

# Eliminating Flooding-related Issues in Electrochemical CO<sub>2</sub>-to-CO Converters: Two Lines of Defense

Soma Vesztergom<sup>a</sup>, Alessandro Senocrate<sup>\*b</sup>, Ying Kong<sup>a</sup>, Viliam Kolivoška<sup>a</sup>, Francesco Bernasconi<sup>b</sup>, Robert Zboray<sup>b</sup>, Corsin Battaglia<sup>b</sup>, and Peter Broekmann<sup>\*a</sup>

**Abstract:** By using silver (Ag) in nanostructured (nanowire, nanosphere, etc.) or thin-layer forms as a catalyst for electrochemical CO<sub>2</sub> reduction, CO-forming selectivity of almost 100% can be achieved. Supported by gas diffusion layers (GDLs), the reactant CO<sub>2</sub> in the gas phase can approach and potentially access active Ag sites, which allows current densities in the range of a few hundred mA cm<sup>-2</sup> to be reached. Yet, the stability of gas diffusion electrode (GDE) based electrochemical CO<sub>2</sub>-to-CO converters is far from perfect, and the activity of GDE cathodes, especially when operated at high current densities, often significantly decays during electrolyses after no more than a few hours. The primary reason of stability losses in GDE-based CO<sub>2</sub>-to-CO electrolyzers is flooding: that is, the excess wetting of the GDE that prevents CO<sub>2</sub> from reaching Ag catalytic sites. In the past years, the authors of this paper at Empa and at the University of Bern, cooperating with other partners of the National Competence Center for Research (NCCR) on Catalysis, took different approaches to overcome flooding. While opinions differ with regard to where the first line of defense in protecting GDEs from flooding should lie, a comparison of the recent results of the two groups gives unique insight into the nature of processes occurring in GDE cathodes used for CO<sub>2</sub> electrolysis.

**Keywords:** Ag nanostructures · CO<sub>2</sub> reduction · Electrocatalysis · Flooding · Perspiration · Wettability



**Soma Vesztergom** obtained his MSc (2010) and PhD (2014) degrees in Chemistry at Eötvös Loránd University, Hungary. He was a post-doctoral researcher with a SciEx fellowship in Prof. Dr. Peter Broekmann's group at the University of Bern for a year (2014), and remains a regular collaborator of the Broekmann group since then. His research primarily focuses on instrumental developments in electrochemistry and on the modelling of electrocatalytic processes. Currently, he is an assistant professor at Eötvös Loránd University, Budapest, Hungary.



**Alessandro Senocrate** obtained his MSc (2013) degree in Chemistry at the University of Pavia, Italy. He obtained his PhD degree in Chemistry (2018) from EPFL carrying out his research work at the Max Planck Institute for Solid State Research, Germany, on the topic of solid-state ionics applied to photovoltaic materials. He joined Dr. Corsin Battaglia's laboratory at Empa in 2019, where he leads the electrocatalysis activities. His research focuses on understanding and improving the selectivity and stability of gas diffusion electrodes for electrochemical CO<sub>2</sub> reduction.



**Ying Kong** received her MSc in Environmental Engineering from China University of Mining and Technology. In 2019, she joined the Interfacial Electrochemistry group of Prof. Dr. Peter Broekmann at the University of Bern. Her PhD project is to study the selectivity and stability of electrochemical CO<sub>2</sub> reduction to valuable chemicals under controlled mass transport conditions.



**Viliam Kolivoška** is an independent researcher and deputy head of the Electrochemistry at the Nanoscale Department of J. Heyrovsky Institute of Physical Chemistry of the Czech Academy of Sciences. He obtained an MSc (2008) in Physical Chemistry at Charles University in Prague and a PhD (2011) in Physical Chemistry at the University of Chemistry and Technology (Prague). From 2011 to 2013 he was a SciEx postdoctoral fellow at the University of Bern in Switzerland, exploring charge transfer and transport phenomena in single molecule electronic elements. His current research interests involve physical electrochemistry and electrocatalysis, focusing on the use of advanced manufacturing techniques in the development of electrochemical devices.

\*Correspondence: Prof. P. Broekmann<sup>a</sup>, E-mail: peter.broekmann@unibe.ch; Dr. A. Senocrate<sup>b</sup>, E-mail: Alessandro.Senocrate@empa.ch

<sup>a</sup>University of Bern, Department of Chemistry, Biochemistry and Pharmaceutical Sciences; <sup>b</sup>Empa, Swiss Federal Laboratories for Materials Science and Technology



**Francesco Bernasconi** obtained his BSc (2018) and MSc (2021) in Materials Science at ETH Zurich, and is a doctoral student in the laboratory of Dr. Corsin Battaglia at Empa since 2021. His research focuses on the fabrication and characterization of gas diffusion electrodes for electrochemical CO<sub>2</sub> reduction.



**Robert Zboray** is group leader for X-ray imaging at the Centre for X-ray Analytics at Empa. After completing his MSc in applied physics at the Technical University of Budapest, Hungary, he earned his PhD in nuclear engineering at Delft University of Technology, the Netherlands. Later, he has been working at the Paul Scherrer Institute, Switzerland, as senior research scientist. Before joining Empa, he held a professorship at Penn State University, United States. His recent research interest includes novel, multi-modal X-ray imaging techniques and image processing methods.



**Corsin Battaglia** obtained his MSc (2004) and PhD degree (2008) in Physics from the University of Neuchâtel. He was a postdoc at EPFL until 2012, and at the University of California at Berkeley and Lawrence Berkeley National Laboratory, USA until 2014. Since 2014 he is head of the Laboratory Materials for Energy Conversion at Empa and is a lecturer at ETH Zurich. His current research focuses on next-generation batteries and synthetic fuels.



