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Book of Abstracts

1st Swiss Workshop on CO2 Electrolysis

June 6th, 2024

Paul Scherrer Institute PSI – Switzerland

Contents

Welcome

Welcome to the 1st Swiss Workshop on CO2 Electrolysis! The event will be held on 6 June 2024 at Paul Scherrer Institut (PSI) in Switzerland.

This workshop aims to gather **international experts** on CO2 electrolysis and allow them to share their latest research and development. Thus, the workshop will be a unique opportunity to **exchange** ideas and opinions, discuss new **opportunities**, and trigger **collaborations**.

Venue and Access

The 1st Swiss Workshop on CO2 Electrolysis will be held on the PSI campus in the Auditorium, on the west side of PSI.
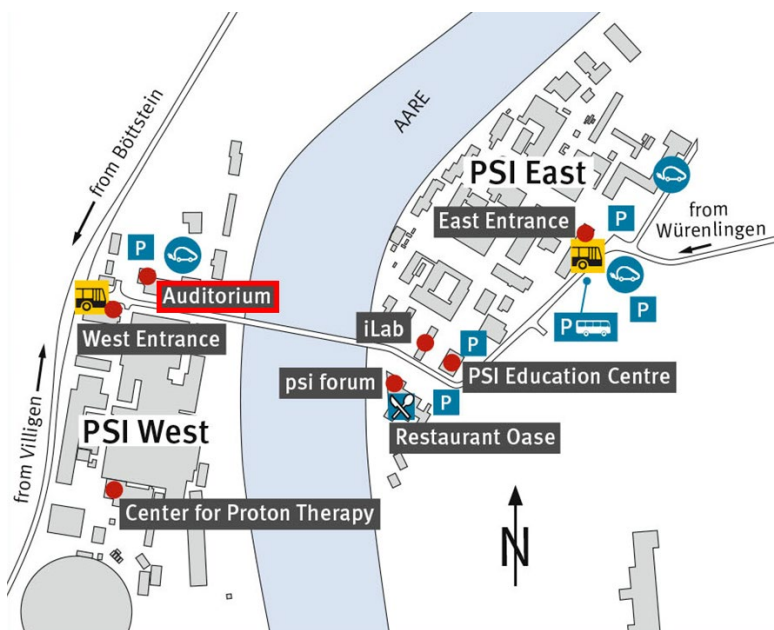
www.psi.ch/en/visit/how-to-find-us

Travel by public transportation

From Brugg SBB Railway station, take Bus 376 and exit at the "Villigen, PSI West" stop.

From Baden SBB Railway station take the local train S27 direction of "Koblenz" or "Bad Zurzach" and change to "Siggenthal-Würenlingen" to Bus 357 and exit at the stop "Villigen, PSI West".

The Auditorium is just a few meters from the "Villigen, PSI West" Bus stop.

Travel by car

There is parking at PSI next to the auditorium (there is a fee to be paid in CHF).

Invited Speakers

Prof. Csaba Janáky

Janaky Lab, Link

University of Szeged, Hungary

Dr. Joey Disch

Group Leader AEM Electrolysis

Electrochemical Energy Systems, IMTEK – Department of Microsystems Engineering

University of Freiburg, Germany Link

Prof. Soma Vesztergom

Laboratory of Electrochemistry & Electroanalytical Chemistry, Eötvös Loránd University of Budapest, Hungary,Link

Biochemistry and Pharmaceutical Sciences, University of Bern, Switzerland, Link

Dr. Baran Şahin

Development engineer specialized in Next Generation Electrolyzers

Siemens Energy, Innovation Center Berlin, Germany

Link1, Link2

Schedule

Time	Speaker	Title
09:00		Registration + Coffee
09:30		Opening
09:40		Session: Catalyst layer - Chair: Lorenz Gubler
	Joey Disch	Invited talk - Catalyst layer engineering and forward-bias bipolar membranes for the electrochemical reduction of CO2 to CO
10:10	Wolfgang Schöfberger	Molecular Catalysts for the electrocatalytic CO2 reduction reaction
10:30	Michele Ferri	Electrochemical synthesis of fertilizers by CO2RR and NO3RR coupling
10:50		Coffee
11:10		Session: Salt Problem - Chair: Matthieu Dessiex
	Soma Vesztergom	Invited talk - Penetration? Perspiration? Flooding? Finding Tools to Study Questions of Electrolyte Management in GDEs for CO2 Electrolysis
11:40	Hunter Simonson	Cation Crossover Limits Accessible Current Densities for Zero-Gap Alkaline CO2 Reduction to Ethylene
12:00	Luca Bohn	Water transport in CO2 electrolysis to CO during pulsed operation investigated by high-resolution neutron imaging
12:20		Lunch + Poster
13:40		Session: Operating conditions - Chair: Sophia Haussener
	Csaba Janáky	Invited talk - System and Process Development for Industrial Carbon-dioxide Electroreduction
14:10	Meng Lin	Mass and thermal management for CO2 electrolyzers enables enhanced performance
14:30	Lydia Weseler	Investigation of Electrochemical CO2 Reduction at Silver-Based Gas Diffusion Electrodes in Flow Cells
14:50		Coffee
15:10		Session: Upscaling - Chair: Felix Büchi
	Baran Sahin	Invited talk - Enhancing Stability of Cu-Based Gas Diffusion Electrodes for Low-Temperature CO2 Electrolysis
15:40	Simone Dussi	Integrated R&D Towards Industrial Ethylene Electrosynthesis
16:00	Kai junge Puring	Improving energy efficiency of CO2 electrolysers in light of process integration with high-pressure stack-technology
16:20		Closing
16:30		Apero

Abstracts of Oral Contributions

Speaker and Authors	Title
(invited) Joey Disch; Khaled Seteiz; Josephine Häberlein; Frederik Brendel; Luca Bohn; Severin Vierrath	Catalyst layer engineering and forward-bias bipolar membranes for the electrochemical reduction of CO2 to CO
Wolfgang Schöfberger; Dominik Krisch	Molecular Catalysts for the electrocatalytic CO2 reduction reaction
Michele Ferri	Electrochemical synthesis of fertilizers by CO2RR and NO3RR coupling
(invited) Soma Vesztergom; Alain Rieder; Ying Kong; Huifang Hu; Menglong Liu; Julia Lorenzetti; Abhijit Dutta; Viliam Kolivoška; Peter Broekmann	Penetration? Perspiration? Flooding? Finding Tools to Study Questions of Electrolyte Management in GDEs for CO2 Electrolysis
Hunter Simonson; Danielle Henckel; W. Ellis Klein; K.C. Neyerlin; Wilson Smith	Cation Crossover Limits Accessible Current Densities for Zero-Gap Alkaline CO2 Reduction to Ethylene
Luca Bohn; Frederik Brendel; Joey Disch; Josephine Häberlein; Severin Vierrath	Water transport in CO2 electrolysis to CO during pulsed operation investigated by high-resolution neutron imaging
(invited) Csaba Janáky	System and Process Development for Industrial Carbon-dioxide Electroreduction
Meng Lin	Mass and thermal management for CO2 electrolyzers enables enhanced performance
Lydia Weseler; Marco Löffelholz; Jens Osiewacz; Thomas Turek	Investigation of Electrochemical CO2 Reduction at Silver-Based Gas Diffusion Electrodes in Flow Cells
(invited) Baran Sahin	Enhancing Stability of Cu-Based Gas Diffusion Electrodes for Low-Temperature CO2 Electrolysis
Simone Dussi; Aviral Rajora; Mark Sassenburg; Francesc Sastre; Michele Tedesco	Integrated R&D Towards Industrial Ethylene Electrosynthesis
Kai junge Puring; Stephan Heuser; Lucas Hoof; Nils Mölders; Kevinjeorjios Pellumbi; Marcus Petermann; Michael Prokein; Ulf-Peter Apfel	Improving energy efficiency of CO2 electrolysers in light of process integration with high-pressure stack-technology

Catalyst layer engineering and forward-bias bipolar membranes for the electrochemical reduction of CO_2 to CO

J. Disch[1], K. Seteiz[1], J. Haeberlein[1], F. Brendel[1], L. Bohn[1], S. Vierrath[1]

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State-of-the-art CO_2 electrolyzers producing CO typically employ pure Ag nanoparticles as CO_2 reduction catalyst. The ideal Ag nanoparticle size in terms of CO_2 reduction selectivity has been found to be ≈5 nm.[1] However, with nanoparticles of that size it is difficult to fabricate catalyst layers with pores for gas transport and nicely distribute the ionomer. Ag nanoparticles supported on carbon black (Figure 1a) with varying surface areas and mesoporosity can be used to independently optimize the required properties of the catalyst layer. Furthermore, this talk will give insights into the potentials and challenges of employing forward-bias bipolar membranes in zero-gap electrolyzers. A porous anion exchange layer can enable long-term stable cell operation as demonstrated in a constant current experiment over 200 hours at 100 mA cm^{-2} (Figure 1b).
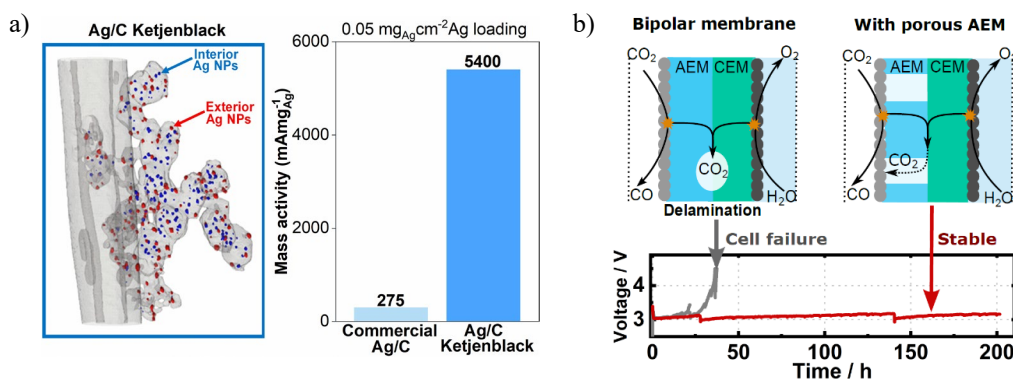

Figure 1 – a) Ag nanoparticles supported on high surface area carbon black (Ketjenblack) and b) concept of forward-bias bipolar membrane with porous anion exchange layer that enables efficient long-term operation. Reproduced from Seteiz et al.² a) and Disch et al.³ b) with permission from the Royal Society of Chemistry and Wiley.

