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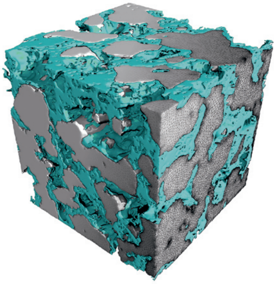

2nd Symposium on Insights into Gas Diffusion Electrodes

From Fundamentals to Industrial Applications

https://www.mpi-magdeburg.mpg.de/gde2022

Plenary Lectures

Hierarchically structured electrodes: Their design, implementation and characterization to make academic developments relevant

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New, micron and nano-sized functional materials play a key role for future technologies that are currently developed in the field of energy conversion (electrolysers, fuel cells) and electrocatalysis (N_2 fixation, CO_2 reduction). While new materials with outstanding properties are continuously developed, they rarely find their way into – urgently needed – large scale production and industrial applications. Overcoming and bridging this “valley of death” is an interdisciplinary endeavour for which chemical engineering and in particular, particle technology is indispensable. To fulfil this bridging function, the field needs to develop in such a way that we i) collect and make efficient use of more data and develop standard procedures that allow us to better understand process-structure and structure-property relationships, ii) replace idealized conditions and model formulations by technically relevant scenarios (testing at application concentration, full complexity of a formulation mixture) and iii) apply relevant processes (scalable dispersion, R2R-coating) already on lab-scale as integrating research tools. In my talk, I will introduce concepts that we developed and apply in my team and in collaborations with colleagues across the Rhine-Ruhr area to generate hierarchically structured electrode layers that can be integrated into full cells.

Electrochemical Reduction of CO2 using Gas Diffusion Electrodes

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Carbon dioxide (CO_2) is a major greenhouse gas which is driving the climate change. CO_2 capture at the emission sources and from air followed by conversion to fuels/chemicals can achieve carbon neutral energy cycle. Electrochemical CO_2 reduction (eCO2R) is one of the most promising methods for the direct production of fuels and chemicals from waste CO_2 and water. eCO2R on copper electrodes favours the production of multi-carbon products including hydrocarbons and oxygenates [1]. The nanostructure engineering and alloying to create a variety of interfaces is a potential route for producing materials with higher catalytic activity and selectivity. Gas diffusion electrode further improved mass transfer of CO_2 to reaction interface resulted in enhanced selectivity for carbonaceous products. High alkalinity with OH groups around catalyst surface improved the reaction kinetics and moreover stabilize the catalyst surface oxygen during the reduction process. Stability of GDE was improved by tuning hydrophobicity of catalyst and gas diffusion layers. Multi-carbon products, C2 and C3, were synthesised with bi-metallic Cu-Ag prepared by electrochemical spontaneous deposition of Ag on Cu_2O nanoparticles [2,3]. From the density functional theory (DFT) analysis, Ag promotes Cu atoms migration towards the surface of the electrode, which seems to adsorb generated CO for the further reduction process to produce higher carbonaceous products (Figure 1). GDE is a promising technology for Sustainability development.

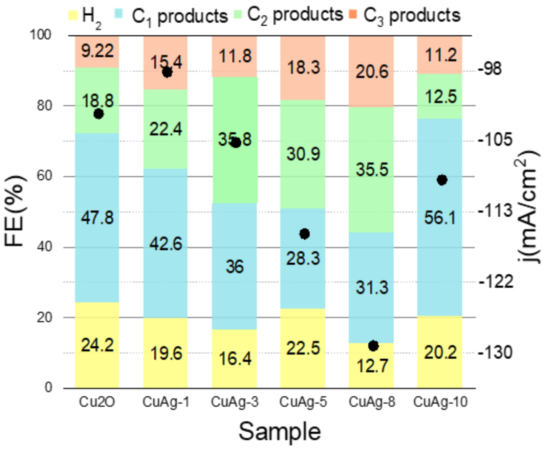

Figure 1. FE(%) for H_2, C_1, C_2 and C_3 products for various CuAg samples

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Importance of Transport in Electrochemical Energy-Conversion Technologies: The Case For Gas-Diffusion Electrodes

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As electrochemical technologies become increasingly important in our energy paradigm, especially hydrogen, there is a need to examine them holistically. Furthermore, for such technologies to become practical, they need to operate at high current densities to minimize various cell costs. This operating space necessitates the need for efficient transport of reactants and removal of products from the reaction site. For example, one of the main challenges towards achieving high-efficiency fuel generators performing CO2 reduction are the mass-transport limitations in traditional aqueous systems due to CO2 interactions/solubility and boundary-layer thickness. To circumvent these issues, gas-diffusion electrodes (GDEs) are considered wherein the reactants and products are fed or removed in a vapor form into a porous 3-D electrode that leverage knowledge from the fuel-cell and electrolyzer fields. In this talk, we will explore the various tradeoffs endemic in GDE architectures for various electrochemical reactions including CO2 and CO reduction and O2 and H2 consumption and evolution. Such tradeoffs are quantified through multiphysics modeling and key diagnostics of the cells including breakdowns of the various limiting phenomena at both the micro and macroscales, where the local conditions and environment around the reaction center impact reactivity in both transient and steady state conditions, enabling metastable states. It will be shown how transport phenomena dominate a lot of the performance and selectivity of the catalysts, which is critical to understand to improve overall performance. In addition, we will explore how different integration schemes can greatly impact overall response, which can overshadow any intrinsic changes due to different electrocatalyst materials, thereby providing different design rules. Different GDE design architectures will be explored and their intrinsic tradeoffs noted including complex interplay of hydration, reactant concentration, and both homogeneous and heterogeneous reactions. In particular, full vapor-phase motifs will be discussed including nonintuitive results when one goes from liquid to solid-state, polymer electrolytes. In addition, experimental data on both GDEs and model, microelectrode solid-state systems for the various electrochemical reactions will be presented and results rationalized through understanding the various concentration and ionic overpotentials.

Invited Lectures

Chemical Design of Carbon-Based Materials for the Electrochemical Activation of Small Molecules

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Carbon-based electrocatalysts stand out by a combination of high (electro)chemical stability, electric conductivity and tuneable porosity/chemical architecture [1]. They are thus intensely studied for the catalytic activation of small molecules. The carbon structure can thereby itself act as catalyst or it can fill the role of a support, that is, the stabilization of metallic catalysts. In recent years, this concept has been widely applied for instance in electrochemically-driven reduction of carbon dioxide or in the oxygen reduction reaction [2,3].

Ammonia synthesis by the electrochemical N_2 reduction reaction (eNRR) is increasingly studied and proposed as an alternative process to overcome the disadvantages of Haber-Bosch synthesis by a more energy-efficient, carbon-free, delocalized, and sustainable process that would be based on water spitting and electricity from renewable sources. An ever-increasing number of scientists are working on the improvement of the faradaic efficiency (FE) and NH_3 production rate by developing novel catalysts, electrolyte concepts, and/or by contributing theoretical studies [4,5]. Despite these intense efforts, eNRR can still not compete with Haber-Bosch synthesis in terms of energy efficiency and space-time yield of ammonia.

The present contribution will provide a critical view on the interplay of different crucial aspects in NRR from the electrolyte, over the mechanism of catalytic activation of N_2, to the full electrochemical cell. Recently developed carbon-based catalysts will be specifically discussed. On the one hand, highly oxidation resistant (“noble”) and microporous carbon materials obtained by template-free thermal condensation of preorganized hexaazatiphenylene-hexacarbonitrile (HAT-CN) precursor molecules will be presented [6]. Such materials have extremely high surface polarity and show properties in gas adsorption that are so far only reported for metal-organic frameworks and zeolites. In combination with a nanocasting approach, hierarchical micro- and mesoporous HAT-CN-derived carbons can be prepared which are suitable for the stabilization of gold single sites and show also intrinsic catalytic activity in eNRR [7]. On the other hand, MOF-derived carbon/titania catalysts as well as boron and nitrogen co-doped materials will be presented and the structure-property relationships will be discussed [8,9].

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From electrocatalyst powder to porous electrode layers: A journey with a lot of pitfalls

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Design and engineering of electrocatalyst materials have attracted great attention in the last 10 years. Improving electrochemical kinetics and transport processes for polymer electrolyte fuel cells and electrolyzers is still a critical challenge. A simple transition from fundamental knowledge obtained from three-electrode half-cell investigations towards single cell investigations is not straightforward due to the multiple processes occurring at the reaction interface of three-phase boundary and their transport losses on different length and times scales. Is there a key strategy at all to successfully transfer from catalyst powder to porous electrode layers, gas diffusion layers or catalyst-coated membranes with similar catalytic performance? A journey with many pitfalls and unknowns to govern and steer electrochemical processes with high conversion and selectivity.

In this talk, I will present our research focussing on various electrocatalytic processes (oxygen reduction reaction (ORR), hydrogen evolution/oxidation reaction (HER/HOR), methanol oxidation reaction (MOR), CO_2 reduction reaction (CO_2RR). We are concerned with the development of new, efficient and robust electrocatalysts with controlled structure, composition, particle size and particle shape. From bimetallic nanoparticles with different elemental arrangements like core-shell nanoparticle motifs towards porous electrode layers will be covered in this talk. Special attention will be paid to the real chemical state of the less noble metals inside so-called core-shell electrocatalysts for ORR and HOR and will bring an old story to new light.[1-2] A broad tool of unique and advanced in-situ and ex-situ high resolution microscopic and spectroscopic techniques is employed in our group to better understand the reaction mechanisms and kinetics of electrochemical processes. A additional focus lies in the transfer of half-cell investigations towards single cell investigations, where a broad tool of diagnostics is applied to gain information about the local reactant concentration, ionomer distribution and mass transport properties within the porous electrode layer.

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Press it, Heat it, Twist it: A Series of Hidden Parameters for the Electrochemical CO_2 Reduction

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The electrochemical reduction of CO_2 from flue gas or direct air capture to relevant syngas mixtures is a promising route towards mitigation of environmental pollution and production of bulk chemicals and fuels. In this context, the application of gas diffusion electrodes is promising due to efficient CO_2 mass transport. Herein, the assembly of the catalytic layer plays a critical role in the electrode performance, as elevated bulk hydrophobicity coupled with good surface wettability is observed to offer highest performance. Obviously, the composition of the GDE has a severe influence on the electrode performance and setting proper hydrophobicity gradients within the electrode is key toward developing a successful electrochemical CO_2 reduction [1]. Yet, the GDE electrode cannot be investigated independent of the reactor it is applied in [2]. Among the different cell types, especially gas-fed zero-gap electrolyzers are promising as energy efficient and scalable devices. Thus, we herein additionally show the influence of operational parameters related to the cathode water management like cell orientation, gas humidification and cathode compression onto CO2R. By a step-wise optimization of our not yet fully optimized electrolyzer, stability could be improved by a factor of three up to 10 h at 3 V and 300 mA cm^{-2}. Faradaic efficiency for CO after two hours of electrolysis was increased from 14 to over 60 %. Controlling the water management is a key parameter as high-water input leads to flooding of the electrodes, whereas lower values decrease performance of the anion-exchange-membrane and reduce catalyst wetting.In conclusion, we herein show that both, a fine-tuned electrode and an optimal reactor environment are key towards a successful CO_2 conversion and cannot be treated independently.

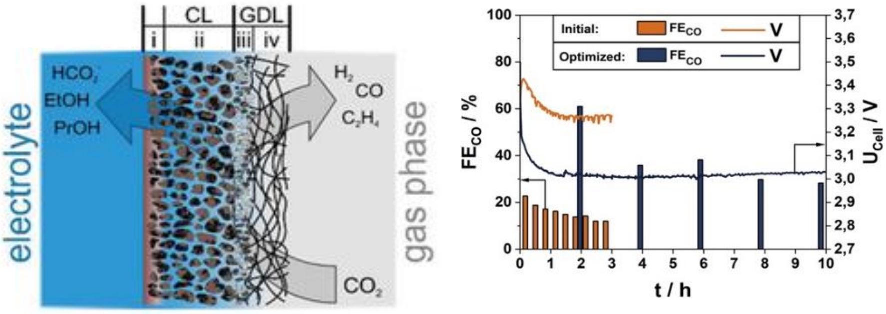

Figure 1*:* (left) Schematic illustration of a GDE used in this work. The electrodes consist of i) an optional ionomer coating, (right) Faradic efficiency for CO (FE_{CO}) and overall cell voltage (U_{cell}) during 3 and 10 h of CO_2 electrolysis of the initial system and with optimized operational parameters at 300 mA cm^{-2}.

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From oxygen reduction to CO_2 reduction in gas diffusion electrodes. Similarities and differences

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At first glance, gas diffusion electrodes seem to be comparatively simple, and the advantages for enhanced mass transport of the gaseous reactants are evident. However, many interconnected parameters have to be considered to enable the fabrication of optimized gas diffusion electrodes, including, among many more, the location of the three-phase boundary, the local pH value, the mass transport of water and OH^- ions in case of proton-coupled electron-transfer reduction reactions, uncompensated electrolyte resistance, counter electrode reaction and the mass transport of the formed gaseous or liquid products, choice of the ion exchange membrane, electrowetting, parasitic side reactions together with in-line product analysis.

In the case of the oxygen reduction reaction and high selectivity for the direct 4-electron transfer, the location of the three-phase boundary inside the gas-diffusion electrode will significantly impact the local pH value and the water and OH^- transport. In contrast, in the case of CO_2 reduction, the location of the three-phase boundary will impact the ratio of CO_2 reduction and parasitic hydrogen evolution up to a level that the CO_2 reduction is largely suppressed.

Using SECM-based local pH measurement techniques, in-situ electrochemistry/Raman spectroscopy and specifically developed measurements routines with in-line gas chromatography together with the design of sprayed model gas-diffusion electrodes 4-electron transfer, we elucidated essential parameters which have to be considered in designing optimized gas-diffusion electrodes for specific reactions.

In this contribution, I want to attempt to dive into the nanoconfined interior of gas-diffusion electrodes to share what my research group and I, together with colleagues, learned in the past 2 to 3 years about the complex interplay of parameters during the oxygen reduction reaction and the CO_2 reduction reaction.

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Development and upscaling of gas diffusion electrodes for wastewater treatment and electrosynthesis of chemicals

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Technologies related to gas diffusion electrodes (GDEs) offer solutions for gaseous reagents taking part in electrochemical reactions. (Bio)electrochemical processes suffer from challenges like high costs of platinized electrodes[1]; rapid catalyst degradation and low performance due to non-uniform electrode quality[2]; difficulties in upscaling. Scaling up microbial fuel cells (MFCs) requires use of large electrodes which are often difficult to fabricate without loss in quality. VITO has developed GDEs tailored for systems with aqueous electrolytes and a gas-water interface, which are characterized by controllable pore diameters in the polymer-bound active layer, mechanical robustness and low water permeability[2]. These cold-rolled (VITOCORE®) and phase-inversion based (VITO CASE®) electrodes enable reproducible quality in sizes from 10 cm² to 1 m². Large-scale VITOCORE® air cathodes were recently developed and tested in 85 L and 255 L MFCs to evaluate the impact of the cathode size on MFC performance[4,5]. For CO_2 electroreduction, GDEs based on Sn, Cu and Pd were developed and evaluated for production of formic acid and oxalic acid.

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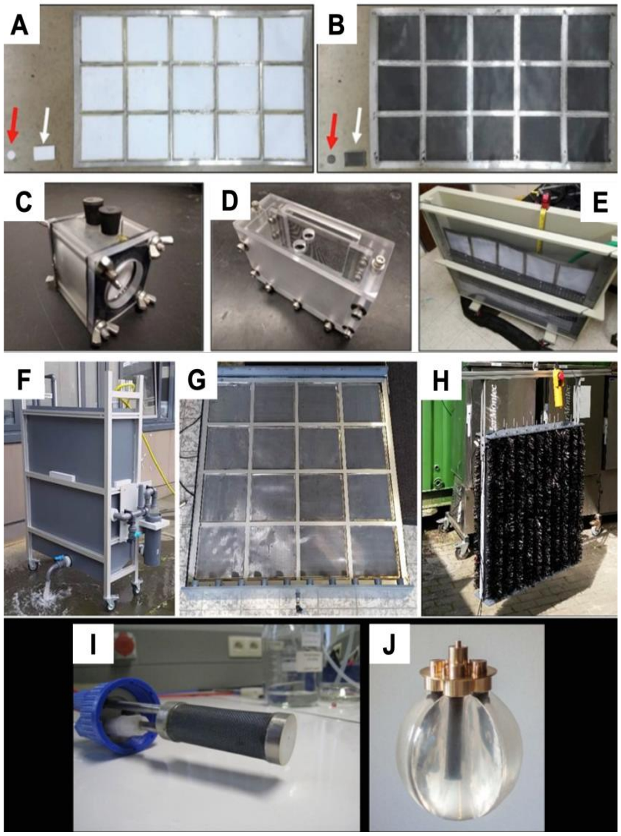

Figure 1. GDE electrode configurations in different sizes and geometries. **(A)** Gas diffusion side of an upscaled GDE **(B)** Electrolyte exposed side of an upscaled GDE. **(C, D)** Lab scale air-cathode MFCs of 10 cm² and 100 cm². **(E)** An 85 L MFC for testing GDE shown in (A) and (B). **(F)** A 255 L MFC reactor **(G)** An upscaled GDE for testing in (F). **(H)** Graphite fibre brush anode used in (F) and tested in combination with (G). **(I)** A tubular GDE. **(J)** A 'spark of life' set up employing a GDE shown in **(I)**.

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Advanced 2D and 3D Microscopic and Spectroscopic Characterization of Gas Diffusion Electrodes for Fuel Cells

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Recent unprecedented push towards clean and renewable technologies places hydrogen fuel cells at the forefront of research, development and commercialization. Lab level and scalable fabrication of fuel cell electrodes, either in the form of catalyst coated membranes (CCMs) or gas diffusion electrodes (GDEs), is typically pursued using a variety of coating approaches such as spray coating, screen printing, rod/bar coating, gravure and slot die methods. A number of parameters affect the quality and the performance of the resulting electrodes, starting from the ink composition and preparation method, to electrode coating parameters, type of substrate, drying conditions, and electrode transfer or membrane electrode assembly (MEA) bonding parameters. Each of the steps affects the microstructure and composition of the electrodes, consequently determining the performance and durability of the electrodes. Within our project, named The Overall Research on Electrode Coating Processes (OREO), researchers from the University of Connecticut, the Colorado School of Mines, the Fraunhofer Institute for Solar Energy in Freiburg, Germany, and the National Renewable Energy Laboratory, seek to reveal the effects of process parameters for each method, both on coating quality as well as on performance. A special emphasis is given on structural and spectroscopy characterization of the layers. This talk will discuss multi-scale 2D and 3D microscopy approaches, as well as spectroscopy studies of the GDEs and CCMs fabricated using a variety of coating techniques. Effect of ink mixing, coating and drying parameters will be quantified through advanced microscopy. In addition, novel imaging approaches, revealing details of electrode degradation will be discussed.

