Symposium on Insights into Gas Diffusion Electrodes
From Fundamentals to Industrial Applications
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Plenary Lectures
Understanding and Optimizing Gas Diffusion Layer Structures

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In polymer electrolyte fuel cells, at high current densities and/or low temperatures, water management in the gas diffusion layers (GDL) is a limiting process. Water transport in the gas diffusion layer is capillary or phase change driven and liquid water, present in the void space of the GDL increases the tortuosity of the gas transport path producing increased mass transport overvoltage losses.

In order to understand the liquid water transport phenomena, improve GDL materials and reduce transport losses, detailed knowledge of the behavior of the liquid water transport is necessary. Imaging techniques offer the possibility to study the liquid water transport in operating cells. X-ray tomographic microscopy [1,2] can reveal the liquid water structure on the scale of the pores in the GDL materials (see Figure 1) with dynamics of up to 10 Hz for 3D-images.

The talk will give an introduction to X-ray microscopic imaging of polymer electrolyte fuel cells and derive the guidelines for improved GDL structures.

Figure 1: Vertical slice of X-ray tomographic microscopy image with a scan time of 1.6 s, showing water in the GDL and channel of the cell.

References:
How can gas-diffusion electrodes leverage enzymatic fuel cells performance

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Enzymatic fuel cells (EFCs) are one class of low temperature fuel cells in which platinum-based catalysts are replaced by very efficient and specific redox enzymes [1]. The intrinsic nature of biocatalyst allows to envision energy production in a fully sustainable manner. Since their proof of concept more than 40 years ago, great improvement has been realized in EFC performances thanks to advanced knowledge in i) catalytic mechanisms involving a wider panel of stable redox enzymes, ii) the molecular basis for efficient enzyme wiring on electrodes, and iii) the required structure to get high surface/volume host matrixes. EFCs using a variety of fuels (sugars, alcohols, H2..) and oxidants (mainly O2 or air) are nowadays reported with power outputs more than 5 mW/cm2. Fundamental research is still going on to get a complete understanding of enzyme behavior on electrified interfaces, in order to push forward the EFC performances. However, one of the main limitations remain substrate and product supply towards/from the enzyme within the electrode volume [2]. This is all the more critical when using gases as fuel or oxidant due to their low solubility in electrolytes while gaseous product accumulation may clog the pores of electrodes.

Gas diffusion electrodes (GDEs) are specifically designed electrodes for use in proton exchange membrane fuel cells, to enable H2 and air to be supplied as gases to the platinum-based catalytic layer [3]. EFCs using air-breathing cathode have been early reported [4], and more recently, gas diffusion type cathode and anode for CO2 reduction and H2 oxidation have also been described [5]. Nevertheless, whereas the behaviour of Pt-based catalysts has been largely studied on GDEs, much less fundamental works have been done when enzymes act as catalysts. It is expected that enzymes that must keep hydrated should be more susceptible to be affected by the triple-phase boundary setting between the porous solid support which harbours the catalyst, the electrolyte and the gas phase. Here, after having presented the latest developments in redox enzyme wiring on porous electrodes, we will highlight and discuss the main challenges to design enzymatic GDEs in comparison with Pt-based membrane electrode assemblies. We will illustrate these concepts with the architectures and performances of already reported gas diffusion electrodes in enzymatic biofuel cells.

References:

Durability of carbon-supported nanostructured electrocatalysts in alkaline environments: more noble is not necessarily more stable!

Clément Lafforgue, Laetitia Dubau, Frédéric Maillard and Marian Chatenet

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Alkaline fuel cells (AFC) are now ready to compete with proton-exchange membrane fuel cells (PEMFC) for the powering of stationary or portable devices [1]. The scientific community often puts forth that AFC electrocatalysts should be more stable than PEMFC ones, owing to the larger stability of many metals and oxides at high pH [2]. This fact is however not granted for carbon-supported Pt and Pd nanoparticles (NPs) used in liquid alkaline electrolytes: mild accelerated stress tests in dilute (0.1 M) NaOH lead to pronounced electrochemical surface area losses [3, 4], associated to major detachment of the Pt (and Pd) NPs from the carbon support. Interestingly, these degradations are not linked to the corrosion of the metal NPs and of the carbon support, as revealed by identical-location transmission electron microscopy (ILTEM). Additional aging tests performed in LiOH, NaOH, KOH, CsOH electrolytes and coupled with in situ Fourier-transform infrared spectroscopy showed that the Pt (Pd) NPs do catalyze the carbon support corrosion (carbon surface oxides form, evolve into CO2, then into carbonate anions and finally into solid metal carbonate precipitates, M2CO3, M = Li, Na, K or Cs) [5]. As a result, the link between the metal NPs and their carbon support is lost, hence the NPs detachment and associated loss of ECSA.

Solid alkaline electrolytes (anion-exchange membrane) enable to reduce the loss of Pt NPs, because the counter-cation of the OH species are immobilized on the polymer backbone and cannot participate to the precipitation of M2CO3, unlike for MOH aqueous electrolytes. Although minor, the degradation of Pt/C NPs in AEM electrolytes are not completely suppressed, though, but instead modified: Ostwald ripening and Pt redeposition proceed. This suggests that the predominant mechanisms of degradation differ in solid versus liquid alkaline environment, as has been previously put forth for solid versus liquid acidic electrolytes [6, 7]. Fortunately, these degradations can be mitigated: non-noble electrocatalysts (e.g. Ni-based) are more robust in alkaline environments [8], and should therefore be more durable in AFC applications.

References:

Multiphase transport in gas diffusion electrodes for fuel cells and electrolyzers: Modelling, imaging, and design

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The polymer electrolyte membrane (PEM) fuel cell and electrolyzer are composed of multiple porous materials, including the catalyst layer, microporous layer, and substrate. Commercial materials, whether by design or not, typically exhibit highly heterogeneous material and chemical properties. For example, in our past work, we extensively examined the heterogeneous microstructure and hydrophobicity of the gas diffusion layer (GDL). In order to reach cost targets for widespread commercial adoption, we must realize materials that enable more effective multiphase flow phenomena than what currently exists. Mass transport losses in PEM fuel cells and electrolyzers are both prohibitively significant. However, designing these materials requires the a priori knowledge of how the heterogeneous properties of the porous materials and their interfacial contacts influence electrochemical performance. These are factors that are currently not fully understood in the literature. In this work, I will discuss these critical design factors (heterogeneous porous materials and nature of interfacial contacts) and how they influence the flow and mass transport behaviour in PEM fuel cells and electrolyzers. I will also discuss the new materials we have designed and fabricated, informed by in-house numerical modelling and tested through a combination of in operando and ex situ X-ray and neutron beam characterization approaches.
Invited Lectures
Optimizing Local Reaction Conditions in Porous Electrodes: Insights from Theory and Computation

Tasleem Muzaffar¹, Jakob Spooner¹, Jun Huang², and Michael H. Eikerling³

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The drastic loading reduction or complete elimination of Pt-group metals from PEM-based fuel cells and electrolysers remains a foremost priority for technology developers. A high emphasis in this realm is placed on developing electrocatalyst materials with high activity and stability. It is however no less important to embed the catalyst material of choice within a well-designed porous composite electrode. The objectives of electrode design are to optimize the local reaction conditions at the dispersed catalyst in view of high and uniformly distributed electrochemical activity towards desired reactions and comply with overall lifetime and durability requirements of cell operation. Furthermore, porous transport media must be developed to guarantee efficient reactant supply and product removal to and from the active electrode layer. Theory and computation provide valuable tools to scrutinize the local variables of interest in this playing field, which are – for the case of an oxygen reduction electrode – proton density and oxygen concentration. Regarding the first variable, results of a molecular modelling study will be presented that reveal the variation in local proton density for a slab-like model of the catalyst-ionomer interface. The width of the water layer between metal surface and ionomer skin layer and the density of charged anionic groups at the ionomer skin are vital parameters in this context. The local concentration of oxygen in the active electrode layer is determined by the macroscale diffusivity of oxygen, which is controlled by water distributions in active and porous transport layers as well as flow conditions in flow field channels. A comprehensive water management model is developed to handle this coupling.
CO₂ electroreduction. From catalyst design to gas diffusion electrodes

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Conversion of CO₂ to useful chemicals aiming toward a closed carbon cycle economy to fight climate change as well as the conversion and storage of sustainable energy requires development of improved electrocatalysts. Specifically, the electrocatalytic reduction of CO₂ (CO₂RR) needs to exhibit high activity, allow high current densities and most importantly should show high selectivity. CO₂RR involves the transfer of up to 12 electrons coupled with protons, leading thus to a multitude of possible products. Beside this, the efficiency of the CO₂RR is limited by the competing parasitic hydrogen evolution reaction (HER), which occurs in the same potential window as the CO₂RR, as well as the low CO₂ solubility in aqueous electrolytes. Recent reports indicate that immobilization of electrocatalysts on gas diffusion electrodes allow the conversion of CO₂ at relevant industrial current densities in alkaline environment supressing thus the competing HER. Design of electrocatalysts for reactions in which multiple proton coupled to electrons can be transferred such as the oxygen reduction reaction (ORR) or the CO₂RR is challenging, since integration of different active sites as well as adsorption/desorption sites at the catalyst is required. Thus, complex catalyst design and complex electrode architecture are required to allow cascade reaction to occur to the aimed product. Recently we showed the importance of the catalyst morphology for the ORR, by designing Pt nanoparticles having distinct channels mimicking thus the enzyme nanostructure, named Nanozymes. The designed Nanozymes obtained by acidic etching of PtNi nanoparticles showed increased catalytic activity by a factor of 3 as compared with Pt nanoparticles having no channel. The nanozyme concept is further exploited for the CO₂RR. We have designed nanozyme electrocatalysts for the CO₂RR which allow cascade reactions to occur under formation of C₂ products. AgCu core-shell nanoparticles showed increased formation of C₂ products at decreased overpotentials. The activity and selectivity of Nanozymes immobilized on carbon cloth will be compared with the ones registered for Nanozymes immobilized on gas diffusion electrodes, showing thus the combined influence of catalyst design and electrode architecture on the CO₂RR selectivity. Moreover, the variability of choosing different catalyst materials nanoparticles immobilized in gas diffusion electrodes on the selectivity of the CO₂RR will be demonstrated.

References:
Benchmarking and tuning the oxygen reduction activity on Pt-based catalysts: from model studies to gas diffusion electrode measurements

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The slow kinetics of the oxygen reduction reaction (ORR) impede the widespread uptake of low-temperature fuel cells. This talk will present some recent strategies aiming to understand, benchmark and tune the activity and stability for ORR electrocatalysts.

Model studies using the rotating disc electrode (RDE) technique are suitable to investigate the ORR activity trends [1,2]. We recently used Cu/Pt (111) near-surface alloys to study the ORR in alkaline electrolyte [4]. Our results show that the ORR shares the same reaction intermediates in both acidic and alkaline electrolytes. On the other hand, we systematically studied the ORR activity and stability trends by controlling the compressive strain of the active phase on Pt-lanthanide alloys [1].

Despite the progress in the development of Pt-based electrocatalysts presenting high enhancement in ORR activity over pure Pt in RDE measurements [2], translating the activity enhancement to real fuel-cell devices remains a challenge. Recently, we have presented a gas diffusion electrode (GDE) setup [4] that overcomes some of the weaknesses of RDEs such as low reactant mass transport. Thus, while RDEs are limited to low overpotentials and current densities, GDEs can be used for benchmarking the activity of Pt-based electrocatalysts at fuel-cell relevant overpotentials (0.6-0.8 V vs. RHE) and high current densities (around 1 A cm⁻²) [5]. Our results illustrate the importance of characterising the ORR electrocatalysts under realistic conditions.

References:
Towards realistic testing conditions for electrocatalysts: Gas diffusion electrodes incorporated into half-cell setups

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In academic research electrocatalysts are usually evaluated in so-called electrochemical half-cells, e.g. using the thin-film rotating disk electrode (TF-RDE) technique. The advantages are that only one reaction is investigated independent of the counter process, that only small amount of catalyst is needed and that the measurements are fast. This enables screening-type investigations. The drawback however is that in general the conditions are far from any realistic conditions concerning mass transport and related achieved current densities as well as operation temperature.

In this presentation, different concepts of electrochemical setups with increased mass transport conditions are discussed [1, 2], in particular a setup developed in our group [3 - 5] that enables the incorporation of gas diffusion electrodes (GDE). It is demonstrated that such setups have significant advantages over standard setups and can be used as an intermediate testing platform before testing at single cell levels.

References:
Operando X-ray Computed Tomography Study of Water Management in Gas Diffusion Electrodes of PGM-free Polymer Electrolyte Fuel Cells

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Atomically dispersed Fe-N-C electrocatalyst is the emerging advanced type of platinum group metal-free (PGM-free) catalyst, its activity arising from multitude of actives sites. In recent years, significant progresses have been achieved to increase the activity and durability of the PGM-free electrocatalysts for oxygen reduction reaction (ORR). Despite substantial advances over the last decade of intensive development, PGM-free electrodes have lower volumetric activity comparing to the traditional Pt-based electrodes due to either lower turnover-frequency or/and lower number of active sites. To compensate for lower volumetric activity, PGM-free electrodes use higher loading of ~4 mg/cm² (as usually the catalyst cost factors are not significant), resulting in order of magnitude thicker electrodes (~100 μm) compared to conventional Pt/C electrodes. This larger thickness can result in overall mass transport and Ohmic losses.

Here, a systematic analysis, both experimental and model-assisted have been performed over three main configurations of PGM-free electrodes in polymer electrolyte fuel cells (PEFCs): catalyst-coated membrane CCM technology is being compared to gas-diffusion electrode (GDE) method of electrode fabrication and juxtaposed to a hybrid/combined GDE-CCM method of membrane-electrode assembly (MEA) fabrication [1]. The corresponding electrodes were evaluated for their electrochemical performance, modeled and studied with in-situ and operando X-ray computed tomography (X-ray CT). The study establishes that through-thickness inhomogeneities play most important role in water withdrawal / water management and affect most significantly PGM-free PEFC performance. The catalyst integration technique results in formation of interfacial regions with increased porosity and surface roughness. These regions form critical interfaces de-facto responsible for flooding type behavior of the PEFC as shown for a first time by operando X-ray CT. The computational model shows that the PEFC performance critically depends on liquid water formation and transport at cold and wet conditions. Lastly, the hydrophobic PGM-free GDEs’ water management was compared to more hydrophilic GDE, where the latter shows higher capacity for water storage, implying that interfacial design might not be as critical.

References:

Gas Diffusion Electrodes in Industry – from Chlorine to CO₂ Reduction

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Chlorine is an important chemical which is involved directly or indirectly in the manufacture of more than 60 percent of all chemical goods. Electrolysis used for chlorine production is currently one of the most energy-intensive processes in chemical industry. Thus, chlorine producers are highly interested to reduce their energy consumption and carbon footprint significantly by optimizing their processes using energy-saving electrolyses technologies.

The state-of-the-art brine or hydrochloric acid electrolyses – both with hydrogen formation at the cathode – are already highly developed. A significant improvement in energy consumption is only possible by a major technology change: By choice of the oxygen reduction as alternative cathode reaction using a gas diffusion electrode – the oxygen depolarized cathode (ODC) – electrical power savings in the region of up to 30% can be obtained.

Though the oxygen reduction reaction (ORR) is already well known from fuel cell technology, the implementation in a chlorine evolving electrolysis and the required gas diffusion electrode manufacturing in industrial scale is a challenge. The new energy saving chlorine production processes using gas diffusion electrodes (see fig. 1) have been realized by interdisciplinary cooperation of industry partners and research institutes, significantly supported by public funding [1].

The talk will highlight the technical requirements and the corresponding developments as well as the ecological and economic aspects of the use of gas diffusion electrodes for chlorine production.

Using electric power generated from renewable resources for the sustainable production of other chemicals using gas diffusion electrodes is a strongly growing research field, and recent results for electrochemical CO₂ reduction to chemicals will be presented.