References:

1. C. Kim et al. "Achieving Selective and Efficient Electrocatalytic Activity for CO_2 Reduction Using Immobilized Silver Nanoparticles" In: J. Am. Chem. Soc. **137**, 13844–13850 (2015).
2. K. Seteiz et al. „Carbon black supported Ag nanoparticles in zero-gap CO_2 electrolysis to CO enabling high mass activity" In: RSC Adv., **13**, 18916-18926 (2023).
3. J. Disch et al. "Bipolar Membrane with Porous Anion Exchange Layer for Efficient and Long-Term Stable Electrochemical Reduction of CO_2 to CO" In: Adv. Energy Mater., **13**, 2301614 (2023)

Molecular Catalysts for the electrocatalytic CO_2 reduction reaction

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Abstract:

In our research work, we focus on converting CO_2 to the industrial feedstock syngas ($CO:H_2$), formic acid, methanol, ethanol, acetic acid via tailored molecular catalysts. We will discuss our synthesis efforts to develop functional materials based on metal complex systems and subsequently show their application as catalysts for CO_2RR.[1-3] As an example, we designed a series of different Ag(I) N,N´-bis(arylimino)-acenaphtene complexes (Ag-BIAN), which are cost-competitive with the industry standard Ag-NPs, while allowing for high tunability of the reactive environment. We tested the different catalysts not only in cell concepts used often in laboratory set-ups but aimed for a rapid transition to industrially relevant cell assemblies and conditions. Contrary to previous reports on comparable matters, we show an exponential performance improvement above 200 mA cm^{-2} by
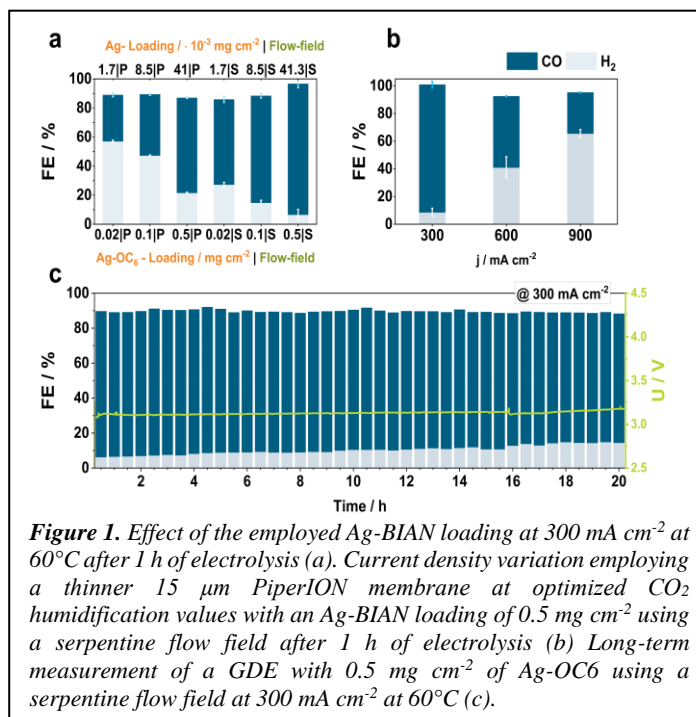
Figure 1. *Effect of the employed Ag-BIAN loading at 300 mA cm^{-2} at 60°C after 1 h of electrolysis (a). Current density variation employing a thinner 15 μm PiperION membrane at optimized CO_2 humidification values with an Ag-BIAN loading of 0.5 mg cm^{-2} using a serpentine flow field after 1 h of electrolysis (b) Long-term measurement of a GDE with 0.5 mg cm^{-2} of Ag-OC6 using a serpentine flow field at 300 mA cm^{-2} at 60°C (c).*

tailoring the cell and condition engineering allows us to reach record-breaking values not only for the subfield of molecular catalysts but also in the field of CO_2 electroreduction overall. Specifically, we reached a mass activity of 100 A mg^{-1} Ag at a current density of up to 900 mA cm^{-2} and high selectivity for CO (90%).

References:

1. Pushing the Ag-Loading of CO_2 Electrolyzers to the Minimum via Molecularly Tuned Environments, K. Pellumbi, D.Krisch, C.Rettenmaier, H. Awada, H.Sun, L. Song, S. A. Sanden, L. Hoof, L. Messing, K. junge Puring, D. Siegmund, B. Roldan Cuenya, W. Schöfberger*, U.-P. Apfel*, *Cell Reports Physical Science* 2023, 4, 101746.
   https://doi.org/10.1016/j.xcrp.2023.101746

2. Electrocatalytic Reduction of CO_2 to Acetic Acid by a Molecular Manganese Corrole Complex, R. De, S. Gonglach, S. Paul, M. Haas, F. Pillwein, S. S. Sreekumar, P. Gerschel, U.-P. Apfel, H. Vuong, J. Rabeah, S. Roy*, and W. Schöfberger*, *Angew. Chem.* 2020, 59, 26, 10527-10534.
   https://doi.org/10.1002/anie.202000601

3. Molecular Cobalt Corrole Complex for the Heterogeneous Electrocatalytic Reduction of Carbon Dioxide, S. Gonglach, S. Paul, M. Haas, F. Pillwein, S. S. Sreekumar, S. Barman, R. De, S. Müllegger, P. Gerschel, U.-P. Apfel, H. Coskun, A. Aljabour, P. Stadler, W. Schöfberger*, and S. Roy*, *Nat. Commun. 2019*, 3864.
   https://doi.org/10.1038/s41467-019-11868-5

Electrochemical synthesis of fertilizers by CO_2RR and NO_3RR coupling

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The material world we are living in lays its foundation on four main pillars: cement, steel, plastics and fertilizers. The production of each of these pillars relies massively on fossil fuels as an energy input and, in the case of fertilizers, also as a feedstock [1].

With a market size estimated in 76 Mtons/year, urea stands out as the most important fertilizer and one of the most fundamental molecules currently produced by the chemical industry. Urea sits at the downstream of the nitrogen fixating process, *i.e.*, is produced by reacting liquid ammonia from the Haber-Bosch (HB) process and CO_2 (from Steam Methane Reforming, the hydrogen source associated with the same HB process). Overall, the fixation of nitrogen and the synthesis of fertilizers come at a substantial energetic and environmental cost. For example, the HB process itself uses *ca*. 5.5 EJ/year, (*ca*. 11% of the energy consumed by the chemical industry), with an associated release of *ca*. 340 $Mtons_{CO_2}$/year into the atmosphere [2].

The coupling of electrochemical CO_2 and nitrate reduction (CO_2RR and NO_3RR) for the direct synthesis of C-N containing molecules is an appealing alternative to electrify the fertilizers industry and produce urea from sustainable feedstock and energy. However, the electrochemical synthesis of urea (E-UREA) is in its infancy and the state of the art lacks several key elements for a proper assessment of its figures of merit. In my talk, I will tackle some of the weakness of the process, ranging from the setups and operative conditions currently employed for E-UREA investigation to the methods for urea detection and quantification [3]. After an overview of the most common pitfalls in E-UREA studies, the discussion will focus on solutions, mostly based on the common good practices in electrocatalysis that have been established by the water splitting and CO_2RR communities. In particular, the attention will be drawn to (*i*) the implementation of *ad-hoc* setups, approaching industrially relevant conditions; (*ii*) a proper electrolyte engineering; and (*iii*) the accurate detection/quantification tools for urea (and all CO_2RR/NO_3RR by-products) [3]. Altogether, these precautions will serve the E-UREA community in achieving sound and industrially relevant results that will hopefully translate in electrofertilizers production technologies.
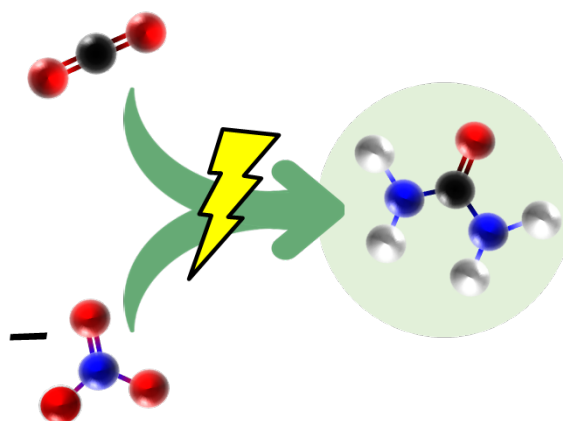

Figure 1 – Table of content: graphical depiction of CO_2 and NO_3^- ions co-reduction to urea

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2. J. Lim et al. "Ammonia and Nitric Acid Demands for Fertilizer Use in 2050." In: ACS Energy Lett. 6 (10), 3676–3685 (2021)
3. M. Ferri " UREAlity check: approaching the rising field of electrofertilizers." In: ACS Energy Lett. 2024, 9, 2394−2400

Penetration? Perspiration? Flooding? Finding Tools to Study Questions of Electrolyte Management in GDEs for CO$_2$ Electrolysis

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The application of gas diffusion electrodes (GDEs) as cathode platforms has recently become a generally followed strategy of achieving industrially relevant (>1 A cm^{-2}) current densities in practical CO$_2$ electrolysers. In a GDE, the catalyst is applied to a microporous layer supported by a looser, fibrous layer, both of which are usually made of conductive carbon. Well-designed GDEs can assure the abundance of all reactants of CO$_2$ electrolysis at the catalyst layer. That is, they create three-phase boundaries where CO$_2$, electrons, and water (the gas-, solid- and liquid-phase reactants of cathodic CO$_2$ reduction) can be brought into reaction by the catalyst and the applied electric field.

To maintain the efficacy of GDEs during electrolysis, ensuring optimal water (electrolyte) management is paramount. While the presence of some amount of water near the catalyst layer is required for CO$_2$ electroreduction, the overhydration of the catalyst is to be avoided, as this can block the access of CO$_2$ to the catalyst particles. Overhydration, or in short flooding, occurs when excess water soaks the entire catalyst layer, displacing the afore-mentioned gas | solid | liquid three-phase boundary to deeper layers of the GDE structure, where no catalyst is present.

The flooding of gas diffusion electrodes can be caused by a variety of factors (pressure imbalances, gas or liquid flow irregularities) that can however be avoided by a careful optimization of process parameters (flow rates, etc.). There is one effect, however, which is hard to avoid, and which will almost definitely cause some electrolyte penetration into the GDE structure: this is the formation of bicarbonate or carbonate precipitates due to a reaction of CO$_2$ with the usually alkaline catholyte. Carbonate precipitation inside and on top of the GDE will eventually start a vicious circle, as it will gradually decrease the original hydrophobicity of the electrode, resulting in a further penetration of electrolyte into the GDE, allowing the formation of more precipitates until —probably after not very long operation times— the entire GDE will become wetted to some extent.

