized spinel, the deep discharge at 2.0 V to form the Jahn-Teller distortion enhances the  $\text{Li}^+$  deintercalation during subsequent charges.

Finally, based on the electronic and atomic geometric structure studies, a cycling protocol has been proposed for the nano-sized  $\text{LiMn}_2\text{O}_4$  spinel particles to achieve an optimal electrochemical performance. The protocol consists of cycling the cathodes repetitively in two different voltage range: 2 cycles at C/20 rate in a

wide range (charging to 4.3 V and discharging until 2.0 V, where the Jahn-Teller distortion takes place), followed by 30 cycles between 3.3 and 4.3 V at C/5 rate. The nano-sized spinel cathode recovered the capacity lost after being cycled only twice in the wide voltage range and presents more defined plateaus in the charge/discharge profiles indicating an improvement of Li<sup>+</sup> diffusivity after deep discharge. Furthermore, this protocol led to increased specific capacity values in long cycling performance with a Coulombic efficiency higher than 99% in the voltage range of 3.3 V to 4.3 V for the nano-sized spinel LiMn<sub>2</sub>O<sub>4</sub> compared to the micron-sized counterpart. Our findings exemplify the structural flexibility of the Li-rich nano-sized spinel and its excellent potential in long term cycling stability in half cell batteries.

## Publications

**Unveiling the (de-)lithiation mechanism of nano-sized LiMn<sub>2</sub>O<sub>4</sub> allows for designing a cycling protocol for achieving long-term cycling stability.**

Juliana B. Falqueto, Adam H. Clark, Łukasz Kondracki, Nerilso Bocchi, Mario El Kazzi.

*Royal Society of Chemistry – Journal of Materials Chemistry A* (2023).

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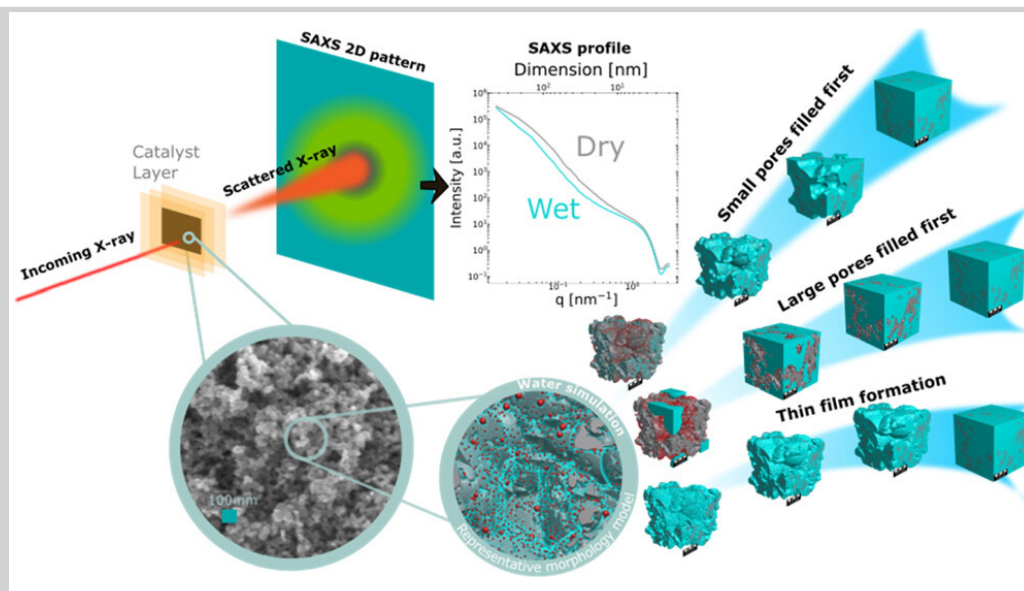
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## Quantification of PEFC Catalyst Layer Saturation via Small-Angle X-ray Scattering

The complex nature of liquid water saturation in polymer electrolyte fuel cell (PEFC) catalyst layers (CLs) greatly affects the device performance. To investigate this problem, a method to quantify the presence of liquid water in a PEFC CL using small-angle X-ray scattering (SAXS) was developed in collaboration with researchers from the Federal Institute for Materials Research and Testing (BAM, Berlin, Germany), the Photon Science Division and the Electrochemistry Laboratory of PSI. The method leverages the differences in electron densities between the solid catalyst matrix and the CL-pores filled with liquid water under dry and wet conditions, respectively.

This small angle X-ray scattering methodology has been applied to porous model materials and a conventional carbon-supported platinum nanoparticle (Pt/C) catalyst layer in both *ex situ* and *in situ* measurements. First, the detectability of liquids in the different nano-porous layers was demonstrated and it was shown that the liquid saturation can be quantified using SAXS. Second, *in silico* experiments and stochastic

modeling were used to interpret the complex multiphase material by generating statistically representative 3D real-space structures of intersected Boolean models. *In silico* simulated SAXS intensity profiles were shown to capture the differences in pore-filling modes, specifically considering whether small or large pores get filled with water first, or if the liquid water forms as a homogeneously-distributed thin film. Third, the



*in situ* wetting behavior of a Pt/C catalyst layer used as the working electrode in a liquid electrolyte flow cell was investigated with the new method. We observed that mainly small pores and a limited fraction of large pores are being filled simultaneously after the liquid electrolyte contacts the catalyst layer. The time resolved *in situ* measurements furthermore showed that the saturation level in the catalyst layer increased sharply to a saturation level of  $\approx 65\%$  within 3 minutes and plateauing thereafter at  $\approx 70\%$ .

The presented SAXS data analysis tools and approach are foreseen to enable the determination of the water saturation level and the water wetting mechanism in catalyst layers given the development of an appropriate SAXS-compatible *operando* setup in the future. This, in turn, will

close the gap of currently available diagnostic methods that cannot provide insights into pore size specific saturation in the catalyst layer under *operando* conditions on a wide nm-scale, and will enable advancements in catalyst layer design.

### Figure 10

*X-ray photons are scattered at different angles due to electron density heterogeneities in a catalyst layer and collected on a 2D detector. The azimuthally integrated scattering data is fitted using 3D morphology models of the catalyst layer under dry conditions. Different wetting scenarios are realized in silico, and the resulting, numerically simulated SAXS data are compared with the measured wet SAXS data to conclude on the most probable wetting mechanism.*

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## Publications

### Quantification of PEFC Catalyst Layer Saturation Via *in Silico*, *Ex Situ*, and *In Situ* Small-Angle X-Ray Scattering.

Kinanti Aliyah, Christian Prehal, Justus S. Diercks, Nataša Diklić, Linfeng Xu, Seçil Ünsal, Christian Appel, Brian R. Pauw, Glen J. Smales, Manuel Guizar-Sicairos, Juan Herranz, Lorenz Gubler, Felix N. Büchi, Jens Eller. *ACS Appl. Mater. Interfaces* **15**, 26538–26553 (2023). DOI: 10.1021/acsami.3c00420

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# DISSERTATIONS 2023

# Fundamental Understanding of Critical Parameters Enabling Lithium Metal Batteries

Eric Winter

Ph.D. Thesis No. 29026, ETH Zürich, January 2023.

Examiners:

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Prof. Dr. Markus Niederberger, ETH Zürich

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## Abstract

Over the past decade, there has been a revival of research activity on lithium metal batteries (LMBs) because these could be a solution for key challenges in electromobility and mobile device autonomy. With an increase in energy density by a factor of 1.5–2 in reach, enabling LMBs in commercial applications would be highly attractive. However, the poor reversibility of Li deposition and stripping is still impeding a breakthrough: especially when only a small reservoir of metal is present, cells fail quickly due to complete consumption of electrochemically active Li. At the same time, processes leading to cell failure are poorly understood, as most studies focus on a suppressing symptoms instead of looking for the root causes. Therefore, three core questions are being clarified in this thesis: what are the critical parameters for reversible cycling of lithium metal, how electrolyte compatibility to metallic lithium can be enhanced, and which tools can help to better understand the kinetics and dynamics of lithium deposition and strip-ping. A baseline study is first looking

into factors that are often neglected during battery characterisation, such as current density, type and quantity of electrolyte and the contribution of more-reactive electrode edges. It is found that the latter play a significant role in the formation of dendrites and thus eventually leads to premature cell failure. On another hand, the excess of lithium metal and electrolyte in a cell conceals detrimental effects that are important, even when cycling takes place at elevated current density. Having identified key factors that influence the outcome of experiments, the modification of carbonate electrolyte with an organophosphate–lithium nitrate mixture has been investigated. Using close-to-industrial conditions with limited excess of metallic lithium and electrolyte at high current density, a positive contribution of the additive is observed, leading to larger particle size, less surface decomposition products and a prolongation of cell lifetimes. The contribution of electrolyte chemistry remains an important topic throughout the thesis and is investigated from a methodology



point-of-view. Potentiostatic lithium plating, inspired from hydrogen pumping, which is a standard test for fuel cell performance evaluation, is explored as a method for fast electrolyte suitability investigation. Scanning electron microscopy helps to establish a link between measured current response and lithium surface coverage before a selection of different electrolytes is used to validate the testing procedure. Electrolyte-specific patterns highlight the potential of the method for electrolyte screening, especially due to an observed direct correlation between measured activation overpotentials and lithium kinetics. Finally, methodology for neutron imaging as a powerful yet facile method for operando tracking of lithium deposition and stripping has been developed. Using a neutron microscope, conventional coin cells are cycled normally, yet in original cell configuration, while the deposition and removal of Li is recorded at high resolution. In addition to providing temporal information on lithium nucleation, a simple processing step also allows determining the

quantitative lateral distribution of lithium metal on the current collector. By using three carbonate electrolytes with varying content of fluoroethylene carbonate additive, the contribution of an electrolyte additive to cycling is further clarified. By combining neutron imaging and operando dilatometry, the density of lithium deposition can also be identified. In summary, this work contributes to the identification of critical cycling parameters, better understanding of the role of electrolyte additives as well as new methodologies. The gained knowledge will help to accelerate progress in the field of Li-metal batteries and systematic experimental design. With a better understanding of metal plating and stripping, it will be possible to address safety concerns and use lithium metal as a safe and long-lived electrode for high capacity cells.

# Antioxidant Strategies for Non-Fluorinated Aromatic Proton Exchange Membranes for Hydrogen Fuel Cells

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Ph.D. Thesis No. 29271, ETH Zürich, May 2023.

Examiners:

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## Abstract

Proton exchange membranes are used in low temperature fuel cells and serve three important functions: conducting protons, providing electrical insulation, and serving as a gas barrier. Currently, most commercial fuel cell membranes are made from perfluorinated polymers such as perfluoroalkylsulfonic acid (PFSA) ionomer. These polymers work well in fuel cells due to their high chemical stability and good performance. However, the EU has announced that non-essential fluorinated materials may be phased out, which could affect fuel cell membrane production. Therefore, there is a need for alternative, environmentally friendly materials.

An alternative group of membranes, aromatic hydrocarbon-based membranes, have shown encouraging fuel cell performance. A major drawback of these membranes is that they are susceptible to oxidative degradation during fuel cell operation. Of the reactive species formed in the fuel cell,  $\text{HO}^\bullet$  was identified to be the most

harmful. Radical attacks lead to deleterious reactions that ultimately cause reduced mechanical strength and premature cell failure. Previous kinetics studies, performed at PSI and ETH, have shown that utilising Ce(III) as a repair agent may mitigate membrane damage by preventing irreversible degradation.