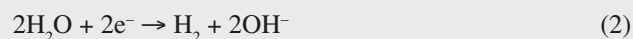
**Peter Broekmann** obtained his MSc in Chemistry (1998) and a PhD (2000) from the University of Bonn. After a post-doctoral stay at the University of Twente, the Netherlands, in 2001, he became project leader at the Institute of Physical Chemistry in Bonn. Since 2008 he holds a lecturer position for electrochemistry at the University of Bern (Switzerland). His research focuses on metal deposition processes for semiconductor and electrocatalysis (CO<sub>2</sub> electrolysis) applications.

## 1. Ag-based Gas Diffusion Electrodes for CO<sub>2</sub> Electroreduction: The Problem of Flooding

The electrochemical CO<sub>2</sub> reduction reaction (*ec*-CO<sub>2</sub>RR) offers a promising pathway to produce synthetic fuels using excess renewable energy, helping to re-establish a balanced global carbon cycle.<sup>[1]</sup> In the past few years, several new catalyst materials have been developed that facilitate *ec*-CO<sub>2</sub>RR at high rate (high effective current density) and with good product selectivity.<sup>[2,3]</sup> Among these, Ag-based catalysts are very promising candidates for the cost-efficient production of CO:<sup>[4,5]</sup> on Ag, the Faradaic efficiency (*FE*) of CO formation from CO<sub>2</sub> according to the reaction



is almost 100%, and the competing (parasitic) hydrogen evolution reaction (HER) remains suppressed, at least at moderate cathode potentials:



Until a few years ago, catalysts were tested by carrying out lab-scale experiments in standard H-type cells<sup>[6]</sup> where the cathode (the actual scene of *ec*-CO<sub>2</sub>RR) is immersed into a usually aqueous electrolyte saturated with CO<sub>2</sub>. Due to its limited solubility in water (max. 32 mmol dm<sup>-3</sup>),<sup>[7]</sup> the rate of CO<sub>2</sub> reduction in this standard laboratory arrangement easily became mass transport limited: that is, if parasitic reactions (such as HER) were to be avoided, the electrolysis could only be conducted at a rather low current density at which most catalysts would essentially remain stable.

With the pursuit of industrially relevant current densities (>200 mA/cm<sup>2</sup>),<sup>[8,9]</sup> the focus has recently shifted from the development of new catalyst materials to studying the possible scale-up prospects of CO<sub>2</sub> electrolysis.<sup>[10,11]</sup> Primarily, this meant that the aforementioned transport limitation had to be overcome. This was achieved using gas diffusion electrodes (GDEs) as cathodes in *ec*-CO<sub>2</sub>RR reactors.<sup>[12–17]</sup>

In typical GDEs, the catalyst is supported by a gas diffusion layer (GDL) that is composed of a carbon fibrous layer (CFL) and a microporous layer (MPL), and this bi-layer structure (Fig. 1a) assures that the gaseous (CO<sub>2</sub>) and liquid (H<sub>2</sub>O) reactants of Reaction (1) would meet each other exactly at the position of the catalyst layer, where the presence of Ag sites enables Reaction (1) to proceed at an appropriately high rate.<sup>[18]</sup> Besides enabling fast reactant delivery, the GDL also facilitates the release of gaseous reaction products (CO in case of Ag catalyst), serves as a mechanical support and electrical contact for the catalyst layer, and plays an important role in controlling the amount of electrolyte (water) accessing the catalyst layer.<sup>[18]</sup>

The latter role of GDLs (that is, electrolyte management) is particularly important,<sup>[19]</sup> given that the presence of some amount of water is required for the *ec*-CO<sub>2</sub>RR to take place, as H<sub>2</sub>O is a reactant in the reduction of CO<sub>2</sub> to CO (Reaction (1)). On the other hand, *too much* water inside the GDE structure is to be avoided, as it can block the access of CO<sub>2</sub> molecules to active catalytic sites. The occurrence of excess water inside the GDE (that is, the phenomenon called *flooding*<sup>[18–23]</sup>) can lead to an immediate and substantial decrease of the Faradaic efficiency towards *ec*-CO<sub>2</sub>RR, in favor of HER. As of today, flooding-related issues present one of the biggest obstacles to the scale-up prospects of CO<sub>2</sub> electroreduction.<sup>[18]</sup>

Different approaches can be taken to eliminate flooding while simultaneously ensuring the appropriate amount of water required for *ec*-CO<sub>2</sub>RR.<sup>[18]</sup> Researchers like Senocrate *et al.*<sup>[24]</sup> (in the group of Corsin Battaglia at Empa) emphasize in their works that the *first line of defense* (a phrase we owe to Kenis<sup>[25]</sup>) against flooding should be the interface where the GDE meets liquid water. By using polymeric and hydrophobic GDL substrates, the wettability of this interface can be minimized and water penetration can be avoided. Other researchers like Kong *et al.*<sup>[22,23]</sup> (in the group of Peter Broekmann at the University of Bern) focus at the same time on a second defense line and emphasize the importance of the ability of GDEs to ‘perspire’ – that is, to alleviate the flooding of GDEs by modifying their structure and composition, allowing an excess electrolyte to harmlessly drain through all layers of the GDE and exit the electrolyser cell with the outward gas flow.

The aim of this paper is to compare these strategies and summarize the important lessons that can be learned on electrolyte management in Ag-based GDEs for *ec*-CO<sub>2</sub>RR.