![Image](image_url)

**Fig.1:** NaCl-ODC electrolyze in Krefeld-Uerdingen, Germany (picture: Covestro Deutschland AG)

Oral Presentations
FIB Tomography of silver-based gas diffusion electrodes with different silver-PTFE ratios

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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. The efficiency of the GDEs is limited by the oxygen reduction reaction (ORR). However, the ORR depends on the microstructure of the GDEs. Therefore, it is of high importance to understand the impact of the microstructure on the ORR for the development and improvement of GDEs. For this purpose, GDEs with different silver-PTFE ratios have been analyzed by focused ion beam (FIB) tomography to measure the distribution of the PTFE depletion and to analyze the form of the silver skeleton and the pore system within the GDEs, like shown in Figure 1. Within the framework of the DFG-Forschungsgruppe FOR 2397 the acquired 3D 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, more specifically, to lower the silver content of the GDEs and/or improve the GDE performance in order to make them more attractive for technical applications.

Figure 1: Visualization of pores with a high probability of electrolyte transport.
Prediction of Electrolyte Distribution in Technical Gas Diffusion Electrodes: From Imaging to SPH Simulations

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The performance of the gas diffusion electrode (GDE) is most crucial for technical processes like chlor-alkali electrolysis. The GDE is responsible for ensuring intimate contact between gaseous reactants, the solid catalyst and the solid or liquid electrolyte. The porous material of the GDE consists of wetting silver and non-wetting Polytetrafluoroethylene (PTFE) which prevents the electrode from being totally flooded. The knowledge of electrolyte distribution in the porous structure is essential for further improvement of GDE preparation.

Electrolyte imbibition is studied by direct numerical simulations using the Smoothed Particle Hydrodynamics (SPH) method. The porous geometry, including the silver and PTFE distribution of a technical GDE, is extracted from FIB-SEM imaging. A segmentation is applied in post-processing to identify the different phases. Modelling of wetting phenomena on continuum scale in such a porous microstructure is challenging, since surface tension and wetting effects at the three-phase contact line must be included physically-consistent. An approach is recently introduced as the contact line force (CLF) model [1].

Simulation results based on a workflow from imaging of the GDE to dynamic SPH simulations of the electrolyte imbibition process will be presented. The influences of non-wetting PTFE on the electrolyte imbibition as well as different electrolyte penetration are analysed by testing several external pressure gradients. We observed that even small parts of PTFE at the pore walls inhibits the pore imbibition under realistic pressure gradient conditions due to its large hydrophobicity. Since modelling a representative volume of a GDE is still impossible by direct numerical simulation we present a hybrid SPH-Pore Network Model approach which combines the advantages of directly incorporating the wettability effects at the fluid-fluid-solid-interfaces with the efficiency of a more simplified single-phase physics.

Figure 1: (a) Focused ion beam, pore system with PTFE depletion (in green) at the silver grain boundaries (b) Snapshots of the phase composition during the electrolyte imbibition process. The electrolyte is shown in blue, the PTFE wall in green and the silver in grey c) Stick-and-ball representation of porous structure.

References:
3D pore-scale lattice Boltzmann modelling of porous electrodes in fuel cells and batteries

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The 3D microstructure of porous electrodes plays an important role in the performance of electrochemical energy devices including fuel cells, batteries and electrolyzers. Computational models are useful as they can provide a direct link between microstructure properties and the complex transport phenomenon and electrochemical performance. A three-dimensional (3D) pore-scale lattice Boltzmann modelling (LBM) framework has been developed at University of Surrey to simulate the transport mechanisms of gases, liquid electrolyte flow, species and charge in the porous electrodes. An electrochemical model based on the Butler-Volmer equation is used to provide species and charge coupling at the interface of active electrode materials and electrolyte. In this talk we will demonstrate the applications of this modelling framework in proton exchange membrane fuel cells (PEMFCs), redox flow batteries (RFBs) and lithium ion batteries (LIBs). We apply this model first to simulate the water transport and oxygen diffusion in the gas diffusion layer (GDL) of PEMFCs, coupled with electrochemical reaction on the catalyst layer. This model is able to predict the time-dependent liquid and gas flow fields within the 3D GDL structure, as well as concentration of oxygen through the GDL and current density distribution [1]. We then further developed the model to simulate a vanadium based RFB and demonstrate that this model is able to capture the multiphase flow phenomenon and predict the local concentration for different species, over-potential and current density profiles under charge/discharge conditions [2]. It is found that the electrochemical performance is reduced with air bubbles trapped inside the electrode [2]. To validate the model, the simulated pressure drop, and electrochemical performance are compared against the experimental measurement based on the same electrode structures [3]. Three electrode structures (SGL paper, Freudenberg paper, Carbon Cloth) are reconstructed from X-ray computed tomography (CT). These electrodes are used in an organic aqueous RFB based on TEMPO. Excellent agreement is achieved between the simulated and experimentally measured electrochemical performance, indicating the validity of our model [3]. The effects of different porous structures on the performance are also investigated and discussed.

Recently the 3D pore-scale LBM framework has been modified and adapted to simulate LIB electrodes. The model is able to simulate the complex transport processes with real electrode geometries and predict electrochemical performance. Li distribution profiles within active materials and the liquid electrolyte are derived [4]. Furthermore, we demonstrate that the model can capture how Li distribution changes with charging/discharging time, and how particle size affects this process [4]. The model can be used to understand the impact of electrode microstructure on electrode performance, and may lead to design principles for creating electrodes with optimal microstructure for LIBs applications.

References: (see next page)


Estimation of effective parameters from pore network simulations

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Pore network models are powerful tools to study invasion processes with multi-phase flow at the pore scale of porous media. These models either incorporate the real pore structure of the porous medium or they are based on idealized 2D and 3D lattices of the best substitute of it. The latter option is very often applied to gain fundamental physical understanding of replacement processes. The mass and heat balances are solved for each individual pore, which essentially allows the study of locally and temporally discrete phenomena and especially invasion processes that result in phase patterns that strongly deviate from ideal macroscopically continuous structures. Pore network modelling is therefore often applied in investigations of fractal invasion fronts with high clustering of the displacing and/or displaced fluids.

Based on the experimental findings, e.g. presented in [1,2], we strongly assume that the oxygen-water distribution in the gas diffusion layer (GDL) at the anode side of electrolysers can become very heterogeneous with numerous branches and clusters if the oxygen production rate exceeds a critical value. This is expected to occur at high current densities. Our assumption is based on the pore structure of the GDL with interconnecting large and small pores and the Young-Laplace equation, with which different invasion pressures are predicted for the various pore sizes. In a first approach, we furthermore assume that a quasi-steady distribution of oxygen conducting fingers and water conducting fingers is obtained for constant process conditions. We thus propose to predict the steady-state oxygen and water distribution for the given process conditions with a pore network model of drainage. Furthermore, we aim to estimate the permeabilities of both fluids based on the pore network simulation and Poiseuille flow (Fig. 1). For this we will in a first step simulate the steady-state distribution of water and oxygen for different realizations of the pore structure (Monte Carlo simulation). Then we will compute the viscous flow of water and oxygen, in respective fluid fingers, on the pore scale. Thus, we will directly incorporate the information from the preceding pore network simulation. From the flow rates measured at the surfaces of the simulated GDL, we will estimate the relative and absolute permeabilities.

![Figure 1: Schematic illustration of the concept of parameter extraction based on pore network Monte Carlo simulation.](image)

References:

Models and experiments for the analysis of ORR product accumulation within porous oxygen gas diffusion electrodes

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In light of our research on gas diffusion electrocrystallization (i.e., GDEx, nanoparticle formation as the result of an electrochemical process using a gas diffusion electrode)1, we investigated the electrolyte composition within a galvanostatically polarized porous oxygen gas diffusion electrode (GDE). GDEx is proposed as a new technique for both the production of nanoparticles and the removal/recovery of metals from solution. In GDEx using an oxygen GDE, the ORR provides products (i.e., OH, H2O, HO2 and H2O2) for the precipitation reaction with metal ions to form nanoparticles (e.g., metal oxides). These products can influence how and which nanoparticles are formed. The process cost is strongly correlated with cell voltage and thus cathode potential. The pH within the GDE (i.e., the GDE pH) strongly influences the equilibrium potential at the cathode and is therefore interesting to investigate to better understand the overall GDEx process. We developed a 1D mathematical model of the ORR product concentration profiles for different bulk electrolyte pH (i.e., the bulk pH) values and different production rates and current efficiencies for HO2 (i.e., the ratio of the two-electron ORR to the four-electron ORR). It is empirical difficult to directly measure the GDE pH. Therefore, we measured the bulk pH and bulk H2O2 concentration in the catholyte during galvanostatic batch experiments with a two-compartment electrochemical flow cell reactor with full recirculation, using an oxygen GDE. Our 1D model clearly demonstrates accumulation of ORR products in the GDE. With our assumptions, at reasonably low (industrial) current densities of 100 A/m2, the pH within the GDE rises above 12, even for low bulk pH values (figure 1, left). Therefore, in most cases, the equilibrium potential of the ORR in porous gas diffusion electrodes can be up to 700 mV lower than expected from the electrolyte pH, influencing also the overall cell voltage. The experimental catholyte pH (as a function of electrochemically added OH) demonstrated significant delays compared to a (additional) bulk pH model (figure 1, right). With reasonable assumptions of diffusion coefficients, diffusion layer thickness, etc., this delay is in the same order of magnitude as the OH accumulation expected from the 1D pH model in the GDE electrode. This is a first indication of the reasonability of the 1D model regarding the internal pH in the GDE. We leave to further developments a more rigorous analysis of these and additional experimental results to proof our 1D pH model.

![Figure 1. pH in GDE and diffusion layer (left) and model and experiment of bulk pH (right)](image)

References:

Dynamics and States of Oxygen Depolarized Cathodes: A Model-Based Analysis

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Silver based oxygen depolarized cathodes are a key component for advanced chlor-alkaline electrolysis processes, which require 30 % less energy than conventional methods. Due to the fast reaction rate of the oxygen reduction reaction at industrial conditions of 80 to 90 °C and the low oxygen solubility, a tailored design of the gas diffusion electrode is needed to enlarge the three-phase-boundary and to minimize diffusion limitation. [1]

In this contribution, the first one-dimensional dynamic three-phase model for analyzing the oxygen reduction reaction in porous silver-based oxygen depolarized cathodes is presented and it is used for a systematic macroscopic evaluation of the interaction of electrochemical reaction and mass transport processes. In the model, the electrode behavior is described by Tafel-Equation, Stefan-flow in the gaseous phase and Maxwell-Stefan-diffusion in the liquid phase, oxygen dissolution following Henry’s law and water evaporation following Raoul’s law. Further, due to the high ionic concentration, the activities of the different species are taken into account for the reaction rate and the phase equilibrium. [2]

With the model, we were able to reveal essential new insights into limiting processes. In particular, the slow mass transport of water or hydroxide ions in the liquid phase was identified as the overall performance restricting factor. As a negative result of the slow mass transport, an enrichment of the hydroxide ions close to the gas-liquid interface causes a shift of the phase equilibrium, which diminishes the oxygen solubility further and leads to a total depletion of oxygen and finally to the limiting current density. Stationary simulation results give insight into the local concentrations and partial pressure profiles of the different species and reveal a stiff gradient of oxygen in the liquid phase (see fig. 2 a) and the enrichment of ions. Dynamic simulations with potential steps (see fig. 2 b) are used to identify the different time constants and to separate overlapping processes. Dynamics of current and local oxygen availability is strongly affected by the slow mass transport of hydroxide ions. Thus, future studies should aim to tackle this limiting process to improve the electrodes. [2]

Figure 2: a) Oxygen concentration dependent on the current density and the diffusion length in the flooded agglomerates under steady state conditions. b) Dynamic simulation of potential steps and the according current density. [2]

References:


Spatially resolved model of oxygen reduction reaction in porous gas-diffusion Electrodes

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Chlorine is one of the most important basic chemicals and is produced mainly by the energy-intensive chlor-alkali electrolysis process. By introducing an oxygen depolarized cathode (ODC), the electrical energy consumption can be reduced by up to 30 % compared to the state-of-the-art membrane process. Due to the low solubility of oxygen at the high process temperature (80 °C), the ODC is designed as a gas diffusion electrode (GDE). However, the GDE is still the limiting component and thus the main cost factor. To improve the efficiency of GDE it is necessary to understand the complex interaction of transport and reaction processes inside the electrodes. In order to investigate these processes a stationary mathematical model is developed, which includes the physical transport processes inside the gas and liquid phase as well as phase transformation and electrochemical reaction kinetics at the three-phase boundary (Fig. 1, left). In contrast to earlier publications [1], recent findings by Botz et al. [2] showed the importance of the electrolyte transport inside the GDE which was underestimated in the current thin-film flooded-agglomerate (TFFA) models. In the improved version of the TFFA model, the electrolyte transport is considered adequately. The electrolyte properties inside the GDE and the resulting process parameters, such as the oxygen solubility, are spatially resolved, allowing a detailed glimpse into the physical and electrochemical processes inside the GDE.

The model is validated by a custom build test setup designed for stationary conditions at the GDE. A large circulating electrolyte system, accurate gas dosing, as well as individual pressure and temperature control for the electrolyte and gas phase guarantee stationary conditions for long-term measurements. A wide range of process conditions can be adjusted and used for model validation. First results show a good agreement between measured and simulated overvoltages (Fig. 1, right).

Figure 1: Left: Schematic of the approach according to the TFFA model [1]. Right: Measured and simulated polarization curves (30 wt. % NaOH, 80 °C) for different oxygen concentrations.

References:
Dynamic Changes of Cathode Morphology During Operation of Li-O₂ Batteries: A Model-Based Analysis

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Carbon based, high surface area gas diffusion electrodes (GDE) are used as cathodes in Li-O₂ cells to enhance the discharge capacities of these batteries. Despite the fast electron transfer at the electrode surface, experimental results show that the very high theoretical energy densities cannot be achieved at the moment. The major reason for this discrepancy is the insoluble, nearly non-conductive main discharge reaction product Li₂O₂. The precipitation of Li₂O₂ at the electrode surface leads to continuous changes in porosity, available reaction surface area and predominant reaction pathway. Modelling is an indispensable tool to analyse the effects of mass transfer resistances and surface blocking in these dynamically changing GDE. [1]

In this contribution, we investigate how the local distribution and the particle size of Li₂O₂ are influenced by the discharge current density by means of a mathematical GDE model. The impact of the distribution and the resulting changes in transport resistance and active surface area on the battery performance are analysed. The presented one-dimensional dynamic model incorporates a nucleation and growth mechanism for Li₂O₂ particles and balance equations for porosity and active surface area. Kinetics are described by the Butler-Volmer-Equation using a two-step reaction mechanism with the soluble species LiO₂ as reaction intermediate. Mass transport is described by Ficks-diffusion and oxygen dissolution by Henry’s law.

With the model, we are able to explain the typical current density dependent discharge behaviour of Li-O₂ cells observed in literature (see fig. 1 a)). [1] The steep potential drop in the beginning of the discharge process and the following relaxation process can be related to the beginning of the nucleation process. Depending on the applied discharge current density, different capacities per carbon cathode surface area are achieved due to different Li₂O₂ particle size distributions which are also observed in experiments (see fig. 1 b)). [2] Our results show that even at moderate current densities the battery capacity is limited by the surface area of the cathode and not by the O₂ concentration. For this reason the solubility and reaction kinetics of the reaction intermediate LiO₂ play a crucial role to enhance Li₂O₂ particle size and with it discharge capacities. The presented results provide detailed insights into the processes that limit the performance of the GDE and clarify the important role of the intermediate LiO₂.

Figure 1: a) Discharge current density dependent potential over cell capacity. b) Particle size distribution at the end of discharge.