At this point it is important to distinguish between the wetting of the GDE (penetration of electrolyte into its structure) and the flooding (overhydration) of the catalyst layer. While several authors interpret electrolyte penetration as a synonym of flooding, it was pointed out recently that even GDEs that are wetted to an extent that the electrolyte already breaks through them, can remain fully functional for electrochemical CO$_2$ reduction, so that their catalyst layer should hardly be considered "flooded" in the classical sense. In fact, electrolyte droplets in the output gas flow of well-operating electrolysers can often be detected — this effect is called perspiration.

That perspiration should not be interpreted as a sign of flooding, but on the contrary, it is an indication of stable operation of the reactor, was pointed out by some of our recent works [1–3] where we emphasized the importance of maintaining efficient perspiration pathways inside GDEs, which the penetrated electrolyte can percolate through, leaving the catalyst layer active and mostly unflooded. This argumentation is supported by a series of investigations where, using newly developed ICP–MS-assisted EDX imaging techniques, we studied the effects of different surface morphologies, binders, catalyst capping agents, etc. on electrolyte perspiration through CO$_2$ electrolysing GDEs. The presentation is focused on these results, and it also gives a detailed introduction to the underlying analytical methods.

1. H. Hu et al. "Effective perspiration is essential to uphold the stability of zero-gap MEA-based cathodes in CO2 electrolysers" In: Journal of Materials Chemistry A 11, 5083 (2023).
2. M. Liu et al. "The role of ionomers in the electrolyte management of zero-gap MEA-based CO2 electrolysers: A Fumion vs. Nafion comparison" In: Applied Catalysis B 335, 122885 (2023).
3. S. Vesztergom et al. "Eliminating Flooding-related Issues in Electrochemical CO$_2$-to-CO Converters: Two Lines of Defense" In: Chimia 77, 104 (2023).

Cation Crossover Limits Accessible Current Densities for Zero-Gap Alkaline CO_2 Reduction to Ethylene

Hunter Simonson[1,2], Danielle Henckel[2], Walter Ellis Klein[1], K.C. Neyerlin[1], Wilson A. Smith[1,2]

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The electrochemical conversion of CO_2 to value-added products is a growing platform to close the loop of captured carbon which is necessary to remediate the effects of anthropogenic climate change. Traditional CO_2 reduction systems fail in an alkaline environment due to the interaction of CO_2 with the alkaline electrolyte phase, forming carbonate and bicarbonate ions which can precipitate out of solution in the form of salt crystals, commonly referred to as "salting out". The presence of the salt crystals causes a reduction in the selectivity of the electrolyzer towards CO_2 conversion. Here, the critical operational variables which elicit the salting out process are investigated, including electrolyte concentration, current density, and membrane thickness. It is shown that salting out is observed when the electrolyzer exceeds a critical total current density, observed by a switch in selectivity from CO_2 reduction to H_2 evolution over the course of an hour, and confirmed by post-hoc cross-sectional SEM-EDS of the electrode. This critical current density is lower when increasing membrane thickness or ionic strength of the anolyte is increased. The salting out process is mediated by the unintended crossover of cations from the anolyte to the cathode across an anion exchange membrane which is imperfectly excluding cations. It is likely that electric-field driven migration drives an increase in concentration of potassium across the membrane, until at the critical current density for that electrolyzer arrangement, the concentration of potassium and bicarbonate exceeds the solubility limit of $KHCO_3$, leading to salting precipitation.
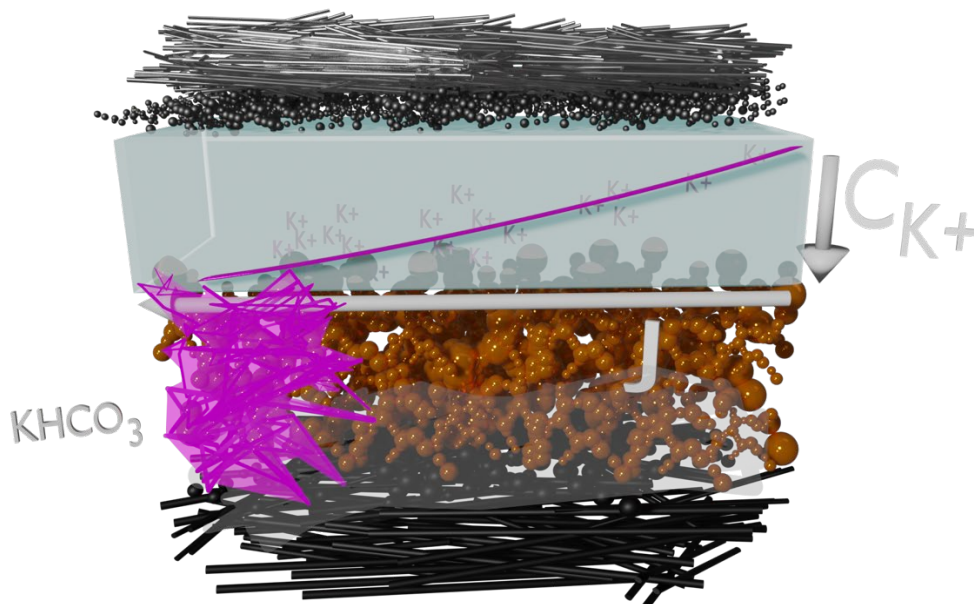
Figure 1: Schematic concentration of potassium ions increasing across the anion exchange membrane with increasing current density.

Water transport in CO_2 electrolysis to CO during pulsed operation investigated by high-resolution neutron imaging

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Even though prototypes of low-temperature CO_2 electrolyzers producing CO are already tested at pilot scale[1] and CO peak partial current densities of 1 A cm^{-2} have been demonstrated[2], achieving sufficient lifetimes still poses a major challenge. A common limiting factor is the precipitation of carbonate salts at the cathode. Pulsed operation of the electrolyzer has been proposed as a strategy to increase the lifetime, as pulsing allows to reduce the local ion concentration.[3,4]

This work investigates the water management, which is closely related to the salt formation, in different operation modes by high-resolution neutron imaging (effective resolution of 4.2 µm, Figure 1b). A PiperION based cell is operated at 50 °C and 400 mA cm^{-2}. Its pulsed counterpart operates repeatedly at 400 mA cm^{-2} for 10 min and is then held at 0 mA cm^{-2} for another minute. While the cell voltage remains stable over the duration of the experiment in both cases, pulsing helps stabilizing the selectivity towards CO. The neutron images reveal an increase in water content of the cathode's gas diffusion electrode while the cell stands idle (Figure 1b). This suggests that pulsed operation does not only reduce the concentration of dissolved ions, but also facilitates the removal of already precipitated salt by repeatedly washing it out.
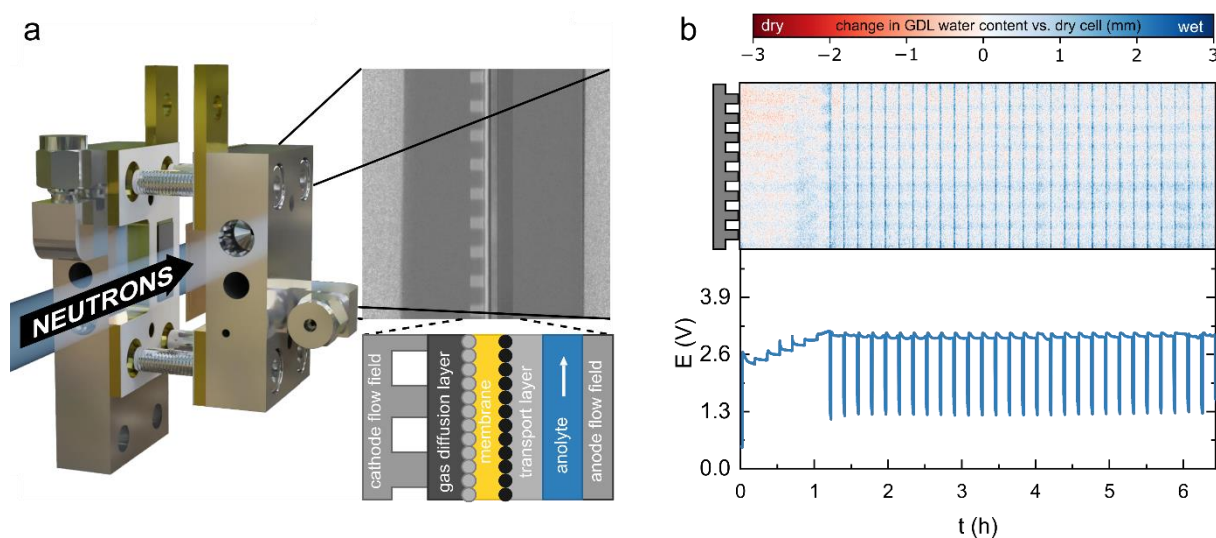

Figure 1 – (a) Adapted zero-gap cell for neutron imaging; (b) change in water content in the gas diffusion layer and cell voltage during pulsed operation at 50 °C and 400 mA cm^{-2}.

References

(1) Masel, R. I.; Liu, Z.; Yang, H.; Kaczur, J. J.; Carrillo, D.; Ren, S.; Salvatore, D.; Berlinguette, C. P. An industrial perspective on catalysts for low-temperature CO_2 electrolysis. Nat. Nanotechnol. 2021, 16, 118–128.

(2) Endrődi, B.; Kecsenovity, E.; Samu, A.; Halmágyi, T.; Rojas-Carbonell, S.; Wang, L.; Yan, Y.; Janáky, C. High carbonate ion conductance of a robust PiperION membrane allows industrial current density and conversion in a zero-gap carbon dioxide electrolyzer cell. Energy Environ. Sci. 2020, 13, 4098–4105.

(3) Xu, Y.; Edwards, J. P.; Liu, S.; Miao, R. K.; Huang, J. E.; Gabardo, C. M.; O'Brien, C. P.; Li, J.; Sargent, E. H.; Sinton, D. Self-Cleaning CO_2 Reduction Systems: Unsteady Electrochemical Forcing Enables Stability. ACS Energy Lett. 2021, 6, 809–815.

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System and Process Development for Industrial Carbon-dioxide Electroreduction

Csaba Janáky[1,2]

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2) *eChemicles zRT, Szeged, Hungary*

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Electrochemical reduction of CO_2 is a promising method for converting a greenhouse gas into value-added products, utilizing renewable energy. Novel catalysts, electrode assemblies, and cell configurations are all necessary to achieve economically appealing performance. In my talk, I am going to present a scalable zero-gap electrolyzer cell, which converts gas phase CO_2 to products without the need for any liquid catholyte. I will show how proper cell components and operational conditions result in unprecedentedly high partial current densities in zero-gap cells. I will demonstrate the role of each component of the membrane electrode assembly, such as the catalysts, the porous transport layers, the membrane, and the ionomers.