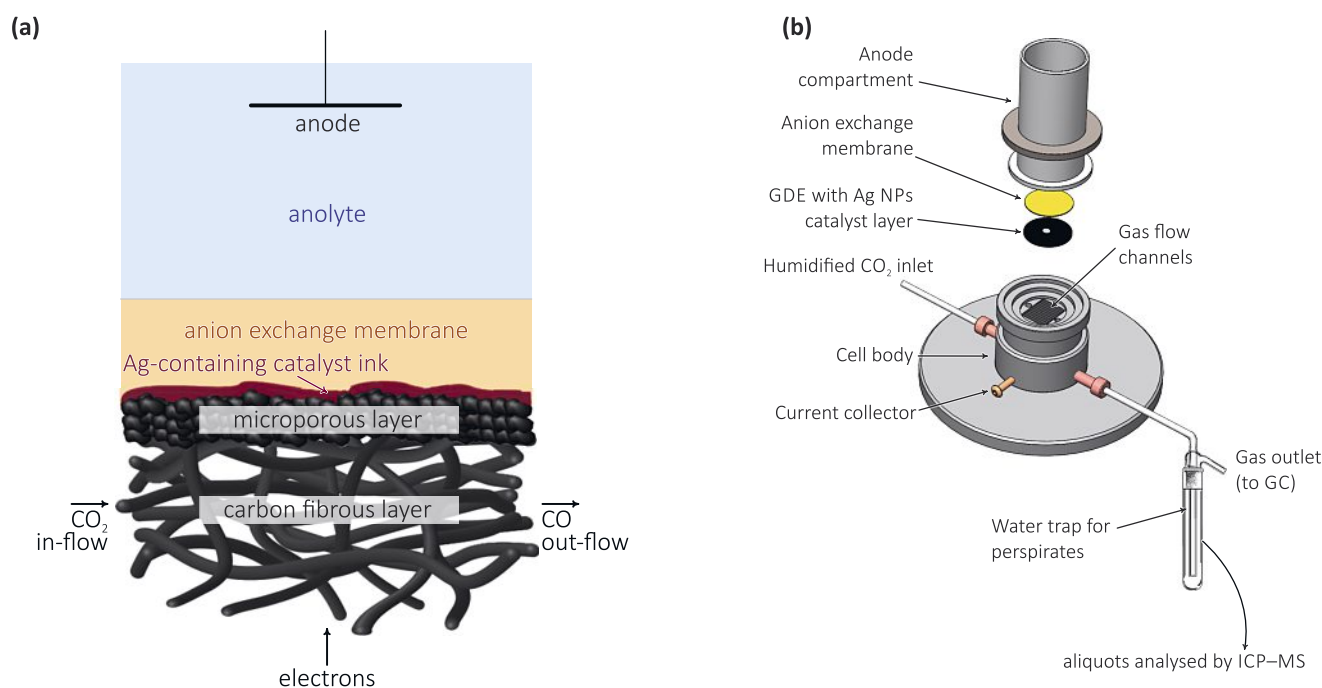


Fig. 1. (a) Scheme (figure not to scale) of a carbon-based bilayer gas diffusion layer (GDL) composed of a carbon fibrous layer (CFL) and a microporous layer (MPL). The GDL supports Ag nanoparticle catalysts and is in direct contact with an anion exchange membrane to form a so-called ‘zero-gap’ membrane-electrode assembly (MEA). (b) Assembly view of a practical model-scale electrolyser. The approach presented here is used by the Broekmann group to study flooding effects hampering the efficiency of CO<sub>2</sub>-to-CO electrolyses.

## 2. The Utilization of ‘Perspiring’ GDEs in a Zero-gap Cathode MEA Configuration: The Approach of the Broekmann Group

One of the most straightforward strategies to not let excess amounts of water and electrolyte ions enter the cathode GDE is to apply a so-called ‘zero-gap’ cathode configuration<sup>[20,21]</sup> (Fig. 1) in which the GDE is directly interfaced to an anion exchange membrane to form a membrane-electrode assembly (MEA), as was shown recently by Kong *et al.*<sup>[22,23]</sup>

The absence of a catholyte phase in this configuration will not be problematic if (like in the case of CO<sub>2</sub>-to-CO conversion with Ag catalysts) *ec*-CO<sub>2</sub>RR yields gaseous products only.<sup>[20,22]</sup> Note, however, that the absence of the catholyte does not mean that the GDE would not be wetted, as some electrolyte amounts will necessarily pass through the membrane and end up on the cathode surface.

Unfortunately, although the cathode GDE is not directly exposed to water in this configuration, wetting by the membrane can still cause flooding of the GDE, and during long-lasting electrolyses conducted at high current densities, a significant drop-down of the Faradaic efficiency of CO production will be observed.<sup>[23–29]</sup>

If instead of large industrial-scale electrolyses, a model-scale device, like the one shown in Fig. 1b is used for electrolysis stress tests, then – mostly due to the more pronounced edge effects arising from the small effective cross-section<sup>[26]</sup> – electrolyser failures appear sooner (within hours instead of days). This renders the device shown in Fig. 1b extremely useful for accelerated durability tests of flooding-related stability losses.<sup>[20–23,27–29]</sup>

One example of such studies is ref. [22], where Kong *et al.* utilized GDLs of different kinds for the preparation of Ag nanowire catalyst-based GDEs (Fig. 2) and found that the presence and distribution of surface cracks in the MPL will create notable differences in the measurable electrolysis stability. As can be seen in Fig. 3, GDLs that contain cracks in their MPLs perform better during high current density electrolyses, retaining their CO production efficiency for much longer times. On the other hand, if GDL substrates with a crack-free surface were used, the stability of the electrolysis was found to decrease quickly and significantly.