References:
Polymer Modified Gas Diffusion Electrodes Containing Hydrogenases or Their Artificial Mimics as Active H₂ Oxidation Catalysts

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The use of highly active but highly sensitive non-noble metal catalysts for energy conversion, i.e. hydrogenases or DuBois-type catalysts for H₂ oxidation is limited by their fragility and the difficulties to connect such catalysts to electrode surfaces. The incorporation of these catalysts into redox polymers overcomes these limitations and the redox polymers simultaneously provide a hydrophilic immobilization matrix and an electron relay matrix that shuttles electrons between the active catalyst and the electrode surface. Moreover, by using low potential redox polymers, air-sensitive catalysts can be protected by the in-situ reduction of incoming O₂ at the polymer electrolyte interface.[¹]

However, in (bio-)electrochemical devices based on flat and non-porous electrode systems the diffusional mass transport of the gaseous substrates typically limits the catalytic current due to their low solubility in aqueous media. Hence, the fabrication of high current density (bio-)electrodes is still a major challenge. The use of gas diffusion electrodes is a promising approach to overcome this limitation. Within these electrodes a three-phase boundary at the electrolyte-catalyst-gas interphase is established to ensure a high local substrate flux and thus high substrate concentrations at the catalytically active sites.

The combination of the benefits of redox polymers, i.e. protection of sensitive catalysts and high catalyst loading with the concept of a gas diffusion electrode (enhanced mass transport) is supposed to ensure high current densities which are desired for the fabrication of high performance (bio-)fuel cells.

In this contribution, we present a dual gas-breathing H₂/air biofuel cell equipped with a H₂ oxidizing bioanode modified with redox polymers/hydrogenase layers and a conventional O₂ reducing, bilirubin oxidase-based biocathode operating in a direct electron transfer regime. The biofuel cell exhibits an open circuit voltage of 1.13 V and delivers an outstanding power output of 3.6 mW cm⁻² at 0.7 V, setting a benchmark for redox polymer/hydrogenase based biofuel cells.[²] Furthermore, we transposed the concept for polymer based gas diffusion electrodes including the protection and wiring ability to an artificial and highly active but also O₂-sensitive DuBois-type catalyst for H₂ oxidation.[³]

References:

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

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Technologies related to gas diffusion electrodes (GDEs) offer solutions for gaseous reagents taking part in electrochemical reactions or being formed as products. However, many (bio)electrochemical processes suffer from several challenges, like e.g. high costs of platinized electrodes¹; rapid catalyst degradation and low product quality due to non-uniform electrode quality²; difficulties in upscaling. Similarly, scaling up microbial fuel cells (MFCs) and other types of bioelectrochemical systems requires the use of very large electrodes compared to sizes typically used in laboratory experiments. Such large electrodes are difficult to fabricate without loss in quality. VITO’s developments in this field originated in the wastewater treatment industry, and are finding their way in the electrification of chemical synthesis e.g. in the electroconversion of CO₂³.

These applications find usage in industries, research labs and academia.

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 permeability². The electrodes can be made via two approaches, namely cold-rolling method (VITO CORE®) and phase-inversion method (VITO CASE®) enabling a reproducible quality in sizes ranging from 10 cm² to 1 m². For wastewater treatment applications, large scale VITO CORE® to be used as air cathodes in microbial fuel cells (MFCs) were recently developed and tested in a 85 L tank to evaluate the impact of the cathode size by comparing the performance of this large cathode with two smaller cathodes made of portions of a single cathode pane in smaller reactors⁴. In this set-up organic waste is oxidized at the anode and oxygen gas, fed through the GDE, is being reduced to water. Using the large cathode and an array of 22 graphite fiber brush anodes, the maximum power density of 0.118 ± 0.006 W m⁻² with a recirculating flow through the chamber (1.3 cm electrode spacing) was obtained. For CO₂ electroreduction, GDEs based on Sn, Cu and Pd were developed and evaluated for a CO₂ electrolyzer of continuous production of formic acid, oxalic acid and CO on a scale of approximately 400 cm⁵. Reproducible, uniform and tailor made GDEs are now available for different applications as wastewater treatment, CO₂ electroreduction and electrolysytosis⁵. In this talk we will discuss the progress and challenges of these applications.

References

Electrochemical conversion of CO2 to methanol – A feasible reaction for large scale?

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CO2 can be considered as one of the main drivers for the anthropogenic climate change with increasing political restriction on its emission. Still, worldwide around 97 million tons are emitted daily. Hence, use of renewable energy sources for production of fuels and chemicals based on CO2 is a profitable and green business strategy, explaining the immense research that has started in this field.

In an electrochemical process, CO2 can be reduced to methanol. Methanol is easier to handle than hydrogen and can be used both, for energy storage and as raw chemical for various types of industries [1]. However, so far, results on CO2 reduction show a large product diversity [2], while high selectivity towards methanol has only been demonstrated at rather low current densities and for short time [3–5]. Moreover, the current results on MeOH selectivity vary and reports with high yield are questioned in recent works [6].

Within this presentation the investigations of different electrode configurations are discussed and compared to literature results in order to identify the trigger for a high MeOH selectivity. Varied parameters are (i) the catalyst composition itself – e.g. shape controlled Cu2O nanoparticles or urchin like Co(CO3)0.5(OH)-0.11H2O [7] – and (ii) the electrode engineering – including the fabrication of a gas diffusion electrode and the operation within in membrane electrode assembly.

This research is carried out within the LOTER.CO2M project [8], funded under the Horizon 2020 program by the European Commission. The goal is to design and realize an improved process consisting of low-cost high selective electrocatalysts, smart membrane design, and optimized stack operations.

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The electrolyte matters: stable systems for high rate electrochemical CO₂ reduction

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Electrochemical CO₂ reduction is a promising technology to reduce greenhouse gas emissions to the atmosphere by using power from regenerative resources. Today, research mainly focuses on the development of catalysts with improved activity and selectivity. However, many studies are conducted at low current densities, unstable electrolyte systems and electrochemical reactors, which are not suitable for industrial application. A paradigm change is needed in order to obtain reliable results at conditions which resemble the industrially relevant environment and which can thus be transferred to reactors with a high capacity. Recently, we have shown that the cell and electrode configuration of an electrochemical membrane reactor highly influences the product spectrum and energy efficiency. [1] In this presentation, we highlight the influence of different electrolytes used as catholyte and anolyte to achieve a stable system for syngas production. Our data shows that the choice of the electrolyte on the anode side requires special care with respect to stable pH and conductivity values. Furthermore, we show the optimized fabrication of the gas diffusion electrode, where each catalyst needs an individual optimization of the polymeric binder as well as the manufacturing process to exploit its full performance potential.

References:
Examination of gas-diffusion electrodes applied in CO$_2$ electrolysis employing electrochemical impedance spectroscopy (EIS)

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Closing the anthropogenic carbon cycle is one of the major challenges for the present mankind. Low-temperature electrochemical reduction of carbon dioxide to useful chemicals can contribute to the solution of this problem by changing the role of CO$_2$ from harmful waste into a valuable feedstock. The electrolyzer can be operated with renewable energy and CO$_2$ taken from concentrated off-gas of industrial plants. One of the main challenges of this process is to bring gaseous CO$_2$ in contact with the catalyst and the aqueous phase to maintain high space-time- yields. By applying porous gas-diffusion electrodes (GDEs) instead of plane electrodes the triple-phase-boundary - reaction zone – and gas transport are significantly enhanced. [1] [2]

Electrochemical impedance spectroscopy is a powerful tool to analyze the nature and velocity of single processes occurring at the microscopic level in electrochemical devices. These insights provide valuable information for a specific optimization of electrodes regarding electrochemical performance and long-term stability. However, there is a lack of knowledge which processes are displayed in the impedance spectrum during alkaline CO$_2$ electrolysis on GDEs. This work focusses on the identification of these processes shown in the impedance spectrum by changing experimental parameters e.g. temperature, CO$_2$ partial pressure & current density and analyzing the obtained response in the spectrum. As it is exemplary shown in Fig. 1 the shape of the impedance spectrum dramatically changes depending on the supplied gas mixture at the GDE. Compared to the absence of CO$_2$ where hydrogen evolution prevails, two additional processes become visible for a pure CO$_2$ gas feed which can be associated to the CO$_2$ reduction reaction.

![Figure 1: Impedance spectrum for a GDE operating with CO$_2$ and CO$_2$ free atmosphere. C-based GDE with SnO$_2$ catalyst, 30 °C, 1 M KOH • aq., 50 mA cm$^{-2}$, Frequency range 10 mHz – 300 kHz](image)

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Beyond Equivalent Circuit Approach: Computer-Enhanced Nonlinear Frequency Response Method

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Dynamic methods have, in general, higher sensitivity for parameter estimation and identification of reaction mechanisms [1] than the steady-state and equilibrium ones. One of these methods is electrochemical impedance spectroscopy (EIS), which analyses the linear response of the investigated electrochemical system to sinusoidal change of the chosen input (usually potential). Since electrochemical systems are inherently nonlinear, much attention has been recently devoted to development of nonlinear dynamic methods. Some examples are nonlinear EIS [2], total harmonic distortion [2], and the here applied Nonlinear Frequency Response (NFR) method [1,3]. In all these methods, the system response to a sinusoidal input signal with relatively high amplitude is studied, whereby the major difference is in the treatment and analysis of the obtained data. Having in mind that EIS is conveniently analysed by using the equivalent circuit approach, which helped its acceptance in a relatively broad electrochemical community, we believe that a similar generalized toolbox would significantly advance more extensive use of the nonlinear methods as well. With that idea, in this contribution a computer aided NFR method is proposed.

Theoretically, the NFR method is based on the concept of higher-order frequency response functions (FRFs) [3]. These FRFs are directly related to the basic and higher harmonics and the non-periodic (DC) term of the NFR and can be estimated from experimental NFR data. The procedure for derivation of the theoretical FRFs assumes that, the mathematical model of the investigated system, defined as a set of nonlinear differential equations, is replaced with a larger set of linear algebraic equations, defining the FRFs of different orders [3]. Finally, by solving this set of algebraic equations, analytical expressions for the FRFs of different orders are obtained [1,3]. However, the derivation of these analytical expressions requires both time and certain mathematical skills from the user, thus making its application unappealing to beginners, especially for very complex mechanisms. Therefore, we developed a software tool for enhancing the NFR method by automatic analytical derivation of the needed theoretical FRFs and data analysis [4]. This computer-enhanced NFR method uses Excel and five Matlab toolboxes. Excel is used as an interface, while Matlab is used for the automatic analytical derivation in the frequency domain and subsequent numerical computations. In this study, the computer-enhanced NFR method was applied for experimental identification, parameter estimation, experimental planning, and process optimization for the oxygen reduction reaction (ORR). Several models were analysed in the frequency domain, and their parameters were estimated for the model that qualitatively matched the experiments best. The application of the computer-enhanced NFR method allowed for a user-friendly modelling interface, fast and automatic derivation of all analytical FRFs of interest, and most importantly, seamless integration with existing numerical algorithms, which enabled fast parameter estimation for the competing reaction mechanisms, and optimization of the operating variables. The presented approach overcomes limitations of the classical equivalent circuit approach, since it does not rely on phenomenological elements, but on particular, fundamental reaction mechanism.

References:

Nanoscale Studies Solve Macroscopic Problems: De- and Reactivation of Oxygen Depolarized Cathodes Under Process Conditions

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Recent efforts to minimize energy consumption in the modern chlor-alkali process include the utilization of gas diffusion electrodes (GDE), the so-called oxygen depolarized cathodes (ODC). Exploiting the cathodic oxygen reduction reaction (ORR) by using the ODC as a substitute for the cathodic hydrogen evolution reaction (HER), as utilized in conventional electrolyzers, enables electrical energy savings of up to 30%. Industrial ODC-ORR catalysis is mediated by a microporous Ag nanoparticle (AgNP)/PTFE structure operating in 10 M NaOH at temperatures above 80 °C. The availability of O₂ can be enhanced by dosage of gaseous O₂ to the backside of the GDE, increasing achievable current densities.

Single AgNP experiments revealed a loss of catalytic activity towards the ORR upon a single O₂ dosage to the AgNP under study.¹ We rationalized the activity deterioration with the formation of surface oxides (Ag₂O) and furthermore explored conditions to recover the catalysts initial activity, seemingly due to indirect involvement of the HER. A similar loss of activity occurs in industrially applicable ODCs and hence we transferred the basic concept of catalyst regeneration from the nanoscale to macro-scaled ODCs (cm²). That allowed for the identification of the species formed on the surface and in the pores during deactivation utilizing a multitude of analytical tools such as X-ray photoelectron spectroscopy (XPS), Raman spectroscopy as well as scanning electron microscopy (SEM) combined with focused ion beam milling (FIB). The recovery is presumably achieved by a combination of the highly reductive potentials as well as the formed “nascent” hydrogen, accounting for additional reductive driving force in the system. This study represents an example, in which knowledge obtained in nanometric experiments facilitates solving industrial challenges.²

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Acknowledgements

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Probing the degradation pathways of PEM water electrolyzers under dynamic operating conditions with advanced microscopy methods

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Understanding the degradation phenomena in polymer electrolyte water electrolyzers (PEWEs) is imperative in view of the high cost of membranes and Ti based components, as well as the scarcity and high cost of Ir, the only material that can presently fulfill the activity and stability requirements of anode electrocatalysis. Herein, a commercial membrane electrode assembly (MEA) with Ir based anode is subjected to different operating modes in the course of 830 h testing at 60 °C; potential sweeping with short and long holds close to the apparent reaction onset (1.4 V) and moderately high potential (1.8 V), in order to simulate conservative PEWE operation coupled with fluctuating renewable energy sources. Steady-state interims were pursued at early testing stages and at the end of the test to serve as reference. The PEWE operation was systematically interrupted to identify degradation modes by in-situ electrochemical methods, while ex-situ physiochemical methods were applied, to discriminate between degradation sources. Enhanced but recoverable performance losses were observed under steady-state conditions. On the other hand, dynamic operation induced irreversible degradation, albeit with significantly lower rate. The post-test analysis revealed the morphological, structural and chemical changes, confined within or close to the anodic catalyst layer/membrane interface. These are attributed to Ir dissolution/re-deposition and the formation of radicals during dynamic operating conditions.

Figure 1: (left) $E_{\text{HFR free}}$ and current density at 1.8 V during dynamic operation (up) and polarisation curves (down). (right) HR-TEM images and EDX spectra of the anode/membrane interface.
Analysing the performance instability of H₂-O₂ Alkaline Membrane Fuel Cell due to water imbalance

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The performance of alkaline membrane fuel cells (AMFCs) has improved considerably during the last decade with power densities rising from 0.1 W·cm⁻² to 2 W·cm⁻² [1]. It has been found that similar to proton exchange membrane fuel cells (PEMFCs), the hydrogen oxidation reaction (HOR) is not a limiting reaction and the oxygen reduction reaction (ORR) is the sluggish reaction [2]. Hence, major power improvements were overly due to appropriate water management. Although now the AMFC performance is on par with state-of-art PEMFC, the high power obtained in AMFC is only stable intermittently. Depending on the membrane and gas diffusion electrodes (GDE) water transport characteristics, either the anode flooding and or cathode dry out takes over in short time causing rapid drop in power. In most cases it could be noticed in the literature that the stable and high AMFC performance is obtained only at high relative humidity (>90%) values and unusually high reactant flow rates. High relative humidity eliminates cathode dry out, but can introduce early anode flooding and sometimes also cathode flooding. To subdue this, unusually high flow rates of H₂ and O₂/air are used to flush out the excess water. However, for a practical AMFC, this operating strategy can lead to high operating cost due to fuel wastage and would require a more powerful air compressor/blower. Hence, insight into the dynamics of water transport across the membrane and GDE, can lead to design of the AMFC such that it can operate at reasonable flow rates.