In the second part of my talk, I will show that while precipitate formation in the cathode gas diffusion electrode is detrimental for the long-term stability, the presence of alkali metal cations at the cathode improves performance. To overcome this contradiction, I will present different approaches which help to extend the lifetime of the electrolyzer cell.

As an outlook, I will present a complex machine learning based approach, through which we aim to find the optimal operating conditions of such CO_2 electrolyzer cells.

References:
1. C. Janáky et. al.: *Multilayer Electrolyzer Stack Converts Carbon Dioxide to Gas Products at High Pressure with High Efficiency,* ACS Energy Letters 4 (2019) 1770-1777
2. C. Janáky et. al.: *High carbonate ion conductance of PiperION membrane allows industrial current density and conversion in zero-gap carbon dioxide electrolyzer cell* Energy & Environ. Science, 13 (2020) 4098-4105
3. C. Janáky et. al. : *Operando cathode activation with alkali metal cations allows high current density operation of water-fed zero-gap carbon dioxide electrolyzers*, Nature Energy, 6, (2021) 439–448
4. C. Janáky et. al.: *Systematic screening of gas diffusion layers for high performance CO_2 electrolysis,* Communications Chemistry, 6 (2023) 41
5. C. Janáky et. al.: *Membrane Electrode Assembly for Electrocatalytic CO_2 Reduction: Principle and Application,* Angewandte Chemie International Edition, 135 (28), e202302789
6. C. Janáky et. al.: *Renewable Syngas Generation via Low-Temperature Electrolysis: Opportunities and Challenges*, ACS Energy Letters 9 (1), 288-297

Mass and thermal management for CO₂ electrolyzers enables enhanced performance

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Electrochemical CO_2 reduction into fuels powered by renewable energy sources presents an advantageous approach for CO_2 mitigation and the storage of intermittent renewable energy into storable, high-energy-density forms. Large-scale industrial applications require efficient and stable electrochemical CO_2 reduction systems operating at high current densities (200 mA cm^{-2}). Despite advancements in the development of electrocatalysts and device architectures, particularly in membrane electrode assembly (MEA)-based cells, sustaining long-term stability at elevated current densities remains a challenge due to limited energy and CO_2 utilization efficiencies, as well as cathodic salt precipitation, which requires a better understanding of mass and heat transport in the electrolyzer. This study utilized a coupled numerical and experimental method to quantify the mass and heat transfer in an MEA-based CO_2 electrolyzer for CO generation. Our 1D non-isothermal numerical model accounts for the fluid flow in gas channels and gas diffusion electrode (GDE), mass transfer of gases, liquid water, as well as ionic species, homogenous and heterogenous reactions in GDE and membrane, and conductive and convective heat transfer. Various MEA designs and operation conditions were assessed, and strategies were sought to improve the electrolyzer's energy and mass utilization efficiencies. Notably, we proposed a non-isothermal operation approach, employing a cooler cathode and a warmer anode to simultaneously enhance device efficiency and prevent salt precipitation. This is achieved by exploiting the Soret effect, which facilitates the thermal diffusion of cations from the cathode to the anode. Additionally, this approach capitalizes on the increased electrochemical activity of the anodic oxygen evolution reaction at higher temperatures and the enhanced selectivity of the cathode due to increased CO_2 solubility at lower temperatures. Our experimental results reveal that a membrane electrode assembly-based CO_2 reduction device, operating with a cathode temperature of 40°C and an anode temperature of 60°C, exhibits no salt precipitation over 13 hours under highly alkaline conditions at a current density of 200 mA cm^{-2}. The mass and thermal management strategies proposed and discussed in this study can push forward the practical implementation of CO_2 reduction technologies, ensuring long-term operational stability with non-compromised energy conversion efficiency.
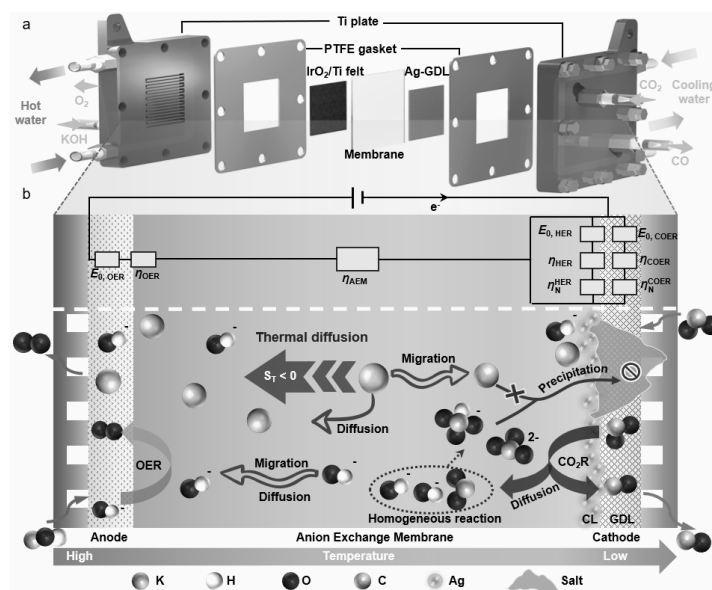

Figure 1 - Schematics of the MEA-base CO2 electrolyzer studied (a) with detailed physics (b).

Investigation of Electrochemical CO_2 Reduction at Silver-Based Gas Diffusion Electrodes in Flow Cells

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As one of the primary contributors to greenhouse gas emissions, CO_2 significantly influences climate change. Excess CO_2 can be converted into valuable chemicals through electrochemical CO_2 reduction (eCO_2R), utilizing renewable energy sources during peak times. However, the efficiency of this process is inhibited by mass transport limitations caused by the poor solubility of CO_2 in aqueous electrolytes. Gas diffusion electrodes (GDEs) are commonly employed to address this issue.

While various catalysts have been explored to produce different C1 and C2 products, not too many studies have investigated eCO_2R at elevated current densities exceeding $2\,kA\,m^{-2}$ [1]. Such investigations are crucial for assessing the industrial viability of electrodes. At higher current densities, mass transport limitations lead to hydrogen evolution dominating the process. The formation of hydrogen bubbles on the electrolyte side of the GDE poses a significant challenge, particularly in flow cells [2]. In the first place, the fluctuating ohmic drop necessitates an online iR correction, e. g. by high-frequency response [3]. Moreover, the differential pressure between the gas and electrolyte sides varies depending on bubble formation. Experimental findings, as illustrated in Figure 1, highlight the correlation between GDE performance and applied differential pressure. Since the latter significantly affects bubble formation, water columns are insufficient for controlling backpressure. Instead, precise pressure control on both gas and electrolyte side of the GDE is recommended [4].

Given the substantial impact of hydrogen evolution, it is imperative to quantify the amount of hydrogen generated on each side of the electrode. Separate gas analysis for the gas and electrolyte compartment can enable this. Figure 2 demonstrates that CO is predominantly formed at the gas side, while a notable amount of hydrogen is released at the electrolyte side. Considering these observations, an improved eCO_2R flow cell setup is proposed based on silver GDEs, with potential applicability to other catalytic systems.
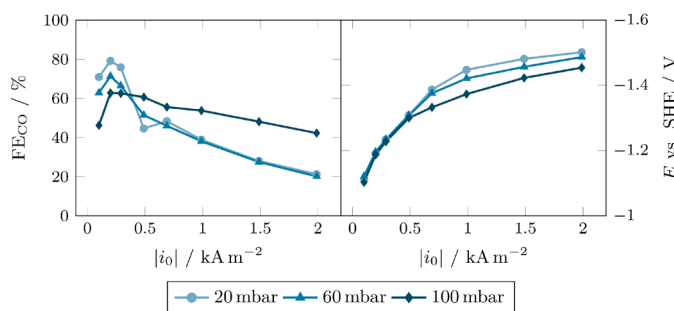

Figure 1 – Faradaic efficiencies (left) and cathode potentials (right) in dependence of differential pressure and current density.
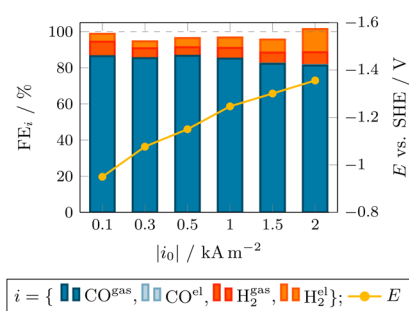

Figure 2 – Faradaic efficiencies on both GDE sides and cathode potentials.

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Enhancing Stability of Cu-Based Gas Diffusion Electrodes for Low-Temperature CO2 Electrolysis

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Despite the growing affordability of renewable energy sources like solar and wind, their inconsistent production remains a hurdle. Short-term storage solutions like batteries are helpful, but a bigger challenge lies in storing large quantities of renewable energy for extended periods, ranging from days to entire seasons. The quest for long-term renewable energy storage goes hand-in-hand with addressing hard-to-decarbonize (or hard-to-defossilize) industries such as chemical, steel and cement industries. They rely heavily on fossil fuels for processes that cannot be easily electrified. In the pursuit of a carbon-neutral economy and the integration of renewable electricity, Siemens Energy initiated more than a decade ago a research program exploring the transformation of CO_2 and renewable electricity into economically valuable products. Low-temperature CO_2 electrolysis presents a game-changing opportunity to leverage the utilization of CO_2 and renewable electricity. This process allows for the production of a wide range of chemicals (carbon monoxide, formic acid, methane, ethylene, ethanol, or *n*-propanol). These chemicals can not only contribute to the defossilization of various sectors but also essentially act as a form of chemical storage for renewable electricity.

Siemens Energy has pioneered CO_2 electrolysis technology for over a decade. Initial lab-scale experiments have successfully transitioned to larger demonstrators. CO_2-to-CO electrolyzers, reaching up to the 5 kW range, feature active cell areas of 300 cm^2 and 5000 cm^2. In a government-funded project, one such demonstrator (capable of producing 0.3 kg/h of CO) was integrated with a fermentation unit for the production of specialty chemicals. This successful integration serves as a real-world example of a complete Power-to-X system in action[1-3].

CO_2-to-C_2H_4 electrolyzers attract significant attention for the possible end use cases in sustainable aviation fuel as well as polymer production. While researchers have achieved high current densities for converting CO_2 using copper-based gas diffusion electrodes, a major hurdle remains - poor long-term stability. Our research in the last years focused on tackles CO_2 conversion stability in copper electrodes by focusing on three key factors: catalyst structural changes, electrode design, and operational conditions[4-6]. The effects of governing operation conditions (such as "back pressure" or liquid product accumulation in electrolyte) on the stability were investigated in detail. Electrode design was optimized for two promising cell design candidates for upscaling. Long-term stability was investigated with all the countermeasures implemented in Siemens Energy test rigs. Internally designed 10 cm^2 flow cells with comparable cell architecture to the cell upscaled to 5000 cm^2 in previous project [7] was run with Cu-based GDEs for this study. 720 hours of stable CO2RR at 100 mA/cm^2 was achieved at FE>20% for C_2H_4. Faradaic efficiency for all C_{2+} products accounted for up to 50%. Increasing current density from 100 mA/cm^2 to 300 mA/cm^2 decreased the stability while enhancing the selectivity. SEM/EDX analyses revealed extensive salt formation as the primary cause for degradation in 100 mA/cm^2 tests, while catalyst agglomeration and restructuring appear to be the initial degradation causes in 300 mA/cm^2 tests.