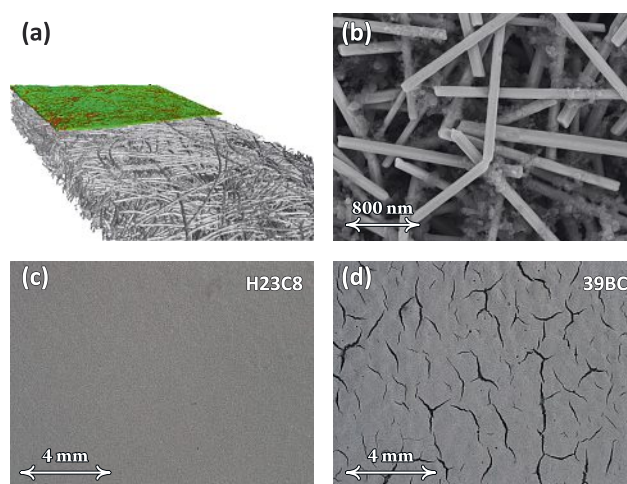


Fig. 2. Ag nanowires-containing GDEs prepared for electrolysis stress tests. (a) X-ray micro tomography image of a H23C8 GDL support with a compact (crack-free) MPL. (b) Scanning electron microscopy (SEM) image of the prepared GDE, with Ag nanowires visible on top of the MPL. (c) and (d) Optical microscopy images of GDLs (H23C8: crack-free, 39BC: cracked MPL surface) coated with an Ag nanowire-containing catalyst ink. Reproduced based on ref. [23], see details there.

That the observed stability losses are due to the flooding of the GDEs was proven by Kong *et al.*<sup>[23]</sup> using post-electrolysis energy-dispersive X-ray (EDX) elemental mapping and scanning electron microscopy (SEM) based imaging of the GDEs. By this method Kong *et al.* could visualize both the deposited potassium (bi)carbonate precipitates on the GDE surface and their transport into the interior of the GDE. These precipitates were formed from KOH that passed through the membrane from the anolyte and recombined at the surface or inside of the GDE with the CO<sub>2</sub> gas flow of the cathode compartment. Note that in most cases, a KOH solution of  $\geq 1 \text{ mol dm}^{-3}$  concentration is applied as anolyte in the electrolyses. Thus, the EDX-based mapping of the surface and

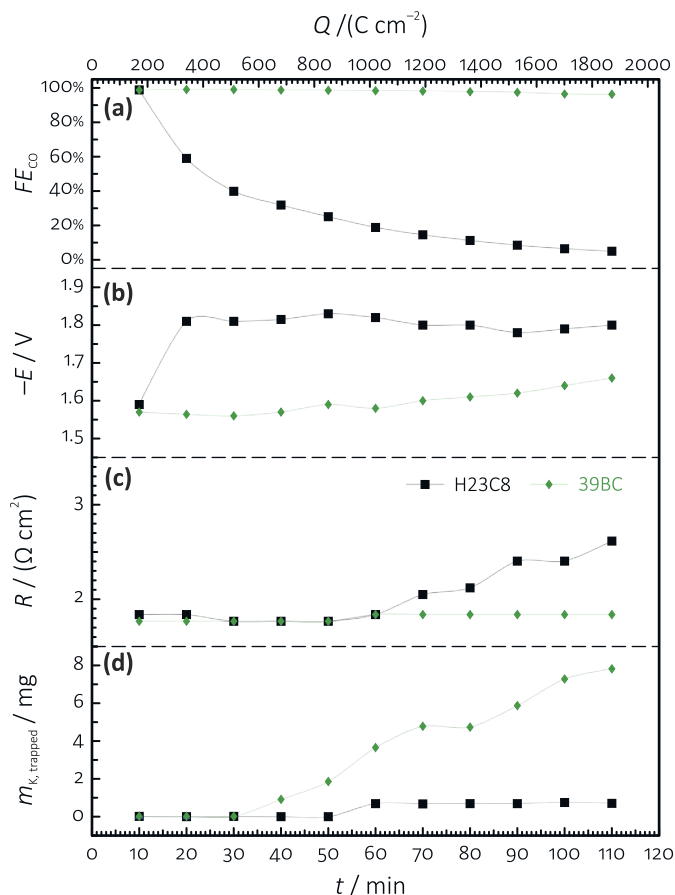


Fig. 3. Results of electrolysis stress tests on Ag nanowire catalyst containing GDEs prepared with crack-free (H23C8) and cracked (39BC) GDL substrates (cf. Fig. 2). The Faradaic efficiency of CO production (a), the measured cathode potential (b), the cell resistance (c) and the total amount of perspired  $K^+$  (d) are shown as a function of time for galvanostatic electrolyses conducted at  $-283 \text{ mA cm}^{-2}$  current density employing aqueous  $2 \text{ mol dm}^{-3}$  KOH as anolyte. A humidified  $\text{CO}_2$  stream was fed to the GDE during the experiment at constant flow rate of  $18 \text{ cm}^3 \text{ min}^{-1}$ . Reproduced based on ref. [23], see details there.

in-depth distribution of  $\text{KHCO}_3/\text{K}_2\text{CO}_3$  salts strongly helped in assessing the proneness of GDEs to allow the entry of electrolytes into their deeper structures (Fig. 4).<sup>[22,23]</sup>

It has to be emphasized here that the emergence of  $\text{K}_2\text{CO}_3$  precipitates inside the GDE structure indicates only that some electrolyte amounts have entered the GDE – the presence of precipitates in the GDE does not necessarily mean, however, that the GDE was flooded during the electrolysis. In their experiments, Kong *et al.*<sup>[23]</sup> also equipped a water trap to the gas outflow of the electrolyser setup (the trap is shown in Fig. 1b) in order to measure the amount of electrolyte that not only entered but also ‘perspired’ through, and then exited the GDE structure. This electrolyte amount leaves the cell in the form of an aerosol carried by the  $\text{CO}_2$  gas flow, and its quantity can be determined by inductively coupled plasma mass spectrometry (ICP-MS) measurements.<sup>[22,23]</sup> Fig. 3d makes it apparent that the effective perspiration of GDEs operated in the zero-gap configuration is in fact essential to uphold stable electrolyser operation. GDLs with a high abundance of cracks present in their MPL show better long-time performance because the cracks provide an efficient perspiration pathway through which electrolyte entering the GDE structure can also leave it. If such drainage pathways are not present, which is the case for GDEs with a compact MPL, perspiration gets disabled and the electrolyte floods the micropores in the MPL as transport channels for  $\text{CO}_2$ , blocking the access of this reactant to the catalyst layer (Fig. 5).