Industrial GDE: Current Applications & Perspectives from De Nora

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Gas diffusion electrode (GDE) technology is critical to the advancement of industrial electrochemical processes that utilize gaseous feedstock or release gaseous products. GDEs are used in membrane water electrolysis to produce green H_2 (and O_2), in fuel cells (FC) to produce electricity, and they are deployed in chlor-alkali electrolysis (CAE) processes as the energy saving electrode [1]

De Nora Industries supply our strategic partners with industrial GDE for CAE and FC, where the oxygen reduction reaction (ORR) overpotential on the cathode plays an important role in their efficient and economic utilization. The oxygen depolarized cathode (ODC) as an alternative cathode in the highly energy consuming CAE has led to an improvement of ~1V of voltage across the cell, an approx. 30% of energy saving during operation. R&D on the ORR cathode in FC, focusing on efficient and cost-effective catalyst materials as well as electrode production, has improved FC performance, galvanizing wide-spread adaptation of FC for stationary and mobile power [2-3]

An upcoming application of GDE is the CO2 reduction reaction (CO2RR). In a GDE-based electrochemical CO2 reactor, or eCO2R, CO2 feedstock from Carbon Capture and Utilization (CCU) will combine with green H2 from electrochemical water electrolysis to produce valuable chemicals and raw materials. In this front, De Nora is actively working to develop the technology towards its commercial exploitation. Particularly within the EU-Funded projects SELECTCO2 and ECO2Fuel, De Nora has the role of Work Package leader and the main role of GDL/GDE developer and supplier. Thanks to the collaborations with industry and academic partners from two EU-wide consortiums, who bring their expertise and R&D infrastructure, it has been possible to set a very ambitious target for the achievement of MW-scale in CO2 electrolysis [4-7]

The talk will first highlight the state-of-the-art of industrial GDE technologies, its advantages, and the scientific as well as economic challenges in the field. Then the focus would be on the research activities trying to overcome these challenges and the promising results coming from both industry and academia. Finally, perspectives from De Nora will summarize industry viewpoints on the GDE technology, especially the development and manufacture of GDE

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Operation of PEM Fuel Cells Exposed to Harsh Environments

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The success of commercialization of proton exchange membrane fuel cell (PEMFC) technology in automotive and stationary markets requires availability of hydrogen infrastructure and reduction of the fuel cell cost production which can be achieved by decreasing of Pt-containing catalyst loading [1]. Evaluation of performance of high- and low-Pt PEMFCs clearly showed that Pt reduction decreased performance and negatively affected durability. Typically, ambient air is used as an oxidant for fuel cells operation and it is very important to understand impacts of common air impurities on high- and low-Pt PEMFC performance and develop a guidance on air quality. In this work we studied impacts of harsh environmental conditions on local PEMFC behavior and evaluated possible recovery strategies.

The experimental work was performed using a test station and a segmented cell system developed at Hawaii Natural Energy Institute as well as commercially available 100 cm^2 membrane electrode assemblies (MEAs) with Pt content of 0.1 and 0.4 mg_{Pt} cm^{-2} for both electrodes. To create harsh environmental conditions, we used air stream with 2 ppm of C_6H_6, NO_2 and SO_2. The poisoning proceeded until the cell voltage reached a steady state, after that the impurity injection was stopped to assess the self-recovery in pure air. The MEA was operated at stoichiometry of 2 for anode and cathode, at 80°C, 150 kPa back pressure and high-power production conditions.

The injection of 2 ppm of any contaminant (SO_2, NO_2, C_6H_6) to air stream led to voltage drop and redistribution of local currents. Table demonstrates that performance of low-Pt PEMFCs was severely affected by the contamination compared to high-Pt PEMFCs. Full self-recovery of the performance was only observed for the low-Pt MEA exposed to C_6H_6, while the cathode poisoning by SO_2 and NO_2 resulted in partial recovery. During the cathode exposure typically, there is a chemical adsorption of the impurity on Pt leading to a decrease in electrochemical surface area and shift of O_2 reduction from 4- to 2-e^- mechanism which caused the observed performance drop. Electrochemical properties of the impurities indicate that their electrooxidation can occur at high potentials (>1.0 V), while electroreduction takes place at potentials lower than 0.5 V [2-4] and these reactions procced in parallel with O_2 reduction at the cathode. The impacts of SO_2 on fuel cell performance were found to be the most drastic due to formation of S^0 on Pt, so evaluation of possible recovery strategies was performed for SO_2 contaminated PEMFCs. Detailed discussion of the results will be presented.

We acknowledge financial support from US Office of Naval Research (N00014-18-1-2127; N00014-22-1-2045).

Table. A comparison of low-Pt (0.1 mg cm^{-2}) and high-Pt (0.4 mg cm^{-2}) PEMFC performance.

Impurity	Low-Pt @0.8 A cm^{-2}		High-Pt @1.0 A cm^{-2}	
	Voltage drop [mV]	Recovery	Voltage drop [mV]	Recovery
2 ppm SO_2	345	partial	285	partial
2 ppm NO_2	130	partial	80	full
2 ppm C_6H_6	460	full	110	full

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Oral Presentations

The Interplay of Oxygen Reduction Reaction and Iron Dissolution from Fe-N-C in Alkaline Media

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For replacing platinum group metals (PGM) in fuel cells, Fe-N-C are promising candidates as earth-abundant and cheap catalysts for oxygen reduction reaction (ORR). While most studies on these materials were done in acidic media, their electrochemical activity and durability are better in alkaline media. [1] In anion exchange membrane fuel cells (AEMFCs), the activities of Fe-N-C catalysts could already be on par with those of PGM, but the stabilities remain challenging. [2] For example, compared to the durability of AEMFCs with PGM-containing electrodes, that with Fe-N-C cathode is more than one order of magnitude worse. [2] Yet, with accelerated stress tests done in aqueous model systems (AMS), the stability of Fe-N-C is reported to be even higher than that of platinum. [3] To address this discrepancy between stability studies using AMS and FCs, a gas diffusion electrode (GDE) half-cell coupled with inductively coupled plasma mass spectrometry (ICP-MS) has been developed to study on-line dissolution in realistic catalyst layers. [4]

In this work, using a GDE-ICP-MS, we investigate the impact of ORR on Fe leaching from realistic Fe-N-C alkaline catalyst layers. [5] For the first time, Fe dissolution is measured online at current densities above $-100\ \mathrm{mA \cdot cm^{-2}}$. The novel results show that compared to the model Ar-saturated environment, the Fe dissolution is dramatically higher during ORR. Furthermore, between 0.6 and 1.0 V_{RHE}, we unveil a direct correlation between Fe dissolution and charge transfer events. This subsequently leads to our hypothesis that the instability of Fe during redox transitions is responsible for the macroscopically measured Fe dissolution from Fe-N-C catalysts in alkaline media in this potential region. These new insights into Fe-N-C catalyst degradation in realistic conditions can lead towards rational design of more efficient, durable, and affordable fuel cells based on PGM-free catalysts.

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Gas Diffusion Electrode Setup Beyond Room Temperature and Ambient Pressure

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For optimal performance, many devices comprised of gas diffusion electrodes (GDEs), such as fuel cells, operate at elevated temperatures and pressures. Meanwhile, most research on GDEs is conducted at ambient conditions due to limitation of the setup design. Phenomena which are more pronounced at elevated conditions might therefore not be properly identified and understood. Therefore, a more commensurate setup is paramount for further elucidation of the GDE.

We further developed our modular 3-electrode GDE setup [1], [2]. Our setup can now operate at temperatures above 110°C and 4 bar absolute pressure. We demonstrate its capabilities by studying common fuel cell reactions, such as oxygen reduction reaction, CO oxidation and hydrogen oxidation, at various temperatures and pressures.

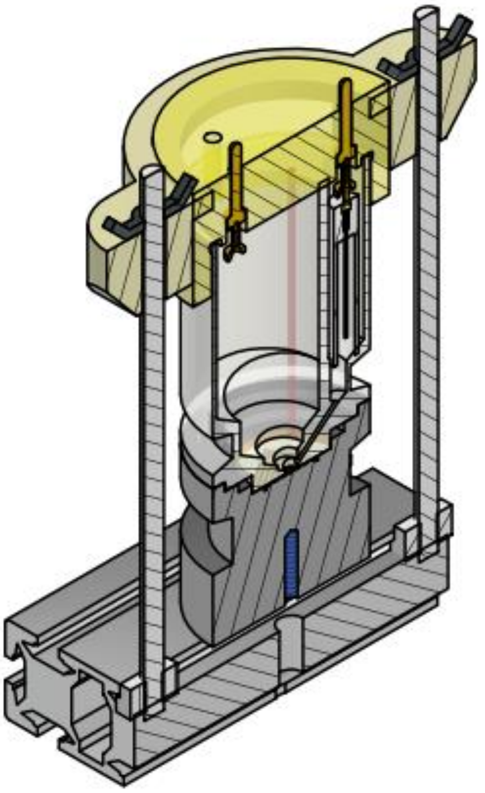

Figure 1: *Cross section of our enhanced GDE setup capable of operating at elevated temperatures and pressures.*

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Bridging the gap between lab and application: A novel Porous Transport Electrode three-electrode setup for degradation studies under realistic current densities of magnetron sputtered Ir-based catalysts in the Oxygen Evolution Reaction

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The development of realistic accelerated stress tests (AST) measurements for Oxygen Evolution Reaction (OER) anode catalysts is an essential target for the commercialization of Proton Exchange Membrane Water Electrolysers (PEMWE). To date, most degradation studies are performed with full-scale membrane electrode assemblies (MEA). However, it can be challenging to study the anode catalyst degradation behaviour individually due to the overlapping with other cell elements and the balance of plant. At the very least, full-scale trials are very material and time-intensive processes, which rely on a series of specialized instruments that are not available to many research groups. On the other hand, current laboratory techniques such as the Rotating Disk Electrode (RDE) have been shown to misrepresent realistic operating conditions due to limitations in mass transport conditions [1]. Hence, realistic current densities and stability data can both not be achieved in RDE measurements. As an alternative, the recently developed Gas Diffusion Electrode (GDE) half-cell technique has been designed to achieve an accurate physical representation of the individual electrode reactions while preserving the fast screening and flexibility wanted for lab techniques. A number of recent studies on fuel cell catalysts has demonstrated its ability to measure catalyst activities in comparable conditions to full-scale systems [2]. However, it was already seen the high current capabilities of this setup had yet to be improved [3]. In this study, we have expanded the GDE method to measure catalyst stability in realistic electrolysis Porous Transport Electrodes (PTE) used in the anode site in PEMWEs. The electrode assembly is formed by an IrOx catalyst material of (Ir loading = 250 µg/cm^2) produced by Physical Vapour Deposition (PVD) on a porous Ti substrate and hot-pressed with a Nafion 117 membrane. With this novel setup, we were able for the first time to reach high current densities >2 A cm^{-2}$_{geo}$ and circulate ultrapure water as a reactant as in MEA setups. In agreement with recent studies that describe the highest degradation conditions obtained from AST [4], we tested a steady-state protocol. To study the evolution in the catalyst performance, a series of CVs and polarization curves up to 2 A cm$^{-2}_{geo}$ were recorded before and after the AST protocol. In the presentation, we will discuss our findings that show that the GDE method can be used to interpret the degradation processes at relevant operation conditions also for OER catalysts.

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Best practice for determining oxygen reduction reaction catalyst activities in gas diffusion electrode half-cell measurements up to current densities above 1 A cm^{-2}

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In order to push forward the energy transition, research and development on technologies enabling storage and release of renewable energies, such as water electrolysis and fuel cells is a vital area in the current decade. For both processes it is essential to collect meaningful data for catalyst activity in terms of transferability to the industrial stage in an early state of catalyst lab-development. Regarding fuel cell catalyst research, gas diffusion electrode (GDE) half-cells are a promising tool for investigation of oxygen reduction reaction (ORR) catalysts at fuel cell relevant current densities and potential regimes. While the commonly used thin-film rotating disk electrode (RDE) technique suffers from major mass transport limitations and is therefore limited to maximum current densities of around 6 mA cm$^{-2}_{geo}$ (for standard conditions in 0.1 M HClO4 and 1600 rpm), GDE half-cells are so far practicable up to 2000 mA cm$^{-2}_{geo}$ at around 0.6 V vs. RHE [1,2].

What was still hindering reliable and well comparable GDE half-cell testing so far, was the application of various setups and different measurement procedures. In our recent joint publication, we compare the ORR activity assessment of a commercial Pt/C and self-prepared Pt/C and PtCo/C gas diffusion electrodes in four different half-cell designs. From this interlab-comparison we demonstrate that comparable results can be obtained if a similar electrochemical protocol is used. From the obtained results best practices and protocols for fuel cell catalyst benchmarking at relevant current densities are proposed [3].

Additionally, we present from our recent publication focusing on a commercially available half-cell (Flexcell, Gaskatel), which pitfalls can generally arise during GDE half-cell testing and how GDE performance can be optimized by tuning the ink composition during catalyst coating [4].

Last but not least, in our most recent results we stress possible limitations in GDE half-cell testing and show what is limiting maximum achievable current densities. Parameters that are found to influence the maximum achievable geometric current densities include the utilized electrolyte concentration, the counter electrode size, position and material, as well as the coated area of the working electrode. Optimization of these parameters allows us to reach astonishing current densities as high as 10000 mA cm$^{-2}_{geo}$.

In sum, the presented results set a basis for a broad-based application of the GDE half-cell technique for evaluation of fuel cell catalysts at technologically relevant current densities.

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An alternative design for state-of-the-art GDEs: OER/ORR active, large macropore-sized, catalyst-coated substrates are competitive

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Gas diffusion electrodes are found in various electrochemical applications such as metal-air batteries [1], unitized regenerative fuel cells [2], and electrolyzers [3]. Moreover, carbon-based materials are not stable in alkaline media during OER and ORR [4]. Therefore, metal-based materials are needed as an alternative. Catalyst-coated (MnO_x) substrates (nickel foam, pressed nickel foam, and stainless-steel fleece) with different macropore sizes (500 - 600 µm; $20 < x \leq 200$ µm; 20 µm) were used as carbon-free GDEs and studied in an alkaline (0.1 M KOH) aqueous half-cell. Their results were compared with a state-of-the-art carbon-based GDE, which has a porous electrode design [5] and a pore size between 0.1 and 6 µm. Accordingly, it was found that the catalyst-coated substrate (CCS) or the carbon-free GDE (CF-GDE) with the largest pore size exhibited lower OER overpotentials (0.37 V @ 10 mA cm^{-2}) than the carbon-based GDE (CB-GDE: 0.59 V @ 10 mA cm^{-2}). The active sites deep within the CF-GDE were provided with reactants. Therefore, a higher electrochemical active surface area was available. This was further studied to understand what parameters and dependencies resulted in this higher activity and how it could be used in different applications like metal-air batteries, unitized regenerative fuel cells, and electrolyzers. Thus, the catalyst-coated substrates were coated with PTFE to stabilize the formation of the electrolyte thin film meniscus in each macropore. This resulted in a CF-GDE with similar OER and ORR activities as the CB-GDE. In addtion, the introduction of PTFE resulted in less O_2-bubble-covered active sites during the OER [3]. Therefore, the PTFE coating on CCS supports the electrolyte thin film formation (ORR activity ↑) and the displacement of the bubble formation towards gas side (OER activity ↑).

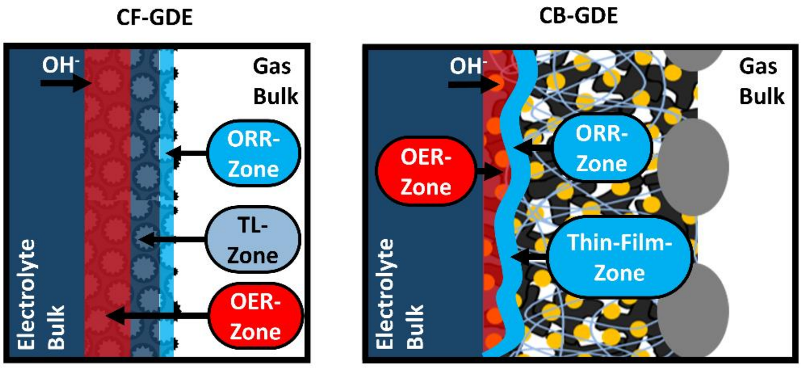

Figure 1. *Schematic depiction of CF- and CB-GDE and their reaction zones (TL: transport limited)*

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Gaining Freedom of Scalable Gas Diffusion Electrode for the CO_2 Reduction Reaction

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Electrochemical CO_2 reduction reaction (CO_2RR) has attracted a lot of research interest, due to its potential for the sustainable synthesis of chemicals and fuels.[1] Typically, planar electrodes with glass H-type cells were widely employed to evaluate the CO_2RR performances.[2] However, in these systems, the electrodes are immersed in electrolytes containing dissolved CO_2 leading to diffusion-limited current densities to tens of $mA \cdot cm^{-2}$, far from meeting the industrial required standards of at least hundreds of $mA \cdot cm^{-2}$.[3] Therefore, extensive effort was recently dedicated to developing gas diffusion electrodes (GDEs) for mitigating the restriction due to CO_2 mass transport.[4] In the common GDE configuration, two dilemmas are inevitable: i) flooding of the GDEs by electrolyte at high current densities resulting in the loss of the three-phase interface; ii) peeling of the catalyst layer as the reaction progresses causing increased parasitic H_2 evolution due to more exposed carbon surface.

To overcome these challenges, we developed a new procedure for the fabrication of self-made GDEs by an automatic airbrush-type spray process, which adds freedom in tuning structural parameters and enables the free arrangement of the gas diffusion layer (GDL), catalyst layer (CL), and supporting materials to stabilize the GDEs structure and the hydrophobic environment (Figure 1a). The thickness impacts the stability and activity of the GDE, while the amount of pore builder and applied pressure have a minor impact. As shown in Figure 1b, the thickness of a GDE was around 340 µm, while the catalyst layer and gas-diffusion layers were around 120 µm. Moreover, the choice of carbon materials has a strong effect on the selectivity of the CO_2RR. For example, using Cu nanoparticles as a model catalyst, carbon XPB-538 enables a high faradaic efficiency (FE) for HCOOH, carbon XPB-633 shows a higher FE for CO, and carbon Super C65 is preferable for the formation of C_2H_4, while carbon SFG-6 and SFG-44 only produce H_2. This work demonstrates a practical method for fabricating the GDEs and provides a transferable strategy for optimizing the major parameters for improving GDEs to get enhanced CO_2RR performance.

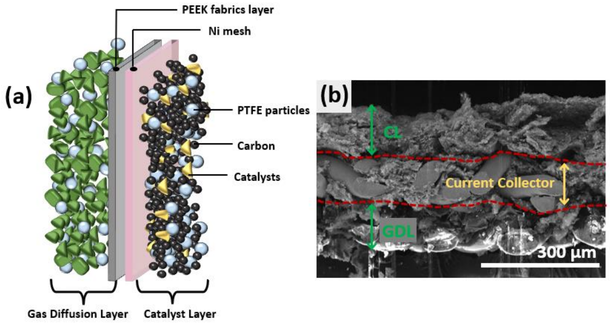

Figure 1: (a) Structure of lab-scale self-made GDE. (b) SEM cross-section image of the self-made GDE.