The aim of this thesis is to promote the understanding of radical-induced chemical degradation of aromatic hydrocarbon-based membranes. This is achieved by studying model compounds and several differently modified membranes. The importance of developing a targeted antioxidant strategy is highlighted by contrasting it to strategies used for perfluorinated materials. The final objective of this work is to develop a repair mechanism that could be applied to aromatic hydrocarbon ionomers generically. This would allow for the production of hydrocarbon membranes that could compete with perfluorinated membranes.

Based on the study of the kinetics of radical attack on aromatic compounds and relevant follow-up reactions, it was shown that Ce(III) can catalytically repair aromatic cation radicals and thereby restore the parent aromatic compound. Important reaction rate constants were determined by pulse radiolysis and stopped-flow experiments. Furthermore, the effect of molecular weight and ionic strength on the formation and decay of intermediates was investigated. Mn(II) was also investigated as a catalytic repair agent, yet its rate of repair was approximately one order of magnitude slower than that of Ce(III).

To test whether this repair mechanism is viable in fuel cell conditions, Ce(III) crown ether complexes were covalently attached to the polymer backbone of a grafted membrane. Cerium-containing membranes showed significantly slower degradation than reference membranes in fuel cell accelerated stress tests. Ce(III) can therefore be utilised as a repair agent in fuel cell membranes.

Further kinetics and fuel cell testing with the same experimental framework as for the Ce(III) investigation were performed on Cu(II)-porphyrin containing membranes. The use of Cu(II)-porphyrins was inspired by hemes. Hemes are a group of chemicals found in biological systems capable of handling highly oxidizing species and thus, are resistant to irreversible oxidative damage. It was found that damage can likely be transferred from the cation radical to Cu(II)-porphyrin complexes. Fuel cell tests with Cu(II)-porphyrin containing membranes showed

increased resistance to radical-induced degradation over a few hundred hours of testing. Post-test results revealed the turnover number of Cu(II) porphyrin to be at least 35, indicating that the repair mechanism is likely catalytic.

In summary, the findings of the work indicate that aromatic hydrocarbon based membranes require a different antioxidant strategy than what is used in PFSA membranes to reach competitive membrane lifetime in the fuel cell. The repair of long-lived intermediates appears to be a promising approach.

# Fuel Cell Performance of a Carbon-Free Pt-Ni Aerogel Catalyst Layer under Automotive-Relevant Conditions

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Ph.D. Thesis No. 29533, ETH Zürich, September 2023.

Examiners:

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## Abstract

Energy is what sustains the well-being and functioning of our society. The global energy demand continues to rise every year to continuously meet the human social and economic development needs of humanity. In order to rapidly meet these needs, fossil fuels (i.e., oil, coal, and natural gas) have been integrated into our daily lives as the primary energy source. Concurrently, it is widely known that the combustion of these fossil fuels emits enormous amounts of greenhouse gases, jeopardizing the environmental stability of our planet and our own way of life. This environmental impact compels us to pursue alternative energy sources, namely renewable energies (i.e., solar and wind). The transportation sector is one of the main contributors to such intensive greenhouse gases emissions, and therefore its rapid electrification is key for minimizing its impact on the global environment. In this context, polymer electrolyte membrane fuel cells (PEMFCs) are highly efficient energy conversion devices that

produce electricity from the oxidation of hydrogen (supplied from renewable energies) and the reduction of oxygen at the cell's anode and cathode, respectively. However, the excessive cost and insufficient durability of PEMFCs limit their extended market implementation. This is caused by the fact that these cells require high amounts of platinum to catalyze the sluggish oxygen reduction reaction (ORR), making this catalyst layer the most expensive component in the fuel cell stack. Furthermore, the insufficient durability is partially caused by the presence of a carbon support in conventional Pt-based catalysts (often referred to as platinum-on-carbon, Pt/C), which oxidizes when high potentials are encountered, as can be the case during PEMFC startup/shutdowns or upon local fuel starvation events.

In this context, bimetallic, carbon-free, Pt-Ni aerogels have been developed to tackle both of these challenges. The bimetallic, alloy nature of

this material leads to a  $\approx 2.5$ -fold higher ORR-activity compared to the conventional Pt/C, and the absence of a carbon support enhances its durability at high potentials, leading to a sustained electrochemical performance over time. Encouraged by these features, this work aimed to perform a full electrochemical characterization of the Pt-Ni aerogel under automotive relevant PEMFC conditions.

Thus, the first part of this thesis focused on the scale-up and optimization of the Pt-Ni aerogel to obtain a homogenous and highly performing catalyst layer in PEMFC at standard measurement conditions (i.e., at  $80^\circ\text{C}$ , 100% relative humidity and 1.7 bar<sub>abs</sub>). Subsequently, the catalyst layer was tested under a broader range of relative humidities and temperatures, as well as submitted to fast load transients. The voltage losses associated with low relative humidity conditions were partially attributed to the cell design and inhomogeneities in the distribution of the current density. Moreover, the effect of the relative humidity on the ORR-kinetics and mass transport losses was further explored by using a coverage-dependent form of the Butler-Volmer equation to extract intrinsic-ORR kinetic parameters and elucidate the fundamental causes of the voltage losses observed for conventional Pt/C catalysts and the Pt-Ni aerogel.

On top of this, this thesis also tackled the electrochemical testing of low loaded Pt-Ni aerogel electrodes (i.e., with  $\approx 0.1 \text{ mgPt}\cdot\text{cm}^{-2}$ ). A drastic drop in performance was initially observed at these reduced loadings, and this was attributed

to the high  $\text{O}_2$ -transport resistance caused by the use of a thin ionomer film in these aerogel electrodes. The subsequent removal of this ionomer from the electrode's formulation resulted in a significant enhancement of the overall fuel cell performance caused by the negligible  $\text{O}_2$  transport resistance. Lastly, a limited water/ice storage capacity of these thin aerogel catalyst layers was observed in isothermal galvanostatic cold-starts at freezing conditions ( $-20^\circ\text{C}$ ), in which the aerogel catalyst layer featured a reduced ice storage capacity compared to conventional Pt/C due to its reduced thickness and volume.

In summary, this work contributed to the development and understanding of the strengths and challenges that Pt-Ni aerogels need to overcome for their full implementation in polymer electrolyte membrane fuel cells.

# Gas Diffusion Layers to Enhance Cold-start Capability and Mitigate Freezing Damage in Fuel Cells

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Ph.D. Thesis No. 29667, ETH Zürich, September 2023.

Examiners:

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## Abstract

The global shift towards the electrification of transportation aims to transition from fossil fuels to renewable energy sources, addressing concerns about greenhouse gas emissions, rising global temperature, and sea level changes. Among the alternatives, polymer electrolyte fuel cell (PEFC) vehicles stand out for their high efficiency, power density, long-range, and zero emission. However, their market share is far behind battery electric vehicles because of high costs, limited lifetimes (< 5000 h), and operation challenges in cold climates. Operation challenges in cold climates are attributed to issues like voltage instability or failures during startup and mechanical damage to cell components due to water freeze in subfreezing conditions. This thesis investigates the influence of the gas diffusion layer (GDL) properties on water freezing behavior, aiming to understand cold-start failures and successes. Based on this, a new design of cross-patterned GDL is proposed to enhance the ice resilience of GDLs and fuel cell cold-start capabilities.

First, initial studies using *ex situ* differential scanning calorimetry (DSC) explore the effects of hydrophobic treatments on GDLs on ice crystallization. Contrary to expectations, increasing GDL overall hydrophobicity does not isolate water clusters from ice nucleation seeds, reducing freezing probability. This is attributed to the uneven coating distribution and limited fiber coverage within GDLs with the dip-coating method but can be improved when waterproofing GDLs under vacuum. In addition, the propagation of freezing in GDLs is fast as soon as ice crystallization initiates. GDLs with patterned wettability are introduced to prevent ice propagation and extend the operation time of the fuel cell, even though ice is formed locally. *Ex situ* DSC measurements show that separating water clusters in GDLs effectively constrains ice propagation, which can be further enhanced by well-defined patterns - reducing the width of hydrophilic pathways and increasing the width of hydrophobic lines.

However, translating *ex situ* results to cell performance posed challenges due to differences in sample sizes and dynamic water distribution. To bridge this gap, an advanced *in situ* DSC setup is developed to investigate the supercooled water freezing behavior in GDL of a single-cell scale and condition without being affected by the membrane electrode assembly. The findings reveal that the freezing temperature of supercooled water shifts to higher temperatures with a larger sample size and higher saturation level. In addition, the broad distribution of freezing-thawing cycles and the noticeable inter-cycle variations demonstrate a good agreement with *ex situ* DSC results.

Finally, the performance of the novel-designed cross-patterned GDL is assessed with isothermal cold-start measurements. Positively, cross-patterned GDLs extend the operation time and reduce the voltage-failure probability of PEFCs under less extreme conditions. It also shows reduced mass transport losses under normal

operation conditions because of advanced water management. In addition, the scattered operation time for isothermal cold-start aligns well with both *ex situ* and *in situ* DSC measurements, highlighting the importance of understanding freezing imitation and stabilization features for future material innovations.

# Development and Application of Spectroscopic Neutron Imaging: Advanced Characterization in Li-ion Battery Materials

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Ph.D. Thesis No. 29629, ETH Zürich, September 2023.

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## Abstract

Due to the increasing demand for alternative energy solutions, batteries have become crucial in the automotive sector owing to their high reliability as energy storage devices. As the needs in this industry drive improvements in terms of fast charging and operation under extreme temperatures, understanding their influence on the battery performance and cycle life has become increasingly important. Current characterization methods, however, rely on experimental designs that do not fully capture the overall internal macroscopic dynamics of these systems, reducing their accuracy, particularly in commercially available designs.

Therefore, a comprehensive spatially resolved method is required, capable of resolving changes in relatively large areas, while providing detailed information on physical, chemical, and electrochemical effects that come into play during the cycling of batteries. Neutron imaging, combined with spectral techniques, provides a solution by offering deeper insights into battery

materials due to the physics behind the interactions between neutrons and matter. This thesis describes these interactions and provides the fundamentals that led to the development of spectroscopic neutron imaging (SNI), a method capable of resolving spectroscopic features in a spatially resolved manner.

Since electrolytes often endure the most damage in battery operation under extreme conditions, this work primarily focuses on the use of SNI to understand the physio-chemical changes that electrolytes experience in connection with the loss of performance caused by cycling batteries at sub-freezing temperatures and fast charge. The application of the SNI to electrolytes includes *ex situ* and *in situ* studies in four beamlines of two different technologies for producing neutrons, i.e., reactor and spallation sources. Throughout the neutron experiments with the SNI in electrolytes, it became evident that to exploit this method to its fullest in current neutron sources, the optimization of parameters govern-



ing this method is key. Therefore, a simulation framework was developed to test its potential and to provide a baseline for the speedy and efficient investigation of materials with the method. Lastly, in a more applied context, SNI was used to study the *operando* intercalation of  $\text{Li}^+$  in graphite anodes that extended its capabilities even further. The investigation aimed to study the state-of-charge in a spatially resolved manner to identify potential deficiencies connected to the battery design and manufacturing that result in loss of performance.