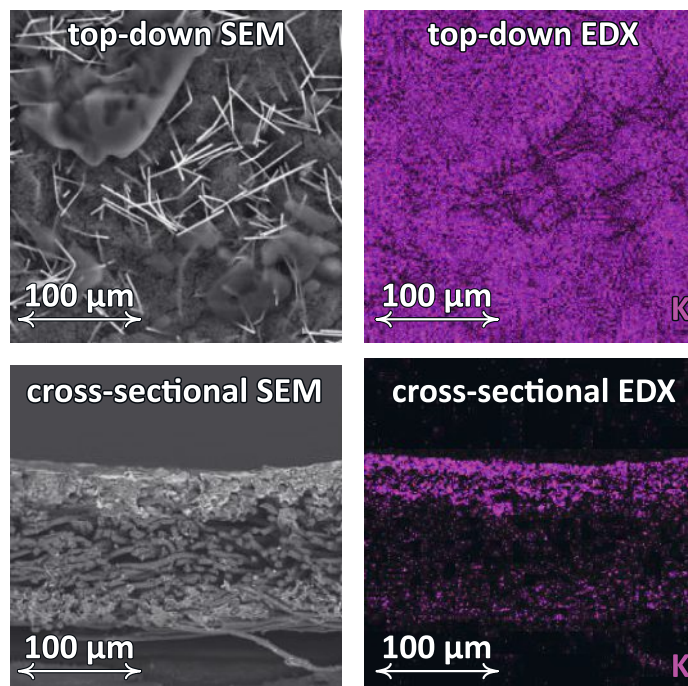


Fig. 4. Post-electrolysis SEM and EDX images of the 39BC substrate-based GDE, following electrolysis. See ref. [23] for details of the measurement.

The main conclusion of Kong *et al.*<sup>[23]</sup> is thus that in a zero-gap cathode GDE-membrane assembly, the penetration of water into the GDE structure is not only unavoidable but even necessary for efficient  $\text{CO}_2$ -to-CO conversion to proceed. Thus in such systems, trying to uphold the first line of defense (e.g., by creating GDEs completely impermeable to water) is not the best strategy; instead, a second defense line is to be created, in the sense that it has to be assured that excess electrolyte amounts entering the GDE structure can efficiently leave it. It is, after all, the trapping of water and electrolyte ions inside the GDE that is the ultimate reason of flooding and related efficiency losses.

That apart from the structure of MPLs several other factors (e.g., the nature and amount of capping agents as well as binders present in the catalyst ink) can also have a strong effect on the perspiration behaviour and hence on the lifetime of  $\text{CO}_2$ -to-CO-converting zero-gap GDE MEAs was further discussed in two recent publications of Hu *et al.*<sup>[28]</sup> and Liu *et al.*<sup>[29]</sup>

As we will see below, when using different electrolyser architectures with a flowing catholyte phase, upholding the first line of defense may, however, still be beneficial.

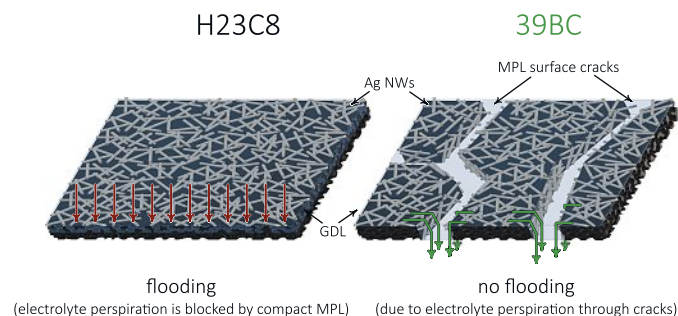


Fig. 5. A scheme illustrating the main findings of Kong *et al.*<sup>[23]</sup> effective perspiration pathways (provided, e.g., by surface cracks present in the MPLs of GDL substrates) are essential to uphold the stability of  $\text{CO}_2$ -to-CO reducing zero-gap GDE-membrane assembly cathodes.