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CO_2 electroreduction selectivity modulation by the gas diffusion electrode architecture

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Activating CO_2 molecule to enable its conversion to basic chemicals, such as CO, ethylene, or other multi carbon products, may play an important role in achieving the aimed closed carbon cycle economy but the discovery of new electrocatalyst materials conditions it. Specifically, the electrocatalysts used to reduce CO2 (CO2RR) need to exhibit high activity, allow high current densities, and, most importantly, show high selectivity. CO_2RR involves the transfer of up to 12 electrons coupled with protons, leading thus to a multitude of possible products. Besides, the efficiency of the CO_2RR is limited by the competing parasitic hydrogen evolution reaction (HER), which occurs in the same potential window as the CO_2RR, as well as the low CO_2 solubility in aqueous electrolytes. Reduction of CO_2 at relevant current densities is possible on gas diffusion electrodes, where the three-phase boundary is a key element to favor CO_2RR over HER.[1,2]

Designing electrocatalysts for reactions in which multiple proton-coupled to electrons can be transferred, such as the CO_2RR is challenging, as it requires integrating different active sites and adsorption/desorption sites at the catalyst is required. Thus, complex catalyst design and electrode architecture are required to allow cascade reactions to occur to the aimed product and provide the optimal mass transfer. In the present communication, we will discuss the importance of the gas diffusion layer and of the electrode architecture in promoting CO_2RR over HER on Cu-based and M-N-C electrocatalysts.[3-5]

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Addressing the issue of carbon efficiency in CO_2 electroreduction at silver gas diffusion electrodes using acidic electrolytes

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In recent times, the reduction of CO_2 emissions has become an increasingly important topic for the chemical industry. A promising technology to achieve this goal is CO_2 electroreduction, as it can not only lower CO_2 emissions, but allows the use of CO_2 as a carbon source for the production of commodity chemicals. A major challenge in the reduction of CO_2 to CO at gas diffusion electrodes (GDEs) is the limited carbon efficiency [1]. This is caused by a strongly alkaline local reaction environment that results from the production of hydroxide ions in the CO_2 reduction reaction (CO_2RR), as has been shown in model studies and experimental work [2]. One possible solution for this problem could be the use of acidic electrolytes. With a low pH in the bulk electrolyte, the resulting steady state pH value inside the GDE is lowered, while still being alkaline enough at high current densities to prevent the competing hydrogen evolution reaction from taking over. While most literature reports low Faradaic efficiencies with acidic electrolytes, recent publications report promising results in the pH range of 2-4 for gold electrodes [3]. In this work, experimental results highlighting the strong effects of catholyte pH on the Faradaic efficiency of CO_2RR on silver gas diffusion electrodes are presented. It is found, that while at low current densities HER is preferred in acidic electrolytes, CO_2RR takes over at high current densities as a result of local alkalization, yielding Faradaic efficiencies that are competitive with the commonly used buffer electrolytes. Meanwhile lower pH values result in an increased carbon efficiency at industrially relevant current densities.

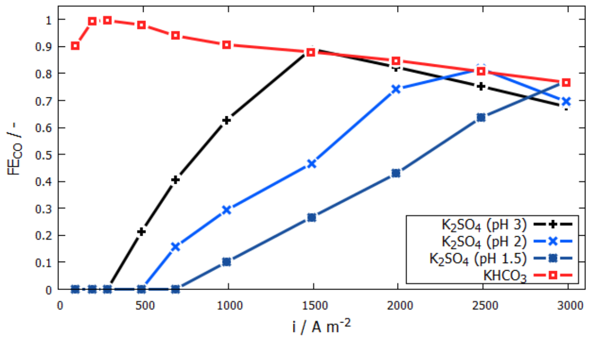

Figure 1: *Faradaic efficiency versus current density for different electrolyte pH values in comparison with $KHCO_3$.*

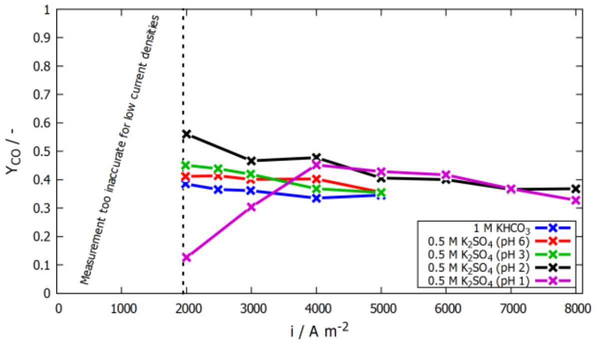

Figure 2: *Carbon efficiency versus current density for different electrolyte pH values in comparison with $KHCO_3$.*

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On the fate of selectivity in zero-gap CO_2 to CO electrolysis using Ni anodes

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Continuous electrochemical reduction of CO_2 to CO has been demonstrated with moderate success using membrane electrode assemblies (MEA) at industrially relevant current densities (≥ 200 mA/cm^2)[1, 2]. In eCO2RR to CO, Ag and Ir are the materials of choice for cathode and anode respectively. Yet the use of Ir-based anodes may be hampered by its low abundance and extreme cost. Based on the similarities with water electrolysis, a viable alternative for the anodic water oxidation are Ni-based electrodes. The application of Ni anodes in MEAs for eCO2RR is challenged by the cathodic poisoning of Ag due to the dissolution of Ni at high current densities (thus high local acidic environment) while water electrolysis doesn't suffer from poisoning due to crossover[3].

Our experiments with Ni sprayed on carbon GDE and Ni foam were very distinct. With sprayed GDE, we experienced a very unstable cell potential and a continuous and rapidly declining selectivity towards CO (starting from 50% FECO at 200 mA/cm^2). The unstable cell potential is attributed to carbon corrosion coupled with the accelerated Ni crossover that favours hydrogen evolution at the cathode (Ag, 100 nm sputtered on GDE). Though using a Ni foam circumvents the instability arising from the carbon substrate at the anode, we will show that cathodic poisoning still exists. Specifically, we observed a momentary decline in CO selectivity (around 0.75 hour) followed by complete transition to water electrolysis in around 2 hours. The XPS analysis of cathode GDE obtained before (sp1), during(sp2) and after(sp3) the initial changes in CO selectivity, as well as the analysis of the GDE after complete transition (sp4) revealed the presence of Ni only for samples originating from points sp2 and sp4 while Ni appeared to be absent at sp1, sp3. In this presentation we will present our understanding of the transient nature of GDE poisoning by Ni and provide insights into inherent process modifications that will help maintaining high selectivity towards CO even when abundant and relatively cost effective Ni anodes are utilized in eCO2RR.

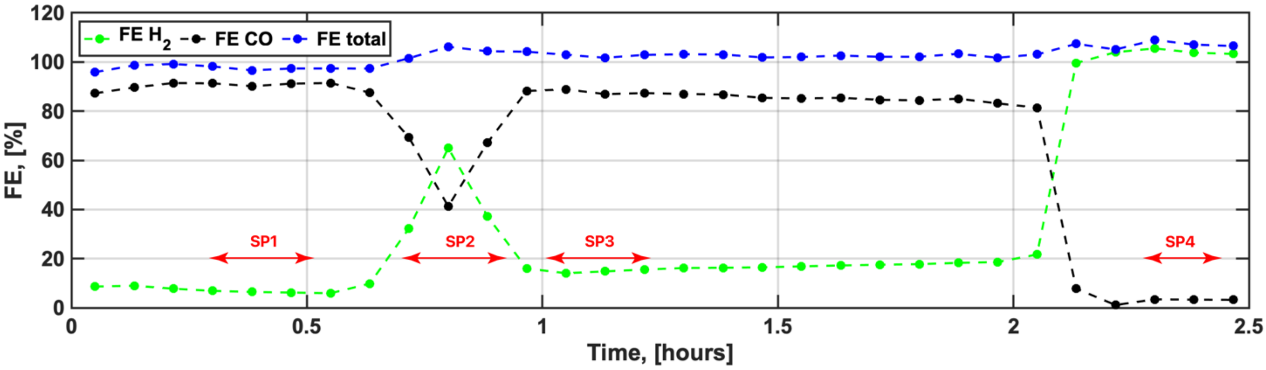

Figure 1: Faradaic efficiency at 200 mA/cm^2. Dashed lines are for visual guide.

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Diagnosis of in-plane and though-plane mass transfer in zero-gap MEA electrolyzer for CO_2 reduction

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The CO_2 emissions increase drastically due to the fast-growing global fossil-based energy demand, leading to urgent environmental crises such as climate change and ocean acidification. To mitigate CO_2 emissions, technologies related to the capture and reuse of CO_2 from the atmosphere or point sources are moving to the fore. In this proposed value chain, electrochemically reducing the CO_2 to value-add products could potentially play a central role.

To date, the electrochemical CO_2 to CO approach has been intensively focused for the intrinsically low overpotential demand and high selectivity, commonly on silver-based gas diffusion electrodes (GDE).[1] Despite over 80% faradaic CO efficiency has been achieved, the scarcity of the raw material and low-purity products stream pose as the current stage obstacles for their large-scale utilization and need further technical development.

In this work, we report the high-efficient electrochemical CO_2 reduction to CO, on novel solid-state single-site Ni-N-C catalyst in the single-pass MEA electrolyzer. Nearly 85% CO faradaic efficiency was achieved at 300 mA cm^{-2} at 3.5 V cell potential, yielding about 60%Vol CO in the product stream. Beyond the apparent single-cell performance, we developed an analytic approach to quantify the CO_2 depletion in the cathodic chamber and demonstrate the mechanistic footprint of cathodic CO_2 consumption. The CO_2 reactant feeds not only electrochemical CO2-to-CO conversion, but also through-MEA anion crossover. Overall, our work provides a diagnostic analysis for the in- and through- plane CO_2 transfer, illuminates the mechanistic details of CO_2 reduction in anion-exchange-membrane derived electrolyzer, and indicates the key performance metric of the catalyst layer manufacture for high current CO_2 electrolysis.

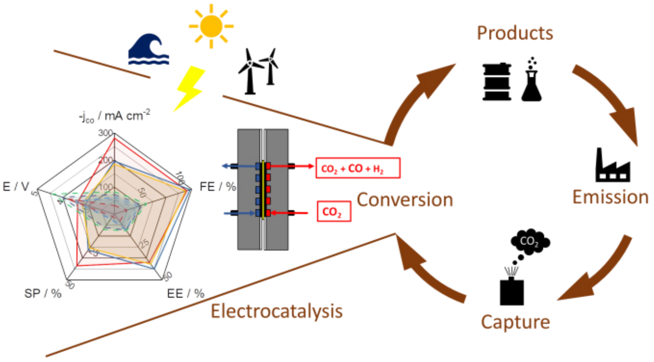

Figure: Proposed scheme of CO_2 reuse upon electrochemical approach and single-cell performance.

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Impacts of Unintended Cation Crossover through Anion Exchange Membranes on the Operation of Zero-gap Cu-based CO_2 Electrolysers

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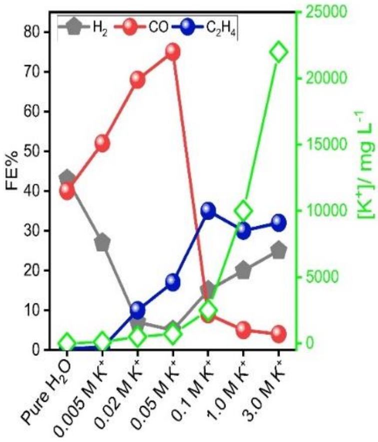
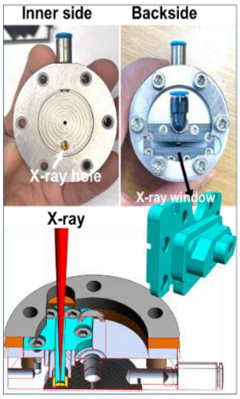
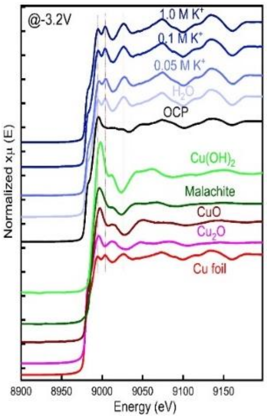
CO_2 electroreduction (CO_2ER) in gas-fed membrane electrode assemblies enable CO_2ER at industrially relevant rates, and hence provide a promising strategy to scale-up this technology for future practical applications. Electrolysers based on anion exchange membranes (AEMs) have been introduced as a strategy for preventing undesired H_2 evolution at the cathode during CO_2ER under zero-gap, catholyte-free conditions. One expects that the anolyte concentration should not significantly impact the performance of AEM-based CO_2 cathodes, since the (an)ion conduction direction is presumed to be from cathode to anode, maintained mainly by CO_3^{2-} and HCO_3^- derived from CO_2. In contrast to this expectation, we observed that varied anolyte concentrations have substantial effects on the behaviors of zero-gap Cu-based cathodes. When using pure water or dilute alkaline anolytes, CO was produced as dominant product, while concentrated anolytes (>0.1M) directed the selectivity towards C2+ products. The parasitic H_2 evolution reaction was also influenced, being more suppressed for the dilute anolytes. Typically, selectivity trends for Cu-based catalysts are correlated to surface speciation (e.g. Cu oxidation states) and/or morphological changes during CO_2ER. To control for these possibilities, we assessed both aspects as a function of anolyte employed. Using an adapted electrochemical reactor with X-ray transparent window, we conducted operando X-ray absorption spectroscopy (XAS) to track the catalyst in the zero-gap cell under true operation conditions. The results indicate complete reduction of the oxidized Cu surface occurs for all the investigated anolytes. Additionally, ex-situ XRD and SEM characterization revealed no obvious structural or morphological changes between samples tested with different anolytes. These observations suggest the varied selectivities we see are not simply explainable by composition or morphological/structural effects. Interestingly, under certain conditions, the unintended but significant migration of K^+ cations from the anolyte to the cathode surface was observed. The amount of K^+ detected at the cathode depends on the anolyte concentration, with a threshold concentration of approx. 0.1 M KOH required before significant amounts of K^+ crossover occurs, correlating with the selectivity switching from CO to C2+ products. This strongly suggests the absence or presence of cations can be a major influencer of CO_2ER selectivity, even in catholyte-free configurations using AEMs. Moreover, cations were found to crossover even under open circuit, and therefore may be diffusing spontaneously along with water uptake by the membrane.







Computational modelling and optimisation of long-channel CO_2 electroreduction flow cells

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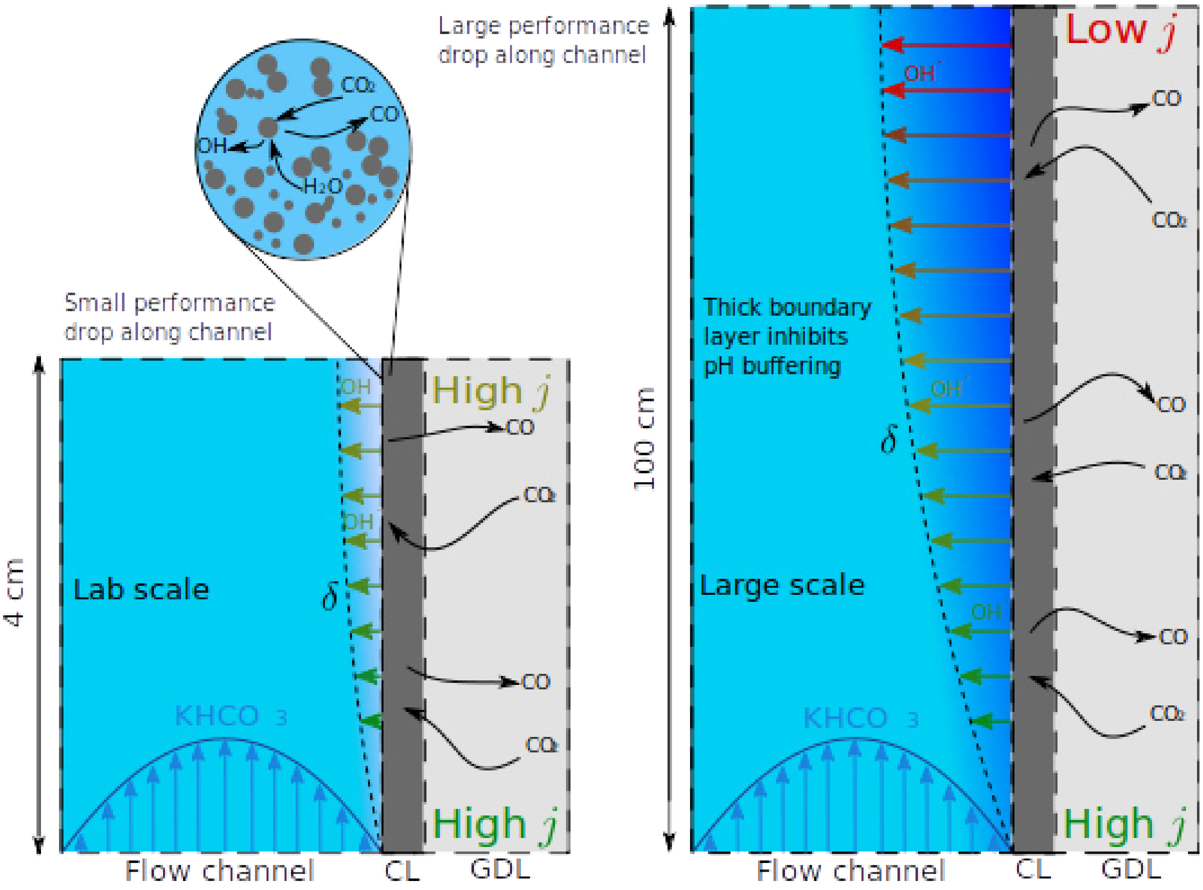
Electrochemical CO_2 reduction is a promising pathway to simultaneously addressing the problems of CO_2 emissions, defossilisation of the chemical industry, and renewable energy utilisation. However, the majority of contemporary research is performed on lab scale electrolyser with no way of capturing effects that only manifest at longer length scales. In this work we develop 2D computational models of microfluidic CO_2 reduction flow cells utilising gas-diffusion electrodes to determine how cell performance metrics like Faradaic efficiency and single-pass conversion are affected by length scale and how to preempt these issues in practice.

Tables and Figure captures*:*



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Micromodel of a gas diffusion electrode tracks in-operando pore-scale wetting phenomena

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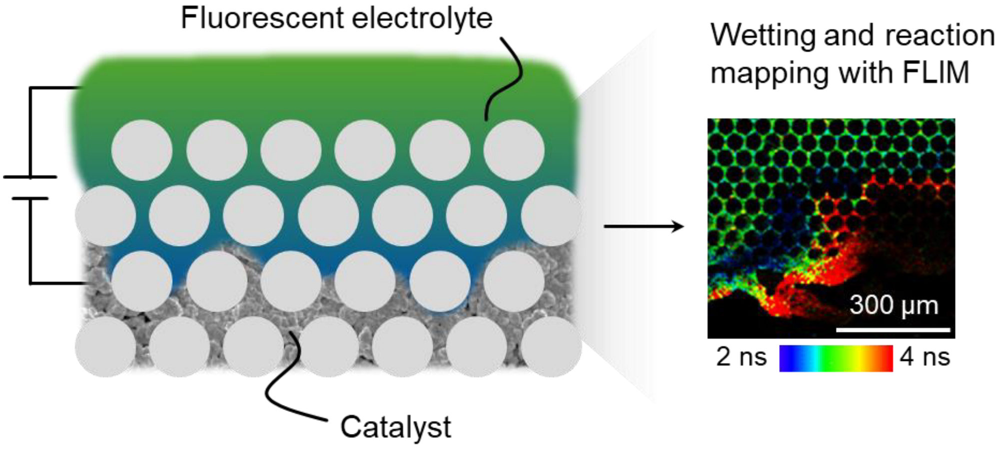

Figure 1: Micromodel of a gas diffusion electrode with combined gas diffusion layer, microporous layer and catalyst layer. Observation with fluorescence lifetime imaging microscopy (FLIM) allows for the observation of wetting phenomena such as electrowetting and reaction mapping at pore scale.