The results in this thesis demonstrate the capabilities of the SNI method to study the dynamics and composition of hydrogenated molecules due to the inelastic scattering of neutrons and matter, as well as materials that undergo changes in their crystalline structure with elastic scattering. One of the major advantages of the SNI is its versatility and possible extension as a characterization method for a broad range of applications well beyond batteries and bat-

tery materials. Therefore, as much as this thesis establishes the fundamentals of this spectral neutron technique, its continuous development and application are essential to strengthening material research in the ever-evolving progress of current technologies.

# Bifunctional Perovskite Oxide Electrocatalysts for the Oxygen Reduction and Oxygen Evolution Reactions

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Ph.D. Thesis No. 29673, ETH Zürich, September 2023.

Examiners:

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## Abstract

The rise in greenhouse gas emissions since the industrial revolution has spurred the development of renewable energy. However, renewable energy sources such as wind and solar experience intermittency issues. Correspondingly, hydrogen based energy conversion systems are of interest to counterbalance this irregular production of energy. Unified regenerative fuel cells (URFC) are promising devices for energy conversion and combine a hydrogen fuel cell and water electrolyzer in one device. However, currently, URFCs suffer from low round trip efficiencies and short lifetimes due in part to the high overpotentials and slow kinetics of the oxygen reduction (ORR) and oxygen evolution (OER) reactions that occur at the oxygen electrode. As a result, the development of high performing and stable bifunctional catalysts is essential for the advancement of URFCs. Motivated by this, this thesis explores perovskites as bifunctional catalysts for ORR and OER, with the focus on

understanding the reaction mechanisms and the catalyst properties that lead to activity.

Operando techniques are invaluable for investigating catalyst changes during a reaction. In this work, *operando* X-ray absorption spectroscopy (XAS) was utilized to uncover insights into the local coordination geometry and electronic structure during the oxygen reduction and oxygen evolution reactions. With high time-resolution, the change in oxidation state of the active site, B-site metal of the perovskite, was elucidated, while cyclic voltammetry was performed. Additionally, device level fuel cell and water electrolyzer measurements are performed to assess the feasibility of the bifunctional catalysts in a more applied setting.

Understanding the oxygen reduction and oxygen evolution reaction mechanisms is essential to improving catalytic activity. Carbon is often added to perovskite catalyst layers to increase

electrical conductivity. These perovskite/carbon composites are theorized to catalyze ORR through a different reaction mechanism. The relationship between carbon and perovskite was further elaborated by investigating the effect of conductive additives on the perovskite  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (BSCF). *Operando* XAS was used to investigate the influence of carbon on the change in the Co oxidation state during ORR and OER.

After the influence of conductive additives is investigated, the catalysts BSCF and  $\text{La}_{0.4}\text{Sr}_{0.6}\text{MnO}_{3-\delta}$  (LSM) are assessed for their bifunctional activity and stability. A URFC will alternate between reducing potentials in fuel cell operation and oxidizing potentials in electrolyzer operation. The bifunctional oxygen electrocatalysts must then also reversibly alternate between ORR and OER, respectively. BSCF and LSM were subjected to alternating OER and ORR potentials, while the change in oxidation

state of their B-site metals was observed. The results revealed performance degradation due to oxidizing potentials. Additionally, key insights into the reversible and irreversible changes that occur during the two reactions were uncovered. Finally, the results of the previous sections are used to design new bifunctional perovskite catalysts. Two design strategies were chosen to incorporate active sites for ORR and OER into the catalyst. The resulting catalysts were screened for activity and stability and *operando* XAS was utilized to study the change in oxidation state of the active sites.

In summary, this thesis started with a fundamental investigation into the reaction mechanisms and concluded with the design of new bifunctional perovskite catalysts. Overall, the knowledge attained during this work allows for the careful design of new bifunctional perovskite catalysts and, ultimately, advances the performance and lifetime of URFC devices.

# Flame-Spray Synthesized Electrocatalysts for Oxygen Evolution Reaction in Alkaline Environment

Dino Aegerter

Ph.D. Thesis No. 29621, ETH Zürich, September 2023.

Examiners:

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## Abstract

Energy conversion and storage systems for a broad time- and capacity range are required to equilibrate the intermittency problem of renewable energy sources and to enable the substitution of fossil fuels on a global scale. A promising solution for the long-term and large scale storage of renewably produced electric energy is the conversion into chemical energy in the form of hydrogen by the electrochemical splitting of water in so-called electrolyzers. Renewably produced hydrogen can then be stored and converted back into electric energy at any time when demanded. Among the different types of electrolyzers, the ones using alkaline conditions have the possibility to facilitate hydrogen production on a global scale as they are composed of abundant and cost-efficient materials. However, today's available products still suffer from low energy conversion efficiencies, which hinders a greater market penetration and thus limits the extent of fossil fuel substitution with renewable energy sources. An important reason for the low energy efficiency of alkaline water

electrolyzers (AWEs) lies in the slow kinetic of the anodic oxygen evolution reaction (OER). The reaction kinetic can be improved by selecting an anode material, which is able to electrocatalyze OER. However, industrial requirements on an ideal OER electrocatalyst include not only a high OER activity and stability, but also the production of nanocatalyst by a scalable synthesis technique from abundant and cost-effective chemicals. Among the variety of tested materials, flame-spray synthesized cobalt-based oxide nanocatalysts are promising candidates as ideal OER electrocatalysts for AWE considering the demanding industrial requirements. Nevertheless, an improvement of the electrocatalytic performance of these materials is still required to further decrease the production costs of hydrogen.

In this context, the first part of this doctoral thesis focuses on the relationship between flame condition and electrocatalytic performance of the produced nanocatalysts. This investigation

shows exemplarily for  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-d}$  that the influence of the flame-spray synthesis parameters on the high-temperature particle residence time and the oxygen partial pressure in the flame allows to directly control OER relevant materials properties such as oxygen vacancy concentration and bulk Co oxidation state. Therefore, the optimization of the flame-spray synthesis parameters can significantly improve the OER activity, which is an important finding particularly for scaling-up the synthesis, where the production rate must be maximized but without losing the electrocatalytic performance.

The second and third part of this thesis focus on the optimization of the Co-to-Fe ratio in two material series of  $\text{Co}_{1-x}\text{Fe}_x\text{O}_y$  and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Fe}_x\text{O}_{3-d}$  (BSCF) to find the best OER performance with the lowest Co-content as possible. Moreover, these two materials series were investigated by using *ex situ* surface-sensitive and *operando* bulk averaging techniques, which delivered new insights into the OER beneficial Co-Fe-interaction and a fundamental understanding how surface and bulk changes can influence the electrochemical behaviour and electrocatalytic performance of Co-Fe-based oxide nanocatalysts.

In summary, this thesis demonstrates the ability to significantly improve the OER activity of flame-spray synthesized Co-based nanocatalysts by optimizing the synthesis parameters, which is an important finding for the scale-up of the synthesis. Moreover, the electrocatalytic performance of these Co-based nanocatalysts

are even further improved by partially substituting Co with Fe. This substitution is more extensively possible for the  $\text{Co}_{1-x}\text{Fe}_x\text{O}_y$  than for the  $\text{BSCo}_{1-x}\text{Fe}_x$  series and is explained with the different optimal Co-to-Fe ratio for the most extensive formation of the OER active Co-Fe-based (oxyhydr)oxide phase as revealed after combining *ex situ* surface-sensitive and *operando* bulk techniques.

# Quantification of Liquid Water in Polymer Electrolyte Fuel Cell Catalyst Layers via *Operando* Scanning Small-Angle X-ray Scattering

Kinanti Aliyah Hantiyana

Ph.D. Thesis No. 29745, ETH Zürich, October 2023.

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## Abstract

Polymer Electrolyte Fuel Cells (PEFC) are seen as a crucial option for decarbonization efforts in mobility applications and hydrogen-based power-to-power cycles. The technology uses hydrogen and oxygen as reactants, with only water and heat as by-products. However, proper water management is essential for efficient PEFC performance, which can be challenging. One of the primary obstacles to maintaining high PEFC performance is preventing water accumulation in the cell's porous layers. If excess water persists, it can impede reactants from accessing the active sites of the catalyst layers.

Conversely, inadequate hydration of the polymer membrane, as well as the ionomer in the catalyst layer, occurs if insufficient water is supplied to humidify the reactant gases. The dehydration reduces their proton conductivity, ultimately compromising the cell's performance. As a result, managing water levels in the catalyst layers becomes critical to ensuring optimal PEFC performance.

Within this thesis, a methodology has been developed using X-ray scattering methods to quantify water levels in PEFC's nanoporous layers and the membrane during cell operation. The methodology includes the development of a small and wide-angle X-ray scattering (S/WAXS) compatible PEFC and data collection in relevant operating conditions. S/WAXS was chosen because of its sensitivity to information in the nanoscale regime which fits to structural features of interest. Scanning S/WAXS was used to isolate the different layers of the PEFC, and a multi-phase Invariant calculation approach was used to quantify the water level in the catalyst and microporous layer. Furthermore, pore size-specific interpretation of liquid water filling the nanoporous media via representative structure modeling has been developed to reveal a likely liquid water distribution.

The methodology is applied to reveal the saturation levels of the catalyst layers as a function of the relative humidity of feed gas,

current density, and operating pressures at relevant operating temperatures. Furthermore, the methodology is applied to investigate the impact of a variation in the adjacent microporous layers on the saturation levels and water distribution in the catalyst layers. It was found that introducing micron-sized pores in microporous layers lowers the hydration level of not only the microporous layer itself but also catalyst layers and the membrane at 3 bar<sub>abs.</sub> and 100% relative humidity. In contrast, the extensive increase of the PTFE content as the binder of the microporous layer enhanced its detected water levels. The impact of the catalyst layer's carbon primary porosity modified via heat treatment on the saturation levels of the catalyst layers and their adjacent layers was also investigated. The membrane electrode assembly using a modified cathode catalyst shows on average a lower saturation level compared to the non-modified catalyst layer, despite the higher current densities it generates.

With the capability of operando S/WAXS measurements to gain insight into the liquid water level in nano-porous layers in actual operating conditions the methodology is expected to improve material design and further advance electrochemical conversion devices as it is not limited to fuel cells but easily transferrable to polymer electrolyte water electrolyzers and other devices, such as CO<sub>2</sub> electrolyzers, nitrogen reduction cells, etc. For example, in water electrolyzers, it could provide insights into the oxygen saturation level in the catalyst layers.

# Synergizing the Porous Transport and Catalyst Layers in Polymer Electrolyte Water Electrolysis

Carl Cesar Weber

Ph.D. Thesis No. 29853, ETH Zürich, November 2023.

Examiners:

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Prof. Dr. Thomas J. Schmidt, PSI Villigen / ETH Zürich

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## Abstract

Polymer electrolyte water electrolysis (PEWE) is experiencing a massive renaissance, driven primarily by the urgency for rapid renewable energy storage solutions. However, the high price and especially the scarcity of iridium, which is needed as an anodic catalyst, are some of the main limiting factors hindering a rapid expansion in capacity installation. Therefore, reducing the iridium content in the system is essential. The porous transport layer (PTL) interaction with the catalyst layer (CL) contributes significantly to the performance and efficient use of the catalyst. However, the mechanistic reasons behind the role of the PTL/CL interface are not well understood. In this work, we focus on the influence of the PTL, the CL, and their interface to reduce the total amount of critical materials in PEWE cells through the synergy of these components.