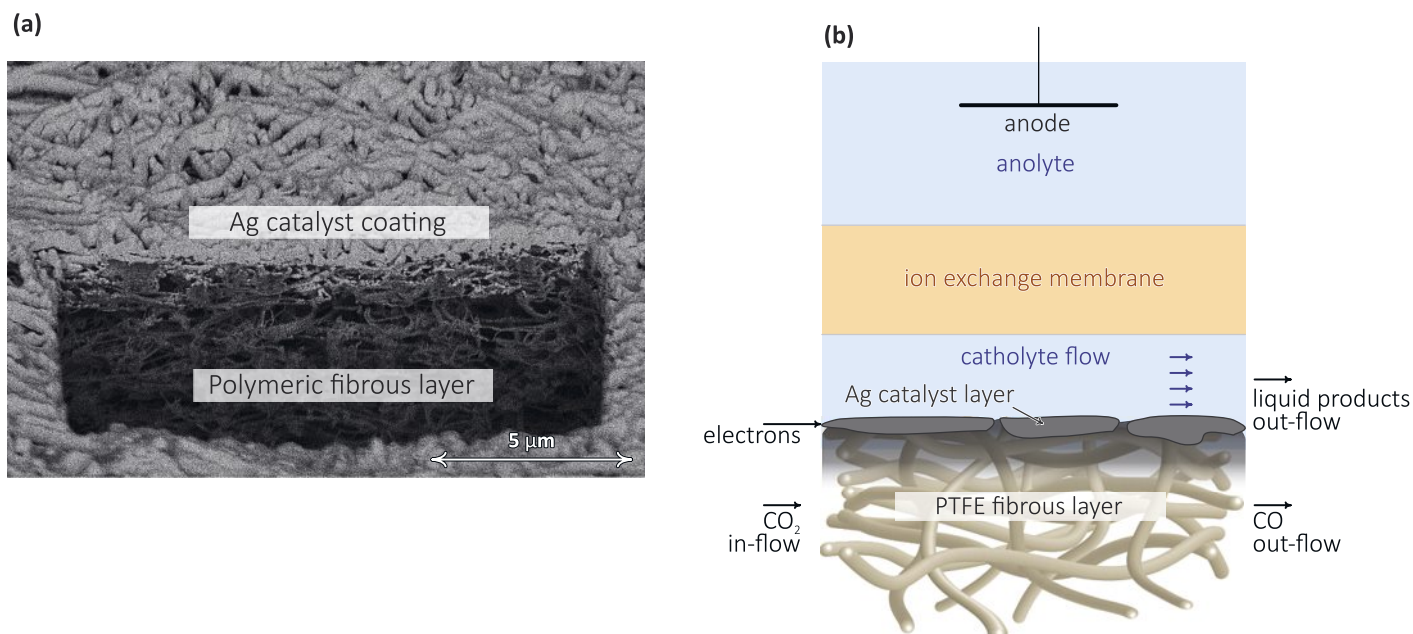


Fig. 6. (a) A fibrous PTFE layer covered by sputtered Ag, used as a GDE for  $ec$ -CO<sub>2</sub>RR. (b) The cell configuration in which the GDE is used in direct contact with a catholyte flow (figure not to scale). Adopted from the work of Senocrate *et al.*<sup>[24]</sup>

### 3. Minimizing the Wettability of GDL Supports: The Approach of the Battaglia Group

In electrolyzers containing a mobile catholyte phase, the importance of the non-wettability of GDEs in upholding stable  $ec$ -CO<sub>2</sub>RR was recently emphasized by the works of Li *et al.*<sup>[30]</sup> and Kenis *et al.*<sup>[25]</sup> and it is often concluded that limiting the wettability of catalyst layers should be the actual first line of defense against flooding. This thought was taken a step ahead by Sargent *et al.*<sup>[31]</sup> who attempted to assure not only the non-wettability of the ionomer coating, but also that of the entire GDL support – at the expense of using completely hydrophobic and, thus, non-conductive polymeric fibrous structures.

In a recent work, Senocrate *et al.*<sup>[24]</sup> at Empa took a similar approach and used fibrous polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) structures with different pore sizes in order to study the effect of pore size on the selectivity and stability of  $ec$ -CO<sub>2</sub>RR. Their polymeric substrates were turned into GDEs by single-sided sputtering of a 500 nm Ag layer, and by contacting this layer electrically (Fig. 6a).

Senocrate *et al.*<sup>[24]</sup> described that the Ag-coated, PTFE and PVDF layers were differently able to resist water/electrolyte penetration due to their different pore sizes. The ability of GDEs to resist water/electrolyte penetration was characterized by the water entry pressure (WEP), that is, the pressure necessary to push water through an initially dry, hydrophobic, porous GDE.<sup>[24]</sup> The authors found that WEP values increase with decreasing average pore size diameters, as well as with higher hydrophobicity (contact angle) of the polymer used. Interestingly, the WEP strongly correlates with selectivity towards CO, an occurrence that can be explained by a more confined electrolyte front and an easier access of CO<sub>2</sub> to the Ag active sites. In addition, also the stability of  $ec$ -CO<sub>2</sub>RR (that is, the tendency of the different GDEs to retain their initially high Faradaic efficiency for CO production) strongly correlated with both the WEP and the inverse pore size values, as shown in Fig. 7. This provides a suitable and scalable strategy to improve both selectivity and stability of GDEs for  $ec$ -CO<sub>2</sub>RR to CO, obtained by acting solely on the GDE substrate microstructure.

### 4. Summary and Outlook

In a recent work,<sup>[24]</sup> Senocrate *et al.* showed for the first time that the morphological modification of hydrophobic polymer-

based GDE supports is a suitable and scalable strategy to improve the selectivity and performance stability of GDEs for  $ec$ -CO<sub>2</sub>RR operated in a catholyte flow-cell configuration. They found, in particular, that the substrate pore size plays a pivotal role in influencing the wetting behavior of GDEs and their ability to resist aqueous electrolyte penetration. Lower electrolyte penetration showed good correlation with increased selectivity towards CO and a longer electrolysis stability.

At the same time, results of the Broekmann group have shown that in catholyte-free ‘zero-gap’ configuration, the hydrophobicity of the GDE seems to be a less important factor, and since in the zero-gap electrolyzers used by the Broekmann group some entry of water to the carbon-based GDE is unavoidable, a second defense line has to be built. That is, in recent works of Kong *et al.*,<sup>[22,23]</sup> Hu *et al.*<sup>[28]</sup> and Liu *et al.*<sup>[29]</sup> the importance of effective perspiration properties (over that of hydrophobicity) was emphasized.

Both the Battaglia and the Broekmann groups identify issues related to GDE flooding as a major challenge for the industrialization of  $ec$ -CO<sub>2</sub>RR. The two teams (collaborating in the framework of the NCCR Catalysis) make use of different electrolyzer architectures, and ultimately found different potential solutions to tackle the flooding problem. In the Battaglia case, the use of flow cells and cathode electrolyte required the implementation of highly hydrophobic GDE substrates to confine the electrolyte and prevent flooding. In the Broekmann case, the use of zero-gap cells in which water is inevitably transported through the anion exchange membrane during electrolysis, led to the requirement of perspiration to avoid GDE instability. The lesson we can learn by comparing the two strategies is that no single solution to the flooding issue can be expected, but rather a tailored approach depending on the electrolyzer architecture employed. The research methodologies applied by the two groups help deepen our understanding of electrolyte management and its effects on GDEs for  $ec$ -CO<sub>2</sub>-RR. In the near future, the two groups will join forces (*e.g.*, by combining hydrophobic polymer-based GDEs with the zero-gap cathode MEA configuration) and combine their respective expertise to take these studies further and ultimately aim at solving the flooding-related stability issues of GDE-based electrochemical CO<sub>2</sub>-to-CO converters.