Converting anthropogenic CO2 emissions into valuable products in gas-fed electrochemical reactors using renewably generated electricity is a promising solution to reduce their impact on global warming[1][2]. However, most gas-fed electrochemical reactors suffer from an unstable long-term operation, which is often associated with the flooding of gas diffusion electrodes (GDEs) within a few hours of operation[3]. In this work, we present a microfluidic structure with multi-scale porosity featuring heterogeneous surface wettabilities to represent the behavior of a conventional GDE realistically. We established a gas-liquid-solid phase boundary within a conductive, highly porous structure. Wire electrodes and a literature-known catalyst layer composed of a silver catalyst and Nafion binder enabled the realistic reproduction of conditions at gas-liquid-solid-interfaces seen on GDE surfaces. In-operando visualization of wetting phenomena was performed using confocal laser scanning microscopy. Non-reversible wetting, wetting of hierarchically porous structures, and electrowetting were observed and analyzed. Applying a potential resulted in the destabilization of the phase boundary and resulted in flooding of the electrode. Moreover, fluorescence lifetime imaging microscopy enabled the observation of reactions on the surface of the model electrode, enabling for the first time the identification of active areas of GDEs in combination with knowledge about their wetting state. The presented results lay the foundations for optimizing process conditions for the long-term operation of full-scale gas-fed electrolyzers.

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A novel pore network model for electrolyte imbibition in gas diffusion electrodes

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The distribution of electrolyte is an important property for the performance of gas diffusion electrodes (GDE). To prevent the electrolyte from flooding of the porous electrode and prevent penetration, the GDE consists of the electrocatalyst (silver in our case) and a non-wetting material such as polytetrafluoroethylene (PTFE). Electrochemical investigations show a high impact of the PTFE content on the electrode performance [1].

The geometrical structure of the GDE's has been locally resolved by FIB/SEM imaging. Based on these inhomogeneous 3D structures detailed hydrodynamic simulations has been carried out using the Smoothed Particle Hydrodynamics (SPH) methods. This allows to track the free electrolyte surface during imbibition as well as to account for the electrowetting [2]. Fig. 1 shows snapshots of electrolyte imbibition. Considering the change in contact angle due to the electrowetting-effect [3] shows a significant change in hydrophobicity and thus the wetting properties. Nevertheless, the approach is computationally expensive and cannot be carried out in larger volumes. To model electrolyte imbibition in large volumes we therefore combined pore network modelling and rigorous hydrodynamic simulations. First, a skeletonize-algorithm is applied to create a skeleton from pore space based on FIB/SEM-images. The skeleton is then segmented from branching point to branching point. Second, characteristic material properties along these paths, pore diameter and fraction of PTFE covering the pore wall, are determined.

To carry out pore network simulations the entry pressure of each path between branching points must be known. In contrast to conventional pore network simulations the entry pressure does not only depend on geometry and **averaged** wettability in case of GDE's. In GDE's the pore diameter and the wettability changes along the pore path. Using either simplifying assumptions or more rigorous simulations by the SPH simulations, the highest entry pressure for each pathway has been determined. Incorporating this data into a pore network, the electrolyte imbibition can be modelled on representative electrode volumes.

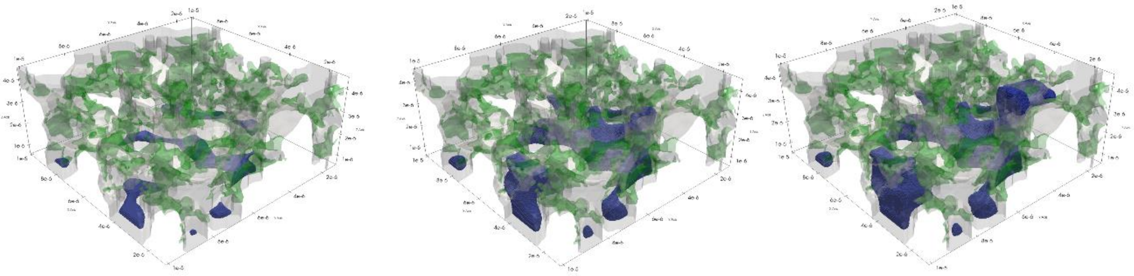

Fig. 1: *Snapshots of the Electrolyte imbibition in a 98 wt-% Silver Electrode for 0, 5 and 10µs. The electrolyte is shown in blue, the silver in grey and the PTFE in green.*

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Operando Synchrotron Imaging of Electrolyte Distribution in Silver Based Gas Diffusion Electrodes During Oxygen Reduction Reaction

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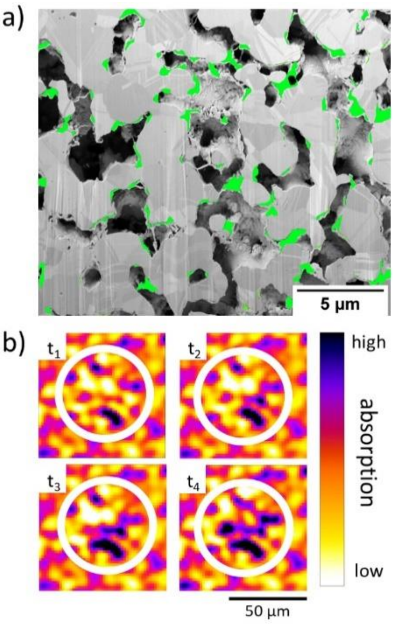

Fig. 1: *a) FIB/SEM, bright silver grains, PTFE (green highlighted) and surround-ding pore system, b) image series of a filling process of a pore system; white circles indicate analysed pore system [adapted from 4].*

Gas diffusion electrodes (GDEs) are used in many important energy converting systems like fuel cells, batteries or electrolyzers. They are complex functional materials and often the most important performance limiting factor in electrolysis. Furthermore, the high costs of silver based GDEs make them a key component of development. Understanding how GDEs are working is crucial to improve their performance, which is limited by the oxygen reduction reaction (ORR). The ORR is mainly influenced by the microstructure of the GDE (Fig. 1a), which is determining the distribution of the electrolyte within it during operation [1-2]. To analyse the electrolyte distribution in 2D and 3D operando synchrotron radiographies and tomographies of chronoamperometric measurements has been carried out under different operation parameters, like temperature, over potential and chemical composition of the GDEs. These measurements gave an insight into the integral fluctuation changes of the electrolyte and allow detailed analyses of dynamic filling processes despite their high attenuation (Fig. 1b) [3-4]. Combined with detailed microstructural analyses carried out by Focused Ion Beam (FIB) technology and Scanning Electron Microscopy (SEM), these analyses lead to a clear picture of the underlying morphology and processes. Within the framework of the DFG-Forschungsgruppe FOR 2397 the acquired data are used for simulation and modelling studies. The aim of this investigation is to obtain fundamental insights into the working mechanisms of GDE materials in general and to improve their performance in order to make them more attractive for technical applications.

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Investigating the Mass Transport in Porous Transport Layers of PEMWE using Neutron Imaging

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The counter-current transport of oxygen and water inside the anodic Porous Transport Layer (PTL) of Polymer Electrolyte Membrane Water Electrolysers (PEMWE) is not yet understood clearly. The limitations to visualise the flow inside the PTLs makes it very inconvenient to study the impact of structure on the two-phase transport. For this purpose, in this study, non-electrochemical flow cells, containing commercial titanium fibre PTLs, were used to visualise the flow phenomena with the help of in-operando neutron imaging. In this cell, the PTL is sandwiched between the water and the oxygen supply channels. As a first step, the PTLs were flooded with water to observe their water imbibition behaviour. Secondly, various flow rates of air were realized which correspond to different current densities, 2, 5, 7, 9 A/cm^2. Based on the results of Panchenko et al.[1], high stoichiometries of the water and air flow rates (100 and 150) were used. In the last step of each experiment, the cells were purged with air to study the drainage patterns. Several radiographies and tomographies were performed and the impact of different structural properties was studied by comparing the image data from PTLs with varying pore size distribution, thickness and overall porosity. One PTL (from Sylatech) had a graded pore structure. It was observed that the water imbibition and gas drainage occur in a periodic manner but the time periods vary for different structures and flow settings. The breakthrough points of gas through the PTLs were also observed to be at almost constant position for each PTL, independent of the flowrates. In addition to that, the PTL with the graded structure showed the quickest breakthrough. The experimental results are analysed based on additional information from CFD and pore network simulation.

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Influence of the Porous Transport Layer Structure on Proton Exchange Membrane Water Electrolyzer Performance

Tamara Miličić[1], Haashir Altaf[2], Nicole Vorhauer-Huget[2], Luka A. Živković[1], Thanh Vu Hoang[1,2], Evangelos Tsotsas[2], Tanja Vidaković-Koch[1]

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Green hydrogen production is one of the main focuses of sustainable economy research. One approach to achieving it is coupling proton exchange membrane water electrolysis (PEMWE) with renewable energy sources. PEMWE allows for high purity of produced hydrogen, high efficiency, and a wide dynamic range of operation, but it still faces both costs and performance challenges. When operated at high current densities, considerable voltage losses appear. A considerable part of these losses is attributed to the porous transport layer (PTL) in the anode compartment of the electrolyzer [1]. A slow counter-current transport of water and produced oxygen occurring in the PTL causes mass transport losses, while poor contact between the catalyst layer and PTL contributes significantly to ohmic losses. Thus, optimization of the PTL structure is essential for reducing both mass transport losses and contact resistance of the PEMWE.

In this contribution, PEMWE performance with commercially available PTLs was studied by employing Nonlinear Frequency Response (NFR) method that can be used for process identification and forced periodic process optimization [2]. Experimentally, forced periodic modulation of the electrical variables was imposed on the electrolyzer and frequency response functions (FRFs) of the linear (first FRFs identical to electrochemical impedance spectroscopy spectra) and nonlinear (second FRFs) part of the response were recorded. The NFR experiments were performed on the electrolyzer with PTLs of different structures that were as well characterized ex-situ using X-ray microtomography. Obtained FRFs were used for the investigation of the PTL structure's influence on the PEMWE performance. Additionally, computer-aided NFR [3] software tool was employed for the derivation of the frequency-domain model. This model allows for the further study of the influence of different operating and structural parameters on PEMWE performance.

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Transient hydrogen crossover in dynamically operated polymer electrolyte membrane electrolysis cells - a model-based analysis

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Hydrogen crossover in polymer electrolyte membrane electrolysis cells is an important phenomenon with respect to faradaic efficiency, flammability hazards, and degradation phenomena. Mass transport resistances in the cathode catalyst layer lead to supersaturation of dissolved hydrogen in the ionomer phase [1], thereby heavily increasing the hydrogen crossover flux to the anode side with current density. The hydrogen crossover flux is usually measured under steady-state conditions downstream of the gas-liquid separation and cooling of the anode outlet gas [2, 3]. However, it is important to understand the gas crossover under dynamic operation conditions, as it may result in the formation of explosive H2-in-O2 mixtures in the anode. Furthermore, it will provide new insights into the reaction and transport processes, since dynamic water electrolysis models are almost non-existent [4].

Capturing the dynamics of the hydrogen crossover experimentally is difficult due to the complex two-phase gas-liquid flow at the anode outlet. As a first step, we analyzed the hydrogen crossover with a 1-D dynamic isothermal macroscopic model. The model includes the distributed dynamic mass and charge balances in the channels, porous transport layers, gas diffusions layers, catalyst layers, and membrane, with a focus on the detailed description of the reaction and mass transport dynamics of hydrogen in the membrane electrode assembly. Dynamic changes in current density, especially large down-steps will lead to transient overshoots in the hydrogen in oxygen content at the anode side. The membrane and ionomer act as short-term mass storage for the dissolved hydrogen, and mass transport lags the instant response of the current density. This phenomenon is influenced by the pressure, temperature, membrane thickness, cathode catalyst hydrogen mass transport resistance, anode water flow rate, and the current density step size. Our results suggest that the hydrogen in oxygen content at the anode side can transiently exceed 50 % of the lower flammability limit under specific conditions. This work provides insights into transient mass transport phenomena and is a step into dynamic model-based analysis of polymer electrolyte water electrolysis cells.

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Poster Presentation

Modeling the Influence of CO_2 Concentration on Electrochemical CO_2 Reduction at Silver Gas Diffusion Electrodes

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Reducing CO_2 emissions by replacing fossil energy sources with renewable ones is an important step in the context of climate change. The electrochemical CO_2 reduction (eCO_2R) is a promising technology to support this shift, since it provides the possibility to store electrical energy in form of high value chemicals, while consuming CO_2, therefore being carbon-negative. It has been demonstrated that the use of gas diffusion electrodes (GDEs) is essential for reaching high current densities, due to the limited solubility of CO_2 in water [1]. To achieve a better understanding of the complex processes in the electrode, the description by a mathematical model is crucial. Based on a thin-film flooded agglomerate (TFFA) model developed for oxygen depolarized cathodes [2], we present a model for the eCO_2R at a silver GDE. The model accounts for electrochemical and homogeneous reactions, diffusion and migration. This enables the prediction of potential and Faradaic efficiency in dependence of the applied current density, while also giving insights into the local reaction environment. The CO_2 mass transport in the electrode is of special interest, since it is the main limitation for the Faradaic efficiency at elevated current densities. We investigated the influence of the CO_2 concentration on the potential and the Faradaic efficiency in the range from 25 to 100 vol.%, and found that the presence of carbon monoxide inhibits the performance of the silver catalyst. This effect is implemented in the model by using a modified Tafel approach for the kinetics of the electrochemical reactions [3].

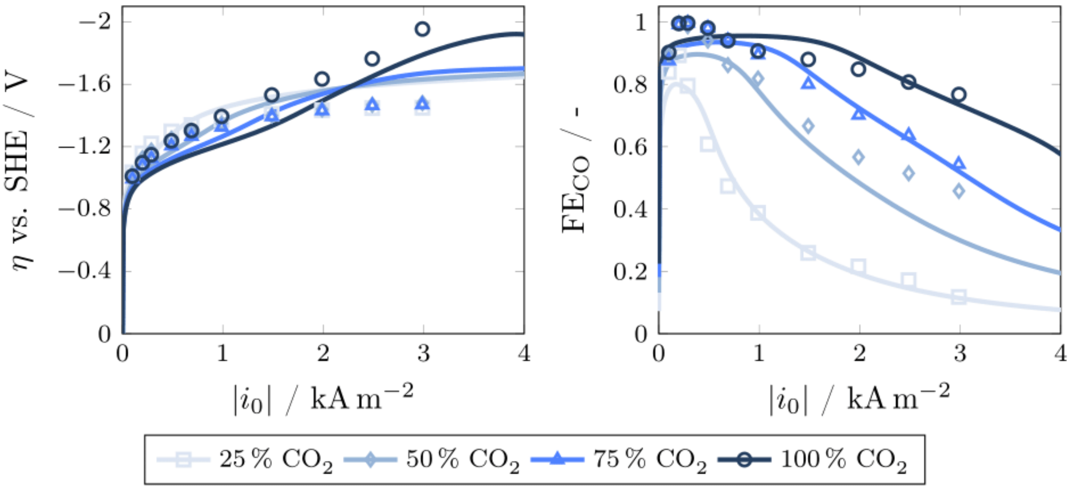

Figure 1*:* Influence of the CO_2 volume fraction on potential and Faradaic efficiency in dependence of the applied current density. The symbols show the experimental data, while the lines show the model results [3].

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Electrochemical CO_2 Reduction: Steady-state vs. Dynamic Investigation

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Electrochemical technologies, such as the carbon dioxide reduction reaction (CO_2RR) for the production of fuels and chemicals, are promising approaches for decarbonatization of energy production, conversion and storage. [1] Improvements in (electro)chemical reactions, their dominant processes and limitations require an in-depth and, above all, quantitative understanding of the reaction mechanisms, their kinetics and their charge and mass transport processes. Dynamic kinetic modelling of heterogeneously catalyzed chemical and electrochemical reactions is a key tool to understand and optimize the behavior and performance of surfaces, electrodes and cells. [2]

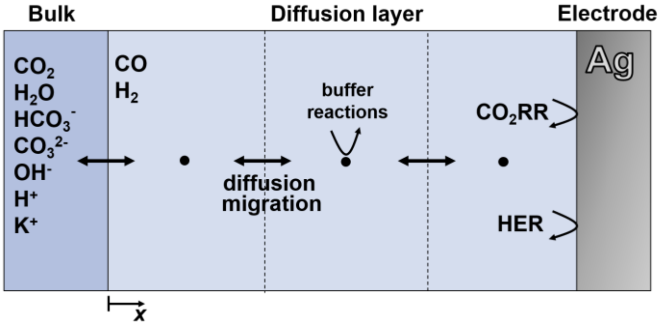

Figure 1: Scheme of dynamic model for the carbon dioxide reduction reaction (CO_2RR) at planar silver electrode with involved dissolved species, transport mechanisms in the diffusion layer, carbonatization and competing hydrogen evolution reaction (HER)

This contribution presents the first dynamic physico-chemical model for the CO_2RR at planar silver electrodes. It considers the dynamic description of reactions at the electrode surface, the transport processes in the electrolyte and the chemical carbonation reactions inside the electrolyte. Model-based analysis provides a detailed insight into the dynamics of the concentration profiles of species and mass fluxes in the vicinity of the electrode and its dependence on operating conditions.

In detail, strong discrepancies between the effect of dynamic and steady-state conditions on current-potential curves are revealed. They originate from the slow transport of reactants, which lead to a strong time dependency of the depletion and recovery of CO_2 at the electrode and a slow buffering effect of the electrolyte system. As a result, during dynamic and steady-state operation, different concentrations are present at the electrode interface and different selectivities of the reaction system follow. This results in differences in the polarization curves recorded by steady state and by potential sweeping. This effect has been largely ignored by researchers, which makes interpretation and comparison of curves erroneous. The understanding about differences and main influencing parameters enable a proper selection of the characterization method, a differentiated interpretation and comparability of experimental results possible.

This dynamic study provides a separation of slow and fast processes. This gives a detailed understanding about the time behavior of involved processes of CO_2RR and the key role of reaction kinetics, transport and carbonatization. The fundamental understanding of these interactions is a prerequisite for mastering CO_2RR in technical gas diffusion electrodes.

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Development of gas diffusion electrodes for applications in electrochemical CO_2 reduction – from laboratory to industrial scale

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In recent years, the possibility of electrochemical conversion of carbon dioxide (CO_2) into high-value chemicals has piqued curiosity, and a large number of articles have been published in this area regarding cell design, operation and catalytic activity. However, scaling up electrochemical CO_2 reduction presents numerous challenges, and there are few research papers on the subject [1]. Furthermore, development of stable and selective catalysts is one of the most important phases in realizing these technologies [2]. Literature has shown that gas diffusion electrodes (GDEs) are the best way to electrochemically convert CO_2 to formate by overcoming the mass-transport limitations of aqueous-based systems [3]. At Avantium (AVT), we are working with electrochemical cells of various sizes from 7 cm^2 to 0.2 m^2.

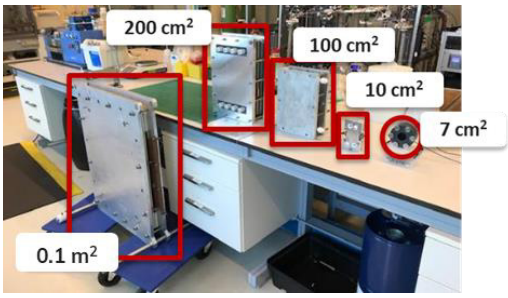

***Figure 1**: Electrochemical cells scale in two dimensions*

To tackle another complexity within the field – catalyst and GDE stability – we designed and built an automated setup which combines multiple high-throughput testing stations with identical configuration allowing for consistency in research on laboratory scale. Thus, conversion of CO_2 into potassium formate with high faraday yield was maintained hundreds of hours online at industrially relevant current densities on a GDE coated with In/Bi catalyst supported on Vulcan carbon.