Reducing PTL thickness can help minimize Ti content and contribute to making PEWE stacks smaller. In this context, we examined how

varying the thickness of the anodic PTL between 0.16 and 2 mm affects cell performance while keeping other PTL parameters constant. A difference of up to 120 mV overpotential at  $4 \text{ A cm}^{-2}$  was observed which we attributed to sluggish water transport below the flow field land in thin PTLs. From our findings, we formulated a guideline that proposes an optimal ratio between PTL thickness and flow field characteristics.

In an effort to better understand the effect of the PTL/CL interface, we designed a matrix of two-dimensional interface layers with a well-known structure. We integrated these structures into PEWE cells between the PTL and the CL. Through a thorough analysis of performance and high-frequency resistances, we were able to determine catalyst utilization. In collaboration with NREL (Golden, USA), we estimated the impact of membrane dry-out and calculated the current distribution in the CL using a 3D-multiphysics model. As the current density



increased, we observed that large parts of the CL became inactive. This is due to two reasons:

- 1) the high electronic resistance of the CL in the open pores space and
- 2) a significant gas accumulation in the CL under the PTL lands, which hinders the distribution of liquid water.

We call this phenomenon gas blinding. Based on our findings, we can conclude that small pore sizes and inter-pore distances of the PTL at the CL interface are crucial in maximizing catalyst utilization.

To identify the challenges in the CL's morphology at lower loadings, we analyzed the 3D nanostructure usingptychographic X-ray laminography in both dry and wet conditions. Our findings showed that interruptions in the percolation network of the particles can limit electronic conductivity. Microporous layers (MPL) with smaller feature sizes can help in bridging the electronic paths in the interrupted CL. To test this hypothesis, we varied iridium loadings ranging from 2.5 to 0.1  $\text{mg}_{\text{Ir}} \text{cm}^{-2}$  in two different configurations: depositing either on the membrane or on the Ti-substrate (MPL). Additionally, we investigated the effect of introducing a thin protective Pt coating on the MPL to decrease the interface resistance. We tested the electrochemical performance of all cell combinations and conducted an in-depth kinetic analysis to reveal information on CL utilization. The findings indicate that cells using MPLs with Pt-coating facilitate the reduction of iridium loadings, allowing them to sustain performance with only modest voltage losses.

In the final section of this thesis, again in collaboration with NREL, a new generation of ultrathin MPL was developed and tailored to increase efficiency and catalyst utilization at low Ir-loadings, simultaneously saving raw material. The structure and surface properties were analyzed using X-ray tomographic microscopy exhibiting a lower surface roughness. Compared with state-of-the-art PTL materials, cells with MPLs showed improved performance, with gains of up to 100 mV at 7  $\text{A cm}^{-2}$  using low platinum group metal loadings of 0.6  $\text{mg}_{\text{PGM}} \text{cm}^{-2}$ . Furthermore, we tested cells with thin membranes (N212), where a significantly lower hydrogen crossover was measured when an MPL was used. This effect was particularly strong at low current densities, which contributes to increasing the turndown ratio.

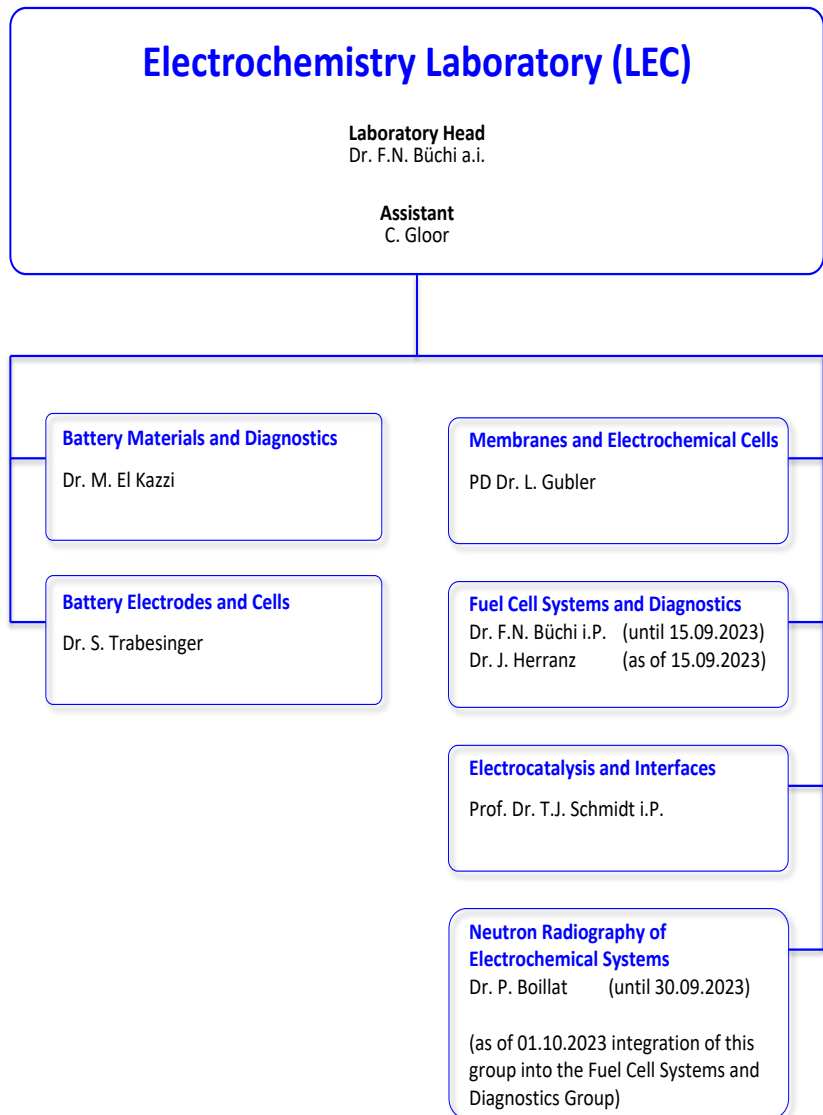
Through a rational design of PTL surface properties, we have shown that high catalyst utilization can be achieved by overcoming the high in-plane resistance of low-loaded catalyst layers. The materials and findings presented in this work will pave the way for advanced PEWE cell components and help minimize the use of critical materials in future electrolyzer systems.