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Integrated R&D Towards Industrial Ethylene Electrosynthesis

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The low-temperature electrochemical conversion of CO_2 to ethylene holds a great potential to defossilize a significant part of the chemical industry. Despite recent breakthroughs obtained in academic settings have shown how the key performance indicators (activity, selectivity, durability) can be improved, knowledge gaps still remain at the level of a single electrochemical cell, as well as many unknowns on multi-cell stack and process design. As a consequence, future market penetration of the CO_2-to-ethylene technology (currently at TRL~3) remains unclear. Integrating R&D at all scales (electrode, cell, stack, process, system) is therefore urgently needed to bring the technology towards industrial implementation.

By combining multiscale modelling, electrode design, testing at different scales, and process development, at TNO we are aiming to identify a suitable scaling-up strategy to advance the CO_2-to-ethylene technology towards industrial implementation in the near future. In this talk, we will present the key results related to the following R&D activities:

1) Development of a multiscale modelling framework from cell- to system-level, to provide guidance for electrode development, stack design, and operational strategies for optimal system integration. We focus on membrane-electrode-assembly (MEA) cell and investigate how different geometrical features, electrode properties, and operating conditions influence I-V curve, Faraday efficiency and the spatial distribution of the key quantities. The isothermal and steady-state model includes gas and liquid flow, the transport of 14 species and heterogeneous/homogeneous reactions. Assumptions and results are compared against existing literature and experimental data.

2) Design and fabrication of process-tailored gas diffusion electrodes with scalable manufacturing techniques. Results from proof-of-principle catalyst synthesis and electrode preparation will be shown. Copper-based nanoparticles are prepared using a water-based synthesis method and deposited on gas diffusion layers using ultrasonic spray coating, ensuring high-degree of tunability of the GDE properties.

3) Identification of upscaling hurdles by testing the technology from lab-scale to 10-kW pilot-scale. The available electrochemical testing infrastructure will be described. Suitable testing protocol and challenges to maximize the performance through the right operating conditions (e.g. gas/liquid pressure balancing) will be highlighted. Preliminary experimental results on the performance of the developed materials will be shown.
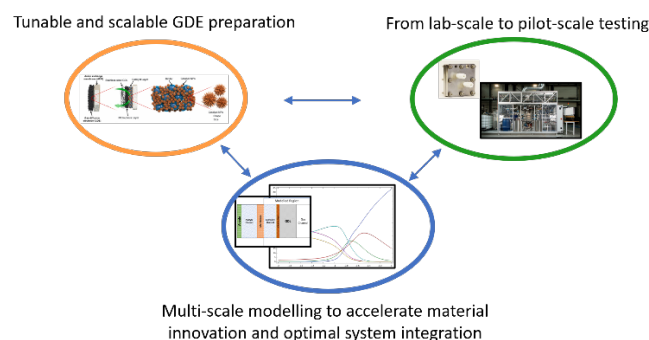

Figure 1 - Overview of the three main pillar of CO_2-to-ethylene R&D activities at TNO.

Improving energy efficiency of CO₂ electrolysers in light of process integration with high-pressure stack-technology

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The electrochemical conversion of CO_2 has in recent years emerged as a promising technology towards allowing the conversion of CO_2 emissions to valuable chemicals and synthons. Among various technologies, CO_2-to-CO electrolysers pose a big opportunity for providing green CO_2-derived carbon synthons for various chemical products such as polymers, paints, varnishes, glues, cosmetics, and aviation / maritime fuels. Despite the significant progress in the field with respect increasing selectivities at high current densities [1], current generation CO_2 electrolysers based on anion exchange membranes (AEM) still encounter inherent challenges due to limited carbon efficiency by high CO_2 cross-over to the anode and sudden degradation events through carbonate formation or flooding [2]. Furthermore, their integration into chemical industry value chains is a major challenge.

Herein, we present a groundbreaking CO_2 electrolysis technology, which tackles the trinity of 1) lacking performance, 2) high cost and 3) poor integrability into state-of-the art chemical process chains. Our differential pressure electrolyser enables conversion of carbon dioxide to CO at pressures up to 120 bar, employing a bipolar membrane (BPM) electrode assembly, enabling the direct coupling without additional compression steps with a multitude of downstream-product separation (membrane or pressure swing adsorption) and subsequent chemical processes such as Methanol and Fischer-Tropsch syntheses. With its high-performance membrane electrode assembly and high-pressure electrochemical cell design the technology improves the carbon efficiency, provides an improvement in energy efficiency of at least 10 % while simultaneously doubling the productivity for CO_2 conversion compared to state of the art. Furthermore, we outline current challenges and opportunities of implementing this technology in the pilot scale project »Leuna100« developing a process chain to methanol [3].
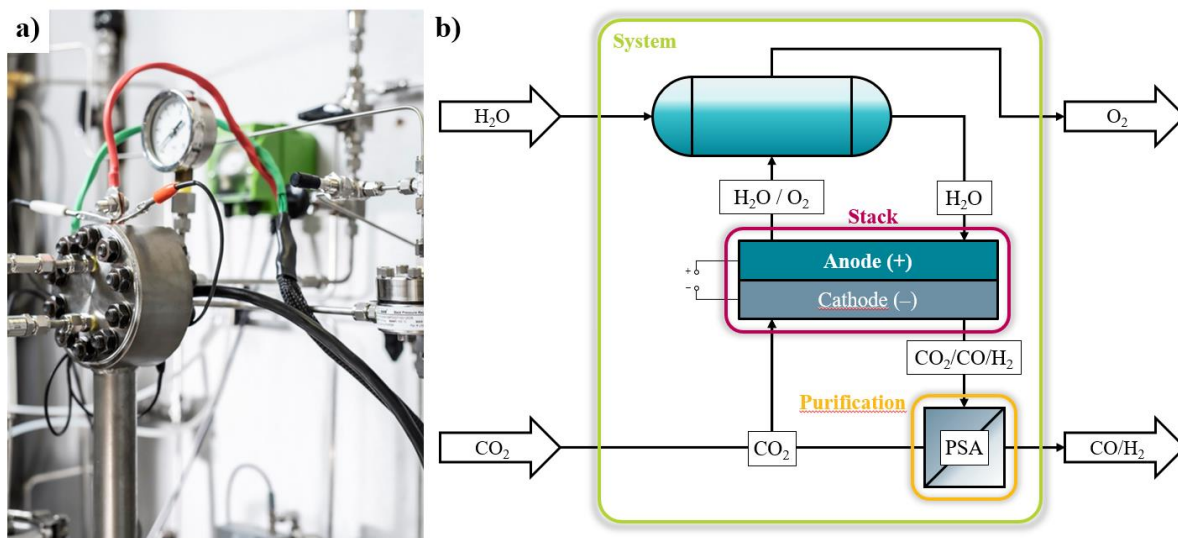

Figure 1. *a) Lab scale high pressure CO_2 electrolyser for differential pressure operation up to 120 bar(g). b) general system design for a CO_2 electrolyser for pure syngas production*

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3. Project »Leuna100«, more information: https://www.leuna100.de/

Abstracts of Poster Contributions

Presenter and Author	Title
Paige Brimley; Ankur Gupta; Wilson Smith; Derek Vigil-Fowler; Jacob Wrubel	A Continuum Nanopore Modeling Framework for Ionic Transport
Frederik Brendel; Luca Bohn; Josephine Häberlein; Severin Vierrath; Joey Disch	Investigating water management in bipolar membrane CO2-to-CO-electrolysis with high-resolution neutron imaging
Robert Fischer; Matthieu Dessiex; Felix N. Büchi	Charge-Current-Damage Relations in Forward Bias Bipolar Membrane CO2 Electrolyzers
Josephine Häberlein; Khaled Seteiz; Philipp Heizmann; Joey Disch; Severin Vierrath	Low loaded carbon supported Ag nanoparticles for CO2 electrolysis towards CO enabling high mass activities
Dominik Krisch; Ulf-Peter Apfel; Houssein Awada; Beatriz Roldan Cuenya; Lucas Hoof; Leonard Messing; Kevinjeorjios Pellumbi; Kai-Junge Puring; Clara Rettenmaier; Sebastian Sanden; Wolfgang Schöfberger; Daniel Siegmund; Luyang Song; He Sun	Minimizing the Ag-loading of CO2 electrolyzers with molecularly tailored catalysts
Niklas Oppel; Philipp Röse; Ulrike Krewer	Unlocking the Potential of Aprotic Electrolytes for CO2 Reduction: Catalyst Composition, Pressure, and Surface Roughness Optimization
Martina Rizzo; Andrea Toma; Hanh Le Thi Hong; Ilka Kriegel; Liberato Manna; Luca De Trizio; Luca Goldoni; Marco Leoncini; Marzia Ferrera; Michele Ferri	Electrochemical Urea Synthesis: Catalytic Insights and Analytical Challenges
Daniel Rottmann; Stefan Haufe; Ricarda Kloth; Karl Mayrhofer	Guidelines for correct product quantification in CO2 electrolysis
Khaled Seteiz; Josephine Häberlein; Philipp Heizmann; Luca Bohn; Severin Vierrath; Joey Disch	The effect of ionomer content and Ag/C catalyst surface area on the performance of CO2 electrolysis to CO
Blaž Tomc; Nejc Hodnik	Dynamic Deactivation of Copper Electrocatalysts During CO2 Reduction
Katharina Trapp; Maria R Lukatskaya	Anion-cation interplay defines the electrolyte effect on the electrochemical CO2 reduction