A big step towards a CO_2 circular economy is recycling of industrial CO_2 into added-value chemicals, including the manufacturing of large size electrodes and electrochemical cells. Pre-pilot demonstrations of CO_2 reduction with CO_2 from real sources are currently ongoing with partners: one at a powerplant, RWE, in Germany (OCEAN) and a cement factory, Titan, in Greece (ReCODE) at commercially relevant current densities targeting CO_2 conversions of ca. 0.5-1 kg/h. We demonstrate efficient (TRL5) formate/ glyoxylic acid/ oxalate production at a scale >100 cm^2 and investigate effects of the GDE structure on electrolyte flooding, breakthrough resistance due to pressure variations between the gas/liquid phases and membrane stability over time.

***Figure 2**: Layout of the electrochemical unit for OCEAN project*

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The application of a MOF-derived FeNC catalyst on commercial GDEs for the CO_2RR

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Atomically dispersed Fe sites in nitrogen-doped carbon matrix (FeNC) have been identified as promising candidates for the electrocatalytic CO_2 reduction reaction (CO_2RR) [1]. Most reports show results obtained with conventional H-type electrochemical cells. Due to the limited CO_2 solubility in the electrolyte solution, high currents as necessary for potential industrial applications cannot be obtained.

In this work, we introduce Fe^{2+} in the matrix of ZIF-8 by a “competitive coordination” strategy firstly reported in [2]. The obtained FeNC materials were further pyrolyzed in Ar and the formation of atomically dispersed Fe sites was confirmed by STEM and EXAFS. The Fe content in the FeNC material is about 1.54 wt%. The prepared FeNC materials showed 98% FE_{CO} at -0.51 V vs. RHE in a conventional H-type reactor cell at a comparatively low current density of only 3.7 mA/cm^2.

In order to mitigate the local depletion of CO_2 and by this to achieve substantially higher current densities, the CO_2RR performance of the FeNC catalysts was evaluated after drop-coating on a commercial GDE. In a typical procedure, the catalysts and PTFE were dispersed in ethanol solution and then dropped on the surface of the commercial carbon-based GDE material. The amount of PTFE was confirmed to be sufficient to enable the formation of a 3-phase boundary during the CO_2RR [3], however, the carbon-based catalyst could not be tightly fixed on the carbon support. The addition of Nafion allowed for improved immobilization of the catalyst particles. By varying the backpressure and the ratio of catalysts, PTFE and Nafion a FE_{CO} of 94% was obtained at a current density of 20 mA/cm^2 at the very low overpotential of only -0.17 V vs. RHE.

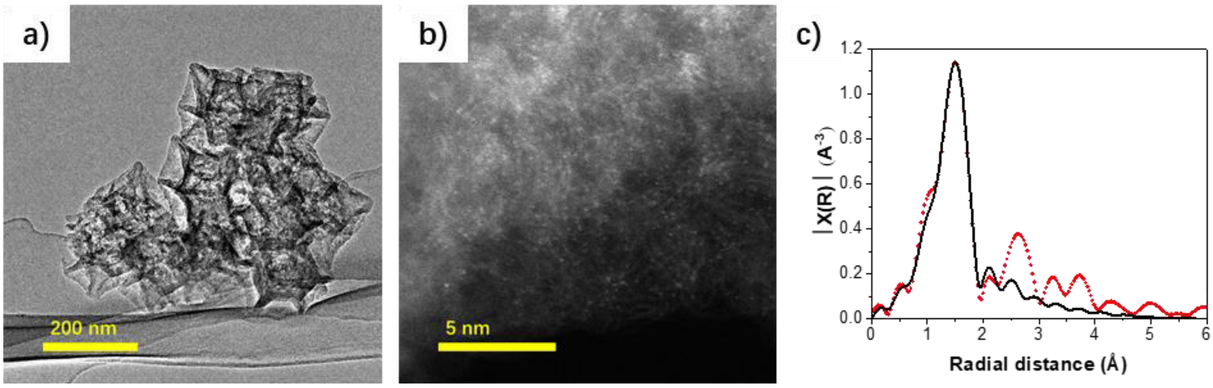

Figure 1*: a) STEM image of FeNC, b) HAADF-STEM image of FeNC, c) EXAFs results of FeNC*

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Fabrication of a CuBZnO Modified GDEs for Back-Pressure Modulated Electrochemical CO_2 Reduction

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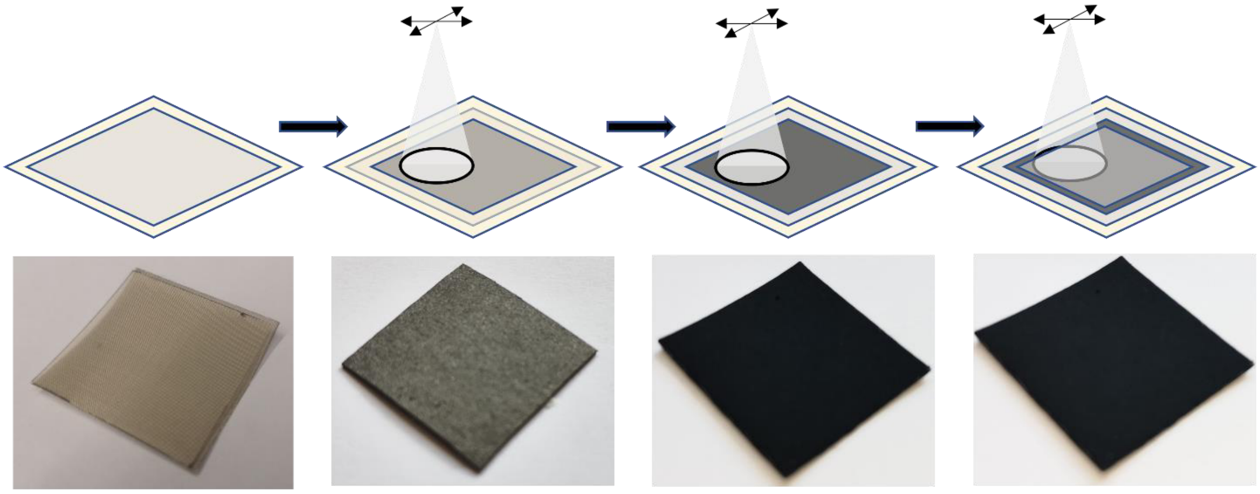
Carbon dioxide (CO_2) emitted by incinerators is a major cause of climate change. It can be intercepted and converted into value-added products through electrochemical reduction (CO_2RR) to create a closed carbon cycle economy. The electrochemical reduction of gaseous reactants on an industrial scale is successfully carried out using gas diffusion electrodes (GDE), which provide short diffusion pathways and thus high reaction rates.[1]
Besides the activity of the electrode, its selectivity for electrochemical CO_2 reduction is equally important and must be optimized to make the process economically lucrative. Reaction rate and selectivity highly depend on the used catalyst and its surroundings embedded in the GDE. For gaining additional control over parameters such as porosity, diffusivity, hydrophobicity, a Ni-gauze and PEEK-gauze supported carbon based self-made GDE was developed. Here, we demonstrate the fabrication process of this self-made GDE (Figure 1), modified with a CuBZnO catalyst[2] and its performance towards CO_2RR embedded in a flow through electrolyzer assembly. Furthermore, we investigated the influence of the applied CO_2 back pressure on CO_2RR in a measuring setup independent of the dynamic pressure changes introduced by the sample loop of the online connected gas chromatograph.



Ni-gauze + PEEK-gauze Gas diffusion layer side Catalyst layer side PTFE layer

Figure 1: *Schematic GDE fabrication process and the obtained result after each respective step.*

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Impact of Catalyst Ink Dispersion Method on Gas Diffusion Electrode Performance for CO_2 Reduction

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Electrochemical carbon dioxide reduction (CO_2R) has the potential to convert captured CO_2 and renewable electricity into valuable fuels and chemical building blocks. Products such as ethanol and ethylene can be generated at high partial current densities by using tailored gas diffusion electrodes (GDEs) along with the right process conditions[1, 2]. However, as the technology is still in the early stages of development, gas diffusion electrodes used for CO_2 reduction are not optimized for this process. A common method for making GDEs is by applying a catalyst ink consisting of a binder, solvent, and catalyst particles onto a gas diffusion layer with an airbrush[3]. To optimize GDEs for CO_2 reduction we need an understanding of how the catalyst ink preparation, dispersion and deposition affects the electrochemical performance. Here, we investigate how the ink dispersion method impacts the ink characteristics, the microstructure of the GDE, and the electrochemical performance of the electrode.

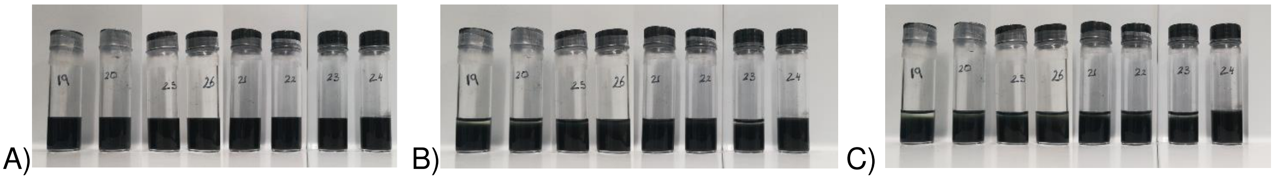

Figure 1*: Catalyst ink sedimentation using either sonication bath or sonication probe with 50% cycle and 50% amplitude listed from left to right as 20 min bath, 20 min probe, 60 min bath, 60 min probe, 90 min bath, 90 min probe, 120 min bath, 120 min probe and results over time A) 0 days, B) 2 day, C) 3 days.*

We have varied the dispersion method of a single catalyst ink formula made up of copper nanopowder, water, isopropanol, and Nafion solution. The inks were sonicated using either a sonication bath or sonciation probe for periods between 20 and 120 minutes. In addition, two soniciation probe paramaters were explored. Amplitude was varied between 20-50% and cycle between 50-100%. The sedimentation tests (see Figure 1) show that the shortest time period of both sonication bath and probe resulted in a relatively quick start of sedimentation. Likewise, the sonication probe of the longest time and intensity (120 minutes with a sonication probe) demonstrated instability. We will also show how the particle size, and viscosity are altered by sonication method and how the deposition of these inks results in differing GDE surface structures.

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Model-based Analysis of CO_2 Reduction Reaction Kinetics on Planar Silver Electrodes

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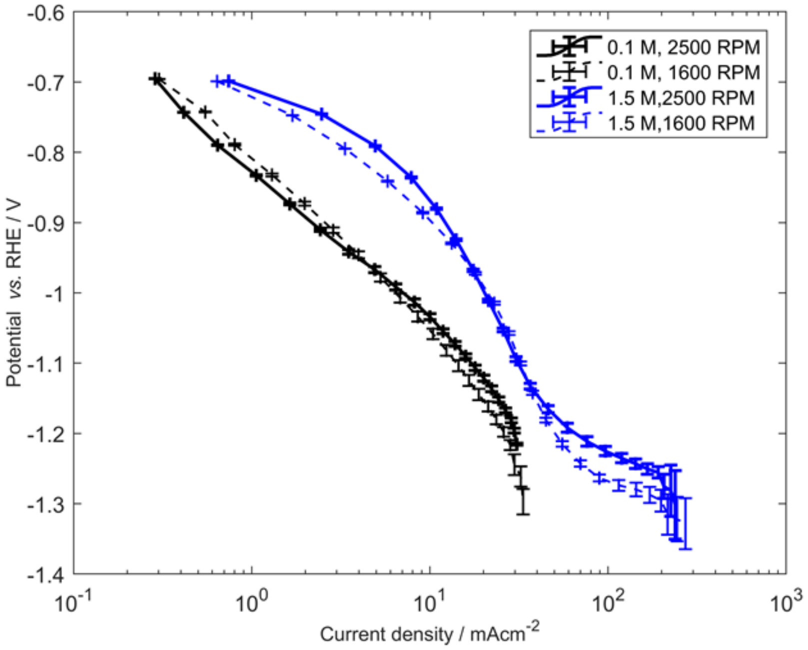
Electrochemical reduction of CO_2 (CO2RR) to value-added products is of considerable interest as a potential platform technology for storage of renewable energies in terms of chemical bonds. This helps in reducing the anthropogenic CO_2 in the atmosphere. Silver is an excellent catalyst for CO2RR as it mostly forms CO and H_2. CO is considered as the primary product and therefore it is desired to increase the CO-faradaic efficiency. It has been reported that different factors can influence product selectivity in CO2RR [1,2]. In this study the focus is on influence of buffer composition/pH and mass transport conditions on CO-faradaic efficiency. To study this effect, planar silver electrodes can serve as a good model. Steady state and electrochemical impedance spectroscopy experiments were performed using an Ag-rotating disc electrode (RDE) under different buffer concentrations and rotation rates as shown in figure (1). Additionally, the product selectivity was analysed using an Ag/Pt rotating ring disc (RRDE) electrode and Gas Chromatography (GC) set-up in tandem. The results from the experiments were used to develop a microkinetic model. The model and experiments show excellent agreement under different conditions.



Figure(1): Tafel plot for CO2RR showing the effect of buffer concentraion (black-0.1 M and blue-1.5 M) and rotation rates (full lines-2500 RPM and dotted-1600 RPM)

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Combined modelling and experimental evaluation of advanced catholyte compartment designs for improved CO_2 reduction towards hydrocarbons in flow cell electrolyzers

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This work aims to understand how electrolyte flow distribution inside a CO_2 flow cell electrolyzer affects its catalytic product formation performance using a Cu-loaded GDE during CO_2 electroreduction to hydrocarbons. Since gas molecules are produced inside the catalyst layer of the GDE and therefore gas bubbles are released into the electrolyte, an effective bubble removal capability is critical for acceptable performance. If gas bubbles cannot be removed effectively, this can result in an inhomogeneous current distribution on the GDE, which can limit the performance at industrially relevant current densities. This contribution analyses computationally, how the geometric design of catholyte compartments affects fluid flow distributions. To verify the computational predictions, a variety of distinct 3D-printed catholyte compartment prototypes were manufactured and their influence on the experimental product faradaic efficiency and production rates inside a CO_2 flow cell electrolyzer setup was investigated and compared.

Exploring the Effects of Mass Transport on the Efficiency of CO_2 Electrolysis Using a Flow Cell Setup

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Electrochemical reduction of the carbon dioxide (CO2RR) could be a key process for the establishment of a society with a reduced anthropogenic impact on the environment [1], including the possibility to recycle the CO_2 into carbon-based products using the excess of energy obtained from renewable resources.

However, one of the main obstacles for technical application is the competition of the CO2RR with the hydrogen evolution reaction (HER). The selectivity between the products, i.e. hydrogen and carbon monoxide, has been found to be influenced by many factors, as for example type of metal catalyst employed, potential applied, electrolyte concentration, pH and mass transport [2].

For investigating the latter effect on faradaic efficiency, flow cell reactors are particularly useful, since they allow to regulate the mass transfer impact. In addition, they can be easily combined with gas chromatography (GC) to quantify the product distribution at the cell outlet, as done in this work for a planar silver electrode. The reaction insights found herein are deemed useful for designing and comparing with gas diffusion electrodes, which are used for technical large-scale applications.

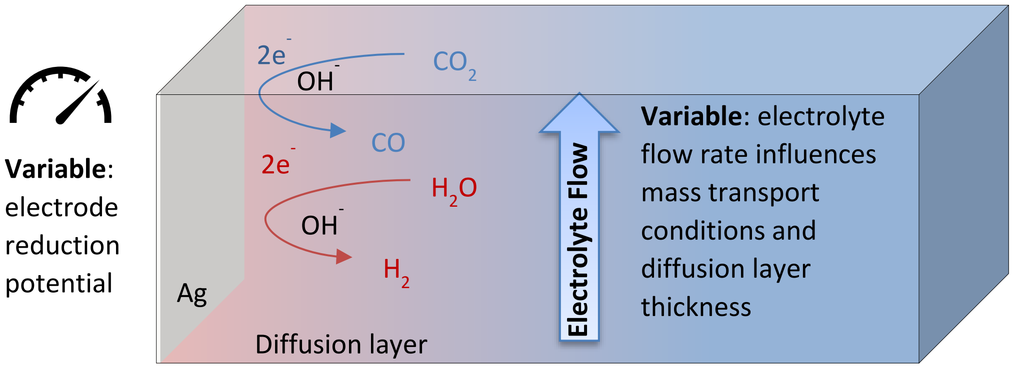

Figure 1: Schematic representation of reduction processes competing on a planar silver electrode in a flow cell

A custom flow cell was designed, that allows to use different flow promoting inserts, which were before simulated with computational fluid dynamics. Experimental evaluation of the selectivity of the CO2RR at different process conditions, i.e. potential, buffer concentration, pH and flow rates were performed and discussed.

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On the fate of selectivity in zero-gap CO_2 to CO electrolysis using Ni anodes

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Continuous electrochemical reduction of CO_2 to CO has been demonstrated with moderate success using membrane electrode assemblies (MEA) at industrially relevant current densities (≥ 200 mA/cm^2)[1, 2]. In eCO2RR to CO, Ag and Ir are the materials of choice for cathode and anode respectively. Yet the use of Ir-based anodes may be hampered by its low abundance and extreme cost. Based on the similarities with water electrolysis, a viable alternative for the anodic water oxidation are Ni-based electrodes. The application of Ni anodes in MEAs for eCO2RR is challenged by the cathodic poisoning of Ag due to the dissolution of Ni at high current densities (thus high local acidic environment) while water electrolysis doesn't suffer from poisoning due to crossover[3].

Our experiments with Ni sprayed on carbon GDE and Ni foam were very distinct. With sprayed GDE, we experienced a very unstable cell potential and a continuous and rapidly declining selectivity towards CO (starting from 50% FECO at 200 mA/cm^2). The unstable cell potential is attributed to carbon corrosion coupled with the accelerated Ni crossover that favours hydrogen evolution at the cathode (Ag, 100 nm sputtered on GDE). Though using a Ni foam circumvents the instability arising from the carbon substrate at the anode, we will show that cathodic poisoning still exists. Specifically, we observed a momentary decline in CO selectivity (around 0.75 hour) followed by complete transition to water electrolysis in around 2 hours. The XPS analysis of cathode GDE obtained before (sp1), during(sp2) and after(sp3) the initial changes in CO selectivity, as well as the analysis of the GDE after complete transition (sp4) revealed the presence of Ni only for samples originating from points sp2 and sp4 while Ni appeared to be absent at sp1, sp3. In this presentation we will present our understanding of the transient nature of GDE poisoning by Ni and provide insights into inherent process modifications that will help maintaining high selectivity towards CO even when abundant and relatively cost effective Ni anodes are utilized in eCO2RR.