# THE ELECTROCHEMISTRY LABORATORY

FACTS & FIGURES

# STRUCTURE 2023



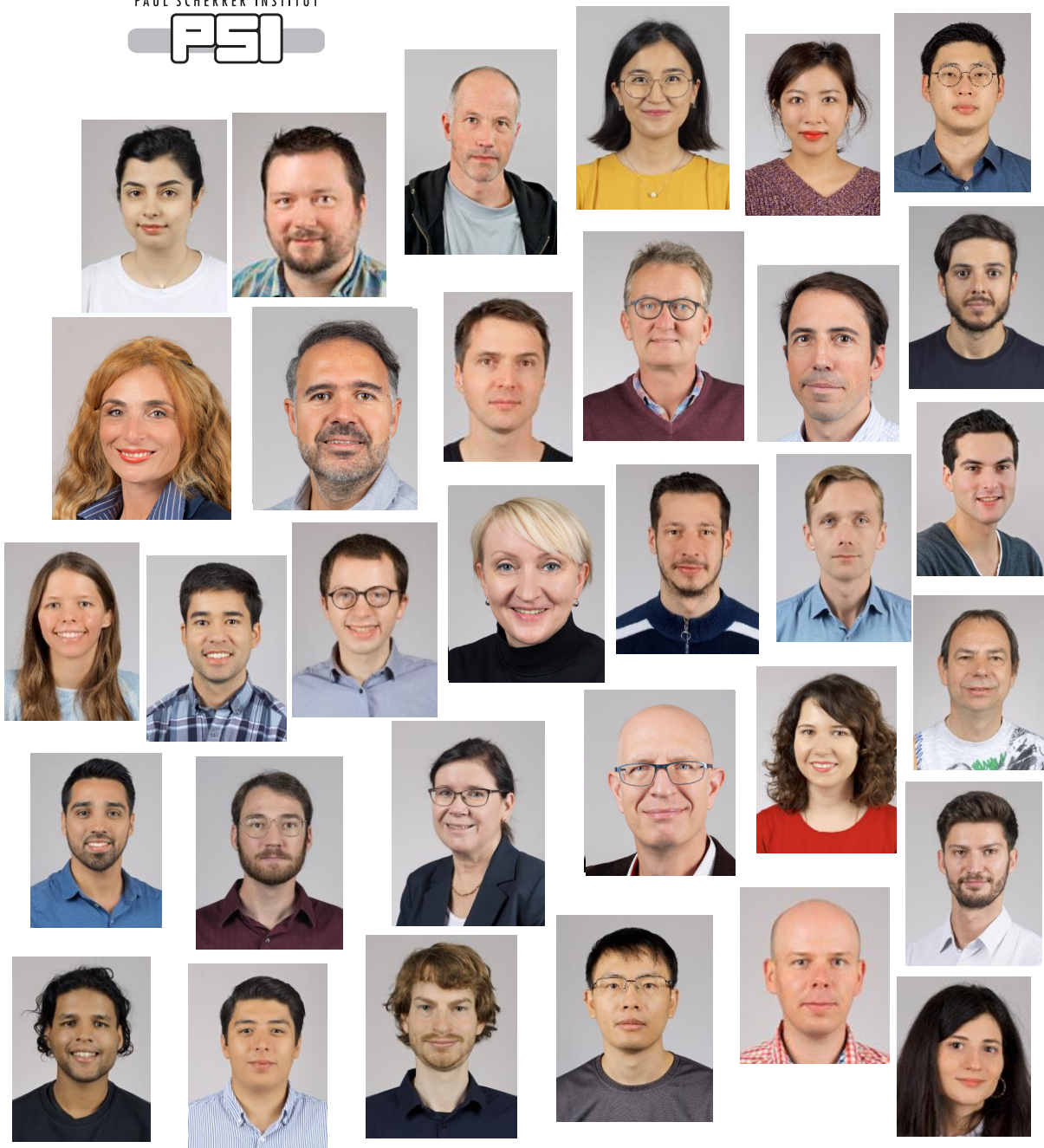
# PERSONNEL 2023

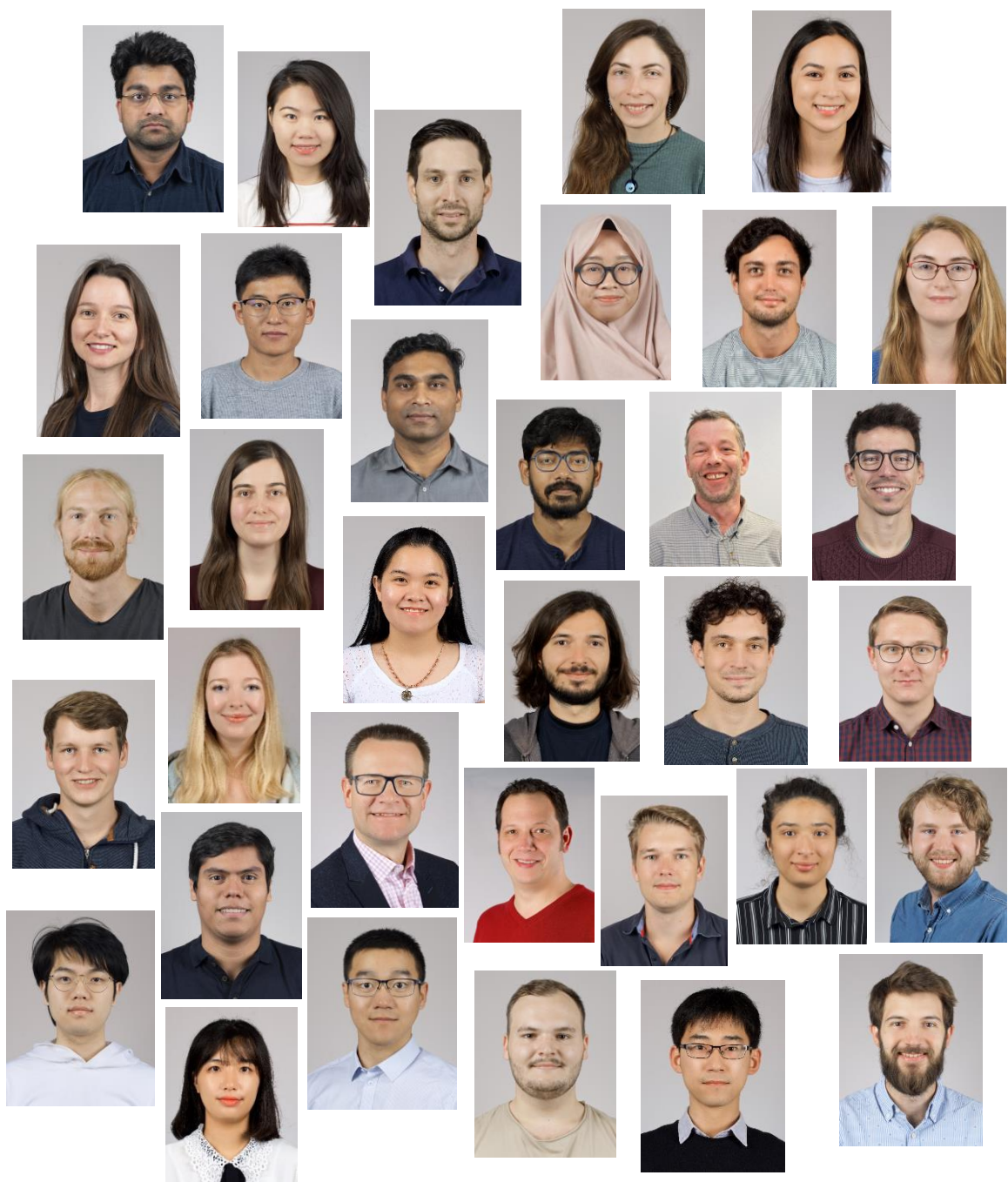
## Staff

Dr. Shima ALINEJAD KHABAZ (Postdoctoral Researcher)  
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Dr. Dominika BASTER (Scientist)  
Dr. Pierre BOILLAT (Group Leader)  
Dr. Juliana BRUNELI FALQUETO (Postdoctoral Researcher)  
Dr. Felix BÜCHI (Laboratory Head a.i. & Group Leader)  
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Dr. Tian LIU (Postdoctoral Researcher)  
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Dr. Tamás NÉMETH (Postdoctoral Researcher)  
Dr. Thi Thu Diêu NGUYEN (Postdoctoral Researcher)  
Dr. Rahul PARMAR (Postdoctoral Researcher)  
Christian PETER (Engineer)  
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Eric Ricardo CARREÓN RUIZ  
Kenneth CROSSLEY  
Tym DE WILD  
Matthieu DESSIEUX  
Tim DÖRENKAMP  
Jacobus DUBURG  
Meriem FIKRY  
Alvaro Jose GARCIA PADILLA  
Samuel GATTI  
Natasha HALES  
Zongyi HAN  
Jiyun KWEN  
Barthélémy LELOTTE  
Julia LINKE  
Wenmei LIU  
Jiaxin LU  
Arnaud SCHULLER  
Leon SKARJAN  
Seçil ÜNSAL DAYANIK  
Carl Cesar WEBER  
Eric WINTER  
Maximilian WINZELY  
Robin Norbert WULLICH  
Linfeng XU  
Jinsong ZHANG  
Zheyu ZHANG





*Members of the Electrochemistry Laboratory in 2023.*

# AWARDS 2023

**Robin Wullich**

## *ETH Medal for Outstanding Master's Theses 2023*

Title: «High Voltage Cathode Surface Modification for Stable Interface in All-Solid-State Batteries».

Event: Master Graduation Ceremony D-CHAB  
December 9, 2023  
ETH Zürich, Switzerland.

Examiners: B. Lelotte, PSI Villigen  
Dr. M. El Kazzi, PSI Villigen  
Prof. Dr. T.J. Schmidt, PSI Villigen/ETH Zürich



# 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 – 2023

(Battery Materials and Diagnostics)

**Masis Marcel Sirim**

Johannes Gutenberg-Universität, Mainz, Germany

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

October 2023 – March 2024

(Membranes and Electrochemical Cells)

**Ting-Wei Weng**

EPFL, Lausanne, Switzerland

*Effect of low-loading unsupported Pt<sub>3</sub>Ni aerogel cathode catalyst on PEM fuel cell cold start for automotive applications*

March – September 2022

(Fuel Cell Systems and Diagnostics)

**Timo Brunner**

ETH Zürich, Switzerland,  
Department of Automatic Control Laboratory

*Fabrication of bipolar membranes and characterization using Hydrogen pump*

January – February 2023

(Electrocatalysis & Interfaces)

**Alvaro Jose Garcia Padilla**

ETH Zürich, Switzerland

*Effect of low-loading unsupported Pt<sub>3</sub>Ni aerogel cathode catalyst on PEM fuel cell cold start for automotive applications*

March – July 2023

(Fuel Cell Systems and Diagnostics)

**Tim Welmers**

ETH Zürich, Switzerland

*Proving the existence of a high-potential trapped state upon H<sub>2</sub>-starvation of a PEFC-anode*

September 2023 – March 2024

(Fuel Cell Systems 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)

# CONFERENCES – SYMPOSIA

39<sup>th</sup> Swiss Electrochemistry Symposium

April 26, 2023  
Culture & Congress House (KuK), Aarau

## Future Materials in Electrochemical Energy Systems

Organizers

Felix N. Büchi, Cordelia Gloor, Lorenz Gubler, Juan Herranz,  
Sigita Trabesinger (Electrochemistry Laboratory)

Contributions from  
(in order of appearance)

Christian Neumann, Heraeus Group, Hanau, Germany  
Isotta Cerri, Toyota Motor Europe, Zaventem, Belgium  
Jake Brittain, Faradion Limited, Oxford, UK  
Antoni Forner-Cuenca, University of Technology (TUE),  
Eindhoven, The Netherlands  
Maximilian Fichtner, Helmholtz Institute Ulm (HIU),  
Ulm, Germany  
Frédéric Jaouen, Institut Charles Gerhardt Montpellier  
(CNRS-UM-ENSCM), Montpellier, France  
Ali Çoskun, University of Fribourg, Fribourg, Switzerland  
Felix N. Büchi, PSI Villigen



### Future Materials in Electrochemical Energy Systems



39<sup>th</sup> Swiss Electrochemistry Symposium

April 26, 2023  
Culture and Congress House  
Kultur- und Kongresshaus KuK  
5000 Aarau, Switzerland

[www.psi.ch/ses23](http://www.psi.ch/ses23)

This Symposium is sponsored by:



### Program

09:00 Welcome Coffee

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

09:40 Poster pitch @ 3 min. each  
(Dr. Neumann unfortunately had to cancel his attendance on short notice)

10:20 Isotta Cerri, Toyota Motor Europe, Zaventem, Belgium  
An automotive perspective on the electrochemical solutions for a sustainable future

11:00 Coffee Break 30 Min.

11:30 Jake Brittain, Faradion Limited, Oxford, UK  
Performance and Structural Chemistry of Layered Oxides as Sodium-ion Cathodes

12:10 Buffet-Lunch, Poster Session and Networking

13:30 Antoni Forner-Cuenca, University of Technology (TUE), Eindhoven, The Netherlands  
Engineering Porous Electrodes for Redox Flow Batteries

14:10 Maximilian Fichtner, Helmholtz Institute Ulm (HIU), Ulm, Germany  
New approaches and materials for Na-ion and Ca batteries

14:50 Coffee Break 20 Min.

15:10 Frédéric Jaouen, Institut Charles Gerhardt Montpellier (CNRS-UM-ENSCM), Montpellier, France  
Non-noble metal catalysts for proton- and anion-exchange membrane fuel cells

15:50 Ali Çoskun, University of Fribourg, Fribourg, Switzerland  
Novel materials and electrolytes for the next generation battery technologies

16:30 Felix N. Büchi, PSI Villigen  
Summary

16:40 End of Symposium Day



3

39<sup>th</sup> Swiss Electrochemistry Symposium  
Future Materials in Electrochemical Energy Systems

# DOCUMENTATION

## Collaborations with Industrial Partners

The Electrochemistry Laboratory had the pleasure to collaborate with the following industrial partners during the year 2023:



INNOLITH

TOYOTA

œerlikon

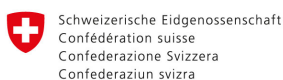


SIEMENS  
ENERGY



## Collaborations with External Partners

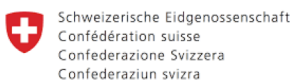
The Electrochemistry Laboratory had the pleasure to collaborate with the following external partners during the year 2023:



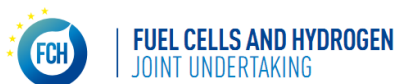
Bundesamt für Energie BFE  
Office fédéral de l'énergie OFEN



SNF Sinergia



Swiss Confederation



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



HELMHOLTZ ZENTRUM  
DRESDEN ROSSENDORF



Technische Universität München

## Teaching Activities

### Teaching

PD Dr. L. Gubler,  
Dr. J. Herranz

*Electrochemical Energy Conversion & Storage Technologies*  
ETH Zürich, FS 2023.

Dr. E. Fabbri,  
PD Dr. L. Gubler,  
Dr. J. Herranz,  
Dr. S. Trapesinger

*Hands-on Electrochemistry for Energy Storage and Conversion Applications*  
ETH Zürich, FS 2023.

Dr. E. Fabbri

*Electrochemistry: Basics and Practice (course number 64133-01)*  
University of Basel, FS 2023.

PD Dr. L. Gubler

*Electrochemistry: Fundamentals, Cells & Applications*  
ETH Zürich, HS 2023.

Prof. Dr. T.J. Schmidt

*Physical Electrochemistry & Electrocatalysis*  
ETH Zürich, FS 2023.

### Contributions to Courses

PD Dr. L. Gubler

*Energy Storage Systems*  
Lucerne University of Applied Sciences and Arts, 2023.