A continuum nanopore modeling framework for ionic transport

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Ion exchange membranes (IEMs) are crucial to the efficient operation of many electrochemical devices but detailed understanding of the microscopic transport mechanisms within an IEM remain elusive. Volume-averaged continuum modeling approaches have typically been applied to the entire IEM domain and are useful for macroscopic properties,[1] however the water domains thought to be responsible for the bulk of ionic transport have rarely been modeled explicitly.[2] In
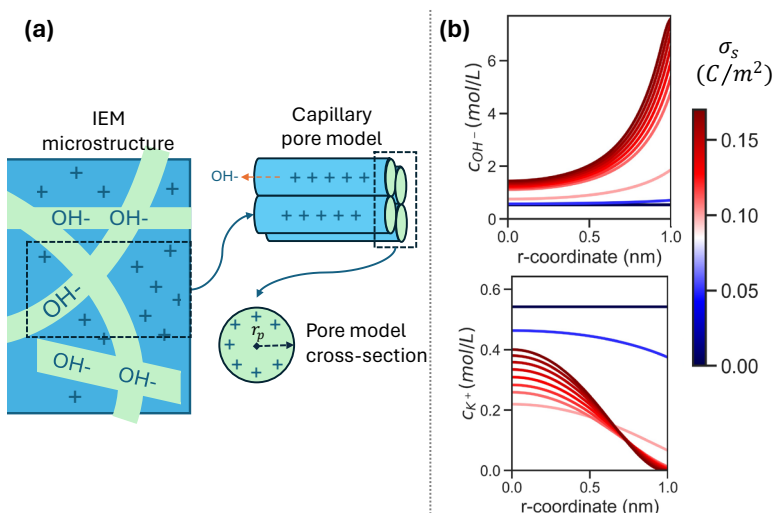

Figure 1 – (a) Schematic representation of nanopore model, (b) ionic radial concentration profiles as a function of pore-wall surface charge density.

this contribution, we build upon previous modeling efforts and assume that water domains can be modeled as cylindrical, charged pores.[3–7] We develop a generalizable, two-dimensional continuum model of a water domain through an ion exchange membrane using a modified Poisson-Nernst-Planck framework.[8] Our model incorporates solvent transport, migration, diffusion, adaptive permittivity and viscosity models, and the finite-size effects of co- and counter-ions. We validate our model to prior, experimentally verified nanopore models of a *proton exchange membrane* (Nafion 117)[4,5] and demonstrate that a shortened pore domain captures many of the characteristic transport features. We then adapt our model to be representative of transport through a model *anion exchange membrane* as has, to our knowledge, rarely been investigated in the literature. By using our model to simulate transport under different operating conditions, we are able to visualize resultant spatial profiles of concentration and potential within a nanopore. Additionally, we quantify the relative contribution of each transport mechanism to the flux of co- and counter-ions through pores of varying properties. The utility of this model is demonstrated through its adaptability and holds many applications for electrosynthesis, carbon removal, and fuel cell technologies.

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Investigating water management in bipolar membrane CO_2-to-CO-electrolysis with high-resolution neutron imaging

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The defossiliziation of carbon-based industries needs environmental friendly carbon sources[1]. CO_2 electrolyzers are an excellent opportunity to convert CO_2 to valuable products. However, they require improvements in energy efficiency and long-term stability for upscaling. Bipolar membranes (BPMs) with porous anion exchange membrane (AEM) have been proposed to enable efficient long-term operation, while mitigating detrimental carbonate crossover. However, compared to state-of-the-art AEM-based CO_2 electrolyzers their electrochemical performance is still lacking behind in terms of maximum CO partial current density and energy efficiency. Further improvement of these bipolar membrane configurations requires a better understanding of the current limitations[2].

Therefore, electrochemical measurements were conducted while observing the spatial water distribution inside a zero-gap CO_2-to-CO-BPM electrolyzer (Figure 1 a) with high-resolution neutron imaging. Current-controlled polarization curves up to 400 mA/cm² were coupled with gas-chromatographic and electrochemical impedance spectroscopy analyses. A perforated AEM was combined with a non-porous cation exchange membrane (CEM). Compared to zero-gap AEM based electrolyzers no cathode dry out could be detected at the catalyst coated gas diffusion layer (GDL) when current density was increased[3]. Instead, a rise in humidity can be observed (Figure 1 b), probably boosting the hydrogen evolution reaction at the cathode by catalyst flooding. This suggests a self-humidification mechanism similar to forward-bias BPM fuel cells[4], which is supported by observing higher humidity in AEM compared to the CEM. This implies using less CO_2-humidfication when high current densities are applied.
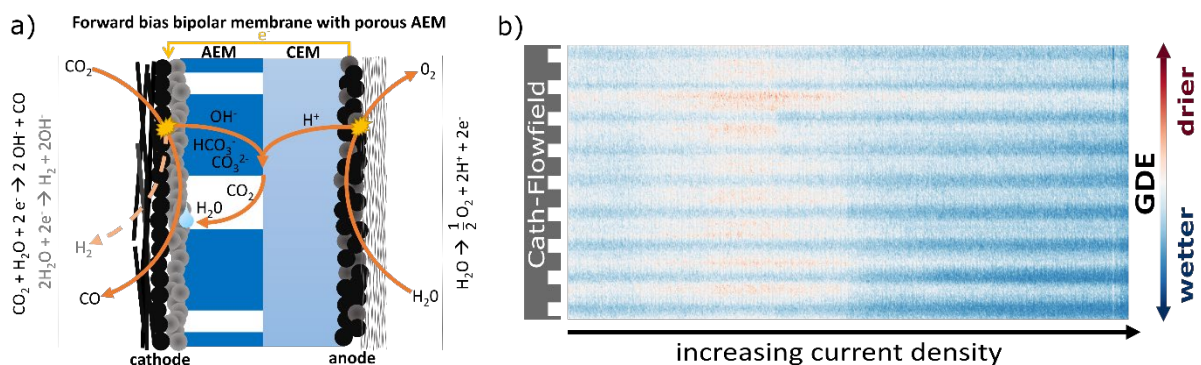

Figure 1 – a) Schematic design of BPM CO_2-electrolyzer with porous anion exchange membrane. The self-humidification is displayed as a droplet at the catalyst coated GDE. b) relative change in local humidity of the GDL over time.

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Charge-Current-Damage Relations in Forward Bias Bipolar Membrane CO2 Electrolyzers

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Bipolar membranes (BPM) are a potential solution to the fundamental issues of pure alkaline exchange membrane (AEM) CO2 electrolyzers (CO2ELY), namely carbonate salt precipitation and high CO2 crossover to the anode. In a forward bias BPM CO2ELY, the anion exchange layer (AEL) faces the cathode and the cation exchange layer (CEL) the anode. Other than in AEM-CO2ELY, the counterions to form carbonate salts are eliminated since there are no other cations than protons present in the system. (Bi)Carbonate ions that are formed at the cathode and conducted through the AEL are recombined with the protons in the CEL at the BPM junction of AEL and CEL. Neutral CO2 and water are formed and the electromigration of CO2 to the anode in the form of (bi)carbonate is prevented.

Previous works showed that gaseous CO2 can lead to membrane delamination[1,2] and anode cathode layer (ACL) disintegration[1]. Imaging experiments[1] also showed that membrane delamination only occurs for elevated current density while ACL damage can be seen for all conditions. There appears to be a balance between CO2 accumulation at the BPM junction driven by the applied current density and diffusive transport to both electrodes determined by CO2 diffusivity and established concentration gradients. A BPM with a macroporous AEL can enhance back-diffusion to the cathode and prevent delamination[2].

Employing laboratory X-ray tomographic microscopy (XTM), we present a systematic study of operating conditions and BPM material combinations on gas induced degradation processes. A miniature electrolyzer cell optimized for imaging is devised to take a full tomographic scan with 3 um voxel size before operation, after operation for a fixed amount of passed charge and after a second period of operation for the same charge. The current density is varied (25, 50, 100, 150 mA/cm2) between samples while accordingly adjusting the operation time to match the same charge (180As/cm^2, e.g. 100mA/cm^2 for 0.5h). We test a commercial BPM (Fumasep), a custom BPM (Fumatech FAA3 + Nafion 115) and a macro-porous BPM (needle punctured FAA3 + Nafion 115). The custom BPM shows strong delamination even for low current density, while the commercial BPM can withstand delamination up to at least 50 mA/cm^2, but shows localized delamination for higher current density. The macro-porous BPM prevents large scale delamination up to 100 mA/cm^2. ACL damage still occurs for all investigated samples indicating that CO2 diffusion to the anode still happens for enhanced back-diffusion pathways to the cathode.

The CO2 transport mechanisms in forward-bias BPM-CO2ELY go beyond CO2 accumulation at the BPM junction and need to be considered for durable application and material design. Employing a porous AEL is a first step towards better performing BPM materials, but does not eliminate all gas induced damages like ACL damage. Dynamic imaging should be employed to investigate if the CO2 back-diffusion pathways work as intended or if there are hidden structural dynamics affecting the redistribution of gaseous CO2. For example, the perforations could act as weak spots that allow bursting CO2 bubbles at the BPM junction for short lived high CO2 pressures, but do not prevent strong CO2 concentration gradients causing diffusion towards the anode during the remaining operation[1]. A microporous AEL could further enhance in-plane transport and homogeneous CO2 back-diffusion to the cathode.

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Low loaded carbon supported Ag nanoparticles for CO$_2$ electrolysis towards CO enabling high mass activities

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Au and Ag nanoparticles are the most active pure metal catalysts for the reduction of CO$_2$ to form CO, whereat Ag nanoparticles are commonly used due to lower material cost. In order to prevent nanoparticle aggregation and enable better catalyst utilization, carbon is applied as support material.[1,2]

In this work, Ag nanoparticles were immobilized via a cysteamine anchoring agent onto carbon black (Ag/C). The synthesis approach was adapted from Kim et al.[3] for different carbon support materials (Super P, Vulcan, Ketjenblack) with varying porosity and surface area. In a zero-gap electrolyzer, all three synthesized Ag/C catalysts achieved high partial current densities (up to 196 mA cm^{-2}) and faradaic efficiencies towards CO above 80% up to a current density of 200 mA cm^{-2}. Furthermore, mass activities (up to 3920 mA mg^{-1} with NiFe$_2$O$_4$ and 5400 mA mg^{-1} with IrO$_2$ anode catalyst) were higher than for commercial Ag/C catalysts and among the highest reported in literature (see Figure 1). The electrochemical performance of the different Ag/C catalysts at very low catalysts loadings (0.07 mg cm^{-2}) was similar, indicating an independence of peak performance and mass activity from the carbon support material and its surface area. It is important to note that this may only apply for very low catalyst loadings and cathodes with PTFE binder, as this was used in this study.
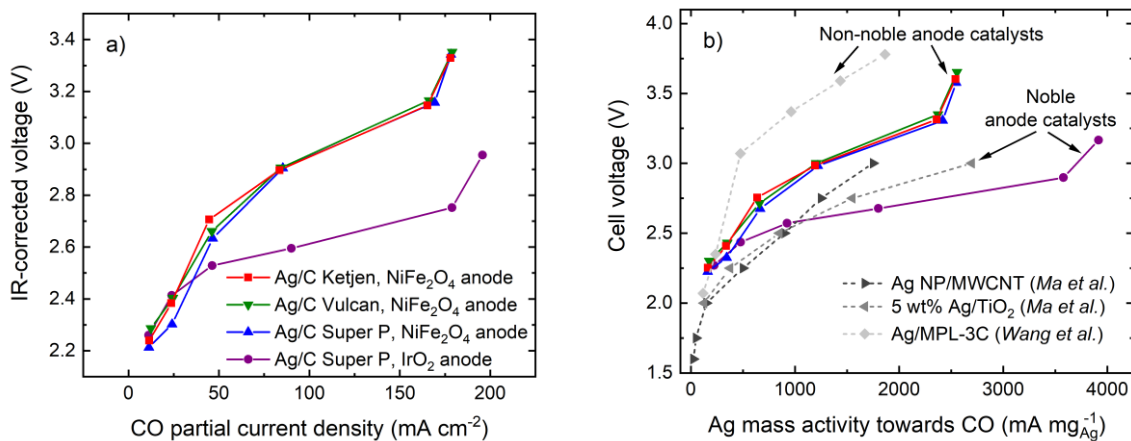