At a given cell potential, the current of the fuel cell is expected to be constant. However, in AMFC the performance fluctuates and drops rapidly. During this current drop, we have observed yet two types of behaviour, periodic undershooting and overshooting of current. To investigate this behaviour, in this work, specially designed heated chambers were installed in the gas lines of inlets and outlets of AMFC. These heated chambers were used to accommodate the humidity sensor and were designed in a way that no condensation occurs inside the chambers or on the humidity sensors. From the humidity sensor measurements, the amount of water entering and leaving the fuel cell is calculated. Further water balance inside the cell gave insight into the dynamic water shift between the anode GDE and cathode GDE when the current overshooting/undershooting occurred. Also, from reference measurements of water diffusion across the membrane, the water drag coefficient was calculated. The results of these studies will be presented in this GDE symposium.

References:
Novel nanoparticles synthesis method by gas-diffusion electrocrystallization

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Gas-diffusion electrocrystallization (GDEx) is a new and rapid one-pot reaction crystallization process steered at the three-phase junction between a porous carbon gas-diffusion cathode, an aqueous electrolyte containing metal ions and an oxidant gas, which serves as a flexible and robust platform to synthesize numerous types of well-controlled crystalline nanoparticles. Figure 1 shows a scheme of GDEx process. An oxidant gas e.g. (O₂) is forced though a hydrophobic backing on the electrically-polarized porous cathode. After it diffuses to the electrocatalytic surface (e.g., activated carbon), the gas is reduced. For instance, by imposing specific cathode polarization conditions (e.g., -0.145 V_SHE), O₂ is electro-reduced to H₂O₂ in a 2 electron (2 e⁻) transfer process and H₂O in a 4 electron (4 e⁻) transfer process, (1), as per the established mechanism of O₂ reduction at non-catalyzed carbon electrodes¹. The products of the electrochemical reduction of the oxidant gas react with the metal ions (Mⁿ⁺) and provide the decisive pH and redox potential conditions to form inorganic nanocrystallites which may remain in a stable colloidal dispersion (2). The nano-crystallites formed grow into nanoclusters or nanoparticles (3), which may eventually sediment to be further recovered as powders (4). The inset TEM photomicrography shows a disperse magnetite nanoparticles of about 20 nm, produced by GDEx.

Figure 1: Gas diffusion electrocrystallization concept for the synthesis of magnetic nanoparticles

Reference:


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Three-phase activity of unsupported high-surface area catalysts towards oxygen reduction in the gas diffusion electrode

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Screening of proton exchange membrane fuel cell catalysts for the oxygen reduction reaction is usually carried out within the rotating disk electrode half-cell arrangement. However, it turned out that the activity measured in the liquid half-cell cannot easily be transferred to the single fuel cell even at the typical slight overpotential of 0.9 V vs. RHE. In addition, the operating overpotential under load in the fuel cell is even higher which questions the significance of the activity measured under mass-transport defined fluid conditions. In order to overcome this challenge, we characterized unsupported high-surface area catalysts in a simple gas diffusion electrode half-cell setup. The gas diffusion electrode is placed beneath the membrane and mimics real fuel cell conditions. This enables rapid screening of the realistic catalyst activity at the three-phase boundary in order to identify the limiting steps of the reaction and enable optimization of the catalyst layer.

For the unsupported catalyst it was measured that the specific activity in the liquid cell is as high as bulk Pt. The mass activity of the unsupported high surface area catalysts in the liquid cell is mainly driven by the electrochemical surface area. Various electrochemical protocols performed in the gas diffusion electrode half-cell setup clarify the behaviour of the thin layers at different potentials, during linear sweeps and under dynamic conditions. The activity of standard supported Pt/C catalyst in the gas diffusion electrode is compared with the advantages and disadvantages of unsupported catalysts. Most important, it can be concluded that due to the lack of carbon and ionomer the availability to oxygen and protons is different and has to be optimized. Furthermore, different magnetron sputtering parameters result in other electrochemical, morphological and mass-transport characteristics of the gas diffusion electrode catalyst layer.

References:

Using GDE half-cell experiments to close the gap between fundamental and applied fuel cell electrocatalysis

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Although modern fuel cells are based on the utilization of solid membranes, fundamental catalyst research is mainly done in aqueous solutions via rotating disk electrode (RDE) or similar techniques. However, due to low solubility of reactant gases (H₂ and O₂) in those electrolytes mass-transfer limitation occurs at potentials relevant for the fuel cell operation (0.6 – 0.8 V vs. reversible hydrogen electrode - RHE [1]). The estimated kinetic parameters from those experiments have to be extrapolated to achieve kinetic data in the relevant potential range. However, there are many open questions on the validity of such extrapolations. Therefore, in addition to RDE measurements, membrane electrode assemblies (MEA) tests are employed to evaluate catalysts in realistic fuel cell conditions. These experiments are complex (as they include a variety of different parameters), time-consuming and require large quantities of catalysts and expensive test equipment. To close the gap between fundamental and applied research intermediary testing methods need to be introduced, which should combine the advantages of both approaches. Half-cell measurements using gas diffusion electrodes (GDE) have recently been considered to be the most suitable method allowing high mass transport catalyst screening in relevant potential ranges and realistic electrode structures. [1-3]

Oxygen reduction reaction (ORR) experiments on Pt/C GDEs revealed that, using this approach, it is possible to achieve current densities of up to 2 A/cm². In contrary to other proposed methods [3], it was thereby possible to overcome mass transport limitations at relevant fuel cell operating potentials. While testing different Pt-loadings, a dedicated testing protocol was established and, using this protocol, good comparability between the various measurements was achieved. The experimental data was compared to full cell experiments and good compliance was confirmed, which proofs the method’s suitability for catalyst evaluation in realistic fuel cell potential ranges. Thus, a new powerful experimental tool for decidedly catalyst layer evaluation for fuel cells or other electrochemical three-phase reactions (e.g. CO₂ reaction) is developed and successfully applied in the fuel cell research.

The further scope is to extend this approach (i) to different catalyst systems and (ii) by enabling high-throughput screening of catalysts. For the latter, a modification to a scanning flow cell (SFC) [4] setup is suggested. With this new device it is possible to rapidly screen the activity of electrocatalysts depending on different material properties (e.g. catalyst loading gradients on one axis and structural property gradients such as pore size, ionomer content of membrane etc. on the other axis) using GDEs. Thus, the most suitable electrodes under realistic fuel cell conditions can be worked out in a fraction of the time required for the conventional methods.

References:
Acid Migration in the Gas Diffusion Electrode of High-Temperature Polymer Electrolyte Membrane Fuel Cells

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As the proton conducting medium, phosphoric acid (PA) plays a vital role in the operation of high-temperature polymer electrolyte membrane fuel cells (HT-PEMFCs). During operation, PA accumulates in the exhaust water, complicating water recycling and corroding the piping and the bipolar plates. Understanding the PA migration during the activation phase and the acid loss during operation would allow for improved HT-PEMFC designs that optimize catalyst utilization to the benefit of overall performance and durability.

In this work, we investigate the PA flow behavior in the gas diffusion electrode (GDE) of HT-PEMFCs. An HT-PEMFC GDE composed of a catalyst layer, a microporous layer (MPL) and a fibrous substrate was assembled, and its three-dimensional (3D) geometry was imaged using synchrotron X-ray microcomputed tomography and focused ion beam-scanning electron microscopy (FIB-SEM). Thereby, the spatial distribution of pores, carbon support, binder and platinum catalyst material were identified. We used pore network modeling to predict the mass redistribution of PA within the catalyst layer and the MPL. It was found, and an equivalent pore network of the GDE was obtained for simulating the PA transport with an invasion percolation algorithm¹. A pore-scale model was employed to compute the effective diffusivity of gas species and ionic/electronic conductivities of the catalyst layer model reconstructed from FIB-SEM images, which had PA distribution simulated using a multi-relaxation time Lattice Boltzmann model. The predicted mass redistribution of PA in the GDE was found that the presence of the MPL encouraged the containment of PA within the catalyst layer² and discouraged acid leaching toward the channel.

Figure: Acid migration in the GDE

References:
Understanding the influence of different porous microstructures derived from diverse drying methods of the cathode catalyst layer in PEMFC

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The heart of the Polymer electrolyte membrane fuel cell (PEMFC) is the membrane electrode assembly (MEA), which consists of gas diffusion medium, active catalyst layer and polymer electrolyte membrane. The catalyst layer (CL) should enable high activity by large interface area and superior gas transport by effective porosity. It is established that transport limitations are significant for PEMFC performance, and it is reported that limited diffusion or accessibility of the reactant gas to the reaction site and poor water management are important. Catalyst-loaded membrane and gas diffusion medium in contact with the electrolyte allows the easy permeation of oxygen from the surrounding atmosphere and its subsequent reduction on supported electrocatalysts. Our group has introduced the freeze drying of CL prepared from suspensions that promotes the porosity of the catalytic layer and correspondingly improves the diffusivity and ionomer distribution [1]. To remove the solvent from the coating, drying step is essential. The major characteristic of freeze drying is removal of solvent by sublimation of the solid state. Thickness of the catalyst layer can also be controlled by controlling the catalyst ink composition in this drying method. Freeze drying of MEAs reduces the mass transport resistance by 20 %. In this work, we have investigated the influence of different drying techniques on microstructure of wet-coated electrodes and the structure performance relationship. We have also performed simulation into a transient 2D physical continuum-model to investigate the effect of the structural properties of the differently dried electrodes on cell performance. This modeling approach determines model parameters that describe a specific electrode structure through an optimization procedure which utilizes data from carefully planned experimental studies.

Reference:
A ternary-based composite as cost-effective, efficient and durable catalyst layer for bifunctional gas diffusion electrodes

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The high theoretical energy density promised by metal-air batteries has prompted large research incentives for the development of more efficient and long-lasting bifunctional gas diffusion electrodes (GDEs). Conventional GDEs are typically made of a two-layered structure: a gas diffusion layer and a catalyst layer. The former must provide both high gas transport rates as well as electrolyte retention capabilities. The latter must exhibit high reactivity and selectivity in reaction products for both the oxygen reduction reaction (ORR, discharge) and the oxygen evolution reaction (OER, charge), and, additionally, it has to demonstrate high stability toward several charge-discharge cycles. Theoretical concepts based on density functional theory [1] showed that the limitation imposed by linear scaling relations implies that the optimum reactivity for both reactions cannot be reached with a single type of catalytic site. State-of-the-art carbon supported Pt and RuO₂ or IrO₂ catalysts are currently the most accepted benchmark electrocatalysts for oxygen reduction and water splitting reaction. However, the prohibitive costs and low abundance of such noble metals pose the limitation of their wide-spread for commercial applications. Thus, finding and a stable, cost-effective and efficient catalyst mixture for bifunctional GDEs is an imperative. Among low-cost alternatives to noble metal electrocatalysts, transition metal oxides and hydroxides based on manganese (α-MnO₂) and nickel (Ni/NiO/NiOOH) have recently gained much attention due to their remarkable catalytic activity for ORR and OER, respectively. Several attempts have been made to couple the electrochemical properties of those transition metal oxides [2-4], but a stable and efficient hybrid Mn-Ni oxide catalyst has still to be identified.

Herein, we present a systematic study on the influence of the catalyst composition for the promotion of the ORR/OER activities. This was performed by combining α-MnO₂, commercial carbon black and Ni nanoparticles into binary mixtures, namely α-MnO₂/C, α-MnO₂/Ni and Ni/C with different weight ratios. We detailed synergetic effects taking place on the different species by comparing their ORR/OER activities by means rotating ring disk electrode (RRDE) techniques. We found that the all these three systems exhibit a volcano-type behaviour with respect to their composition, suggesting an optimum utilization of the available catalytic sites. Benefiting from these activity-composition relationships, we designed a α-MnO₂/C/Ni ternary-based catalyst with promising ORR and OER activities. Further insights down to the atomic scale level and describing the electrocatalytic processes on this material were gained from in operando XAS studies and will be discussed in this communication. Finally, the catalyst mixture was embedded as bifunctional GDE that showed remarkable performances, displaying higher power density and high cycling stability than the state-of-the-art Pt/C/IrO₂ ternary systems, and high stability after successive charge/discharge cycles. The work will provide a rational design for efficient and cost-effective bifunctional OER and ORR catalysts for rechargeable alkaline metal-air batteries.

References:
Development of new carbon free electrode for application in secondary zinc-air cells

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The development of rechargeable zinc-air batteries is a hot topic because of the advantages of these systems: high energy density, high capacity and low cost. The main problem with their commercialization is the lifetime, which is related to the degradation of the electrodes during cycling. In respect to the gas diffusion electrode, the main difficulty comes from carbon oxidation during charging. The problem-solving approach is the replacement of carbon with non-carbon material. One possibility is the application of solid oxides with perovskite structure. This work presents an innovative solution for development of monolithic solid gas diffusion electrode produced by standard ceramic technology (cold pressing and sintering) based on Lanthanum Strontium Manganite (LSM). The presentation gives more detailed description of the technological procedure for production of samples with sufficient porosity and hydrophobicity [1]. The first results of the performed electrochemical tests show that the samples are stable for more than 1000 cycles.

Acknowledgements:

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References:

[1] Zinc Air Secondary innovative nanotech based batteries for efficient energy storage (ZAS), EU Horizon 2020 framework NMP Project GA 646186, https://www.sintef.no/projectweb/zas
Effect of wetting behaviour on the electrochemical performance of bifunctional gas diffusion electrodes for electrically rechargeable zinc-air batteries

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Increasing electricity generation from renewable sources such as wind and photovoltaics leads to fluctuating feeding of electricity into the power grid and at worst risking instabilities in the supply. One solution is to store surplus energy electrochemically using electrically rechargeable batteries, which can be discharged when electricity is needed [1]. Though lithium-ion (LIB) and lead-acid batteries (LAB) are used predominantly, electrically rechargeable zinc-air batteries (ZAB) are considered a very promising alternative. Compared to LIB and LAB, ZAB possess sufficient material availability, enhanced operational reliability, environmental friendliness and considerably high energy density [2]. However, the development of stable and durable bifunctional gas diffusion electrodes (GDE) for ZAB is still a challenge as they must enable both the Oxygen Reduction Reaction (ORR) and Oxygen Evolution Reaction (OER) in KOH aqueous electrolyte while withstand the harsh conditions under repeated cycling and therefore not at least mainly depend on the (bifunctional) activity and (electro-)chemical stability of the applied electrocatalysts. State of the art GDEs consist of an oxygen/air permeable gas diffusion layer (GDL), metal mesh current collector and reactive layer using carbon-supported precious metal catalysts and hydrophobic polymer binders to avoid flooding of the reactive layer and thus creating a three-phase reaction zone to specifically address ORR active sites. Bifunctional GDEs must fulfil additional requirements regarding the wetting behaviour of the reactive layer: Whereas the ORR requires three-phase reaction sites, the OER needs a two-phase reaction zone (solid (catalyst)/liquid (electrolyte) interface) and thus requires a meticulously adjusted proportion of hydrophobic as well as hydrophilic properties within the reactive layer [3, 4].

This contribution highlights the development of a durable and active bifunctional GDE for ZAB including the synthesis and characterisation of two non-precious metal catalyst materials, α-MnO₂ and Co₃O₄ as ORR and OER catalyst respectively, fabrication of GDEs and finally their testing in a full cell ZAB. Bifunctional GDEs are fabricated through electrode slurries containing the most active catalysts, carbon black, graphite flakes and a binder, which are applied on commercial GDLs using a blade coating technique. As binder a mixture of hydrophobic Styrene-butadiene rubber (SBR) and hydrophilic Sodium carboxymethyl cellulose (Na-CMC) is used. The electrochemical performance of the GDEs is evaluated in full cell ZAB configurations using El-Cell® ECC Air test cells by means of discharge/charge polarisation measurements, electrochemical impedance spectroscopy and repeated charge/discharge cycling. The wetting behaviour of the reactive layers is characterised by means of contact angle measurements. Through a successive variation of the ratio of SBR and Na-CMC the effect of contact angle on the electrochemical performance of GDEs is evaluated and the optimum wetting behaviour for the highest activity of both catalysts is identified.