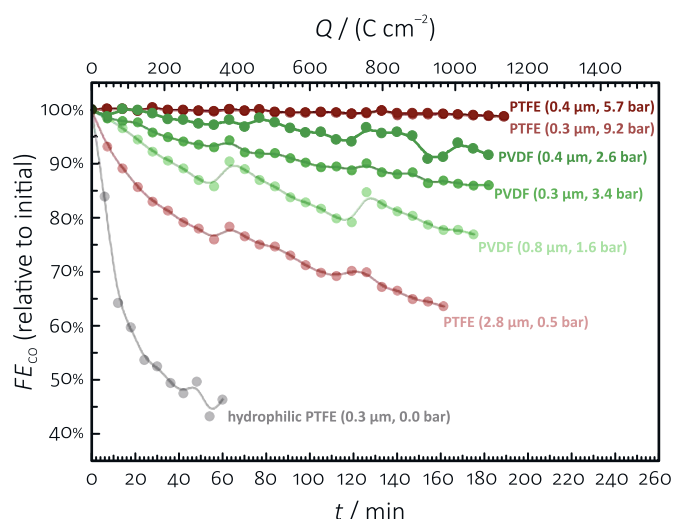


Fig. 7. Results of electrolysis stress tests conducted on polymeric fibrous layer-based GDEs. Fibrous layers of smaller pore size and higher WEP (both values are indicated in the figure) retain their Faradaic efficiency for CO production for longer times. Experiments are carried out at 100 mA cm<sup>-2</sup> current density, with both the catholyte and anolyte compartments filled with 1 mol dm<sup>-3</sup> CO<sub>2</sub>-saturated KHCO<sub>3</sub> solution. See ref. [21] for further details.

### Acknowledgements

This work was supported by NCCR Catalysis (Grant Number 180544), a National Centre of Competence in Research funded by the Swiss National Science Foundation. S. V. acknowledges support from the Lendület (Momentum) program of the Hungarian Academy of Sciences (grant LP2022–18/2022) and from the National Research, Development and Innovation Office of Hungary (NKFIH grants FK135375 and K129210). A. S. and C. B. acknowledge the support from the ETH Board in the framework of the Joint Strategic Initiative ‘Synthetic Fuels from Renewable Resources’. A. S., F. B., and C. B. acknowledge the support of Dr. Peng Zeng of the Scientific Center for Optical and Electron Microscopy (ScopeM) at ETH Zurich for the FIB-SEM imaging. Y. K. acknowledges the financial support of the Chinese Scholarship Council (CSC). V. K. acknowledges financial support from the Czech Science Foundation (project number 23–07292S).

Received: December 18, 2022

- [1] D. R. Feldman, W. D. Collins, P. J. Gero, M. S. Torn, E. J. Mlawer, T. R. Shippert, *Nature* **2015**, *519*, 339, <https://doi.org/10.1038/nature14240>.
- [2] J. Li, S. U. Abbas, H. Wang, Z. Zhang, W. Hu, *Nano-Micro Lett.* **2021**, *13*, 216, <https://doi.org/10.1007/s40820-022-00879-5>
- [3] H.-R. M. Jhong, S. Ma, P. J. A. Kenis, *Curr. Opin. Chem. Eng.* **2013**, *2*, 191, <http://dx.doi.org/10.1016%2Fj.coche.2013.03.005>.
- [4] S. A. Mahyoub, F. A. Qaraah, C. Chen, F. Zhang, S. Yan, Z. Cheng, *Sustain. Energy Fuels* **2020**, *4*, 50, <https://doi.org/10.1039/C9SE00594C>.
- [5] D. Sun, X. Xu, Y. Qin, S. P. Jiang, Z. Shao, *ChemSusChem* **2019**, *13*, 39, <https://doi.org/10.1002/cssc.201902061>.
- [6] K. P. Kuhl, E. R. Cave, D. N. Abram, T. F. Jaramillo, *Energy Environ. Sci.* **2012**, *5*, 7050, <https://doi.org/10.1039/C2EE21234J>.
- [7] M. König, J. Vaes, E. Klemm, D. Pant, *iScience* **2019**, *19*, 135, <https://doi.org/10.1016/j.isci.2019.07.014>.
- [8] J. Durst, A. Rudnev, A. Dutta, Y. Fu, J. Herranz, V. Kalignedi, A. Kuzume, A. A. Permyakova, Y. Paratcha, P. Broekmann, T. Schmidt, *Chim. Int. J. Chem.* **2015**, *69*, 769, <https://doi.org/10.2533/chimia.2015.769>.
- [9] T. Burdyny, W. A. Smith, *Energy Environ. Sci.* **2019**, *12*, 1442, <https://doi.org/10.1039/C8EE03134G>.
- [10] Z. Yang, D. Li, L. Xing, H. Xiang, J. Xuan, S. Cheng, E. H. Yu, A. Yang, *ACS Sustainable Chem. Eng.* **2020**, *9*, 351, <https://doi.org/10.1021/acssuschemeng.0c07387>.
- [11] A. Gawel, T. Jaster, D. Siegmund, J. Holzmann, H. Lohmann, E. Klemm, U.-P. Apfel, *iScience* **2022**, *25*, 104011, <https://doi.org/10.1016/j.isci.2022.104011>.
- [12] D. Higgins, C. Hahn, C. Xiang, T. F. Jaramillo, A. Z. Weber, *ACS Energy Lett.* **2019**, *4*, 317, <https://doi.org/10.1021/acsenrgylett.8b02035>.
- [13] D. M. Weekes, D. A. Salvatore, A. Reyes, A. Huang, C. P. Berlinguette, *Acc. Chem. Res.* **2018**, *51*, 910, <https://doi.org/10.1021/acs.accounts.8b00010>.