Figure 1 – a) Electrochemical performance: iR-corrected cell voltage over CO partial current density and b) mass activities for synthesized Ag/C catalysts compared to selected supported Ag catalysts from literature.[4-6]

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Minimizing the Ag-loading of CO_2 electrolyzers with molecularly tailored catalysts

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Electrochemical reduction offers a promising way of transforming the inert CO_2 molecule into beneficial feedstock chemicals like e.g. CO, thus advancing the dream of closed carbon cycles. Yet in order to render electrocatalytic CO_2 reduction (CO_2R) industrially applicable, catalytic systems have to meet steep demands with high selectivity, faradaic efficiency (FE) as well as long term stability under high current densities while also being cost effective. [1] In an effort to satisfy these requirements, an array of scalable Ag(I) bis-BIAN complexes featuring a variety of stereoelectronic properties was synthesized and thoroughly characterized (Figure 1A). Homogeneous electrochemical experiments asserted these compounds excellent selectivity of CO_2R over HER (hydrogen evolution reaction) and a clearly augmenting effect of electron donating ligands on the catalytic activity. [2] The most active derivatives were subsequently examined in a zero-gap cell electrolyzer, plus utilized to comprehensively optimize operating parameters such as membranes, flow fields and CO_2 feed humidification. As a result, the best performing catalyst [Ag(4-*n*-hexyloxy-BIAN)$_2$]BF$_4$ exhibited a FE_{CO} of 92% at 300 mA cm^{-2}, 51% at 600 mA cm^{-2} and 30% at 900 mA cm^{-2} at a loading of just 0.5 mg cm^{-2} under optimized conditions (Figure 1B). This excellent catalytic performance was furthermore proven to be stable for at least 110 h at 300 mA cm^{-2} and 80 h at 600 mA cm^{-2} with a FE_{CO} decay rate of merely 0.01% h^{-1}. The resultant mass activities of silver for CO generation surpass the ones reported for nanoparticle-based catalysts highlighting the advantage in catalytic efficiency of well dispersed single atom catalysts. [3]
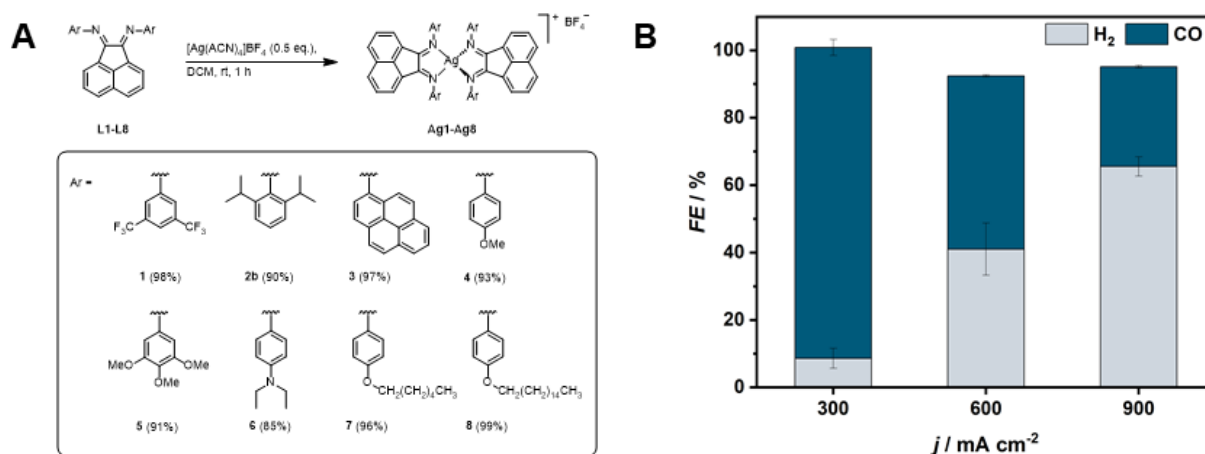

Figure 1 – A) Synthesis of investigated silver(I) bis-BIAN complexes. [2,3] B) Current density variation at optimized conditions in a zero-gap cell electrolyzer with an Ag7 loading of 0.5 mg cm^{-2} after 1 h of electrolysis. [3]

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Unlocking the Potential of Aprotic Electrolytes for CO_2 Reduction: Catalyst Composition, Pressure, and Surface Roughness Optimization

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Copper-based electrocatalysts have emerged as promising materials for the CO_2 electrolysis to valuable products in aqueous electrolytes. However, the inherent limitations of aqueous electrolytes, including low CO_2 solubility and competing hydrogen evolution reaction (HER), hinder their widespread application.[1] Aprotic organic electrolytes (e.g., acetonitrile) offer a potential solution by providing higher CO_2 solubility and suppressing HER.[2] Yet, fundamental understanding of CO_2 reduction in aprotic media remains limited, hindering further progress in this field.

In this contribution, we present a comprehensive analysis of the CO_2 reduction kinetics on Cu-based electrocatalysts in acetonitrile. Using a combination of dynamic electrochemical techniques (e.g., cyclic voltammetry) alongside mathematical modeling of the microkinetics and continuum transport, we elucidate reaction and transport phenomena and uncover underlying performance limitations. In addition, we systematically investigate the influence of pressure, surface roughness and catalyst composition by alloying Zn, to overcome these limitations and improve CO_2 reduction efficiency.

Our results show that Cu electrodes in aprotic electrolytes exhibit a bottleneck in CO_2 adsorption,[3] in contrast to the CO_2 transport limitations observed in aqueous solutions.[4] Furthermore, increasing the pressure, surface roughness, and Zn content leads to improved CO_2 reduction performance, which we attribute to enhanced CO_2 adsorption kinetics: elevated pressure favorably shifts the adsorption equilibrium, increased surface roughness exposes additional adsorption sites, and Zn alloying increases the intrinsic CO_2 adsorption capacity, resulting in higher catalyst utilization.

Overall, our study provides valuable insights into the effects of catalyst design and reaction conditions on the performance of CO_2 electrolysis in organic electrolytes. These insights facilitate knowledge-based customization of electrocatalysts and optimization of operating conditions, paving the way for the scale-up of this application and the exploration of more complex reaction systems such as electro-organic syntheses or CO_2 electrolysis with protic additives.
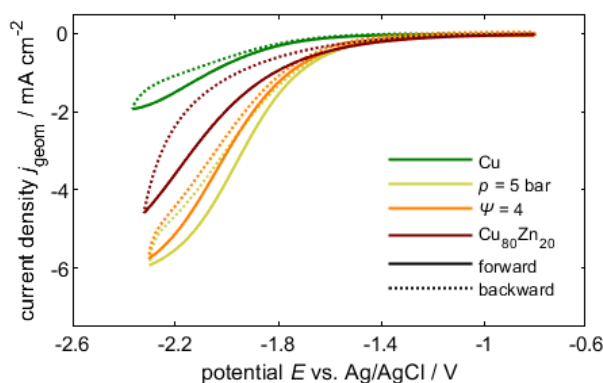

Figure 1 – Simulated cyclic voltammograms in CO_2 saturated 0.1M $TBABF_4$ in acetonitrile on planar polycrystalline Cu (green), planar Cu at p = 5 bar (yellow), roughened Cu with roughness factor Ψ = 4 (orange) and planar polycrystalline $Cu_{80}Zn_{20}$ alloy (red).

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Electrochemical Urea Synthesis: Catalytic Insights and Analytical Challenges

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Urea stands out as the predominant synthetic nitrogen fertilizer and in the last decades it has played a key role in increasing crop production and feeding a growing population[1]. Traditional urea synthesis heavily relies on the energy-intensive, fossil fuel-driven Haber-Bosch and Bosch-Meiser processes, collectively responsible for over 2% of global energy consumption[2]. Conversely, the electrochemical coupling between CO_2RR and NO_3RR can provide novel and sustainable routes to synthesize urea[3].

Most of the findings concerning the electrochemical synthesis of urea have been achieved in limited and non-scalable systems (e.g., H-cells), while there is still a lack of a comprehensive research in an industrially relevant configuration and environment. Furthermore, the results reported are derived from analytical methodologies susceptible to inaccuracies, thereby impeding precise quantification of urea and, subsequently, assessment of the faradaic efficiency of the systems utilized in its production[4].

The DAMO-TSC spectrophotometric method measures the absorbance of the compound obtained from the reaction of urea with diacetyl. However, the presence of nitrite ions can alter the absorbance, leading to inaccurate results[5]. Adding sulfamic acid to the sample helps mitigate this effect[6], but our research shows that other reaction products can also affect urea quantification, potentially causing its underestimation.

The indirect colorimetric method involves quantifying urea by determining the concentration of ammonia (via the indophenol reaction) before and after the hydrolysis of urea into CO_2 and NH_3 through the action of urease.

^{1}H-NMR is instead hampered by the currently low concentration of urea in post-electrolysis samples, and it is necessary to adjust the pH of the sample according to the stability of the target product. Methods based on liquid chromatographic separation and detection emerge as the most reliable for precise and unbiased urea quantification, but there is no standardized protocol for the quantification of both CO_2RR and NO_3RR products.

Our research provides an in-depth study of urea quantification methods, proposing an ad-hoc analytical methodology aimed at avoiding false positives and negatives.

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Guidelines for correct product quantification in CO₂ electrolysis

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Electrochemical CO_2 reduction (ECO2R) is a promising technique for converting CO_2 to high value chemical feedstocks using renewable energy. As of today, multiple challenges for the ECO2R process still need to be solved before its operation on an industrial scale is feasible[1].
The first step towards meaningful research on CO_2 electrolysis is to build a setup, which allows to determine the product distribution of the electroreduction process correctly and reproducibly. For the gaseous products (e.g., CO, H_2, C_2H_4…) gas chromatography (GC) has been established as the main method for product quantification, while liquid products (e.g., ethanol, propanol, formic acid…) have been quantified via multiple analytical methods such as high-performance liquid chromatography (HPLC), nuclear magnetic resonance (NMR) spectroscopy or headspace GC[2,3]. However, many obstacles must be overcome to avoid over- and/or underestimation of products.