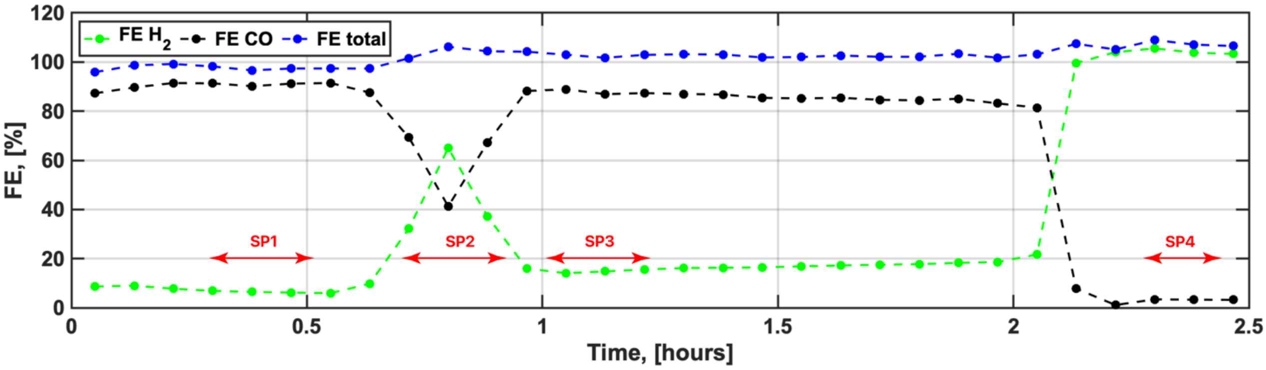

Figure 1: Faradaic efficiency at 200 mA/cm^2. Dashed lines are for visual guide.

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Optimization of the zero-gap half-cell for electroreduction of CO_2 to multi-carbon (C_{2+}) products

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The efficient electrochemical reduction of CO_2 (e-CO_2RR) to valuable energy dense chemicals and synthetic fuels such as ethylene (C_2H_4) and ethanol (C_2H_5OH) is an attractive route for enabling negative carbon emissions.[1] However, e-CO_2RR is kinetically sluggish as this reaction involves multiple coupled electron-proton transfer steps and therefore inherent large energy barriers need to be overcome. The e-CO_2RR activity and selectivity are further impacted by catalyst surface structure, CO_2 mass transport, pH and the choice of electrolyte[2]. Although the knowledge on designing electrocatalysts for e-CO_2RR exists, challenges are associated with developing CO_2 electrolyzers which are relevant for industrial operation. The reactor where the e-CO_2RR is performed influences the performance of the electrocatalyst. In this regard, zero-gap reactors (also called membrane electrode assemblies) have emerged as a technological solution in comparison to the catholyte-based counterparts where high ohmic losses, electrolyte percolation through the gas diffusion electrode (GDE) and CO_2 crossover in the form of HCO_3^-/CO_3^{2-} results in decreased energy efficiency (EE)[3]. In the zero-gap arrangement, an ion conductive membrane is sandwiched on either side with cathode and anode catalyst, acting as a solid electrolyte and product separator, and the protons required for e-CO_2RR are fed through humidified CO_2. Due to the very small inter-electrode distance, the ohmic resistance from the overall cell is significantly minimized translating in increased EE. Moreover, due to an improved water management, they can be operated at high current densities (>-500 mA cm^{-2}) while maintaining high faradaic efficiency (FE) for the target products.

To accelerate relevant testing of catalytic materials which can be identified as potential candidates for developing a e-CO_2RR technology, we aim to investigate CO_2 electrocatalysts by screening cathode electrodes in a zero-gap half-cell[4]. In this half-cell, only the cathode GDE is placed in close contact with the membrane and the counter electrode is placed in the compartment above which is filled with electrolyte. This particular design for the half-cell resembles a three-electrode setup. The influence of the electrolyzer on the activity and selectivity for e-CO_2RR will be studied by optimizing parameters such as the electrocatalyst to be used, the mass loading, the electrolyte and its concentration, the relative humidity on the cathodic side, and CO_2 flow rate. Moreover, the flexible architecture of this cell allows us to reconfigure different GDEs and anion-exchange membranes (AEM) which will be employed to achieve enhanced e-CO_2RR to C_{2+} products.

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Tuning pH profiles in Gas Diffusion Electrodes for Formic Acid Production

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In a previous study carried out at the Institute of Technical Chemistry, University of Stuttgart [1], electrochemical reduction of CO_2 was studied with acidic electrolytes. Single layer gas diffusion electrodes based on the ODC technology of Covestro [2] were applied consisting of PTFE and tin oxide supported on carbon black. Numerical simulations were conducted to get the pH profiles inside the GDE. The simulations showed that, regardless of electrolyte pH, there are alkaline conditions in the reaction zone of the GDE. In the end, it was concluded that a zero-gap anode can provide the protons to the electrolyte and keep it acidic, whereas in the reaction zone alkaline conditions are maintained. By working in acidic condition bicarbonate/carbonate ions can diffuse or migrate into the acidic bulk catholyte, where they are protonated to carbonic acid which decomposes to CO_2.

Considering the results of the previous study, in the current project funded by BMWi (81033805) electrochemical reduction of CO_2 to formic acid under acidic condition using a zero-gap anode and an optimized GDE cathode is further investigated. In this study bismuth oxide nanoparticles, which are more stable [3], will be used as catalyst. Bismuth oxide nanoparticles are expected to further enhance the geometrical current density in GDEs [4]. For more sustainable formic acid production, GDEs with extra layers will be used in order to control pH gradients and protect the reaction zone against the acidity of the bulk electrolyte. Numerical simulation will be carried out to estimate the pH of electrolyte inside the GDEs as well as to optimize thickness of the protective layer on GDEs. An electrodialysis unit will be used to separate the products and recirculate the electrolyte back to cell.

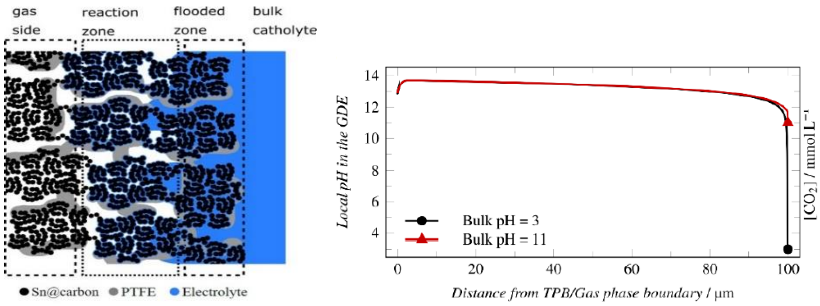

Figure 1. Schematic view of the zones formed inside the polarized GDE & Predicted pH profiles within the flooded and reaction zones of the GDE

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PTFE degradation and morphology investigation in Gas Diffusion Electrodes after electrochemical performance

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PolyTetraFluoroEthylene (PTFE) is a fluorocarbon-based polymer belonging to the oliefins class of polymers. Due the usual high physical and chemical stability under very harsh environmental and experimental conditions, PTFE is major applied where properties such electrical insulation, mechanical strength and surface protection (lubricity and nonstick e.g) are required[1]. The intermolecular forces due to the fluorine atoms oriented along the chain with helical conformation provide a shielding effect that leads to chemical inertness and hydrophobicity[2]. PTFE has been recently applied in gas diffusion systems (GDE) ensuring that the pore wall of the electrode will selectively act upon the gas passage and not be blocked by the aqueous solution during the cell performance[3]. Despite the good performance of the electrodes, the real stability of the polymer throughout the NaOH electrolyte penetration process still needs attention. Hence, we examined the silver-based gas diffusion electrodes with 10 wt% and 2 wt% of PTFE before and after electrochemical tests. For a clear understanding of what was the most important parameter on PTFE instability, we investigate also the influence of parameters such temperature, time and voltage potential. Thermogravimetry analyse coupled with mass spectroscopy (TGA-MAS) shows that all samples present two secondary mass loss temperature (85°C and 380°C) below the PTFR thermal degradation temperature (550 °C). The first degradation is accompanied by the emission of OH and Oxygen ions. Differential scanning calorimetry (DSC) confirmed that before this temperature degradation, samples present an endothermic peak transition characteristic of water bonded salt solution evaporation, indicating an accumulation of electrolyte in the polymer channels. Infrared spectroscopy (FTIR) reveals the presence of carboxyl group (signet at 1700 cm^{-1}) formed as a sub product during the electrolyte penetration. Raman spectroscopy was able to identify polymer debris in the electrolyte side, possible caused by the electrolyte penetration and a significant reduction of crystallinity of PTFE in the gas side, especially decreasing with the time. Furthermore, Raman shows a peak associate with the sodium carbonate (Na_2CO_3) at 1080 cm^{-1} that agrees of FTIR results. These results together shows that the PTFE is sensible to the electrolyte penetration over the electrochemical tests and gives a little description how the interface are changing during the process. It's very clear that the electrolyte solution retention lead to a degradation of the polymer and the gas permeation promote the, so to speak, amorphization of the crystalline polymer, probably due to the interaction between the gases and the fluorine, promoting a disorganization of the polymers chains.

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Determining the electrochemical active surface area of fuel cell catalyst layers in a gas diffusion electrode half-cell setup

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In recent years, gas diffusion electrode (GDE) half-cell setups have attained increasing interest to evaluate the performance of realistic fuel cell catalyst layers.[1-3] As a bridge between research on a catalyst material level and on a full cell level, GDE half-cell setups enable electrochemical characterization of catalyst layers on a component level at relevant mass transport condition while maintaining the comparability, rapidity, and simplicity of conventional three electrode testing.[4] Thereby, the determination of the electrochemical active surface area (ECSA) is inevitable to evaluate and compare the intrinsic activity and stability of different electrocatalysts as well as its utilization in catalyst layers. Different methods were used in GDE half-cell setups to derive the ECSA, yet a detailed comparison is missing.[1-4]

To allow a rigorous comparison and discuss the applicability of these methods in GDE half-cell setups, here we compare results from underpotential deposition of hydrogen (H_{upd}) and copper (Cu_{upd}) as well as CO-stripping in acidic and alkaline electrolyte for Pt and PtRu-alloy containing catalyst layers (Figure 1). Thereby, we have found comparable results for CO-stripping and Cu_{upd} presenting them both as suitable method to derive ECSA. Additionally, the application of Cu_{upd} offers the possibility to derive electrochemically the elemental surface ratio in PtRu-alloy catalysts. By discussing advantages of each method, we hope to guide future research to rigorously determine ECSA and, hence, the intrinsic performance of fuel cell catalyst layers.

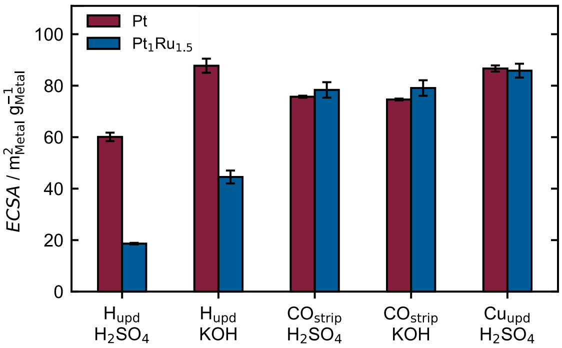

Figure 1: *Derived values for the ECSA using different methods and electrolytes for Pt and PtRu supported on high-surface area carbon containing catalyst layers. Error bars are indicating the standard deviation of two independently measured samples.*

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Efficient Methods to Characterize the Morphology of Highly Porous 3D Metallic Foam Electrodes

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3D porous metal foams can be used as tailored model electrodes in gas-consuming electrochemical reactions, such as the oxygen reduction reaction (ORR) and the CO_2 reduction reaction (CO_2RR). They offer a self-supported structure, an enlarged surface area by continuous hierarchical pore systems and high mass transfer coefficients[1, 2]. One efficient way to produce these foam electrodes is the Dynamic Hydrogen Bubble Templation (DHBT) method by Shin et al.[3]. With this approach, metal foam electrodes can be produced within seconds. At sufficiently high negative potentials, the hydrogen evolution reaction (HER) will occur simultaneously to metal deposition. Numerous hydrogen bubbles at the substrate surface work as a dissolving negative template, forming macro-porous layers and nanoscale interconnecting foam walls [4–6]. This method is also a very promising approach to decorate hierarchically structured metal films onto conductive gas diffusion layers to manufacture highly porous gas diffusion electrodes (GDE).

To fully evaluate the complex structure of DHBT-synthesized foams on the macro and nanoscale attempting for a semi-quantitative description, this work aims to shed light on Ag model electrodes. We provide a selection of methods to analyze the two-scale morphology of these highly porous electrodes qualitatively and quantitively demonstrating that conventionally used methods are not enough to show the complete picture. By using the Laser confocal scanning microscopy (LCSM) technique, 3D information by line-scans was converted into 3D information and a calculated macro porosity of the foam electrodes. Adding morphology analysis by Focused Ion Beam tomography, the pore size distribution of the nano-porous foam walls was obtained (Fig. 1).

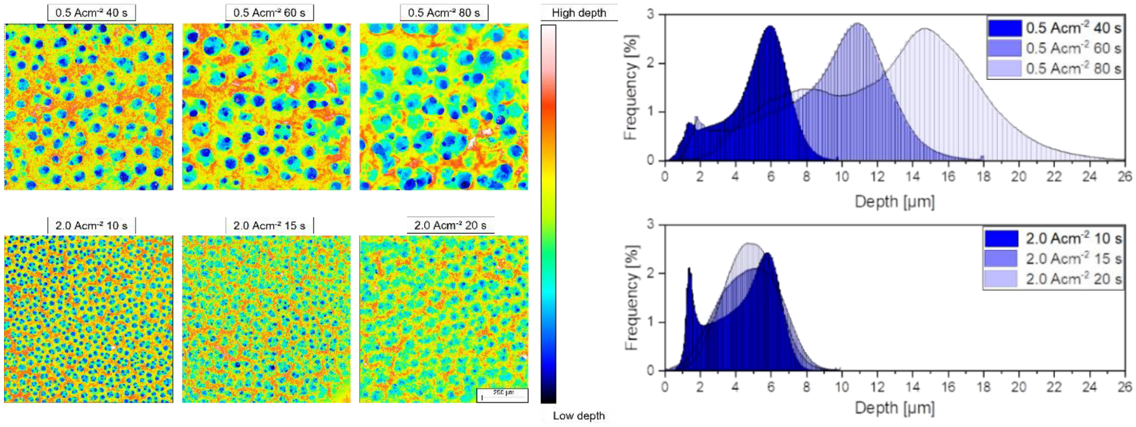

Figure 1: Coloured 2D LCSM images of the tested samples with high (red to white) and low (blue to black) pore depth (left) and distribution of the pore depths of the macro-pores of all tested samples (right).

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Predictive, Multiphysics simulation of effective electrical conductivity, permeability, porosity, and specific active area of Gas Diffusion Electrodes (GDE)

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The conversion of carbon dioxide into valuable fuels has attracted in recent years due to reduced emissions and fuel production capability. Whereas, due to its low solubility and diffusivity, systems using dissolved CO_2 lead to low Faradaic efficiency, and ineffective CO_2 utilization. As a result, the electrode current density is far below what is economically viable. Gas diffusion electrodes (GDEs) are able to deliver orders of magnitude greater current densities compared to conventional electrodes [1]. The low conductivity of reactant flow compared to carbon makes it difficult to predict their properties simultaneously. Moreover, its complex structure makes it even more difficult to predict its properties [2]. The configuration of the porous electrode can strongly influence the mass transfer in this multiphysics system. Thus, improving the microstructure and nanostructure design requires a thorough study of the interaction of nano- and mesoscale physical phenomena.

The electrical and hydrodynamic performance of a model including carbon particles is studied using numerical simulation and coupling fluid dynamics and electrical/ionic charge transport. Three different models are shown in Figure 1a, Figure 1b shows the velocity and streamlines of reactant flow for models, and Figure 1c shows the electrical current density distribution inside each model. Detailed results for each configuration are presented below the figures. By increasing the volume fraction of solid particles the electrical conductivity is increased. However, the porosity and permeability of the solid particles are decreased, which means the availability of reactant flow to active surfaces is limited.

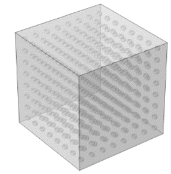
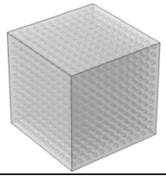
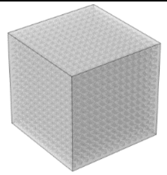
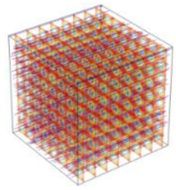
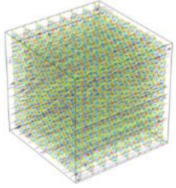
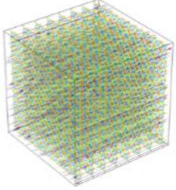
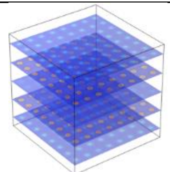
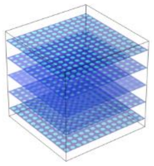
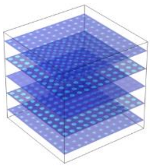
a			
b			
c			
Porosity	0.965	0.884	0.81
Permeability [1 m^{-2}]	5.95×10^{-3}	9.67×10^{-4}	3.98×10^{-4}
Specific active area [1 m^{-1}]	2.1626	7.95	13.695
Effective electrical conductivity [S/m]	273.53	575.83	915.43

Figure 1. (a) Configuration of different case studies, (b) contour of velocity and streamline, and (c) contour of electrical current inside the models

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Probing the activity and stability of oxygen evolution electrocatalysts using a modified GDE setup

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Since their introduction, gas-diffusion electrode (GDE) half cells were used over the last decades for benchmarking different electrochemical reactions. [1,2] In particular, GDEs have proven to be excellent systems to characterize electrocatalysts for CO_2 and oxygen reduction reaction (CO2RR and ORR) at elevated, application-relevant current densities as they mitigate reactant mass transport limitations. [3,4] However, GDE half cells have rarely been employed for another very important electrochemical reaction, namely the oxygen evolution reaction (OER) taking place during water electrolysis. [5] Regardless, GDE half cells might be used to elucidate why the high activity and, most importantly, the lifetime some advanced OER catalysts show in aqueous model systems was not yet translated to applied systems. To bridge this knowledge gap, our study evaluates the usage of GDE half cells towards the investigation of OER catalysts.

To determine the influence of the reactant and porous transport layer (PTL) on the measured OER activity, both humidified argon and liquid water were used as a feedstock, being supplied to the backside of a carbon gas-diffusion layer (C-GDL), as well as a titanium PTL supporting the catalyst layer (CL). Only with the combination of a hydrophilic Ti PTL and membrane, using liquid water as reactant, high current densities up to 1.5 A cm^{-2} were reached, while avoiding flooding with acidic electrolyte.

After assessing the GDE half-cell's applicability towards the OER, CLs consisting of different Ir-oxide based catalysts were prepared via spray-coating, and electrochemically evaluated. Catalysts based on amorphous IrOx showed higher activity at kinetically dominated as well as application-relevant, elevated current densities, compared to crystalline IrO_2 supported on TiO_2. Additional offline ICP-MS measurements corroborate the trade-off between activity and stability seen for different Ir-oxide based OER catalysts. [6] In conclusion, comparison to full cell measurements confirm the feasibility of our GDE setup to achieve application-relevant current densities. We thus believe that GDE half cells can be an asset for realistic benchmarking of OER catalysts before being used in full cell systems.