## Publications

### Peer Reviewed Papers

- D. Aegerter, E. Fabbri, N.S. Yüzbasi, N. Diklić, A.H. Clark, M. Nachttegaal, C. Piamonteze, J. Dreiser, T. Huthwelker, T. Graule, T.J. Schmidt *Co<sub>1-x</sub>Fe<sub>x</sub>O<sub>y</sub> Oxygen Evolution Nanocatalysts: On the Way To Resolve (Electro)Chemically Triggered Surface-Bulk Discrepancy* ACS Catalysis **13**(24), 15899–15909 (2023). DOI: 10.1021/acscatal.3c04138
- K. Aliyah, C. Prehal, J.S. Diercks, N. Diklić, L. Xu, S. Ünsal, C. Appel, B.R. Pauw, G.J. Smales, M. Guizar-Sicairos, J. Herranz, L. Gubler, F.N. Büchi, J. Eller *Quantification of PEFC Catalyst Layer Saturation via In Silico, Ex Situ, and In Situ Small-Angle X-ray Scatterings* ACS Applied Materials & Interfaces **15**(22), 26538–26553 (2023). DOI: 10.1021/acscami.3c00420
- C.E. Beall, E. Fabbri, A.H. Clark, N.S. Yüzbasi, T. Graule, T.J. Schmidt *Influence of carbon on the dynamic changes in Co oxidation state of Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub> perovskite catalyst during the oxygen reduction and evolution reactions* EcoMat **5**(7), e12353 (2023). DOI: 10.1002/eom2.12353
- K. Crossley, D. Montinaro *Insights into strontium zirconate-induced interface pressures in solid oxide electrolysis cells* Journal of Power Sources **589**, 233747 (2024). DOI: 10.1016/j.jpowsour.2023.233747
- T. de Wild, T. Nemeth, P. Becker, D. Günther, T. Nauser, T.J. Schmidt, L. Gubler *Repair of aromatic hydrocarbon-based membranes tested under accelerated fuel cell conditions* Journal of Power Sources **560**, 232525 (2023). DOI: 10.1016/j.jpowsour.2022.232525

- T. de Wild, J. Wurm,  
P. Becker, D. Günther,  
T. Nauser, T.J. Schmidt,  
L. Gubler, T. Nemeth
- A Nature-inspired Antioxidant Strategy based on Porphyrin for Aromatic Hydrocarbon Containing Fuel Cell Membranes*  
ChemSusChem **16**(21), e202300775 (2023).  
DOI: 10.1002/cssc.202300775
- J.S. Diercks, J. Herranz,  
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M. Georgi, P. Chauhan,  
A.H. Clark,  
M. Nachttegaal,  
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- Spectroscopy vs. Electrochemistry: Catalyst Layer Thickness Effects on Operando/In Situ Measurements*  
Angewandte Chemie International Edition **62**(16), e202216633 (2023).  
DOI: doi.org/10.1002/anie.202216633
- J.B. Falqueto, A.H. Clark,  
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M. El Kazzi
- Unveiling the (de-)lithiation mechanism of nano-sized LiMn<sub>2</sub>O<sub>4</sub> allows the design of a cycling protocol for achieving long-term cycling stability*  
Journal of Materials Chemistry A **11**(45), 24800–24811 (2023).  
DOI: 10.1039/D3TA04660E
- N. Hales, T.J. Schmidt,  
E. Fabbri
- Reversible and irreversible transformations of Ni-based electrocatalysts during the oxygen evolution reaction*  
Current Opinion in Electrochemistry **38**, 101231 (2023).  
DOI: 10.1016/j.coelec.2023.101231
- D. Hua, J. Huang,  
E. Fabbri, M. Rafique,  
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- Development of Anion Exchange Membrane Water Electrolysis and the Associated Challenges: A Review*  
ChemElectroChem **10**(1), e202200999 (2023).  
DOI: 10.1002/celec.202200999
- F. Jeschull, H.Q. Pham,  
A. Ghamlouche,  
P.K. Thakur,  
S. Trabesinger,  
J. Maibach
- Interphase Formation with Carboxylic Acids as Slurry Additives for Si Electrodes in Li-ion Batteries. Part 2: a Photoelectron Spectroscopy Study*  
Journal of Physics: Energy **5**(2), 025002 (2023).  
DOI: 10.1088/2515-7655/acbbee
- F. Jeschull, L. Zhang,  
Ł. Kondracki, F. Scott,  
S. Trabesinger
- Interphase Formation with Carboxylic Acids as Slurry Additives for Si Electrodes in Li-ion Batteries. Part 1: Performance and Gas Evolution*  
Journal of Physics: Energy **5**(2), 025003 (2023).  
DOI: 10.1088/2515-7655/acbbdd



- S. Luh, R. Kannan, R. McKenna, T.J. Schmidt, T. Kober *How, where, and when to charge electric vehicles—net-zero energy system implications and policy recommendations* Environmental Research Communications **5**(9), 095004 (2023). DOI: 10.1088/2515-7620/acf363
- M. Fikry, J. Herranz, S. Leisibach, P. Khavlyuk, A. Eychmüller, T.J. Schmidt *PEMFC-Performance of Unsupported Pt-Ni Aerogel Cathode Catalyst Layers under Automotive-Relevant Operative Conditions* Journal of The Electrochemical Society **170**, 114524 (2023). DOI: 10.1149/1945-7111/ad0e45
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- E. Marelli, J. Lyu, M. Morin, M. Leménager, T. Shang, N.S. Yüzbası, D. Aegerter, J. Huang, N.D. Daffé, A.H. Clark, D. Sheptyakov, T. Graule, M. Nachtegaal, E. Pomjakushina, T.J. Schmidt, M. Krack, E. Fabbri, M. Medarde *Cobalt-free layered perovskites  $R\text{BaCuFeO}_{5+6}$  ( $R = 4f$  lanthanide) as electrocatalysts for the oxygen evolution reaction* EES Catalysis **2**, 335–350 (2024). DOI: 10.1039/D3EY00142C
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- M.D. Obrist, R. Kannan, R. McKenna, T.J. Schmidt, T. Kober *High-temperature heat pumps in climate pathways for selected industry sectors in Switzerland*  
Energy Policy **173**, 113383 (2023).  
DOI: 10.1016/j.enpol.2022.113383
- W.L. Soon, M. Peydayesh, T. de Wild, F. Donat, R. Saran, C.R. Muller, L. Gubler, R. Mezzenga, A. Miserez *Renewable Energy from Livestock Waste Valorization: Amyloid-Based Feather Keratin Fuel Cells*  
ACS Appl Mater Interfaces **15**(40), 47049–47057 (2023).  
DOI: 10.1021/acsami.3c10218
- 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 **19**(7), 2206252 (2023).  
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- L. Stermieri, T. Kober, R. McKenna, T.J. Schmidt, E. Panos *Impacts of Digitalization and Societal Changes on Energy Transition: A Novel Socio-Techno-Economic Energy System Model*  
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- L. Stermieri, T. Kober, T.J. Schmidt, R. McKenna, E. Panos *Quantifying the implications of behavioral changes induced by digitalization on energy transition: A systematic review of methodological approaches*  
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- Y. Surace, F. Jeschull, P. Novák, S. Trabesinger *Performance-Determining Factors for Si–Graphite Electrode Evaluation: The Role of Mass Loading and Amount of Electrolyte Additive*  
Journal of The Electrochemical Society **170**(2), 020510 (2023).  
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C. Appel, D. Karpov,  
M. Mermoux, F. Maillard,  
V.A. Saveleva, V. Tileli,  
T.J. Schmidt, J. Herranz  
*Decoupling the Contributions of Different Instability Mechanisms to the PEMFC Performance Decay of Non-noble Metal O<sub>2</sub>-Reduction Catalysts*  
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J. Herranz  
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DOI: 10.1016/j.electacta.2023.142024
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*Conditions for profitable operation of P2X energy hubs to meet local demand with energy market access*  
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S. De Angelis, F.N. Büchi  
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ACS Applied Materials & Interfaces **15**(29), 34750–34763 (2023).  
DOI: 10.1021/acsami.3c04151
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*Sulfonated Poly(Phenylene sulfone) blend membranes finding their way into proton exchange membrane fuel cells*  
Journal of Power Sources **563** (2023).  
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- W. Yoshimune,  
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J. Wook Choi, A. Coskun  
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ACS Energy Letters **8**, 3180–3187 (2023).  
DOI: 10.1021/acseenergylett.3c01004
- T. Zhou, Y. Zhao,  
P.W. Fritz, A. Timur,  
D. Baster, M. El Kazzi,  
A. Coskun  
*Molecular regulation of electrolytes for enhancing anode interfacial stability in lithium–sulfur batteries*  
Chemical Communications **59**, 8286–8289 (2023).  
DOI: 10.1039/d3cc01179h
- T. Zhou, Y. Zhao,  
K. Seob Song, D. Baster,  
M. El Kazzi, A. Coskun  
*Boosting Polysulfide Conversion in Lithium–Sulfur Batteries via Palladium-Based Environmentally Friendly Porous Catalyst*  
Chemistry of Materials **35**, 5362–5367 (2023).  
DOI: 10.1021/acs.chemmater.3c00544

## Talks

### Invited Talks

- M. El Kazzi *Operando XPS: an emerging reliable and valuable technique for all-solid-state batteries*  
8<sup>th</sup> XPS workshop, KIT, Karlsruhe Institute of Technology, Germany, June 22, 2023.
- M. El Kazzi *Recent Advances in Operando X-Ray Photoemission/Absorption Spectroscopy to Probe the Electrolyte/Electrode Interfaces in All-Solid-State Batteries*  
Stanford Synchrotron Radiation Lightsource (SSRL), Stanford University, USA, April 12, 2023.
- M. El Kazzi *The role of the interface to enable Li metal/Li-free anodes for liquid and all-solid type batteries*  
IBatmeeting, CSEM, Neuchâtel, Switzerland, October 5, 2023.
- J. Eller *PNoninvasive Local Impedance Determination in Polymer Electrolyte Fuel Cell Stacks*  
PlugPower Technical Seminar, Online, November 17, 2023.
- E. Fabbri *Steps towards the understanding the oxygen evolution reaction enigma by operando techniques supported by computational studies*  
E-MRS-2023 Spring Meeting, Strasbourg, France, May 29–31, 2023.
- E. Fabbri *Steps towards Understanding the Oxygen Evolution Reaction Enigma by Operando Quick X-ray Absorption Spectroscopy*  
Operando VII Conference 2023, Grindelwald, Switzerland, May 9–10, 2023.
- L. Gubler *Degradation Studies of Hydrocarbon Fuel Cell Membranes*  
Beyond-PFSA Project Meeting, ZSW, Ulm, Germany, March 3, 2023.
- L. Gubler *Degradation Studies of Hydrocarbon Fuel Cell Membranes*  
EMEA-2023 Workshop on Ion Exchange Membranes for Energy Applications, Bad Zwischenahn, Germany, June 20–22, 2023.

- L. Gubler *Electrochemical CO<sub>2</sub> Separation*  
Carbon Atlantis, Ismaning, Germany, November 10, 2023.
- S. Trabesinger *Analytical Approaches for Rechargeable Batteries*  
Seminar at the Adolphe Merkle Institute, Fribourg, Switzerland,  
March 20, 2023.
- S. Trabesinger *Charge Transfer for Energy Efficient Batteries*  
Energy Efficiency Movement, The Symposium, ABB Research Center,  
Baden, Switzerland, September 25, 2023.
- S. Trabesinger *Effects and Working Mechanisms of Battery Electrolyte Additives*  
4<sup>th</sup> International Battery Manufacturing Days – Webinar Series, On-  
line, September 14, 2023.
- S. Trabesinger *Importance of (Advanced) Analytics for Battery Interfaces*  
Saltus! Workshop, University of Freiburg, Germany, February 17,  
2023.
- S. Trabesinger *Keynote: Importance of Advanced Analytics for Battery Interfaces*  
12<sup>th</sup> Gotion Technology Conference, Hefei, China, May 19–20, 2023.