Liquid products are prone to migration to the anode side and/or evaporation into the gas stream, which can lead to unnoticed product loss. For gaseous products the correct determination of the volume flow is essential. Assuming the volume flow does not change over time can lead to large overestimation of the gaseous products as dimerization, formation of liquid products and solvation of CO_2 into the typically alkaline electrolyte diminish the gas flow[4].

In this work it is aspired to present guidelines for correct product quantification within a gas diffusion electrode-based flow-cell electrolyser. Loss of liquid product to the anolyte is avoided by using an almost impermeable bipolar membrane. Furthermore, evaporated liquid products are regained in a collection vessel by cooling the product gas stream behind the cell. For the correct determination of the gaseous product flow, an additional N_2 line is installed, which allows monitoring the flow. This is possible as the N_2 signal within each GC injection is depending on the volume flow of the gaseous products.

The figure below illustrates the implementation of all these measures in a test stand:
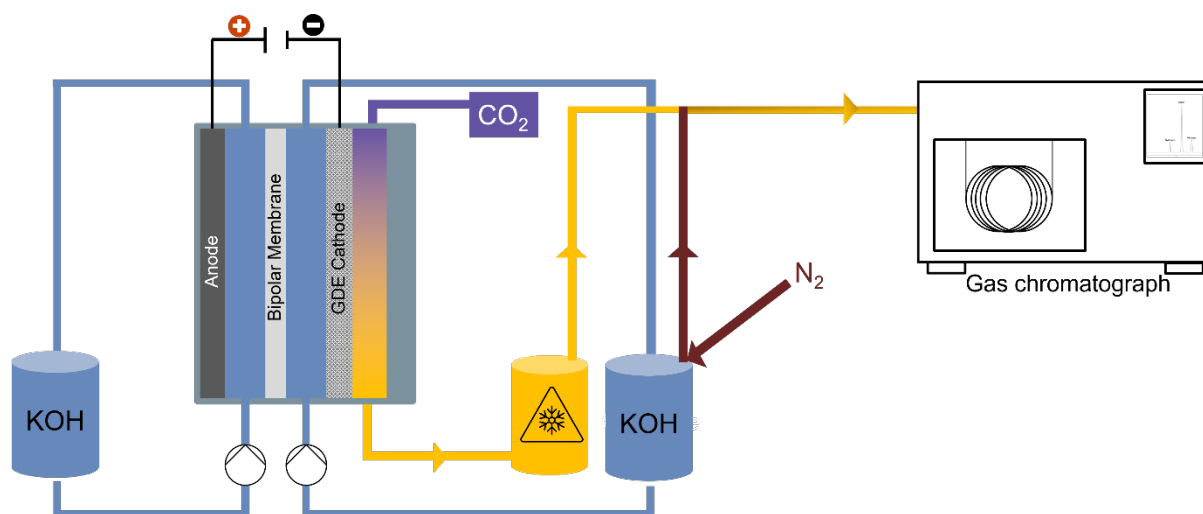

Figure 1 - Design of the test stand for correct product quantification including a bipolar membrane, a cooling vessel and an additional N_2 line.

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The effect of ionomer content and Ag/C catalyst surface area on the performance of CO_2 electrolysis to CO

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Carbon supported silver catalysts have proven high activity and durability in electrochemical CO_2 reduction to CO.[1-3] This work investigates the impact of cathode catalyst layer composition on performance by varying the ionomer content and Ag/C catalysts with differing BET surface areas ($33 \ m^2g^{-1}$ to $455 \ m^2g^{-1}$). For optimal performance, there is a positive correlation between optimal ionomer binder content and catalyst surface area: 5 wt% PiperION for $Ag/C_{Super P}$, 15 wt% for Ag/C_{Vulcan}, and 25 wt% for Ag/C_{Ketjen}. The top-performing cells exhibited remarkably high CO faradaic efficiencies of 93 % for Ag/C_{Vulcan}, 91 % for $Ag/C_{Super P}$, and 90 % for Ag/C_{Ketjen} (all at 400 $mAcm^{-2}$ with 0.01 M CsOH as anolyte). Long-term measurements at 300 $mAcm^{-2}$ over 100 hours revealed the lowest FE_{CO} loss for Ag/C_{Vulcan}, decreasing from 93 % to 87 %, followed by $Ag/C_{Super P}$ (91 % to 79 %), and Ag/C_{Ketjen} (90 % to 63 %).
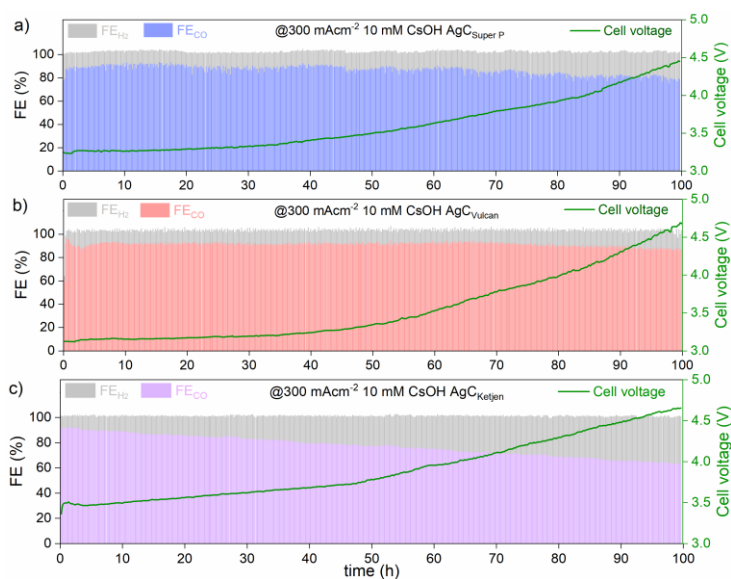

Figure 1: Long-term measurements at 300 $mAcm^{-2}$ of top-performing cells: A) 5 wt% Piperion $Ag/C_{Super P}$, b) 15 wt% Piperion Ag/C_{Vulcan} and c) 25 wt% Piperion Ag/C_{Ketjen} in 0.01 M CsOH at $50 \pm 1 \ °C$.

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Dynamic Deactivation of Copper Electrocatalysts During CO$_2$ Reduction

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Commercial applications of electrochemical CO$_2$ reduction (ECR) demand a catalyst with high faradaic efficiency and current density for a specific product and, of equal importance, long-term operational stability.[1] Addressing the challenge of uncontrolled restructuring and deactivation of copper (Cu) catalysts during operation (Figure 1) is essential for the regulation of this phenomenon. The detection of dissolved Cu species during electrolysis confirms the proposed intermediates mediated Cu^0(s) dissolution mechanism at ECR-relevant potential.[2] A dynamic equilibrium between dissolution and subsequent redeposition leads to morphological restructuring. Additionally, our findings suggest that the electrodeposition of dissolved Cu species is biased towards less active sites due to their lower coverage by reaction intermediates such as adsorbed CO. The iterative cycles of the dissolution-redeposition mechanism at ECR-relevant potential lead to the growth of the less-active Cu surface at the cost of the more-active one. This gradual yet persistent restructuring mechanism consequently shifts selectivity towards hydrogen production (Figure 1).
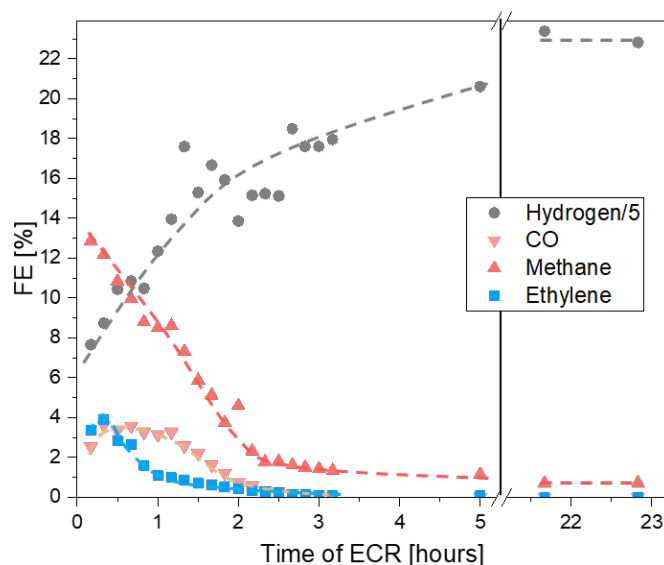

Figure 1 –Faradaic efficiency changes for different gas products vs. time leading to complete Cu catalyst deactivation.

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Anion-Cation interplay defines the electrolyte effect on the electrochemical CO₂ reduction

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The urgency to reduce net CO_2 emissions and the depleting of fossil fuel resources calls for the development of new processes for industrial feedstocks. The electrochemical CO_2 reduction (eCO₂RR) is a promising alternative to produce essential building blocks (e.g., carbon monoxide, ethylene) for the chemical industry using renewable energy sources and simultaneously closing the carbon cycle.[1] However, eCO₂RR faces several challenges that must be addressed before it can become a viable option for industrial applications. Two main issues are low product selectivity, including inefficiencies caused by the competing hydrogen evolution reaction, and high reaction overpotentials. In order to tune the faradaic efficiencies towards desirable products, a profound understanding of the reaction pathways and the system properties that influence it, is required. While conventional catalyst design is one approach to fine-tune eCO₂R, creating high-performance electrolytes is equally important.[2]

The electrolyte controls several crucial properties of the electrode/electrolyte interface e.g., pH, electric field modulation, interfacial mass transport and intermediate adsorption/stabilization.[3,4] Although recent research efforts are leading to an advanced understanding in this field, the knowledge of the highly complex structure of the electrolyte interface is still limited to a small group of electrolyte systems and the nature of electrolyte effects is in numerous cases still subject of debate. Therefore, it is essential to drive further efforts in electrolyte research to unlock the full potential of eCO₂R. In this work, a series of aqueous electrolytes was investigated for their utilization in CO_2 electroreduction. Cationic and anionic organic molecules with different structures are probed as electrolyte components to unravel structure-activity relationships. Gold served as catalyst, as the singular CO_2 reduction pathway towards CO formation provides a suitable model system. Differential electrochemical mass spectrometry (DEMS) was utilized as product detection method due to its high time-resolution, that enables tracking of product formation during linear sweep voltammetry. This study advances the understanding of the electrode-electrolyte interface and helps to design improved systems for eCO₂RR.

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