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Electrochemical characterisation of the ORR in realistic catalyst layers with a GDE

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The activities of advanced fuel cell catalyst materials achieved in an ideal rotating disk electrode (RDE) environment are often extremely promising but can frequently not be transferred to technologically relevant membrane electrode assemblies (MEAs). This can mainly be ascribed to a non-optimal catalyst layer structure, which significantly affects the management of educts and products in the catalyst layer during the oxygen reduction reaction (ORR). Therefore, the structure of the catalyst layer has enormous potential to significantly improve the performance of these systems in MEA. However, it has to be optimized for each individual catalyst system. Currently, MEA experiments have to be employed for catalyst layer optimization.[1] However, such investigations are time consuming, expensive (large quantities of catalyst and extended test equipment needed) and do not allow independent investigation of either cathode or anode catalyst layer. In order to accelerate catalyst layer optimization screening, the gas diffusion electrode (GDE) half-cell setup for investigating realistic catalyst layers was recently proposed.[2]

In a Pt loading study, it was previously shown that similar performance trends compared to MEA experiments can be achieved.[2] In the present work, we introduce advanced electrochemical characterization methods, such as *Oxygen Transport Resistance*[3, 4] and *CO-Displacement*[5], which have been developed for MEA technique, to the GDE method. By using a commercial Pt on Vulcan catalyst system, we investigate the impact of Nafion loading on the electrochemical performance. The results show, that high ionomer loadings lead to severe O_2 mass transport limitations, whereas for small loadings, lower ionomer coverage are measured. Both result in a significant performance loss at high current densities. Therefore, an intermediate ionomer loading which forms a thin layer of ionomer leads to an optimal performance for the Vulcan carbon support.

This work demonstrates that advanced electrochemical methods can also be applied to GDE setups to shed light on the optimal composition of the triple phase interface of catalyst layers. This is an innovative step for the future to efficiently optimise catalyst systems and to gain fundamental insight into the understanding of catalyst layers.

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Optimisation of Gas Diffusion Electrode for Alkaline Fuel Cell with Liquid Electrolyte

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Alkaline fuel cells (AFC), utilizing concentrated liquid KOH electrolyte as separator of electrode compartments, represent the first practically usable device of this kind. However, in the last decades most of the attention was paid to the alternative type using proton exchange polymer membrane (PEM) as separator of electrode compartments. PEMFC offers, among the others, the advantage of the simpler operation as no liquid electrolyte has to be circulated through the cell. On the other hand, due to the stability issue, expensive Pt catalysts are almost exclusively used in order to enhance the performance of the PEMFC. High price of PEMFC thus slows down their commercialisation.

Alkaline environment offers the possibility to use cheap non-Pt catalysts. This represents the reason for growing interest in AFCs. In alkaline environment, the anion-selective polymer membrane can be used to separate electrode compartment and ensure the ionic contact. Significant improvement in the performance of the alkaline membrane fuel cells (AMEFC) has been achieved since 2006 [1], however, the long term stability of AMEFC is strongly limited [1]. This is due to the drying-out of the anion-selective polymer membrane at the cathode side, which leads to the nucleophilic attacks of functional groups by OH^- ions [2]. AFC using liquid electrolyte represents the simple solution of this issue.

The crucial part of AFC is represented by the gas diffusion electrode (GDE). The role of GDE is to establish contact of the gaseous reactant with electron and ionic conductors (i.e. three-phase boundary). The properties of the GDE thus must be tuned to achieve three-phase boundary of maximal area and prevent the flooding of the catalyst layer. This is the role of the polymer binder in the catalyst layer. Polytetrafluoroethylene (PTFE) represents the most spread material for this purpose. The reason lies in its excellent chemical stability and hydrophobicity.

In this work, we firstly optimize the content of the PTFE in catalyst layer with respect to amount of the catalyst HiSPEC 40 wt. % Pt/C. In the next step, NiCoSe based catalyst was used on cathode as possible replacement of the Pt/C catalyst.

The results shows that higher PTFE content has negative impact on the AFC performance, however, it increases its stability. In order to achieve reasonable stability of the AFC during continuous operation, it is necessary to use at least 40 wt.% PTFE in catalyst layer. Despite the fact that NiCoSe based catalyst showed promising results, its performance is lower when compare to Pt/C catalyst.

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Investigation of PEMFC Multiphase Transport in Cathodic Gas Diffusion Layers Using a Co-Simulation Concept

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Polymer electrolyte membrane fuel cells (PEMFC) convert energy, which is stored in fuels to electrical energy, whereby the running redox processes are separated with an ion exchange membrane. A central challenge in optimizing PEMFC performance is the supply of the catalyst layer with gaseous fuels or oxidants and the removal of formed liquid products like water in the gas diffusion layers. For optimizing gas diffusion layer structure, on the one hand experimental assessment, on the other hand modelling the multiphase transport are needed to gain fundamental insights. Here, a concept for a co-simulation of detailed multiphase transport within a representative element of the gas diffusion layer coupled to an overall 1D simulation of the membrane electrode assembly (MEA) of a low temperature PEMFCs operated with hydrogen as fuel is introduced. A fast, 1D model of a MEA based on the groundwork of Vetter and Schumacher[1], is thus linked to a detailed multiphase transport model using the hybrid interface resolving two fluid model approach from Marschall and Hinrichsen.[2]

Methods

The co-simulation consists of three parts. First, a very fast, transient and one dimensional model for fuel cell performance is implemented. This pseudohomogenous approach accounts for electric losses in electrode and electrolyte, temperature profile, mass transport due to Fick-diffusion mechanisms and the water management in the membrane as well as in the gas diffusion layers. For the anode and cathode kinetics, Butler-Volmer equation is employed. Within this simulation a potential scan from the electrode potential (Nernst equation) to 0 V and the calculation of the resulting current density is realized. The resulting polarization curve shows all domains from kinetic losses at high potential, over the resistance losses due to mass and heat transfer, up to the mass and heat transfer limitation at low potential.

Next, a modelling approach for multiphase flow is implemented. In this hybrid interface-resolving two fluid model by Marschall and Hinrichsen[2] the two-phase flow features are grouped in unresolved and resolved portions, like it is known from large eddy simulation for turbulence modelling, which leads to a stable method. This approach will be used to model two phase flow in cathodic gas diffusion layers in a PEMFC and investigate gas diffusion layer structure.

The third part is the connecting process. Linking the two solvers with preCICE[3] enables us to let them communicate with each other and exchange parameters, data mapping or coupling schemes for each time step. With that, a combined model for investigation of two phase flow in gas diffusion layer with a relative low calculation time can be achieved.

Results

Currently the 1D model has been successful implemented and validated in Comsol Multiphysics® and parameter variations to study transport and kinetic influences on fuel cell performance has been done. The model is translated currently to FOAM-Extend and validated against the Comsol model. Linking via preCICE the 1D Model in FOAM-Extend with the existing two fluid model will be carried out with simple model 3D mesh structures.

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Microfluidic PEM Water Electrolyzer Cell to Investigate the Two-Phase Flow in the Anodic Pore-Network Structure

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Abstract

Driven by the political and societal endeavors to drastically reduce CO_2 emissions in several sectors within the next decades, such as in the transport or the industrial production sectors, the substitution of fossil fuels by "green" hydrogen is widely considered. Electrochemical splitting of water inside polymer electrolyte membrane water electrolyzers (PEMWEs) is one possibility for efficient and sustained production of "green" hydrogen.

In this work, a prototype model of a novel microfluidic PEMWE cell for experimental examination of the two-phase flow inside the anodic PTL is presented. The cell is made of transparent PMMA (Poly-Methyl-Methacrylate) to allow monitoring of the fluid flow. The anodic PTL is represented by a quasi-2D pore network with uniformly distributed pore sizes, similar to previous work (1,2). However, in contrast to previous works, the microfluidic device is realized as a complete electrochemical cell. Thus, the gas phase is not injected at a discrete point but generated at an electrically activated catalyst coated membrane with iridium ruthenium oxide on the anode side and carbon-supported platinum on the cathode side. Platinum meshes were used as current collectors on both sides.

The microfluidic electrochemical cell is used to study the correlation of gas-liquid invasion patterns in dependence of the applied current densities and stoichiometry of flow rates. In contrast to more advanced measurements, like operando neutron imaging (3), the simplified quasi-2D structure allows studying the invasion profiles directly. In addition, a very easy comparison of the experimentally recorded profiles to simulation results, e.g., from Lattice Boltzmann simulation (4), is possible via simple image processing algorithms.

Keywords: microfluidic PEMWE cell; anodic porous transport layer (PTL); counter-current transport; invasion regimes; current density; pore-scale physics, Lattice Boltzmann simulation.

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Distribution of Relaxation Times as a Diagnosis Tool for Polymer Electrolyte Membrane Electrolysers

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Hydrogen plays a central role in the energy transition and it is an excellent storage form for the energy generated from the renewable energy systems. In that regard, water electrolysis is a favourable hydrogen production method and Polymer Electrolyte Membrane Electrolysers (PEMEL) are of particular interest due to its high-power density, high-pressure operation possibility and partial load capability.

To improve the performance of these PEMEL cells it is necessary to understand the different loss processes. To identify and quantify these processes, electrochemical impedance spectroscopy (EIS) can be used, which has already been proven to be applicable for the characterization of electrochemical systems such as fuel cells and electrolysers. In general, EIS can be used to distinguish between physicochemical processes with different time constants. However, it remains challenging to distinguish the different processes overlapping in the frequency domain and to identify the underlying physicochemical mechanisms. To resolve the polarization processes and set up physicochemical meaningful models systematic and comprehensive parameter variations combined with high resolution deconvolution techniques are required. A valuable diagnosis tool, which gives direct access to the quantities of interest in the measurement data by providing a higher resolution in the frequency domain is the distribution of relaxation times (DRT) [1]. The benefits of this approach have been successfully demonstrated for fuel cells and lithium-ion batteries [2-4].

For the first time, we will present this approach for PEMEL. Impedance measurements in a frequency range of 100 mHz to 100 KHz have been conducted. The impedance data quality was ensured by Kramers-Kronig validity test [5]. To eliminate lateral gradients in temperature and current density, small active electrode areas and high water flow rates are used. Hence, we can achieve a homogenous operational state over the entire cell area during one measurement, which sharpens the peaks in the DRT and increases the resolvability of individual processes in the impedance spectrum.

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The performance of different iron compounds in gas diffusion electrodes for a novel alkaline water electrolysis process

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Clean hydrogen is one of the key areas in the European green deal for the decarbonisation of the industry [1]. Hydrogen production via alkaline water electrolysis (AEL) is particularly economical due to the use of low-cost materials [2]. A new hybrid AEL concept with only one electrolyte cycle, a zero-gap assembly and the use of gas diffusion electrodes (GDE) to reduce the cost even further was proposed by Koj et al. [3]. These authors integrated iron into nickel GDEs using nickel particles, hydroxyethylmethyl cellulose, polytetrafluoroethylene (PTFE), water and iron (II) acetate. In combination with their hybrid AEL concept those GDEs reached similar performance as a classical AEL cell up to current densities of 400 mA cm^{-2} [3].

Since iron (II) acetate is an expensive iron compound, we evaluated iron (II) lactate and iron (II) gluconate alternatives. Additionally, a combination of iron (II) lactate and iron (II) gluconate was tested as well to try to combine their advantages. The main difference between these three iron sources is their solubility and molecular weight. The ratio of integrated iron to nickel differs depending on the molecular weight of the iron compound. Thus, we produced GDEs with a constant ratio of iron compound to nickel and GDEs with a constant ratio of molecular iron to nickel.

In this work, the influence of different iron sources was investigated at constant iron contents of 2 wt.% and 6 wt.%. It was shown that the physical properties of the GDE change with the iron source and the iron content within the GDE. Thus, a comparison with the results of Koj et al. [3] is possible for the physical and electrochemical measurements. Electrochemical techniques showed that the GDEs with 2 wt.% iron have an overpotential of about 246 mV at 10 mA cm^{-2}. The comparison of linear sweep voltammetry scans showed that the GDEs with 2 wt.% iron have an improved electrochemical activity. We demonstrate that a cheaper iron source can achieve a comparable electrochemical performance to that of the GDEs from Koj et al. [3]. However, additional improvements can still be realized by variation of the hydroxyethylmethyl cellulose and PTFE content or by further increasing the iron nickel ratio in the GDE.

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Scale-up of microbial fuel cells using large-area gas diffusion electrodes

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Energy-efficient and resource-conserving water management can make an important contribution to the energy transition in future. Due to their ability to purify wastewater and generate electricity at the same time, microbial fuel cells have increasingly become the focus of research [1]. Microbial fuel cells enable direct energy conversion from chemically bound energy in raw sewage into electrical power. With this technology, exoelectrogenic microorganism are cultivated on the anode, which metabolize the organic substances in the wastewater and thereby release electrons. These electrons reach the cathode via an external circuit, where atmospheric oxygen is reduced. For the large-scale application of microbial fuel cells, a number of challenges still have to be overcome. The focus is on improving cell performance and reducing costs [2]. One way to save costs when scaling up is to use gas diffusion electrodes since proton exchange membranes and a cathode chamber are not required. Moreover, the mass transfer of oxygen is optimized because gas diffusion electrodes use oxygen directly from air, which means that no additional energy is required to aerate the wastewater, which is the electrolyte. The goal of this work is the development and demonstration of an energy-efficient bio-electrochemical wastewater treatment plant on a technical scale for approx. 300 population equivalents using gas diffusion electrodes. For this purpose, a manufacturing process for large-area gas diffusion electrodes and a reactor concept using them were developed.

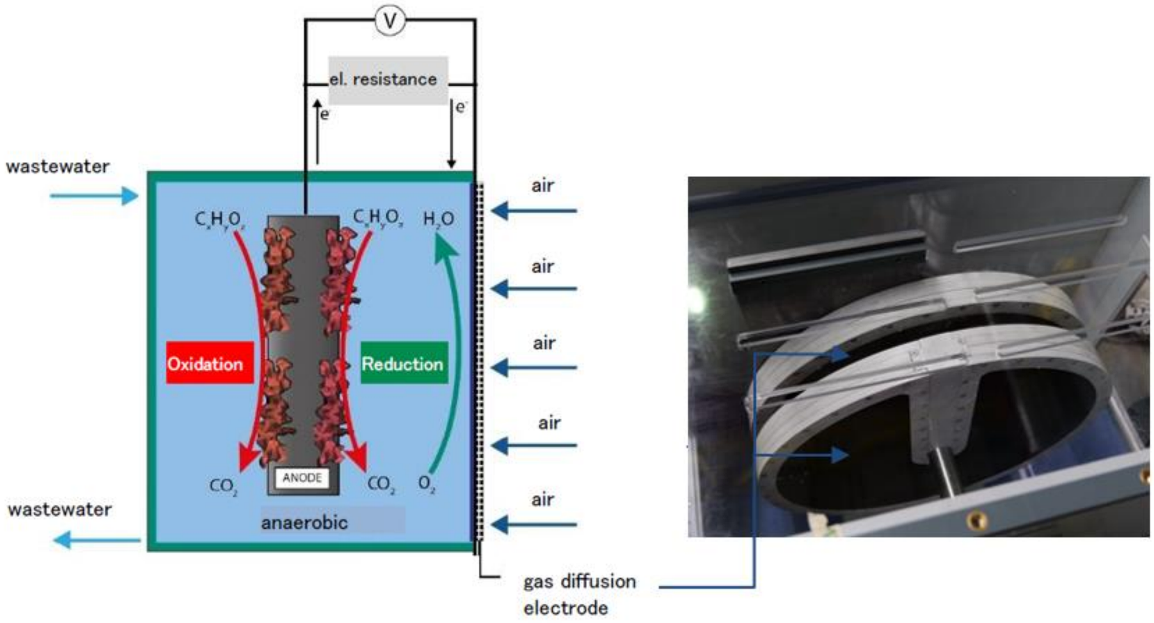

Figure 1: *Functional diagram of a microbial fuel cell (left) and reactor construction as a stack with four gas diffusion electrodes for scale-up (right)*

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Carbon monoxide electroreduction in catholyte-free gas diffusion electrolysers: Overcoming operational challenges and developing operando methods

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Closing the anthropogenic carbon cycle by valorizing CO_2 using electrochemical means has shown considerable promise under laboratory conditions but there are system level challenges hindering industrial application. Studies showing high production rates of C_{2+} products at low overpotentials, are conventionally carried out in alkaline conditions under which the loss of OH^- and CO_2 due to the CO_2/CO_3^{2-} equilibria results in low single pass CO_2 conversion yields.[1] Breaking the CO_2 to C_{2+} reaction into two subsequent cascade reactions; $CO_2 \rightarrow CO$ and $CO \rightarrow C_{2+}$ in different reactors tailored to each reaction is a possible solution, since $CO_2 \rightarrow CO$ doesn't require alkaline conditions for industrial scale reactors, and CO doesn't have the CO_2/CO_3^{2-} equilibria problems that persist with electrochemical carbon dioxide reduction (CO_2R). Most current studies on CO_2R employ GDE cells with flowing liquid catholyte which imply higher cell resistances than catholyte-free electrolysers. Industrial applications would require shifting to catholyte-free electrolysers to minimise total cell voltages and improve the energy efficiency of the cell.[2] Changes in cell configuration and geometry are shown to have a huge impact on the cell performance therefore it is essential to carry out testing in cells that are scalable for industrial application with minimal changes. In our approach we carry out *CO electroreduction* under alkaline conditions using *catholyte-free zero-gap electrolysers* to overcome challenges associated with CO_2/CO_3^{2-} equilibria and scalability of electrolysers. It was observed that using a Cu-based electrode in the same configuration used for effective CO2R but fed instead with CO, resulted in 80% FE towards hydrogen and negligible COR. This is attributed to much lower solubilities of CO in aq. electrolytes highlighting the importance of a three-phase interface for COR. To address this, we altered the electrode microenvironment by incorporating a hydrophobic ionomer facilitating better water management and thereby reduced CO diffusion distances. We observed a drastic increase in the C_{2+} efficiencies and suppression of H_2 upon the incorporation of the hydrophobic ionomer. To further study the mobility of water through the catalyst-membrane interface and electrode surface speciation, we developed operando radiography and XAFS cells which replicate the selectivity and high current densities achieved in the cell used for electrochemical characterisation. This was achieved by incorporating an X-Ray transparent window in the electrolysis cell without altering the gas flow pattern and the overall cell geometry, to ensure reproducibility of laboratory results during operando measurements.