## Contributed Talks

- K. Aliyah, A. Berger,  
T. Lazaridis, C. Appel,  
A. Menzel, H. Gasteiger,  
F.N. Büchi, L. Gubler,  
J. Eller  
*Investigation of Catalyst Layer and Microporous Layer Liquid Water Saturation Level in Polymer Electrolyte Fuel Cell by Operando Small&Wide Angle X-ray Scattering*  
Interpore-2023, Edinburgh, UK, May 22–25, 2023.
- K. Aliyah, A. Berger,  
T. Lazaridis, C. Appel,  
A. Menzel, H. Gasteiger,  
F.N. Büchi, L. Gubler,  
J. Eller  
*The Effect of Catalyst Layer and Microporous Layer Saturation Level in Polymer Electrolyte Fuel Cell Revealed By Small and Wide Angle X-ray Scattering*  
European Fuel Cell Forum 2023, Lucerne, Switzerland, July 4–7, 2023.
- K. Aliyah, A. Berger,  
T. Lazaridis, C. Appel,  
A. Menzel, H. Gasteiger,  
F.N. Büchi, L. Gubler,  
J. Eller  
*Effects of Operating Conditions on Membrane Electrode Assembly Saturation and Hydration Revealed by Operando Small & Wide Angle X-ray Scattering*  
ECS-2023 244<sup>th</sup> The Electrochemical Society Meeting, Gothenburg, Sweden, October 8–12, 2023.
- C. Beall, E. Fabbri,  
A. H. Clark, V. Meier,  
N.S. Yüzbaşı, D. Aegerter,  
N. Diklic, T. Graule,  
T.J. Schmidt  
*The Reversible and Irreversible Changes in Perovskite Catalysts While Alternating Between the Oxygen Reduction and Evolution Reactions in Alkaline Environment*  
ISE-2023 74<sup>th</sup> Annual Meeting of the International Society of Electrochemistry, Lyon, France, September 3–8, 2023.
- M. Dessieux, R. Fischer,  
S. Haussener, F. Büchi  
*Mass transport in a gas-fed CO<sub>2</sub> electrolyzer with a forward-bias bipolar membrane*  
ECS-2023 244<sup>th</sup> The Electrochemical Society Meeting, Gothenburg, Sweden, October 8–12, 2023.
- M. Dessieux, R. Fischer,  
S. Haussener, F. Büchi  
*Stability Investigation of a CO<sub>2</sub> Electrolyzer with a Bipolar Membrane*  
EFCF-2023 26<sup>th</sup> European Fuel Cell Forum, Luzern, Switzerland, July 4–7, 2023.
- T. Dörenkamp, F. Büchi,  
T. Schmidt, J. Eller  
*Capillary Pressure Controlled Water Pathways in GDL for PEFC Designed by Additive Manufacturing*  
ECS-2023 244<sup>th</sup> The Electrochemical Society Meeting, Gothenburg, Sweden, October 8–12, 2023.

- T. Dörenkamp, F. Büchi,  
T. Schmidt, J. Eller      *Percolation Pathways in Gas Diffusion Layers for PEFC Designed by Additive Manufacturing*  
EFCF-2023 26<sup>th</sup> European Fuel Cell Forum, Luzern, Switzerland,  
July 4–7, 2023.
- T. Dörenkamp,  
F. Marone, M. Sabharwal,  
J. Eller      *Insights into Water Cluster Instabilities in Gas Diffusion Layers of Polymer Electrolyte Fuel Cells*  
Interpore 2023, Edinburgh, UK, May 22–25, 2023.
- J.C. Duburg, B. Chen,  
S. Holdcroft, L. Gubler      *Hexamethyl-p-terphenyl Polybenzimidazolium Membranes for Use in Vanadium Redox Flow Batteries*  
EMEA-2023 Workshop on Ion Exchange Membranes for Energy Applications, Bad Zwischenahn, Germany, June 20–22, 2023.
- M. El Kazzi      *Recent advances in ex-situ/operando X-ray photoemission/absorption spectroscopy to probe the electrolyte/electrode interfaces in Li-ion batteries*  
MRS-2023, Spring Meeting of the Materials Research Society, San Francisco, USA, April 10–14, 2023.
- R. Fischer, M. Dessieux,  
F. Marone, F.N. Büchi      *Degradation Processes in Bipolar Membrane CO<sub>2</sub>-Electrolysis Studied by Time-Resolved X-Ray Tomography*  
ECS-2023 244<sup>th</sup> The Electrochemical Society Meeting, Gothenburg, Sweden, October 8–12, 2023.
- R. Fischer, M. Dessieux,  
F. Marone, F.N. Büchi      *Dynamic X-Ray Imaging of Flooding And Degradation in CO<sub>2</sub>-Electrolysis*  
EFCF-2023 27<sup>th</sup> European Fuel Cell Forum, Luzern, Switzerland,  
July 4–7, 2023.
- R. Fischer, M. Dessieux,  
F. Marone, F.N. Büchi      *Water Dynamics during Gas Fed CO<sub>2</sub>-Electrolysis Revealed by 4D X-ray Imaging*  
Interpore-2023, Edinburgh, UK, May 22–25, 2023.
- N. Hales, T.J. Schmidt,  
E. Fabbri      *Operando Transformations of the Perovskite Ba<sub>0.5</sub>Sr<sub>0.5</sub>Ni<sub>0.5</sub>W<sub>0.5</sub>O<sub>3-δ</sub> during the Oxygen Evolution Reaction*  
MRS-2023, Fall Meeting of the Materials Research Society, Boston, US, November 26 - December 1, 2023.



- J. Huang, T.J. Schmidt,  
E. Fabbri *Operando/ex situ X-ray adsorption spectroscopy to monitor the cobalt oxidation state during oxygen evolution reaction*  
4<sup>th</sup> Asia-Pacific Conference on Energy Storage and Conversion, Xiamen, China, November 25–28, 2023.
- Ł. Kondracki, J. Stropp,  
S. Steiner, D. Wierzbicki,  
A. Wach, S. Trabesinger *Superstructure-Suppressed Oxygen Evolution in Co-free Materials for Na-ion Batteries*  
Swiss Battery Days 2023, PSI Villigen, Switzerland, September 18–20, 2023.
- J. Kwen, J. Herranz,  
T.J. Schmidt *Forward-Bias 3D-Junction Bipolar Membranes for Electrochemical CO<sub>2</sub> Reduction to CO*  
ECS-2023 244<sup>th</sup> The Electrochemical Society Meeting, Gothenburg, Sweden, October 8–12, 2023.
- B. Lelotte, V. Pelé,  
C. Jordy, C.A.F. Vaz,  
C.N. Borca,  
T. Huthwelker, L. Gubler,  
M. El Kazzi *Interface Evolution of the LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub>/Li<sub>6</sub>PS<sub>5</sub>Cl Solid-State-Battery Bathode During Cycling*  
LiBD-2023 Lithium Batteries Discussion Conference on Electrode Materials, Arcachon, France, June 18–23, 2023.
- J. Linke, T. Rohrbach,  
A.H. Clark,  
M. Andrzejewski,  
N.P.M. Casati,  
M. Ranocchiari,  
T.J. Schmidt, E. Fabbri *Operando Investigations of Reversible and Irreversible Transformations of MOF based Catalysts during OER*  
ECS-2023 244<sup>th</sup> The Electrochemical Society Meeting, Gothenburg, Sweden, October 8–12, 2023.
- M. Fikry,  
A. Garcia-Padilla,  
J. Herranz, P. Khavlyuk,  
A. Eychmüller,  
T.J. Schmidt *Challenges of ultra-thin Pt<sub>3</sub>Ni aerogel catalyst layer during cold starts in PEM fuel cell*  
ECS-2023 244<sup>th</sup> The Electrochemical Society Meeting, Gothenburg, Sweden, October 8–12, 2023.
- M. Fikry, T. Welmers,  
J. Herranz, P. Khavlyuk,  
A. Eychmüller,  
T.J. Schmidt *Toward low Pt loading of unsupported Pt-Ni aerogels cathode catalyst layer in PEMFCs*  
EFCF-2023 27<sup>th</sup> European Fuel Cell Forum, Luzern, Switzerland, July 4–7, 2023.

- D. Masiello, L. Gubler,  
A. Muroyama *Simulation-Driven Enhancement of an Alkaline CO<sub>2</sub> Capture Electrochemical Cell*  
ECS-2023 243<sup>rd</sup> Electrochemical Society Meeting, Boston, USA,  
May 28 – June 2, 2023.
- A. Muroyama,  
D. Masiello, L. Gubler *Electrode Design for Effective Electrochemical Regeneration of an Alkaline CO<sub>2</sub> Capture Solution*  
ECS-2023 243<sup>rd</sup> Electrochemical Society Meeting, Boston, USA,  
May 28 – June 2, 2023.
- T. Nemeth, Z. Han,  
L. Gubler *PVDF-based Aromatic Hydrocarbon containing Proton Exchange Membranes with High Performance in the Hydrogen Fuel Cell*  
Carisma 2023, Lefkada, Greece, October 1–6, 2023.
- T. Nemeth, T. Nauser,  
L. Gubler *On the Radical-Induced Degradation of Quaternary Ammonium Cations for Anion-Exchange Membrane Fuel Cells and Electrolyzers*  
EMEA-2023 Workshop on Ion Exchange Membranes for Energy Applications, Bad Zwischenahn, Germany, June 20–22, 2023.
- A. Schuller, J. Eller *Noninvasive Local Impedance Determination in Polymer Electrolyte Fuel Cells Stacks*  
19<sup>th</sup> Symposium on Fuel Cell and Battery Modeling and Experimental Validation, Duisburg, Germany, March 23, 2023.
- A. Schuller, T.J. Schmidt,  
J. Eller *Noninvasive Local Impedance Determination in Polymer Electrolyte Fuel Cells Stacks*  
ECS-2023 244<sup>th</sup> The Electrochemical Society Meeting, Gothenburg, Sweden, October 8–12, 2023.
- V. Siller, B. Lelotte,  
C.A.F. Vaz, M. El Kazzi *Probing the instable interface between LPSCI solid electrolyte and NCM622 high voltage cathode with operando X-ray spectroscopy*  
Swiss Battery Days 2023, PSI Villigen, Switzerland, September 18–20, 2023.
- V. Siller, B. Lelotte,  
C.A.F. Vaz, M. El Kazzi *Probing the instable interface between solid electrolytes and high voltage cathodes with operando X-ray spectroscopy*  
LiBD-2023 Lithium Batteries Discussion Conference on Electrode Materials, Arcachon, France, June 18–23, 2023.