References:
**Stable carbon materials for metal/air batteries and PEM fuel cells GDEs**

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In this contribution, we report on recent investigation of GDE materials for both alkaline Zinc/Air Battery (ZAB) and PEM Fuel Cell (PEMFC). Especially, carbon material plays a preponderant role regarding catalyst and gas diffusion electrode stability. While in electrically rechargeable ZAB carbon acts as an electronic booster and is usually mechanically mixed with the bifunctional catalyst, in PEMFC, carbon is commonly used as support structure for nano-dispersed Pt-based catalyst.

Market penetration of electrically rechargeable alkaline ZAB is hindered by principally low energy efficiency (<60%), carbonate & dendrite formation as well as poor stability of bifunctional GDE mostly due to catalyst collapse but also to limited carbon stability. In that context, we have characterized several commercially available carbon and graphite materials by means of electrochemical, thermal and physical techniques and founded that appropriate balance between BET surface and graphitic domains is of great importance for carbon and consequently for GDE long-term-stability. By mixing the best commercial carbon sample with a BaSrCoFeO$_3$ (BSCF) bifunctional catalyst, an outstanding stability was observed for over 3600 h during oxygen reduction/evolution reactions (ORR/OER) cycling in 6 M KOH at 10 mA cm$^{-2}$ for 2.5 h each step [1].

Also, in PEMFC, carbon plays a key role especially in the cathode where severe degradation mechanisms occur. It is meanwhile well-accepted that some carbons with a spherical shape and mesoporous surface structure are more capable to stabilize Pt catalyst that microporous benchmark materials. Since hart-template synthesis routes are highly time-consuming and mostly not suitable for industrial production scale-up, we have investigated feasibility of carbon synthesis by soft-template route. Promising results in terms of particle and pore size were obtained from a hydrothermal route with F127 as template, Resol as carbon source and HCl as cross-linking agent. Activity for ORR and stability of two as-prepared Pt/C was investigated under RRDE and GDE half- cell conditions and compared to that of a commercial Pt/C$_{Vulcan}$ catalyst.

References:

Poster Presentations
The Developments of Carbon-based Gas Diffusion Electrodes (GDEs) at IEES

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Currently, using the developed at IESS innovative technology for high energy mixing of teflonised carbon [1], efforts were concentrated on the development of secondary Zn/Air batteries with an accent on the bi functional oxygen electrode (BOE). The innovative technology for high energy mixing of teflonised carbon, which ensures extremely homogeneously distribution of the basic components for the gas diffusion layer Teflon on to carbon particles (with a high level of teflonisation up to 60%), exhibited that the produced electrodes with several commercial catalysts (including cobalt oxide, NiCo₂O₄ and silver) show good stability for more than 1000 cycles. That may be regarded as one of the best results achieved.

Acknowledgements:

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References:

Controllable Preparation of Graphene-based air electrode for Efficient Rechargeable Mg–Air Batteries
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The catalytic material of the air cathode is mixed with manganese dioxide, graphene, acetylene black, silver oxide and polytetrafluoroethylene in different proportion. The proportion of graphene in the materials is about 8%. The air electrode was prepared by rolling the multi-layer materials (catalytic layer, waterproof layer, collector network, waterproof layer) together on the framework of copper network. The addition of graphene greatly enhanced the catalytic efficiency and time of the air cathode.

Figure: SEM image of Graphene-based air electrode
Highly Mesoporous Carbon Derived from Cigarette Butt as Efficient Electro catalysts for Zinc-Air Batteries

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Zinc-air batteries are promising candidates for various future energy applications due to their low cost, safety, high specific energy density, and environment-friendliness. The air cathode is a critical factor determining the overall performances of the batteries as they are mostly hindered by the sluggish kinetics of oxygen reduction reaction (ORR) of the air cathode. Therefore, the development of high-efficiency ORR catalysts, as well as high-performance air cathodes, is significant in improving the performances of the batteries. To fabricate the air cathode, ORR catalysts are dispersed with carbon black and binder, and subsequently, deposited on a current collector with a porous gas diffusion layer. Nevertheless, it is difficult to reach a uniform dispersion. Besides, the introduced binder could result in a loss of active sites and degradation of conductivity. Various approaches to fabricate highly efficient catalyst were proposed such as efficient metal, well dispersion metal on the substrate, high porous substrate, applying bimetals, conductive binders and etc.

To address this problem, we propose a facile and cost-effective approach to fabricate an air cathode for zinc-air batteries via an in-situ synthesis of mesoporous carbon using cigarette butts as a soft template. The resulted mesoporous carbon structure exhibited a decent degree of accessible porosity, high surface area, high electrical conductivity and high chemical, thermal and mechanical stability. Also, non-ionic surfactants Pluronic F-127 was separately used as a soft template. The impact of the acid amount and the surfactant/carbon precursor ratio were examined to determine the optimum ratio of the polymer solution. The optimum surfactant/carbon precursor ratio was selected based on electrochemical properties cyclic voltammetry, impedance spectroscopy, and potentiodynamic polarization. The highest peak current, lowest resistance with less negative rest potential of potentiodynamic polarization were yielded for a polymer solution containing P127 and g cigarette butt with ratios 40:60 wt\%, respectively. By adding MnO\textsubscript{2} as the ORR catalyst to the polymer solution and casting over Ni foam, a high-performance air cathode for the zinc-air batteries was fabricated without using any binders. Performances of the fabricated air cathode were then investigated in home-made zinc-air flow batteries.
Wetting behavior of electrolyte in a GDE and how it affects performance in Zn-air batteries

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One of the major drawbacks for today’s energy market of renewable energy production is that there is no cost efficient possibility to store produced energy for times when renewable energy production is less then energy consumption. Despite the success of Li-ion batteries, there is a push towards the open cell architecture of metal-air batteries and the use of metallic anodes, both together resulting in a high energy density. Because of that lighter batteries can be build and the only limiting factor is the amount of reversible active usable metal inside the battery. Zinc-air and Lithium-air batteries have attracted the most attention. Primary Zinc-air batteries are well developed and commonly used as button cells in hearing aids. Besides this, zinc has more advantages, zinc is a cheap metal which is commonly occurring in the environment, production of Zn-Air batteries can be done in any atmosphere which makes it cheap in production and zinc is environmentally benign. Because of all these advantages these Zn-Air batteries are of high interest for stationary energy storage systems.

Before commercialization of electrical rechargeable some challenges have to be overcome. Deterioration of cathode material leads to flooding of the cathode eventually to cell failure. Beside this long-term influence changing wettability, during each discharge conversion of Zn to ZnO leads to higher electrolyte pressure which might result in increased electrolyte uptake of the porous cathode. To mimic this behavior of the zinc anode and study its influence an electrolyte intrusion cell was build to record pressure saturation curves [1] for cathodes with varying pore size distributions and states of health. With the help of these measurements the influence of cell life on wettability of the cathode could be shown. Furthermore, the influence of electrolyte pressure caused by volume increase of the anode could be shown by comparison of pressure saturation curves and correlation of these with U-I Curves for varying electrolyte pressures up to 25 mbar.

References:
Caffeine modified active carbon as catalyst layer in gas-diffusion electrodes for aprotic metal-air systems

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The metal-air and fuel cells are among the most promises candidates as successor technology of lithium-ion and lead-acid batteries.\([1]\) The cheap and effective alternative for Oxygen Reduction and Evolution Reactions (ORR/OER) of noble metal catalysts is needed to accelerate commercializing of metal-air systems. Finding of a nature friendly solution of that challenge is preferred.

In this study, we are presenting behaviour of doped with caffeine and thermal treated active carbon Norit NK. So prepared active carbon, was used as catalytic layer of a gas-diffusion electrode made by patented technology.\([2]\) Physicochemical (SEM imaging, XRD spectroscopy) and electrochemical (Cyclic Voltammetry, Charge-Discharge curves) analyses were made, and the results of caffeine doped Norit NK were compared to 5% Platinum doped Norit NK. The electrochemical measurements are made in two electrodes cell, in which for counter and reference electrode lithium foil with diameter 18 mm is used. As electrolyte 4M LiNO\(_3\) in DME to DMSO 1:2 is used. The catalyst layer contains 20 mg.cm\(^{-2}\) of caffeine- Norit NK or platinum- Norit NK mixtures.

During the thermal treating process of caffeinated Norit NK under argon, more than 90% of the caffeine sublimes. The SEM image shows the complex morphology of the active carbon crystallites, after that process. The XRD pattern show a small amount from caffeine residues. The observed cyclic voltammetry curve shows a broad oxygen reduction peaks for both of catalysts. Five charge-discharge cycles at 0.25 mA in an air atmosphere for both catalysts were did.

![Fig. 1A](image1.png) ![Fig. 1B](image2.png)

**Figure 1A:** SEM image of caffeine doped Norit NK catalyst at 10000x, **1B – CV of caffeine doped Norit NK, compared to Platinum doped Norit NK at scan rate 0.5mV/s**

References:


Performance Improvement of Lead Acid Batteries by Crystallized Graphite Powders in Negative Electrodes

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This research explores the application of carbon materials to lead paste for conductivity improvement, battery capacity increment and cycle performance enhancement. The experiments used carbon black (CB), activated carbon (AC), graphite carbon powder (Graphite Carbon, GC) and other additives into lead powder to make a lead paste, then through ripening and chemical processing steps [1, 2]. The produced active substances can effectively inhibit the crystal growth of lead sulfate and further increase battery cycle life (Cycle). The experiments included three groups of samples, 0.3 wt% GC + 0.3 wt% CB, 0.3 wt% AC + 0.3 wt% CB, 0.6 wt% GC, and two types of batteries, WP5-12/12 Volt 5Ah, WP6-12/12 Volt 6Ah, then analyzed their performances. The experiments used Raman spectroscopy and X-ray Diffraction (XRD) to measure the carbon materials properties and active substances. Fig. 1 shows the graphitization measurement by using Raman spectroscopy for different carbon materials. The high peak at 1580 cm⁻¹ represents a high degree of graphitization, eg. the top line of N908 carbon in Fig. 1. The XRD results showed the high graphitization carbon with crystallines. The appearances of the carbon materials and the active materials were observed by a Scanning Electron Microscope (SEM). Finally, the results show that 0.6 wt% GC with crystalline structure has a relatively high initial capacity of 4.97 Ah and 4.86 Ah, and it has relatively high energy efficiency in cyclic charge and discharge about 98%.

![Graphitization measurement comparison of different carbon materials.](image)

References:
Towards realistic benchmarking of fuel cell catalysts – Bridging the gap between RDE and MEA.

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Low-temperature polymer electrolyte membrane fuel cells (PEMFCs) are of fundamental importance for sustainable energy conversion. The energy efficiency is largely determined by the slow kinetics of the oxygen reduction reaction (ORR); as a result, high platinum loadings at the cathode currently inhibits the widespread commercialization of PEMFCs. In recent years, remarkable progress has been made on improving the mass activity of ORR catalysts. In liquid half-cells using thin-film rotating disc electrode (TF-RDE) numerous model catalyst concepts have presented activities far surpassing the performance targets given by the Department of Energy (DOE). However, so far, these impressive results haven’t been translated to actual fuel cell devices e.g. membrane electrode assemblies (MEA).

Herein, we present a gas diffusion electrode (GDE) half-cell setup [1] that combines the strength of both RDE and MEA. Similar to RDE, the GDE allows rapid and inexpensive testing using small quantities of catalyst. Notably the GDE resembles the MEA in terms of reaction environment and reactant mass transport, thus allowing catalyst activity benchmarking at high current densities [2], opposite to RDE where benchmarking is limited to low overpotentials (typically 0.9 \( \text{V}_{\text{RHE}} \)) due to poor \( \text{O}_2 \) transport in the liquid electrolyte. By applying similar conditions to actual fuel cell devices (e.g. temperature, membrane and humidification), we show that the performance data obtained from GDE measurements can be directly compared to that obtained in MEA tests, hereby lowering gap between model systems and real devices.

**Figure (a)** Schematic of the GDE cell, **(b)** Comparison of I–V curves obtained from the GDE cell and the MEA test for the commercial 46.5 wt% Pt/C catalyst.

References:


In situ estimation of the effective (Nafion® & Anion) membrane Water diffusion coefficient in a PEMFC

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Estimation of In situ Diffusion coefficient in membrane is a difficult task as different experimental setups and uncertainties have their values ranged from 10⁻⁵ – 10⁻⁹ cm²/s [1]. What does not change is the (p/EW) as depicted in [2]. In our research, we calculated diffusion through membrane by Fick’s law in Nafion® membrane as a function of temperature. Relative humidity and thickness. Water balance method [3] is used for the calculations figure (1). An interesting observation is analysed relating $D_t$ (Fick’s Diffusion constant) calculated through our experiments and $D_l$ observed from [1]. Experiments are also conducted with Nafion® 212, Nafion® 211 and Anionic A201 Tokuyama and interesting results are analysed, few are tabulated in Table (1). A relation between $D_l$ and $D_t$ is explained and the values presented below are multiplied by the factor of (p/EW) where p = 1970 kg/m³ and EW = 1.1 kg/mol. Results were also calculated with the entire fuel cell set up considering GDL, Membrane and the catalysis layer. Interesting results are approach with water balance approach in the system.

![Figure 1: Fuel cell water Balance Setup](image1)

![Figure 2: Conditions to measure the flux](image2)

<table>
<thead>
<tr>
<th>Anode section and cathode section</th>
<th>Fuel cell Temperature-70 Diffusion coefficient ($D_t$) (m²/s) Nafion®</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Humidity</td>
<td></td>
</tr>
<tr>
<td>A - 20 C - 40</td>
<td>3.17 * 10⁻¹¹</td>
</tr>
<tr>
<td>A - 20 C - 60</td>
<td>4.5 * 10⁻¹¹</td>
</tr>
<tr>
<td>A - 20 C - 80</td>
<td>4.83 * 10⁻¹¹</td>
</tr>
<tr>
<td>A - 80 C - 60</td>
<td>7.25 * 10⁻¹¹</td>
</tr>
<tr>
<td>A -100 C - 80</td>
<td>9.02 * 10⁻¹¹</td>
</tr>
</tbody>
</table>

Table 1: Effect of Relative Humidity across fuel cell for Nafion® Membrane

References:

Permeability for gaseous reactants – a key characteristic of PEM FC gas diffusion layer

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Gas diffusion layer (GDL) is an inherent part of a gas diffusion electrode (GDE). GDL ensures conductive connection, access of fuel and oxidant to the catalytic layers and serves as physical support in polymer electrolyte membrane (PEM) fuel cells (FCs). Characterization of GDL is not an easy task due to its properties.

Within this work, GDLs without micro-porous layer were studied. In other words, only the macro-porous substrates of GDL underwent throughout characterisation. The results are presented for GDL from Freudenberg, type H23, which is non-woven carbon fibre GDL. Both through-plane and in-plane permeability were determined in flow-through cells using hydrogen and nitrogen gas.

Schemes of both cells are presented in Figure 1. Through-plane permeability was measured using several layers of GDLs to achieve sufficient pressure drop. The obtained dependence of overall pressure drops on linear velocity of streaming gas was used to evaluate GDL permeability. Darcy's law was used for this purpose. In case of through-plane permeability only uncompressed samples were studied. It was because of experimental difficulties and due to the fact, that for this direction the GDL compression impact on its permeability is less significant. On the other hand, in-plane permeability was determined for various degrees of compression. The channels 125, 159 and 168 µm thick corresponding to the GDL compression of 35, 17 and 13 % respectively were used. The size of a single layer GDL sample was 5 × 4 cm². Results obtained reveals strong dependence of in-plane permeability on GDL compression. Also, in case of in-plane permeability, its value is evaluated by means of Darcy's law.