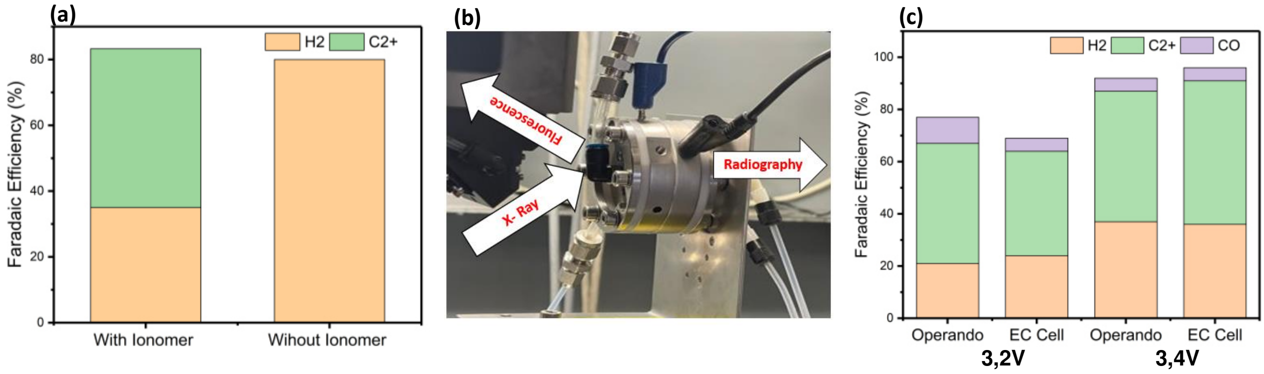

Figure 1 a) Influence of hydrophobic ionomer on HER suppression in CORR, b) Operando Cell for XAS and Radiography studies, c) Selectivities in the Operando and EC Cell (>100mA/cm^2)

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Wetting behavior of electrolyte in a silver GDE and how it affects performance in Metal-air batteries

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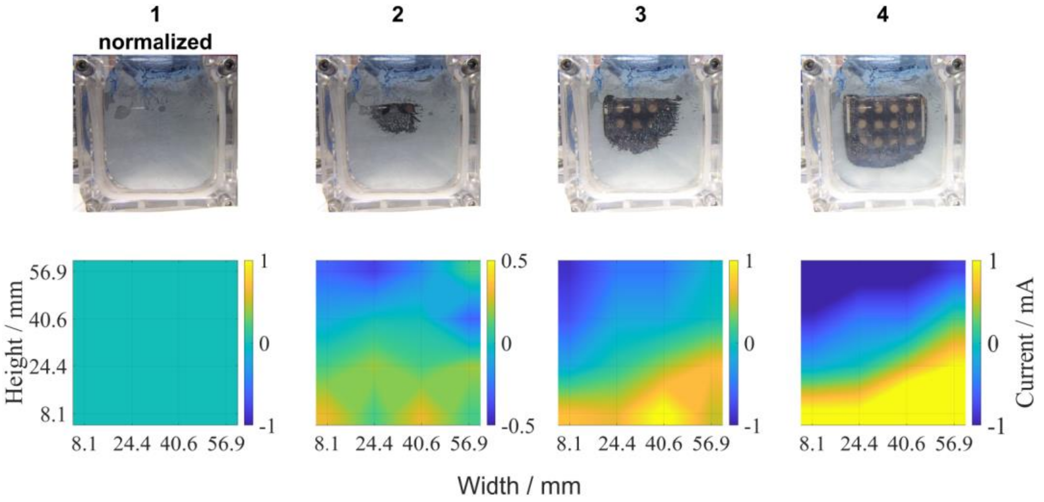
Metal-air batteries are attractive candidates for energy storage due to their high theoretical capacities. As for commercialization larger batteries are needed the influence of heterogeneous current distributions growths. If vertical cell configurations are used, hydrostatic pressure results in higher penetration of electrolyte into the cathode porous system in the lower cell parts. This leads to lower current densities in these regions. This heterogeneity on the cathode side is reflected by heterogeneous dissolution of the anode.[1]



Due to the high overpotentials during charge and discharge, the cathode material undergoes several oxidation/reduction reactions. This leads to an increase of the influence of the hydrostatic pressure as during charge metal oxidizes and therefore shows higher wettability. As could be shown by our segmented cell technique, this leads to a shift of current density to the upper regions of the battery.

To further validate this behavior a cell was used to specifically set the electrolyte pressure and measure overpotentials and impedance for the oxygen reduction reaction showing the penetration behavior of electrolyte with increasing electrolyte pressure and the loss of performance.

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Switchable Oxygen Depolarized Cathodes for flexible Chlor-Alkali Electrolysis

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The worldwide energy sector is facing the challenge of reducing carbon dioxide emissions, mitigating global warming, and revolutionizing energy generation. The increasing proportion of renewable energy production intensifies fluctuations in supplied energy. In our work, we aim to reduce the energy demand of chlor-alkali-electrolysis and adapt the process to flexible production conditions.

Switchable ODCs[1] (sODC) enable an energy-saving oxygen-consuming mode and an energy-intensive hydrogen-evolving mode. Thus, the oxygen mode is employed in times of large energy amounts, whereas in times of low energy quantities the hydrogen mode is applied. Experiments on a lab-scale focused on the system's stability for the two cathode reactions. A comparison of the oxygen mode of the switchable with a conventional ODC without the ability for switching demonstrates the high potential of the sODC with a difference of 0.07V only. Long-term experiments with up to 1,000 switching cycles, including short-term oxygen and hydrogen modes at 6.7kA/m^2, interrupted by a nitrogen flush, aimed to mimic a realistic application of more than 500 days with regular switching. The long-term experiments revealed a potential increase of up to 7.8% over the whole course of switching cycles, which I will discuss in more detail in the presentation or poster.

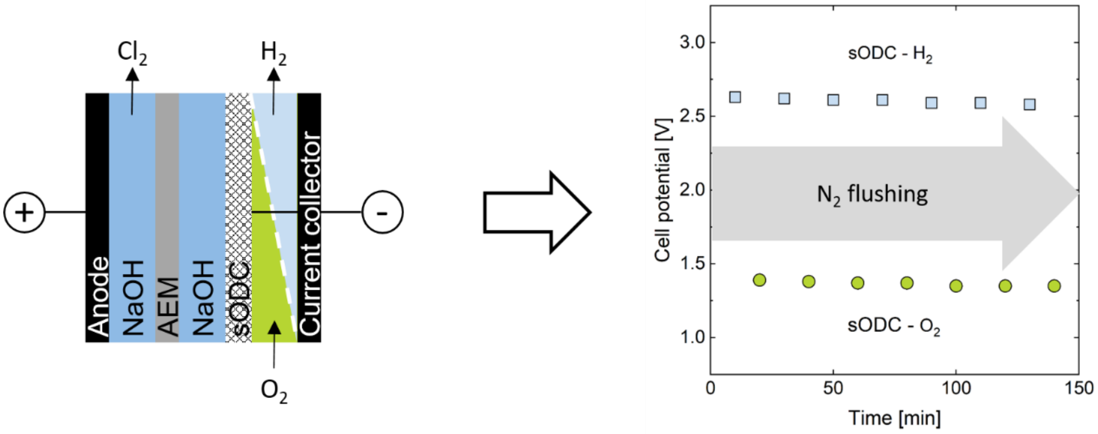

Figure 1: sODC is implemented in up to 1,000 automated switching cycles between H2 and O2 mode

This high potential of the sODC is supported by intensive economic studies showing that the sODC in chlor-alkali electrolysis can reduce operational costs by 6.5% and accommodates the expected strong fluctuations in future renewable energy supply[2].

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Preparation of an air-diffusion cathode based on Printex L6 carbon supported on carbon cloth for H_2O_2 electrogeneration in water treatment: Catalysis and viability

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Current advances on homogeneous processes for electrochemical wastewater treatment demand the development of new designs of gas-diffusion electrodes (GDEs) to be employed under actual conditions for H_2O_2 electrogeneration [1]. This work presents a catalytic and economic comparison between a commercial GDE and a new GDE made of carbon black/PTFE supported on carbon cloth. The electrode area was scaled up from 3 cm^2 (tested in a 150-mL electrochemical cell) to 20 cm^2 (fitted into a filter-press reactor) to assess the H_2O_2 electrogeneration. The new GDE was produced using a hot press method, by employing a Printex L6 carbon (loading of 15 mg cm^{-2}) mixed with 20% of PTFE and compressing the suspension on a carbon cloth (model PX30-PW03 from Plain Weave Fabric) at 0.5 ton over 15 min at 270 °C. The electrodes were physically characterised by scanning electron microscopy (SEM) and contact angle analysis, further evaluating the H_2O_2 electrogeneration in galvanostatic mode by applying different current densities (*j* from 5 to 80 mA cm^{-2}). Fig. 1a displays the SEM image of the PL6C/PTFE-based GDE, demonstrating a well dispersed and homogeneous catalytic surface showing no exposure of the carbon cloth. The very low conctact angle (~47°) of the water droplet onto the electrode surface confirmed the hydrophobic nature of the resulting GDE. Once evidenced its suitable structure for electrochemical application, H_2O_2 electrogeneration tests were performed at small scale in a 50 mM Na_2SO_4 solution at pH 3 using the GDE as cathode and a commercial DSA® as the anode, both of 3 cm^2. Fig. 1b shows a good catalytic performance for H_2O_2 accumulation, achieving high values ~2500 mg L^{-1} after 300 min at j = 80 mA cm^{-2}. Since the energy consumption was excessive at such high *j* values (Fig. 1c), the subsequent trials in a pre-pilot plant with a 20-cm^2 were carried out at lower input current. Furthermore, our investigation also focused on the comparative behavior of a commercial GDE under the same conditions at smaller and greater scale.

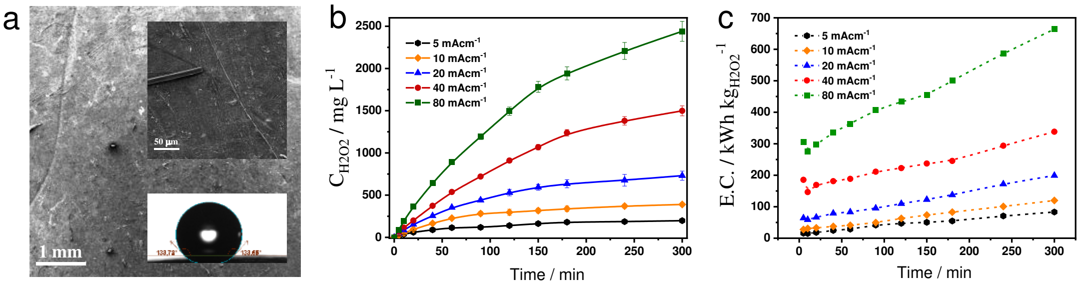

***Figure 1. (a)** SEM images of PL6C/PTFE-based GDE. **(b)** Accumulation tests of H_2O_2 and **(c)** energy consumption (E.C.) in 150 mL of a 50 mM Na_2SO_4 solution at pH 3, using the GDE as cathode and a comercial DSA® as the anode, both of 3 cm^2, at j = 5, 10, 20, 40 and 80 mA cm^{-2} under air-flow of 200 mL min^{-1}.*

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Bifunctional silver-based gas diffusion electrodes for electrically rechargeable zinc-air flow batteries: Challenges and perspectives

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The vast majority of proposed cell concepts for secondary zinc-air batteries uses a three-electrode setup [1]. However, the battery management system is complex in this case and a higher voltage loss might result from the electrode gap. An obvious solution is the use of a bifunctional gas diffusion electrode (GDE) where oxygen evolution and reduction would occur. The requirements for the catalysts are, on the one hand, high chemical stability in the strongly alkaline electrolyte and, on the other hand, sufficient long-term stability regarding the oxygen reactions. Especially the evolution of oxygen during charging causes a high stress to the electrode matrix. Wittmaier et al. reported about a promising bifunctional silver-based GDE with cobalt oxide as an additional catalyst [2]. In cooperation with the company Covestro Deutschland AG we fabricated similar electrodes and varied the composition of the components. The electrodes were tested in a half-cell setup for a duration of 60 h (20 cycles) at a current density of 50 mA cm^{-2}. Surprisingly, we found that the long-term stability of the GDEs is much higher, if no cobalt oxide is present in the electrode. The best GDE, which also enables prolonged experiments in a full cell setup, is the commercial silver-based GDE from Covestro Deutschland AG. This electrode was developed for the oxygen reduction reaction in the chlor-alkali electrolysis and is usually not used as oxygen evolving electrode. However, the aging of the electrode in a full cell setup is even reduced compared to the half-cell tests. This is presumably due to the zero gap arrangement (see Fig. 1 (left)), which minimizes the degradation of the electrode surface due to oxidation processes. The full cell could be cycled over a long time period of about 760 h (215 cycles) with a short interruption, which was caused by a decrease in the Coloumb efficiency. Due to the promising results of the commercial GDE, further experiments with self-made spray-coated electrodes were done. The electrodes were produced with different binder proportions and thicknesses in a wide range. As a result, the content of binder has a high impact on the stability and performance of the electrode. With the increase of the binder mass fraction the oxygen reactions start earlier. Furthermore, the potential is higher during discharging compared to that of the commercial electrode (see Fig. 2 (right)).

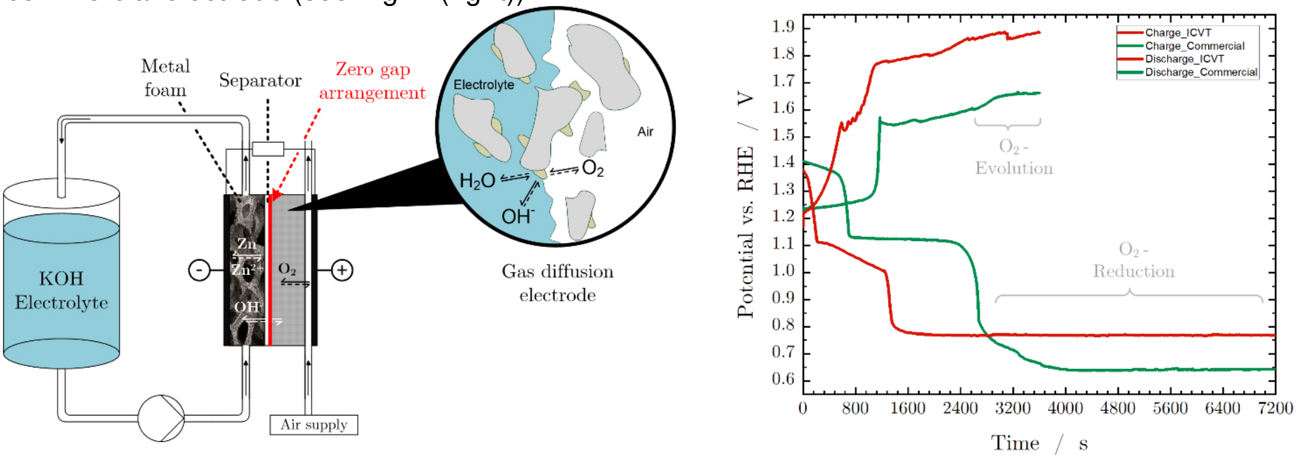

Figure 1: Full cell setup with zero gap arrangement of the cell components (left). Potential curves of a commercial and spray-coated GDE (ICVT) during the 20th cycle in a half cell setup.

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Gold Recovery and Nanoparticle Synthesis by Gas-Diffusion Electrocrystallization (GDEx)

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Gas-diffusion electrocrystallization (GDEx) is an electrochemical technology that allows to recover metals in the form of (hydr)oxides or in a zero-valent state, forming nanoparticles (NPs) [1]. The electrochemical device to conduct GDEx includes a gas diffusion electrode (GDE) used as a cathode, which allows the percolation of a gas that will be electrochemically reduced within the porous electrode. This results in the formation of oxidizing or reducing species, depending on the gas supplied. When the gas supplied is CO_2, and the medium is aqueous, CO and H_2 are formed, which act as reducing agents, obtaining metallic NPs if the reduction potential of the metal ion species in solution is sufficiently high (Pt, Pd, Rh, Ru, Ag, Au).

This work focused on the proof of concept and optimization of Au(III) recovery from synthetic streams, resulting in the simultaneous nanoparticle synthesis. The optimization was conducted by operating under different cathode polarization and gas-flow overpressure. In addition, different GDE materials were investigated in order to favor the selectivity of the electrogenerated (reducing) reactive species, leading to a better understanding of the reaction mechanism and optimal efficiency (i.e., near 100% recovery).

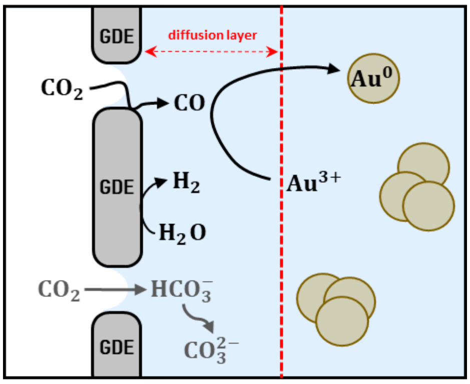

Figure 1. Au(III) ions reduction in the GDEx process.

Results show that Au(III) ions are mainly reduced by CO in the bulk of the catholyte [2]. Depending on the gas overpressure value, CO availability in the catholyte can be promoted, favoring Au(III) reduction rates in the catholyte. The current collector material plays a key role in a successful Au recovery and formation of Au^0 nanoparticles.

References:

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Porous Electrodes for Electrochemical NAD(P)H Regeneration

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Nicotinamide adenine dinucleotide and its phosphate NAD(P)H form are among the most important co-factors in biocatalysis. Since their price is very high it is not economic to add them in stoichiometric amounts. Instead, they have to be regenerated in the process. Among different possibilities for co-factor regeneration, direct regeneration at the electrode surface is especially promising. For the direct co-factor regeneration, the use of carbon materials and their combination with metals like silver or nickel is of particular interest. Carbon materials themselves, e.g. glassy carbon electrode, show activity for NADH regeneration. However, for technical applications use of carbon nanobased materials would be of advantage, since surface-to-volume ratio could be increased and reactant or products supply/removal from/to gas phase could take place, resulting in higher productivity and lower mass transfer limitations.

There are several common approaches to prepare porous electrodes, like: drop casting, dipping, spray coating, or spin coating [1]. Most of these methods are not able to control the structure of the porous layer. Since this is detrimental for optimal activity, new methods leading to optimized electrode structures are required. In this contribution, a process developed at OvGU [2], so-called aerosol coating, is used to produce carbon-based porous electrodes and benchmarked against conventional spray-coated porous electrodes with respect to NAD^+ reduction.

References:

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Rational design of 3-D porous enzymatic electrodes for the production of gluconic acid in bioelectrochemical system

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Electroenzymatic systems are very promising for development of new sustainable biotechnological processes. This concept is based on utilization of redox enzymes as catalysts where cofactor regeneration can be controlled via electric current or potential. [1] However, the performance of these systems for practical application is still low. Major challenges are related to electrode performance *i.e* low activity and stability of enzymatic electrodes and system integration. Therefore, the focus of this research is on rational design of porous enzymatic electrodes based on *horseradish peroxidase* (HRP) and *glucose oxidase* (GOx) as biocatalysts for gluconic acid production. The aim was to understand the bottlenecks for the highest biocatalyst utilization within the complex porous structures and to evaluate influence of different immobilization strategies on the electrode performance. The optimized electrodes were then tested in a half-cell and flow-through reactor without any separation in-between. The anode has been made with GOx using tetrathiafulvalene (TTF) as mediator, while cathode comprised enzyme cascade, GOx and horseradish peroxidase (HRP) or bilirubin oxidase (BOD). The influence of the electrode preparation procedure, structural and operating parameters on the biofuel cell performance has been checked.

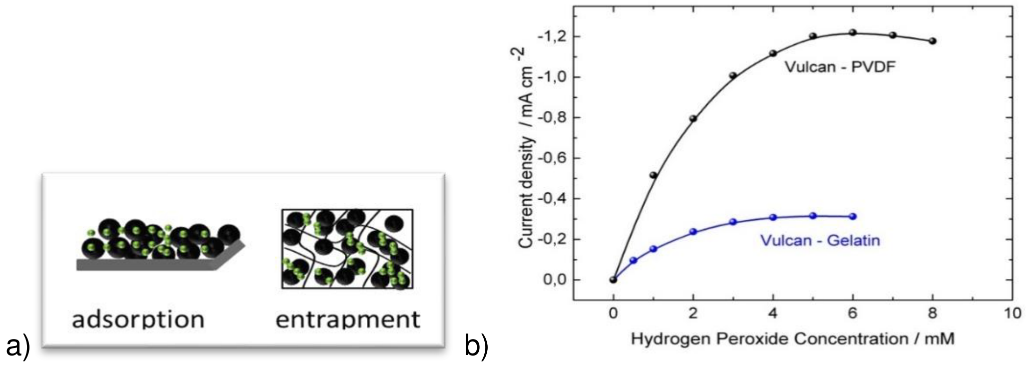

Figure: a) Schematic presentation of different immobilization strategies for preparation of 3-D electrodes b) The electrode performance of HRP-electrode based on different immobilization strategies in different hydrogen peroxide concentrations

References:

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