- Y. Surace, D. Leanza,  
M. Mirolo, L. Kondracki,  
C.A.F. Vaz, P. Novák,  
M. El Kazzi,  
S. Trabesinger
- Deciphering the True FEC Reduction Mechanism and its Implications to the Understanding of the SEI in Li-ion Batteries*  
ECS-2023 244<sup>th</sup> The Electrochemical Society Meeting, Gothenburg, Sweden, October 8–12, 2023.
- Y. Surace, D. Leanza,  
M. Mirolo, L. Kondracki,  
C.A.F. Vaz, P. Novák,  
M.El Kazzi, S. Trabesinger
- Deciphering the True FEC Reduction Mechanism and its Implications to the Understanding of the SEI in Li-ion Batteries*  
ISE-2023 74<sup>th</sup> Annual Meeting of the International Society of Electrochemistry, Lyon, France, September 3–8, 2023.
- Y. Surace, D. Leanza,  
M. Mirolo, L. Kondracki,  
C.A.F. Vaz, P. Novák,  
M.El Kazzi, S. Trabesinger
- Is FEC a truly film-forming additive?*  
LiBD-2023 Lithium Batteries Discussion Conference on Electrode Materials, Arcachon, France, June 18–23, 2023.
- C.C. Weber, R. Meinert,  
C. Appel, M. Holler,  
L. Gubler, S. De Angelis,  
F.N. Büchi
- Challenges of ultra-thin Pt<sub>3</sub>Ni aerogel catalyst layer during cold starts in PEM fuel cell*  
ECS-2023 244<sup>th</sup> The Electrochemical Society Meeting, Gothenburg, Sweden, October 8–12, 2023.
- C.C. Weber, T. Schuler,  
J.A. Wrubel, L. Gubler,  
G. Bender, F.N. Büchi
- Hybrid Design of Thin Titanium Microporous Layers for Polymer Electrolyte Water Electrolysis*  
EFCF-2023 26<sup>th</sup> European Fuel Cell Forum, Luzern, Switzerland, July 4–7, 2023.
- C.C. Weber, T. Schuler,  
J.A. Wrubel, L. Gubler,  
B. Pivovar, G. Bender,  
F.N. Büchi
- Novel microporous layers for PEM electrolysis with low iridium loadings and thin membranes*  
ICE-2023 4<sup>th</sup> International Conference on Electrolysis, Sun City, South Africa, August 27 – September 1, 2023.
- M. Winzely,  
J.S. Diercks, O. Safonova,  
P. Rüttimann, A.H. Clark,  
M. Nachttegaal,  
T.J. Schmidt, J. Herranz
- An Electrochemical Cell for Operando Grazing-Incidence X-ray Absorption Spectroscopic Studies of Low-Loaded Electrodes*  
ECS-2023 244<sup>th</sup> The Electrochemical Society Meeting, Gothenburg, Sweden, October 8–12, 2023.

J. Zhang, T.J. Schmidt,  
M. El Kazzi

*Impacts of cell physical parameters on the cycling of metallic lithium in sulfide-based all-solid-state batteries*

ISE-2023 74<sup>th</sup> Annual Meeting of the International Society of Electrochemistry, Lyon, France, September 3–8, 2023.

Z. Zhang, A. Baudy,  
Z. Han, A. Testino,  
L. Gubler

*Towards Next-Generation Catalyst Coated Membranes for Polymer Electrolyte Water Electrolyzers*

ICE-2023 4<sup>th</sup> International Conference on Electrolysis, Sun City, South Africa, August 27 – September 1, 2023.

## Posters

- A. Baiju, V. Siller,  
F. Okur, K. Kravchyk,  
M. Montazerian,  
N. Shepelin, D. Pergolesi,  
M. Kovalenko, Y. Ekinci,  
T. Lippert, M. El Kazzi
- LiMn<sub>2</sub>O<sub>4</sub> a Promising Cathode for Lithionic Memristors: Electronic Conductivity Evolution Relative to the State of Charge*  
Swiss Battery Days 2023, Villigen, Switzerland, September 18–20, 2023.
- D. Baster, A.H. Clark,  
T. Schmitt, C.A.F. Vaz,  
T.C. Asmara, Y. Wei,  
Z. Tao, M. El Kazzi
- Unveiling the charge compensation mechanism and surface degradation of Na<sub>0.67</sub>Mn<sub>0.6</sub>Fe<sub>0.25</sub>Al<sub>0.15</sub>O<sub>2</sub> high-voltage cathode for Na-ion batteries*  
Swiss Battery Days 2023, Villigen, Switzerland, September 18–20, 2023.
- D. Baster, C.A.F. Vaz,  
A.H. Clark, M. El Kazzi
- Unveiling the degradation mechanism of Na<sub>0.67</sub>Mn<sub>0.6</sub>Fe<sub>0.25</sub>Al<sub>0.15</sub>O<sub>2</sub> high-voltage cathode material for Na-ion batteries*  
39<sup>th</sup> Swiss Electrochemistry Symposium, Aarau, Switzerland, April 26, 2023.
- M. Dessieux, R. Fischer,  
S. Haussener, F. Büchi
- Stability issue in Gas-Fed CO<sub>2</sub> Reduction Devices with Bipolar Membranes*  
Gordon Research Conference 2023 – Carbon Capture, Utilization and Storage, Les Diablerets, May 29, 2023.
- J.C. Duburg, B. Chen,  
S. Holdcroft, L. Gubler
- Optimising Polybenzimidazolium Membranes for Use in Vanadium Redox Flow Batteries*  
IFBF International Flow Battery Forum 2023, Prague, Czech Republic, June 27–29, 2023.
- Á. García-Padilla,  
M. Fikry, J. Herranz,  
P. Khavlyuk,  
A. Eychmüller,  
T.J Schmidt
- Behaviour of unsupported Pt-Ni aerogel cathode catalyst layers upon PEMFC cold-start*  
27<sup>th</sup> European Fuel Cell Forum, Luzern, 2023.

- S.F. Gatti, S. Trabesinger,  
A. Testino *What Limits Performance in Sidorenkite-Type  $\text{Na}_{2.81}\text{Fe}(\text{PO}_4)(\text{CO}_3)$  in NIBs?*  
Swiss Battery Days 2023, Villigen, Switzerland, September 18–20, 2023.
- K. Crossley, J. Huang,  
T.J. Schmidt, E. Fabbri *Towards oxygen evolution reaction catalyst activity descriptors using model hydroxide perovskites*  
European Materials Research Society 2023 Spring Meeting, Strasbourg, France, May 30, 2023.
- Ł. Kondracki, J. Stropp,  
S. Steiner, D. Wierzbicki,  
A. Wach, S. Trabesinger *Superstructure-Controlled Oxygen Evolution in Co-free Materials for Na-ion Batteries*  
BatSynch: The battery Challenge at Synchrotrons, Trieste, November 29–30, 2023.
- Ł. Kondracki, J. Stropp,  
S. Steiner, D. Wierzbicki,  
A. Wach, S. Trabesinger *Superstructure-Suppressed Oxygen Evolution in Co-free Materials for Na-ion Batteries*  
ISE-2023 74<sup>th</sup> Annual Meeting of the International Society of Electrochemistry, Lyon, September 3–8, 2023.
- B. Lelotte, V. Pelé,  
C. Jordy, C.A.F. Vaz,  
C.N. Borca,  
T. Huthwelker,  
L. Gubler, M. El Kazzi *Interface Evolution of the  $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2/\text{Li}_6\text{PS}_5\text{Cl}$  Solid-State-Battery Bathode During Cycling*  
Lithium Battery Discussions (LiBD), Arcachon, France, June 18–23, 2023.
- D. Masiello, L. Gubler,  
A. Muroyama *Electrochemical  $\text{CO}_2$  Direct-Air Capture*  
ModVal-2023 Symposium on Modeling and Experimental Validation of Electrochemical Energy Technologies, Duisburg, Germany, March 21–23, 2023.
- M. Winzely, J.S. Diercks,  
O. Safonova,  
P. Rüttimann, A.H. Clark,  
P. Leidinger, S. Phadke,  
T.J. Schmidt, J. Herranz *A novel electrochemical cell for the in situ X-ray absorption spectroscopic investigation of cluster-based  $\text{CO}_2$ -electroreduction catalysts*  
ISSPIC XXI, Berlin, Germany, September 3–8, 2023.

- M. Winzely, J.S. Diercks,  
O. Safonova,  
P. Rüttimann, J. Coroa,  
A.H. Clark, T.J. Schmidt,  
J. Herranz
- An electrochemical cell for operando grazing-incidence X-ray absorption spectroscopic studies of low-loaded electrodes*  
Operando VII, Grindelwald, Switzerland, May 7–11, 2023.
- T. Nemeth, T. Nauser,  
L. Gubler
- On the Radical-induced Degradation of Anion Exchange Fuel Cell Membranes*  
Miller Conference on Radiation Chemistry, Corsica, France, June 3–8, 2023.
- R. Parmar, S. Trabesinger
- Impact of Lithium Metal Anode Thickness on its Performance*  
Swiss Battery Days 2023, Villigen, Switzerland, September 18–20, 2023.
- J. Płotek, Ł. Kondracki,  
S. Trabesinger,  
J. Molenda
- Impact of carbonate-, ester- and ether-based electrolytes on the effectiveness of sodium plating and stripping*  
Swiss Battery Days 2023, Villigen Switzerland, September 18–20, 2023.
- H.V. Ramasamya,  
C.A.F. Vaz, B. Lelotte,  
V. Siller, K. Yalamanchili,  
H. Rudigier, M. El Kazzi
- Deciphering the electrode/electrolyte interface reaction of High voltage  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2/\text{Li}_6\text{PS}_5\text{Cl}$  solid state batteries*  
Swiss Battery Days 2023, Villigen Switzerland, September 18–20, 2023.
- H.V. Ramasamya,  
C.A.F. Vaz, V. Siller,  
B. Lelotte,  
K. Yalamanchili,  
H. Rudigier, M. El Kazzi
- Understanding the interface reactivity of high voltage  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  (NCM811) cathode cycled in all-solid-state lithium ion batteries*  
Lithium Battery Discussions (LiBD), Arcachon, France, June 18–23, 2023.
- V. Siller, B. Lelotte,  
V. Pelé, C. Jordy,  
C.A.F. Vaz, M. El Kazzi
- Probing the instable interface between solid electrolytes and high voltage cathodes with operando X-ray spectroscopy*  
LiBD-2023 Lithium Batteries Discussion Conference on Electrode Materials, Arcachon, France, June 18–23, 2023.
- V. Siller, B. Lelotte,  
C.A.F. Vaz, V. Pelé,  
C. Jordy, M. El Kazzi
- Probing the instable interface between solid electrolytes and high voltage cathodes with operando X-ray spectroscopy*  
Swiss Battery Days 2023, Villigen Switzerland, September 18–20, 2023.

- Y. Surace, D. Leanza,  
M. Mirolo, L. Kondracki,  
C.A.F. Vaz, P. Novák,  
M. El Kazzi,  
S. Trabesinger
- Is FEC a truly film-forming additive?*  
LIBD-2023, Lithium Batteries Discussion Conference on Electrode  
Materials, Arcachon, France, June 18–23, 2023.
- L. Xu, J. Zhang,  
J. Le Houx, V. Kachkanov,  
J. Eller, T.J. Schmidt,  
M. El Kazzi
- X-ray Computed Tomography to Elucidate Mechanical Failures in All  
solid state Li metal Batteries*  
74<sup>th</sup> Annual International Society of Electrochemistry, Lyon, France,  
September 3–8, 2023.
- L. Xu, J. Zhang,  
J. Le Houx, V. Kachkanov,  
J. Eller, T.J. Schmidt,  
M. El Kazzi
- X-ray Computed Tomography to Elucidate Mechanical Failures in All-  
solid-state Li-metal Batteries*  
Swiss Battery Days 2023, Villigen Switzerland, September 18–20,  
2023.
- J. Zhang, T.J. Schmidt,  
M. El Kazzi
- Impacts of cell physical parameters on the cycling of metallic lithium in  
sulfide based all solid state batteries*  
Swiss Battery Days 2023, Villigen, Switzerland, September 18–20,  
2023.



## Conference Organizations

E. Fabbri  
(Organizer)

*Solid State Ionics Symposium of the EMRS Spring conference .*  
Strasbourg, France, May 29 to June 2, 2023.

L. Gubler  
(Member of the Scientific Committee)

*IFBF International Flow Battery Forum 2023*  
Prague, Czech Republic, June 27–29, 2023.