![Figure 1: Schema of flow through cells for measuring of pressure drop, left: for through-plane permeability right: for in-plane permeability.](image)

Both cells underwent through long development and now provide reliable results. The reproducibility of results, regardless used gas, is very good.

The work was supported from European Regional Development Fund-Project "Fuel Cells with Low Platinum Content" (No. CZ.02.1.01/0.0/0.0/16_025/000741).
Tuning the structure of Pt-Co catalyst materials for the oxygen reduction reaction in PEM fuel cell applications

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Polymer electrolyte membrane (PEM) fuel cells will play an important role in the clean and versatile energy conversion for mobile and stationary applications in the near future. However, high loadings of very costly and scarce platinum group metal (PGM) electrode materials and insufficient long-term performance hinder the wide commercialization of PEM fuel cells to date.[1] Thus, the development of highly efficient and robust catalyst materials is essential. In this context, a promising approach to accelerate the kinetics of ORR is the utilization of nano-structured Pt-Co alloy catalyst materials.[2]

The target of this work is the preparation and characterization of various Pt,Co 1-x (1<x<0) alloy nanoparticles supported on carbon under real hydrogen/air fuel cell conditions. The chemical composition and structure of the as-prepared Pt-Co nanoparticles are controlled by variation of the synthetic parameters during the wet impregnation method. Transmission electron microscopy (TEM), X-ray absorption spectroscopy (XAS), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD) are employed for characterization. The goal is to find a correlation of the Pt-Co catalyst structure with their catalytic ORR performance. Therefore, catalyst-coated membranes were prepared via decal transfer and investigated in a full cell under real hydrogen/air fuel cell conditions. With increasing Co content, we show an enhancement of the Pt surface area-based specific activity and the Pt mass-based activity for the ORR compared to commercial Pt/C. The next steps are further optimizations regarding the phase boundaries by minimizing the proton conducting resistance and oxygen mass transport resistance inside the cathode electrode layer.

Based on our results, we present a promising Pt-Co catalyst system to boost the ORR activity for PEM fuel cell applications.

References:
Micro-CT imaging of electrolyser gas diffusion layers to extract pore space information for pore network modeling

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At the anode side of an electrolyser, water must be supplied efficiently to the electrode and oxygen (product) must be removed simultaneously. This counter current flow occurs within the gas diffusion layer (GDL), a porous medium. An electrolyser, when operated at high current density, shows a significant decrease in the performance due to the mass transfer resistances. This is primarily due the high oxygen production rate which obstructs the supply of water towards the reaction zone. The rate of reaction, and therefore the efficiency of the system, is reduced because of this insufficient water supply. The removal of oxygen is thus a very important factor to maximize the water supply and hence the performance. This requires a deep understanding of the pore scale distribution of gas and liquid phase. Due to the microscale nature of GDL porous media, it is not convenient to study experimentally the transport phenomena within. Pore network modeling (PNM) conceptually represents the porous media and provides a micro-scale approach with relevant two-phase flow physics to study the transport in GDLs. PNM is suitable for low capillary numbers and takes wetting characteristics into account. It is assumed that the gas produced in high quantities, to a certain extent, drains out the water from the GDL. It can be shown by PNM that the tortuosity of the gas paths penetrating the GDL and the water and oxygen permeability essentially depends on the pore structure, local temperature and wettability of the GDL as well as local pressure differences. Parameters (e.g. permeability) can then be extracted from the steady-state quasistatic simulations. As the GDL is a thin porous medium, the size of the pore network can be adjusted to the size of the GDL. Micro-CT measurements can be used to extract information of porous medium and used in PNM. As shown in the figure below, first of all, micro-CT images are obtained for the GDL porous medium. After that, in-plane slices of these images are binarized and then used as an input to a pore extraction algorithm. Bigger voids are approximated as pores and relatively smaller ones are throats. The output obtained is the size and volume of pores and throats present in the medium and also their locations, which can then be used in the pore network model to simulate a GDL using its actual attributes.

![Image](image-url)

**Figure:** Transformation of porous media to a pore and throat network [1] [2]

References:


Simple and straight-forward thermal preparation of metal oxide nanocatalysts from commercially available metal precursors for electrochemical water oxidation

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One of the efficient sources of energy is water to fulfill the high demands of global energy, which could undergo electrochemical splitting to produce green fuel in the form of hydrogen gas. In the production of hydrogen by electrochemical or photoelectrochemical methods, efficient water oxidation \((2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + 4e^- + \text{O}_2)\) is important since the necessary proton for production of molecular hydrogen fuels is generated in this step. As a result, the efficiency of electrochemical generation of hydrogen from water partially depends on favorable catalysts to promote the oxygen evolution reaction (OER). In the last few decades, the earth-abundant metal catalysts have been focused by the researchers that could possibly substitute the benchmark oxygen evolution reaction (OER) catalysts, Ru, Pt, and Ir. However, much attention has been gained by catalysts based on earth-abundant metals (cobalt, nickel, and manganese) as several catalysts based on chalcogenides, phosphides, phosphates, and oxides of these elements have been developed for water splitting. Particularly, there have significant improvement in preparation of nanomaterials of oxides of these elements to meet the demands of electrochemical water oxidation. Several methods to synthesize oxides of earth-abundant metal and their composites with different nanostructures and improved electrochemical performance have been reported. Even though many efforts have been expended to prepare nano-\(\text{Co}_3\text{O}_4\), the development of novel methods to prepare \(\text{Co}_3\text{O}_4\) using simple processes and at low cost remain a topic of interest. Recently, we developed simple and straight-forward method for preparation of nano-\(\text{Co}_3\text{O}_4\) by thermal decomposition of commercially available \(\text{Co(NO}_3)_2\cdot 6\text{H}_2\text{O}\) for OER [1, 2]. We have evaluated the effect of \(\text{Co(NO}_3)_2\cdot 6\text{H}_2\text{O}\) thermal decomposition temperature on the nano-\(\text{Co}_3\text{O}_4\) product morphology and electrocatalysis of water oxidation [2].

This developed thermal decomposition method has been expanded to prepare nano-\(\text{MnO}_x\)-coated carbon and nano-\(\text{Co}_3\text{O}_4\)-coated carbon using the corresponding commercial available metal precursor and homemade carbon for OER reaction. To check the electrocatalytic properties of our developed nanocatalyst toward OER, we used filter paper derived porous carbon electrode (FPCE) as substrate electrode. It took advantages of low charge transfer resistivity, high conductivity, low cost and its high porosity to easy immobilization of the prepared nanomaterials by simply drop-drying method.

Here, we will present the straight-forward preparation of (i) nano-\(\text{Co}_3\text{O}_4\), (ii) nano-\(\text{MnO}_x\)-coated carbon and nano-\(\text{Co}_3\text{O}_4\)-coated carbon by direct thermal decomposition and their characterization. Besides, we will present their electrochemical properties toward OER upon immobilization them on filter paper derived carbon electrode.

References:
Catalytic active Manganese Oxide on Hydrophobic Nickel-Mesh for Application as Gas Diffusion Electrodes

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Technologies like alkaline electrolyzers, alkaline fuel cells and metal-air-batteries are limited by low conversion efficiency. One reason for that is their slow oxygen conversion reaction [1]. It is necessary to optimize gas diffusion electrodes to provide the latent high energy density.

The integration of a hierarchic surface architecture similar to the surface of floating fern is a suitable option therefore. The combination of a macroscopic hydrophobic metal-mesh or –foam with a microscopic hydrophilic bifunctional (OER/ORR) catalyst forms a hierarchic surface architecture. This specific microstructure results in a stable air layer on the gas diffusion electrode surface in an aqueous media. Thus, a stable three-phase boundary will be formed, whereby the charge and discharge reactions are accelerated. Because the oxygen transport to the catalytic active regions will be improved [2].

Furthermore, carbon material weaknesses of conventional gas diffusion electrode designs result in poor long-term stability [3]. However, this can be overcome by a carbon free design and with that higher performance and efficiency can be achieved [4, 5].

It was possible to maintain a hydrophobic surface on a nickel-mesh after an electrodeposition of manganese oxide. Firstly, the nickel surface was etched in hydrochloric acid, temperature treated at 350 °C and immersed in stearic acid to generate a hydrophobic surface. Afterwards, manganese oxide was electrodeposited on the treated nickel mesh. The used electrolyte was composed of manganese(II) acetate tetrahydrate and sodium sulfate. These gas diffusion electrode prototypes were electrochemically characterized in a symmetric cell setup to evaluate the electrochemical activity. The specific surface area (nitrogen sorption), surface structure (SEM) and manganese oxide phase structure (XRD, TEM and EDS) were determined.

References:

Electrochemical Reduction of CO₂ on Copper Phosphide Catalysts in a Near Zero-gap Electrolytic Cell

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Using electrochemical reduction of carbon dioxide (CO₂), chemically converting CO₂ into value-added organic compounds, is a great solution to solve the CO₂ accumulation. Especially the electrochemical conversion of CO₂ can be carried out at ambient temperature and pressure. The biggest advantage of electrochemical conversion is product selectivity on depending on the catalyst. Among variety of catalyst, Copper based catalysts offers the route to synthesize multi-carbon fuels and chemicals from CO₂ (e.g., ethylene, ethanol and n-propanol). [1,2] In this study, Copper Phosphide was synthesized by oleate method and used as a catalyst in a near Zero-gap CO₂ gas-phase electrolytic cell for CO₂ reduction reaction. By using a hydrophobic GDL, PDMS treated, exhibited the formation of three phase interphase during the CO₂ reduction reaction. For studying the mechanism of the reactions, in-situ surface analysis using ATR-SEIRAS for checking the onset point of CO adsorption which is the intermediate of most products by CO₂ reduction reaction. Finally, gas/liquid product analysis was done by GC-MS and UV-Vis.

Figure 1. The graphical illustration of the gas-phase electrolytic cell. (a) 2D illustration of the cell, (b) 3D illustration of the cell and (c) 3D exploded view of the cell

References:
Gas-Diffusion Electrodes for Practical CO₂ Reduction: Challenges & Strategies

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Carbon dioxide reduction (CO₂R) into fuels and commodity chemicals is an attractive approach toward mitigating global climate change and developing a carbon neutral society. Significant developments have been achieved in designing selective catalyst materials for CO₂R, however limited studies have been focused on manufacturing practical CO₂ electrolyzers. In this perspective, the use of gas-diffusion electrodes (GDEs) is a promising tactic to scale-up CO₂R for future industrial application via overcoming the mass-transport limitations of aqueous-based systems. Since CO₂R product selectivity depends greatly on the local reaction environment, translation of knowledge from aqueous-cell CO₂R into practical application on optimized GDEs is not straightforward. Due to the significant operational differences (e.g., much higher current density, pH changes, triple-phase interfaces), many parameters must be tuned in order to optimize the performance of GDE for CO₂R.

Herein, we discuss the influence of these different parameters, such as the reactor design, operational conditions, and properties of the catalyst (e.g., loading, morphology, etc) and support material (e.g., porosity, hydrophobicity, etc), on the performance and selectivity of GDE towards CO₂R. For instance, the employed catalyst fabrication technique showed significant effects on the obtained CO₂R current, product distribution and stability. These influences are attributed to the great impacts of the used fabrication strategy on the properties of the loaded catalyst, including electrochemically active surface area, catalyst utilization, morphology, etc. We found that the in-situ deposition approaches, such as electrodeposition techniques and our recently developed dancing water droplets approach¹, in which the catalyst is directly formed onto the porous substrate (e.g., GDL) in one-step, exhibit improved performance for CO₂R.

References:
High-entropy alloys as novel electrocatalysts for the CO₂ reduction reaction

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The development of alternative energy technologies based on the usage of renewable sources and the conversion of CO₂ into fuels and feedstock chemicals has the potential to mitigate the current observed climate changes. However, technical limitations inhibit the establishment of a closed carbon cycle economy, such as the discovery of stable and active catalyst. Cu is the most studied catalyst and one of the few materials capable of producing C₂ products – e.g. ethylene and ethane.[1,2] Nonetheless, copper based catalysts require large overpotentials and lack selectivity.[2] Therefore, the discovery of novel selective catalysts for electrochemical CO₂ reduction reaction (CO₂RR) is of high importance.

The combination of Ag with Cu is an example of how mixed metals catalysts can impact on the product distribution of the CO₂RR.[2] With this in mind, we investigate the use of high-entropy alloys (HEA) as novel electrocatalysts for CO₂RR. HEA comprise at least five elements and in some instances form a single-phase solid solution, hence potentially exhibiting unusual mechanical, physical or chemical properties.[3] Recently, a HEA system was discovered using combinatorial materials science which revealed an outstanding activity towards the oxygen reduction reaction.[4] Such material systems are now considered as potential new catalysts for the CO₂RR. In this communication, the fabrication of HEA materials by co-sputtering onto gas-diffusion electrodes and the evaluation with respect to the CO₂RR will be shown including potential dependent activity and product distribution and the impact of the HEA composition on the selectivity.

References:

Solvent effect on the ink preparation of Copper-based gas diffusion electrodes: A product distribution evaluation on the electrochemical reduction of CO2

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Gas diffusion electrodes (GDE) have been widely utilized in the electrochemical reduction of CO2 due to the advantages of its so-called triple phase boundary (gas-catalyst-electrolyte), which provides easier product removal and higher mass transport to the catalytic sites. In this field, lots of effort have been applied to optimize the catalyst performance, but less attention has been devoted to the environment surrounding the catalyst particles, mainly within an ink formulation. The choice of a proper ionomer-solvent combination might generate a catalyst layer containing more exposed active sites, a proper catalyst wettability by the electrolyte and an optimum catalyst layer thickness, which might improve the electro-catalyst activity [1].

In the present study, we prepared copper-based gas diffusion electrodes (Cu-GDE) by modifying the solvent during the ink preparation in order to evaluate how the solvent changes the electrochemical properties of the electrode and the product distribution on CO2 electro reduction. In that sense, inks were prepared using Copper powder (1 µm size, 99%), Nafton as ionomer and four different solvents: Isopropanol (IPA), Dymetil sulfoxide (DMSO), Ethylene glycol (EG) and N-Methyl-2-pyrrolidine (NMP). Electrochemical reduction of CO2 was conducted in a continuous flow reactor, containing the cathode (Cu-GDE) and anode (IrO2-GDE) separated by a membrane (Nafton 112) and a flowing anolyte chamber (0.3 M KHCO3). Preliminary results showed that from all solvents, DMSO and NMP have provided the catalyst layers with the lowest charge transfer resistance (Rct) and highest electrochemical catalytic surface area (ECSA). A low Rct favours the interaction between catalyst and electrolyte as well as a high ECSA means more exposed active sites. It was initially found a correlation of higher ECSA with higher ethylene (C2H4) production.

![Figure 1: ECSA values of Cu-GDE catalysts (a) and faradaic efficiency to carbon products (b).](image-url)

Silver and Copper Nanoparticle Modified Gas Diffusion Electrodes for the CO2 Reduction Reaction. Impact of CO2 Back Pressure

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The usage of intermittent renewable energy resources requires advanced energy storage and conversion technologies. Energy can be effectively stored via electrochemically driven reactions such as the electrochemical CO2 reduction (CO2RR). The CO2RR does not only offer energy storage options, but also minimizes the CO2 emission while forming higher value products. In order to achieve significant decrease of CO2 emission CO2RR has to be performed at relevant industrial current densities (>300 mA cm⁻²). However, the low solubility of CO2 (~ 30 mM) in aqueous electrolytes limits the reaction rate of CO2RR. In order to overcome this limitation, gas diffusion electrodes (GDEs) are employed. Within a GDE, the formation of a three-phase boundary occurs and is composed of the solid electrode surface, the liquid electrolyte and the gaseous reactant. The average CO2 diffusion pathway (~50 μm) is around three orders of magnitude shorter than in planar electrode systems due to the CO2 supply in direct proximity to the electrode surface, which prevents mass transport limitation and significantly increases the achievable current densities.[4]

The exact position of the three-phase boundary within the GDE remains an important open question. Here, we will present a measuring setup to investigate the influence of the variation of the CO2 back pressure on the CO2RR. Silver and copper nanoparticle modified GDEs exhibit significant changes in activity and selectivity in dependence from the CO2 back pressure indicating different locations of the three-phase boundary within the GDE.