- [14] T. Burdyny, W. A. Smith, *Energy Environ. Sci.* **2019**, *12*, 1442, <https://doi.org/10.1039/C8EE03134G>.
- [15] N. T. Nesbitt, T. Burdyny, H. Simonson, D. Salvatore, D. Bohra, R. Kas, W. A. Smith, *ACS Catal.* **2020**, *10*, 14093, <https://doi.org/10.1021/acscatal.0c03319>.
- [16] E. W. Lees, B. A. W. Mowbray, F. G. L. Parlane, C. P. Berlinguette, *Nat. Rev. Mater.* **2021**, *7*, 55, <https://doi.org/10.1038/s41578-021-00356-2>.
- [17] W. Ju, F. Jiang, H. Ma, Z. Pan, Y. Zhao, F. Pagani, D. Rentsch, J. Wang, C. Battaglia, *Adv. Energy Mater.* **2019**, *9*, 1901514, <https://doi.org/10.1002/aenm.201901514>.
- [18] K. Yang, R. Kas, W. A. Smith, T. Burdyny, *ACS Energy Lett.* **2020**, *6*, 33, <https://doi.org/10.1021/acsenrgylett.0c02184>.
- [19] A. Reyes, R. P. Janssonius, B. A. W. Mowbray, Y. Cao, D. G. Wheeler, J. Chau, D. J. Dvorak, C. P. Berlinguette, *ACS Energy Lett.* **2020**, *5*, 1612, <https://doi.org/10.1021/acsenrgylett.0c00637>.
- [20] M. de J. Gálvez-Vázquez, P. Moreno-García, H. Xu, Y. Hou, H. Hu, I. Z. Montiel, A. V. Rudnev, S. Alinejad, V. Grozovski, B. J. Wiley, M. Arenz, P. Broekmann, *ACS Catal.* **2020**, *10*, 13096, <https://doi.org/10.1016/j.jcat.2021.10.016>.
- [21] M. Liu, Y. Kong, H. Hu, N. Kovács, C. Sun, I. Zelocualtecatl Montiel, M. de J. Gálvez Vázquez, Y. Hou, M. Mirólo, I. Martens, J. Drnec, S. Vesztergom, P. Broekmann, *J. Catal.* **2021**, *404*, 371, <https://doi.org/10.1016/j.jcat.2021.10.016>.
- [22] Y. Kong, H. Hu, M. Liu, Y. Hou, V. Kolivoška, S. Vesztergom, P. Broekmann, *J. Catal.* **2022**, *408*, 1, <https://doi.org/10.1016/j.jcat.2022.02.014>.
- [23] Y. Kong, M. Liu, H. Hu, Y. Hou, S. Vesztergom, M. de J. Gálvez Vázquez, I. Zelocualtecatl Montiel, V. Kolivoška, P. Broekmann, *Small Methods* **2022**, *6*, 2200369, <https://doi.org/10.1002/smt.202200369>.
- [24] A. Senocrate, F. Bernasconi, D. Rentsch, K. Kraft, M. Trottmann, A. Wichser, D. Bleiner, C. Battaglia, *ACS Appl. Energy Mater.* **2022**, *5*, 14504, <https://doi.org/10.1021/acsaem.2c03054>.
- [25] U. O. Nwabara, A. D. Hernandez, D. A. Henckel, X. Chen, E. R. Cofell, M. P. de Heer, S. Verma, A. A. Gewirth, P. J. A. Kenis, *ACS Appl. Energy Mater.* **2021**, *4*, 5175, <https://doi.org/10.1021/acsaem.1c00715>.
- [26] K. Ehelebe, D. Seeberger, M. T. Y. Paul, S. Thiele, K. J. J. Mayrhofer, S. Cherevko, *J. Electrochem. Soc.* **2019**, *166*, F1259, <https://doi.org/10.1016/j.jelecom.2020.106761>.
- [27] U. O. Nwabara, M. P. de Heer, E. R. Cofell, S. Verma, E. Negro, P. J. A. Kenis, *J. Mater. Chem. A* **2020**, *8*, 22557, <https://doi.org/10.1039/D0TA08695A>.
- [28] H. Hu, Y. Kong, M. Liu, V. Kolivoška, A. V. Rudnev, Y. Hou, R. Erni, S. Vesztergom, P. Broekmann, *J. Mater. Chem. A* **2022**, in press, <https://doi.org/10.1039/D2TA06965B>.
- [29] M. Liu, H. Hu, Y. Kong, I. Zelocualtecatl Montiel, V. Kolivoška, A. V. Rudnev, Y. Hou, R. Erni, S. Vesztergom, P. Broekmann, *Appl. Catal. B Environ.* **2022**, under review.
- [30] M. Li, M. N. Idros, Y. Wu, T. Burdyny, S. Garg, X. S. Zhao, G. Wang, T. E. Rufford, *J. Mater. Chem. A* **2021**, *9*, 19369, <https://doi.org/10.1039/D1TA03636J>.
- [31] C.-T. Dinh, F. Pelayo García de Arquer, D. Sinton, E. H. Sargent, *ACS Energy Lett.* **2018**, *3*, 2835, <https://doi.org/10.1021/acsenrgylett.8b01734>.

### License and Terms



This is an Open Access article under the terms of the Creative Commons Attribution License CC BY 4.0. The material may not be used for commercial purposes.

The license is subject to the CHIMIA terms and conditions: (<https://chimia.ch/chimia/about>).

The definitive version of this article is the electronic one that can be found at <https://doi.org/10.2533/chimia.2023.104>