![Figure 1: Average intensity of formed CO at different potentials and different CO2 back pressure using an Ag-nanoparticle modified GDE in 0.1 M KHCO3.](image)

References:
Frequency Response Analysis of Oxygen Reduction Reaction in Concentrated Alkaline Solutions

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In chlor-alkali electrolysis, the oxygen reduction reaction (ORR) takes place at silver electrode, under strongly alkaline conditions and at elevated temperatures. Currently there is a little knowledge on ORR micro kinetics under conditions relevant to this process. In this contribution the kinetics of ORR on model silver electrodes was studied by using nonlinear frequency response analysis (NFRA) [1-3]. The NFRA method is based on frequency response measurements, performed by sinusoidal modulation of the chosen input (usually potential) and analysis of the periodic response of the chosen output (usually electric current). It is essentially an extension of the Electrochemical Impedance Spectroscopy (EIS) method, but uses higher input amplitudes, which makes the system nonlinearity visible. In our previous studies we have shown that NFRA has a high potential for discrimination of different reaction mechanisms [3]. A great advantage of this method is that one obtains a set of frequency response functions (FRF), which contain different information about the properties of the electrochemical system. The first order FRF corresponds to the linear part of the response and is identical to the electrochemical admittance (inverse of the electrochemical impedance). On the other hand, the higher orders FRFs reflect the nonlinearities of the system response. The second order FRF was proven especially useful for model discrimination [3]. In the NFRA experiments, relatively large amplitudes of the sinusoidal modulation of the potential input were applied to the ORR system and the output current response was measured and converted to frequency domain by using fast Fourier transform (FFT). The experimental first and second order FRFs obtained under conditions of different sodium hydroxide concentrations (0.1-11 M) and at different temperatures are presented. The formation of possible intermediate products was studied by using a rotating ring disk electrode (RRDE). Finally, the experimental FRFs are compared with the theoretical ones derived from a nonlinear model of the ORR system by using software for computer aided derivation of the analytical expressions of theoretical FRFs [4].

References:
Workfunction of the Metal as Descriptor for Active and Durable Carbon Nanofiber Support Alkaline Oxygen Reduction Electro catalyst

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Widespread application of hydrogen fuel cell and hydrogen generator is vital for the acceleration of a sustainable energy landscape. But, since the high price of platinum (Pt) electrocatalysts, it is essential to design the super active and durable nonnoble oxygen reduction reaction (ORR) electrocatalysts. Herein, we suggest a optimal design of nonnoble metal-containing and heteroatom-containing carbon nanofiber electrocatalysts. Collaboration of experimental and computational approach, we drew an ORR activity volcano of metal embedded-CNFn using the work function of the embedded metal as the descriptor. Though Fe located on the top of the volcano, poor durability is originated from the carbide formation which limits the role of stable carbon layer. Vicinity at the top of the activity volcano, the metal inside the carbon was additionally optimized by modulating the Fe1-xCo composition to accomplish high catalytic activity and durability at the same time. This work suggests the mechanistic significance of tuning the charge transfer between the metal and carbon layers, providing guideline for the design of nonnoble embedded ORR electrocatalysts using stable carbon-layer-surrounded metals.

Figure 1. Optimized ratio of nonnoble metal embedding carbon nanofiber with the descriptor using the electron transfer from metal to interfacial carbon layer due to the workfunction difference.

References:

Design of an In-Operando Cell for X-Ray and Neutron Imaging of Oxygen-Depolarized Cathodes in Chlor-Alkali Electrolysis

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Chlorine is an important base chemical involved in the manufacturing of more than 60 percent of all chemical products. A significant improvement in its efficiency can be made when the oxygen reduction reaction (ORR) is chosen to be the cathode reaction instead of the reduction of water. As a result, the cell voltage can be lowered by 1.23 V under standard conditions, yielding energy savings up to 30%. The currently used technical GDEs use a combination of silver flakes as active material, PTFE as hydrophobic component and methylcellulose as a pore building agent, which is being burnt during the preparation. These electrodes have only low pore volumes and contain up to 98% silver, which is only in part active for the ORR catalysis. Imaging techniques like tomography with X-rays and neutrons can be used to obtain further information of the GDE structure and the interaction with the electrolyte. X-ray radiography is extremely suited as it allows to measure the electrolyte movement very fast in the GDEs.

However, the direct correlation between specific electrode structure and electrochemical performance is difficult. The aim of this work was to design and adapt an in-operando cell for X-ray (micro computed tomography, synchrotron) and neutron imaging of an operating oxygen-depolarized cathode under realistic operation conditions, enabling the investigation of the electrolyte invasion into and distribution inside the porous electrode for the first time. We show how the cell was build taking into account all critical operation conditions (30 wt. % NaOH, 80 °C, high current densities) and first results of in-operando measurements. We were able to monitor the saturation of the GDE with electrolyte in correlation to the applied potential and other processes happening at the GDE.

Figure 1: Microstructure of silver PTFE GDE, a) X-ray radiography, Ni mesh with pores, b) focused ion beam, pore system with PTFE depletion (in green) at the walls, c) synchrotron tomography: analysis of pore system, d) in-operando through-plane measurement of GDE obtained with self-designed half-cell compartment taken by lab x-ray [1].

References:
Characterization of Bi-functional Oxygen Electrocatalysts

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The presentation describes double layers gas diffusion electrodes. The catalysts are mixture of silver and nickel cobaltite. The following stationary methods have been used: (i) stationary steady state polarization curves; (ii) Δ E curves characterizing diffusion limitations in gas face; (iii) polarization curves (Δ E/ Δ i) proportional to ionic resistance in hydrophilic pores of the active layer; (iii) evaluation of wetted (active) area of the catalysts using charging curve method; (iv) comparison of catalytic activity by Tafel slopes[1-4].

Long term tests suitable for industrial application have been performed and presented.

Acknowledgements:

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References:
NiCoPₓ Catalyst Based Electrode for Reversible Alkaline Fuel Cell

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Due to the increase consumption of energy, remarkable efforts have been already devoted to the search for new, sustainable energies as alternatives to fossil fuel based sources. Due to this, fuel cells of all kinds have attracted a global attention in the last few decades. The reason for this lies in their adaptable size, broad range of the operational temperatures, low emissions and high efficiency. However, so called low-temperature fuel cells, e.g. proton exchange membrane fuel cells (PEMFC), direct alcohol fuel cells (DAFC) or alkaline fuels cells (AFC), which are considered as a most promising option for mobile and small stationary units are still facing several barriers preventing them from wide spread. In the case of PEMFC and DAFC the reason is connected with the costs of the fuel cell. It is from significant part driven by the necessity of utilizing the noble platinum group metals as the catalyst for the electrode reactions. Another barrier is represented by the sluggish kinetic of the oxygen reduction reaction (ORR). In the case of AFC, the situation is slightly different. The alkaline environment allows to use even the non-platinum metals like Mn, Co, Fe, Ni based catalysts for electrode reactions. They are under these conditions stable and their catalytic activity is comparable with Pt-based catalysts [1]. The transition metal phosphides were recently investigated as highly promising materials for ORR [2]. At the same time, these materials are investigated as promising catalysts for alkaline water electrolysis. It is due to their bifunctional character. From this point of view, they represent highly promising material for reversible fuel cells, which combine the alkaline water electrolyzer and AWE in one unit. Recently, it was shown, that the properties of transition metal phosphides can be further tuned by combining different metals of this group.

In this work, NiCoPₓ catalyst was synthesized by simple method of cathodic electrodeposition on Ni substrate from solution of corresponding salts. Subsequently, it was tested with respect to utilization as bifunctional catalyst in reversible fuel cell for oxygen evolution reaction (OER) and ORR. After careful characterisation, the material is foreseen for incorporation into a gas-diffusion-electrode. Alkaline polymer electrolyte will be used as a binder. Unsupported catalyst will be used in the first step in order to avoid problems with carbon phase degradation in the water electrolysis phase of the cell operation.

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References:


Production of Bifunctional GDE for alkaline solutions

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Gas diffusion electrodes are essential for conversion of gases into liquids – like for example fuel cell. But also for the reverse processes like electrolysers the GDE’s have an inherent advantage: They separate the gas from liquid inside of the electrode. Compared to simple expanded metals that give the possibility to reduce ohmic losses due to gas bubble shadowing in the electrolyte gap of the cell. GDE are at least essential, when discussing a bifunctional electrode for fuel cell and electrolysers in one unit.

Gaskatel produces now for several years GDE for industrial applications (Biplex®). Because of the corrosion issue we focused our development onto the inexpensive materials in alkaline environment. Carbon, Nickel, Manganese and silver are the typical material we use. But of course bifunctional catalysts are the most interesting topics, as they reduce the investment costs of an electrochemical cell for energy conversion.

For the Hydrogen Electrode this catalyst is the activated Nickel (tradename Raney-Nickel), which catalyses the HOR as well as the HER with similar very little overvoltages. It will be shown, that the HER works well with metallic Nickel as well as with Nickeloxides with similar activity, whereas the HOR takes place only at metallic activated Nickel surfaces. To achieve a metallic Nickel surface a thermal treatment of the electrode at medium temperature of 50°C is essential [1]. The reason is not fully understood, but the electrodes are available in large scale amounts for industrial applications. Focus on that electrode should therefore be in the near future to reduce the activation temperature to room temperatures.

A more challenging task is the bifunctional Oxygen electrodes, which catalyses the OOR as well as the ORR in alkaline solutions. Besides of corrosion resistant carbons there is also the approach with various alloys like Ni/Li [2], Ni/Fe, Ni/Co or lanthanium cobalt alloys. We would like to share our results with mixture out of Nickel alloys and carbon with the community.

As essential for a bifunctional electrode is a three layer structure- consisting out of a microporous hydrophilic layer, a porous catalytic layer and a liquid repelling gas diffusion layer. We like to present our approach for the continuous production of that three layer electrodes.

References:


Novel alkaline water electrolysis process with nickel-iron gas diffusion electrodes for oxygen evolution

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Hydrogen production by water electrolysis is one of the most promising energy storage technologies in the context of an increasing share of renewable energies. Alkaline water electrolysis (AEL) has recently gained renewed interest as it was shown that comparable performance to PEM electrolysis can be achieved with nickel-based catalysts using optimized electrodes and separators [1]. Remaining challenges in AEL are related to the electrode activity especially for the oxygen evolution reaction (OER) due to its slow kinetics, insufficient catalyst stability and ohmic losses resulting from gas bubbles detachment [2]. Moreover, the purity of the product gases at lower current density and under dynamic operation, which is mainly affected by the gas solubility in the mixed electrolyte cycles [3], may lead to electrolyzer shutdown for safety reasons. Therefore, our research focusses on the improvement of alkaline water electrolysis with special emphasis on new types of OER electrodes and novel process concepts. In the present work, we propose a novel AEL concept (Fig. 1) with a GDE as anode, a conventional electrode as cathode, and a separator. In this configuration, the electrolyte is only circulated through the cathode compartment, which greatly simplifies the process. Moreover, the gas purity during dynamic operation should be increased since dissolved hydrogen is no longer transferred to the anode side. In a first series of measurements, we employed GDE obtained by spraying a mixture of nickel particles and a PTFE suspension on a nickel net as current collector followed by hot pressing. Iron as an active electrocatalyst was introduced through addition of iron acetate to the spraying suspension which was subsequently decomposed during sintering. The electrodes were characterized with physico-chemical methods and subjected to electrochemical measurements in a lab-scale electrolysis cell at 353 K, atmospheric pressure and 32.5 wt.% KOH. Figure 2 shows the cell voltage for a GDE cell compared to a classical electrolysis cell with electrolyte flow in both half cells using an iron-coated nickel foam as anode. It can be seen that almost the same performance could be obtained up to a current density of 400 mA cm\textsuperscript{-2} [4].

\textbf{Figure 1: AEL process with anodic GDE} \hspace{1cm} \textbf{Figure 2: Polarization curve for GDE cell [4]}

These first results reveal that AEL with a GDE anode is a very promising new concept and we expect that even better results can be achieved by optimisation of the GDE pore system.

References:

One-Step Preparation of Ruthenium-CNT-Microtubes as Gas Diffusion Electrode for Electrochemical Ammonia Synthesis

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The Haber-Bosch process consumes approximately two percent of the world’s commercial energy to produce ammonia (NH₃) under harsh conditions, resulting in substantial carbon dioxide emission. The electrochemical nitrogen (N₂) reduction reaction (eNRR) offers an ideal alternative path to produce NH₃ using renewable energy sources under ambient conditions. The eNRR represents an attractive prospect for NH₃ synthesis, which requires lower activation energy (about 12.3 kJ/mol) than the traditional Haber-Bosch process (57 kJ/mol) [1]. However, this process suffers from low NH₃ yield due to the high triple bond dissociation energy of N₂. Previous studies proved that ruthenium (Ru) is the most promising catalyst for eNRR with high activity and selectivity [2]. Moreover, the low N₂ solubility in aqueous solutions limits the NH₃ yield by using bulk electrodes. A gas diffusion electrode (GDE) can prevent the reaction in the diffusion-controlled mode since the gas can be bubbled through the highly porous GDE into the electrolyte.

Here, we investigated a novel homemade microtubular GDE fabricated with Ru loaded carbon nanotubes (Ru-CNT) for the electrochemical NH₃ synthesis. The microtubular Ru-CNT GDEs were typically prepared by a two-step process. 1) Ru was loaded on CNT nanoparticles by the chemical reduction method using sodium borohydride (NaBH₄) in ethylene glycol (EG). Subsequently, the Ru-CNT nanoparticles were collected after the filtration, purification and drying processes [3]. 2) The obtained Ru-CNT nanoparticles were dissolved in water again to form an aqueous suspension by adding Triton-X 100. The CNT microtubes were obtained by filtering the above suspension through a microfiltration hollow fiber membrane in dead-end mode [4]. This work aims to optimize the preparation method of the microtubular Ru-CNT GDE from two steps to one step by using different solvent (water:EG, w/EG) ratios. As a result, the simplified fabrication with w/EG ratio of 50/50 was suggested as the best method, due to the stable structure of the produced GDE and its higher physical and electrochemical surface areas. One-step produced Ru-CNT GDEs were employed for NH₃ synthesis achieving a high current efficiency of 24.5% and large NH₃ yield of 13.9 µg/mg·cat·h under 0.1 V vs. RHE, which shows similar catalytic performances compared to two-step productions.

References:
Minimizing the influence of the electrolyte hydrostatic pressure on the potential distribution of hydrogen peroxide generating gas diffusion electrodes through electrode design and process parameter

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Electrochemical methods offer the opportunity for in-situ generation of oxidants for wastewater treatment, as disinfectant for apparatuses and production sites as well as rocket fuel. An innovative concept for removing trace elements is a combination of a boron-doped diamond electrode and a gas diffusion electrode (GDE) for generating highly oxidative species at both electrodes simultaneously. [1] Such a system is not commercially available yet, mainly due to the absence of efficient hydrogen peroxide (H₂O₂) GDEs working at high current densities and which are scalable to technical relevant sizes.

A major challenge is the uniform operation of the GDE over the entire active surface, as the electrolyte hydrostatic pressure has a considerable influence on the GDE performance. Figure 1 shows the potential distribution of a GDE consisting of 60 % Vulcan XC 72 and 40 % PTFE on a gold-plated nickel net. It is obvious that the electrode reduces oxygen in the upper part but is already operating in hydrogen evolution mode in the lower part. The influence of the hydrostatic pressure is immense and higher current densities are not applicable.

Therefore, the influence of the manufacturing and process parameters on the potential distribution and H₂O₂ yield were investigated and a considerable influence of the oxygen differential pressure (dp), the material load and GDE composition could be determined.

![Figure 1: Potential distribution through 25 Luggin capillaries over the active area of 10 cm x 10 cm. All measurements were performed at 15 °C, 1 M NaOH, 3.6xO2 and dp of 35 mbar. The classification of columns and rows are given in the legend above](image)

References:
The expanded Micro Flow Cell for the side by side production and electrochemical detection of Hydrogen Peroxide

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Hydrogen peroxide (H₂O₂) is commonly produced via the anthraquinone process, but it still suffers from high energy consumption and the generation of a variety of by-products. A promising alternative is the electrochemical pathway. We present the micro flow cell as a suitable method for the production of hydrogen peroxide via two-electron oxygen reduction using benchmark carbon catalysts [1].

The presented micro flow cell is designed to imitate realistic conditions and allows the scale-up for industrial purposes. The set-up enables to adjust the reaction conditions, e.g. catalyst loading on gas diffusion layers, flow rate, current density and long-time productivity. However, due to the instability of hydrogen peroxide the detection of the produced amount remains difficult.

Inspired by the rotating ring disk electrode (RRDE) method an expanded micro flow cell was introduced, using a build in second working electrode for the oxidation of the produced hydrogen peroxide. Converting the resulting current at a constant potential into the produced amount of hydrogen peroxide, allows the direct sensing of the catalytic activity.

References:
Systematic building of an electroactive material library via gas-diffusion driven electrosynthesis

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Here we report a rapid, room-temperature, scalable, electrosynthesis route for an unprecedented range of nanocrystalline manganese and cobalt oxides and hydroxides: Co-doped Na-birnessite, cubic/tetragonal spinels, and layered double hydroxides (CoMn-LDH), with unique synthetic identities. An air-fed, carbon/PTFE, gas diffusion electrode (GDE) is used to drive the oxygen reduction reaction, which fuels the oxidative electrosynthesis. A crucial first step to elucidate catalytic performances of materials is taken by producing a large range of materials under the same synthetic conditions. With fixed electrochemical parameters at the electrode, simply changing the Co and Mn concentration in the feed solution results in tailored products in terms of: morphology (spins vs nanosheets), composition (Co/Mn stoichiometry), structure (tetragonal/cubic-spinel, birnessite, LDH), particle size (15 – 35 nm), crystallinity (polycrystalline particles vs single-crystals) and phase purity. Some of the materials tested exhibit remarkable catalytic properties for the oxygen evolution reaction. Our work opens the door to a new systematic way of working towards producing optimized and affordable materials with gas diffusion electrodes.

![Figure 1](image.png)

**Figure 1:** The main components of the gas diffusion electrode are shown and described, with the gas flow and diffusion path through the electrode leading into the metal-ion containing electrolyte. The result of the synthesis is summarized with the structural control over the resulting nanoparticle crystalline structure via changes in the charge/metal ratio and metal stoichiometry depicted on the chart.
Application of a gas diffusion electrodes in an electrochemical advanced oxidation process treating different synthetic wastewaters

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The release of contaminants into natural waters can cause harm to terrestrial and aquatic ecosystems. Although pharmaceutical products have been discovered in traces (μg/L-ng/L) in rivers, groundwaters and lakes, they are able to influence public health and environment unfavourably [1]. Main sources for pharmaceuticals in the environment are human excrements or improper disposal introduced into municipal wastewater streams. For a variety of pharmaceutical substances, conventional treatment processes in municipal wastewater treatment plants (MWWTP) are equipped for a sufficient degradation or removal. Many pharmaceutical active ingredients such in X-ray-contrast media, are persistent to the applied biological treatment or are not able to adsorb onto the activated sludge. Consequently, persistent trace substances can be found in the efflux of MWWTPs.

The removal of the undesired organic compounds from water and wastewater streams is challenging due to both the properties and the concentration of the compounds. However, many processes have been investigated for the removal of pharmaceuticals including electrochemical methods.

In this contribution, the scientific approach is the elimination of persistent organic compounds by the reaction with radicals. The radicals, in particular hydroxyl radicals (OH radicals), are produced electrochemically. Therefore, this method is counted among the so-called Advanced Electrochemical Oxidation Processes (AEOP) [2]. The boron-doped diamond electrode (BDD, CONDIAS GmbH) is one of the favourable electrodes used to synthesize OH radicals \textit{in situ} by electrolysis. Unlike other electrode materials, e.g. graphite or platinum, the BDD has a higher overpotential for water electrolysis. This enables reaching potentials where the formation of OH radicals starts. Furthermore, the combination of a BDD electrode as anode with a gas diffusion electrode (GDE, Covestro Deutschland AG) as cathode offers advantages for the whole process. Depending on the applied catalysts it is possible to produce hydrogen peroxide at GDEs via the two-electron oxygen reduction pathway. The additionally produced hydrogen peroxide complements the oxidation process with another strong oxidizing agent. At the same time the use of a GDE suppresses hydrogen evolution reaction. The investigations with the novel electrode combination showed that the use of the GDE reduced the cell voltage, which reduces the energy requirement of the overall elimination process. Compounds of the X-ray contrast agents and of the anti-inflammatory group have been chosen as model substances for the degradation and/or removal from different wastewaters matrices. Different influence factors on degradation rate such as current density, cell design, and electrolyte compositions were investigated. The degradation experiments showed that with the presented combination of electrodes in a 200 % cell the complete mineralization is almost possible even for very stable and persistent compounds.

References:

Corrosion Current Density Related to Gas Diffusion Electrodes Durability Study

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Several gas diffusion substrates were fabricated for corrosion studies by measuring their corrosion current densities. Gas diffusion substrates with different physical parameters were prepared by the commercial producer, CeTech Co. Ltd. Those samples included bare substrate, added 30 wt.% substrate, gas diffusion layer including MPL, and gas diffusion layer added 30 wt.% including MPL. Because gas diffusion electrodes are widely used for various fuel cells and electrolyzers [1, 2, 3], their degradation are directly related to the electrode corrosion during operations. The carbon corrosion accelerated tests were studied to examine the key parameters to the electrode corrosion resistance. The Tafel analysis was used to investigate the electrode corrosion current density as shown in Fig. 1. Through SEM surface observation and profile analysis, it’s confirmed that the carbon electrode was corroded after the accelerated corrosion test. It’s found that electrode microstructures were changed. Mass analysis, water droplet contact angle measurement, four-point probe measurement and XPS analysis were used to analyze the electrode corrosion phenomenon. The relative corrosion rate was calculated by comparing the difference between before and after corrosion. According to these analyses, the gas diffusion layer added 30 wt.% PTFE including MPL has the lowest corrosion current density 4.8 μA.cm-2 among those samples. The electrodes added with PTFE or MPL, the corrosion resistance is obviously improved and these are benefit to the electrode durability in the operations of the fuel cells and electrolysers.

Fig. 1 Tafel test results of the electrode corrosion samples

References:
Microbial reversible fuel cell integrated in membrane electrode assemblies

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Microbial reversible fuel cells (MRFCs) are devices that convert chemical energy to electrical energy or vice versa catalyzed by microorganisms. The microbial fuel cell (regime of electricity generating) consists of anode and cathode compartments separated by a cation specific membrane. Microbes in the anode compartment oxidize fuel (electron donor) generating electrons and protons. Electrons are transferred to the cathode compartment through the external circuit, and the protons through the membrane. Electrons and protons are consumed in the cathode compartment reducing oxygen to water. In the electrolysis mode, the MRFC generates hydrogen by applying external voltage, which, however, is even less than the theoretical value (1.23 V) for conventional water electrolysis. The most important part of the microbial hydrogen converter cells is the gas diffusion layer. In this work, different types of commercial gas diffusion layers are investigated. The electrodes are sintered in a temperature range of 320 – 360 °C in order to change pore structure of the electrode surface. The prepared electrodes were integrated in a prototype fuel cell developed in IEES–BAS and investigated concerning both cathodic and anodic reactions in regime of reversible fuel cell. A Zircon perl 500 was used as a polymer separator. The electrochemical performance was characterized by cyclic voltammetry in a potential window of both reactions with scan range 10 mV.s⁻¹ and steady state polarization curves with slope 1 mV.s⁻¹. Long term tests are in progress.

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Fabrication of bioanode for use in microbial electrolysis cell

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One of the latest technologies for hydrogen production, developing only for a decade, is the so-called Microbial electrolysis. Although it combines the principles of conventional water electrolysis and microbial fuel cells, the concept of microbial electrolysis was first demonstrated only in 2005 as an innovative approach to the production of hydrogen from organic matter, including sewage and other renewable resources. The main advantage of microbial electrolysis is that the theoretical voltage required to generate hydrogen on the cathode is significantly less than that (1.23 V) for conventional water electrolysis. Of crucial importance for the whole performance of microbial electrolysis cells is the formation of electrochemically active biofilm, which is the aim of this study. Applying a certain potential to a carbon electrode in the presence of model bacteria, the topology of the biofilm as well as its metabolic activity has been influenced. The stages of the biofilm formation and the mature biofilm have been investigated by CV, DPV and EIS. The bioanodes has been also assembled with cathode separated by membrane and the membrane-electrode pack assembly has been analyzed in recently designed microbial electrolysis cell.

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Performance of gas-diffusion electrode as cathode for hydrogen generation in microbial electrolysis cell

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Microbial electrolysis cells (MECs) are attracting increasing attention as an emerging technology for valuable chemicals production, including hydrogen, from wastewater and other waste streams. Assisted by specific bacteria (called exoelectrogens), serving as biocatalysts for the anodic reaction, the microbial electrolysis requires much less external voltage (0.2 – 0.8 V) than water electrolysis to run the hydrogen generation on the cathode. The production of efficient cathodic catalysts for HER is a major challenge for the development and practical application of MECs because due to the presence of microorganisms they typically operate at mild conditions (near-neutral pH and ambient temperature), at which the electrocatalysts used possess low catalytic activity. In this study, the performance of gas-diffusion electrodes with different types of gas diffusion layers, was examined in neutral electrolyte in respect to potential application as cathodes in MEC. Initially, the prepared GDE were tested in phosphate buffer saline (pH 7) at abiotic conditions by means of linear voltammetry and chronoamperometry. The hydrogen production rate and overpotential for HER was estimated from obtained electrochemical data. Then, the GDE together with bioanodes, developed in microbial fuel cells, were assembled in MEC and tested at different applied voltages. The hydrogen production yield, cathodic hydrogen recovery and energy efficiency achieved with explored GDE were estimated and compared.

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Gas Diffusion Electrodes for CO₂ Reduction to Formate

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At Avantium, we are working on converting CO₂ to formate using a gas diffusion electrode. We've analyzed reported data from over 90 papers and patents on this reaction; all of it shows that gas diffusion electrodes are the best way to electrochemically convert CO₂ to formate. The sources that use GDEs for this reaction are very limited, and a significant amount of them operate a GDE in a bulk electrolyte solution where there is no three phase boundary. Additionally, the studies that do operate a GDE with a three phase boundary take a one factor at a time approach at optimization which can result in failure to identify the influence of critical interactions between the gas diffusion layer and catalyst layer characteristics on the overall performance. Furthermore, these studies are limited to a scale of 10cm² and they operate for less than 8hr (one working day). At Avantium, we are efficiently producing formate at industrial relevant current densities at a scale >100cm² for extended operational times.

Figure 1: Current Efficiency of Formate vs Current Density for different electrode styles¹⁻⁶⁶
Figure 2: Current Efficiency of Formate vs Scale for different electrode styles and current density ranges

Figure 3: Current Efficiency of Formate vs Experiment Time for different electrode styles
Analysis of publications is being prepared for submission to journal

References:


Multiscale analysis of the limiting mechanisms in the gas phase oxidation of hydrogen chloride employing an oxygen depolarized cathode

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The increasing production capacities of the polyurethanes and polycarbonate underline the importance electrochemical oxidation of HCl to Cl\textsubscript{2}, which then can be refed into the above-mentioned industrial processes. \textsuperscript{1}Hereby, the gas phase oxidation of HCl employing an oxygen depolarized cathode (ODC) has proven to be significantly more efficient than the current state-of-the-art process based on the oxidation of aqueous hydrochloric acid \cite{1}. First experimental results showed a limiting current behavior, which we recently assigned mainly to a saturation of the catalyst surface with adsorbed Cl\textsuperscript{-} species and a subsequently rate limiting desorption step forming chlorine \cite{2}. When looking at the overall reactor employing an ODC, our recent studies identified several indications for two additional physical phenomena inducing the experimentally observed limiting behavior at current densities of 350-450 mA/cm\textsuperscript{2} \cite{3}. This limiting current of the reactor employing an ODC is significantly lower than the reaction limited current observed in the HClOR half-cell experiments under comparable conditions. Also, its temperature dependence is implying a different underlying cause. In the present work, a non-isothermal multiphase agglomerate model of the HCl gas phase oxidation reactor employing an ODC is developed to investigate the origin of this limiting behavior. A major focus of the model is the mass transport within the GDL and agglomerates of the catalyst layer, taking into account the presence of both gaseous and liquid water, as well as the HClOR microkinetics proposed in \cite{2}. It is shown that depending on the employed process conditions two diametric reasons, flooding of the cathode catalyst layer (CCL) versus dehydration of the anode catalyst layer (ACL) and the adjacent membrane, are at cause. The model is able to predict the seemingly contradicting temperature dependence of the limiting behavior and the conditions under which either one of the two underlying mechanism inducing the limiting current, occurs. Based on this, process conditions can be suggested that predict the feasibility of an operation at significantly higher current densities than the ones achieved experimentally so far. Additionally, reactor optimization strategies are proposed and evaluated in order to even further increase the efficiency of the electrochemical gas phase oxidation of HCl.

References
Long-term Operation of Homogeneous Gas Diffusion Electrodes for High Rate Production of Formate

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Electrochemical low-temperature conversion of CO\(_2\) is a promising way to reduce emissions and to valorize CO\(_2\) as a carbon-source to produce basic chemicals and/or to store excess electricity from renewable resources. Formic acid or formate is a well-known candidate for these tasks. Recently we reported the potential of formate as energy carrier and demonstrated the coupling of CO\(_2\) electrolysis and subsequent energy recovery in a direct formate fuel cell (DFFC).\(^{[1]}\)

\[
\text{CO}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{HCOO}^- + \text{OH}^- \quad \phi_0 = -0.665 \text{ V (vs. SHE, pH = 10)}
\]

Gas diffusion electrodes (GDE) have become a state of the art electrode system for CO\(_2\) reduction reaction (CO\(_2\)RR), independent of the product formed. They overcome the low solubility of the reactant causing severe mass transport limitation and allow industrial relevant current densities.

We are using and emphasizing homogeneous GDEs with SnO\(_x\) nanoparticles as catalyst.\(^{[2-4]}\) The main difference to the better-known design incorporating a hydrophobic gas diffusion backbone and a more or less flooded catalyst layer, is the homogenous distribution of large gas transport pores and smaller, electrolyte filled pores throughout the whole electrode. This design potentially offers a larger contact area between gaseous CO\(_2\) and the electrolyte covering active sites. However, stabilization of the reaction zone and achieving sufficient mechanical stability while maintaining a great performance is difficult. We just reported the high potential of this GDE design under optimum reaction conditions, which allowed a maximum current density of 1000 mA cm\(^{-2}\) for 45 min, maintaining an average Faraday efficiency (FE) of 80 \%.\(^{[5]}\) Currently, the long-term stability is under investigation. Catalyst loading, type and amount of binder, temperature as well as Electrolyte composition play a crucial role in suppressing the parasitic hydrogen evolution reaction (HER). A consistent optimization of said parameters already allowed a time on stream of 168 h. Identification and quantification of different parameters contributing to the increasing HER are the current object of research.

References:


Figure 1: FE to formate and H\(_2\) as well as cathode potential for different GDE compositions over time on stream.
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