

Eliminating Flooding-related Issues in Electrochemical CO₂-to-CO Converters: Two Lines of Defense

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Abstract: By using silver (Ag) in nanostructured (nanowire, nanosphere, etc.) or thin-layer forms as a catalyst for electrochemical CO₂ reduction, CO-forming selectivity of almost 100% can be achieved. Supported by gas diffusion layers (GDLs), the reactant CO₂ 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⁻² to be reached. Yet, the stability of gas diffusion electrode (GDE) based electrochemical CO₂-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 CO₂-to-CO electrolyzers is flooding: that is, the excess wetting of the GDE that prevents CO₂ 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 CO₂ electrolysis.

Keywords: Ag nanostructures · CO₂ reduction · Electrocatalysis · Flooding · Perspiration · Wettability



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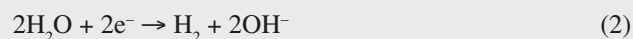
Peter Broekmann obtained his MSc in Chemistry (1998) and a PhD (2000) from the University of Bonn. After a post-doctoral stay at the University of Twente, the Netherlands, in 2001, he became project leader at the Institute of Physical Chemistry in Bonn. Since 2008 he holds a lecturer position for electrochemistry at the University of Bern (Switzerland). His research focuses on metal deposition processes for semiconductor and electrocatalysis (CO₂ electrolysis) applications.

1. Ag-based Gas Diffusion Electrodes for CO₂ Electroreduction: The Problem of Flooding

The electrochemical CO₂ reduction reaction (*ec*-CO₂RR) offers a promising pathway to produce synthetic fuels using excess renewable energy, helping to re-establish a balanced global carbon cycle.^[1] In the past few years, several new catalyst materials have been developed that facilitate *ec*-CO₂RR at high rate (high effective current density) and with good product selectivity.^[2,3] Among these, Ag-based catalysts are very promising candidates for the cost-efficient production of CO:^[4,5] on Ag, the Faradaic efficiency (*FE*) of CO formation from CO₂ 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^[6] where the cathode (the actual scene of *ec*-CO₂RR) is immersed into a usually aqueous electrolyte saturated with CO₂. Due to its limited solubility in water (max. 32 mmol dm⁻³),^[7] the rate of CO₂ 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/cm²),^[8,9] the focus has recently shifted from the development of new catalyst materials to studying the possible scale-up prospects of CO₂ electrolysis.^[10,11] Primarily, this meant that the aforementioned transport limitation had to be overcome. This was achieved using gas diffusion electrodes (GDEs) as cathodes in *ec*-CO₂RR reactors.^[12–17]

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 (CO₂) and liquid (H₂O) 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.^[18] 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.^[18]

The latter role of GDLs (that is, electrolyte management) is particularly important,^[19] given that the presence of some amount of water is required for the *ec*-CO₂RR to take place, as H₂O is a reactant in the reduction of CO₂ 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 CO₂ molecules to active catalytic sites. The occurrence of excess water inside the GDE (that is, the phenomenon called *flooding*^[18–23]) can lead to an immediate and substantial decrease of the Faradaic efficiency towards *ec*-CO₂RR, in favor of HER. As of today, flooding-related issues present one of the biggest obstacles to the scale-up prospects of CO₂ electroreduction.^[18]

Different approaches can be taken to eliminate flooding while simultaneously ensuring the appropriate amount of water required for *ec*-CO₂RR.^[18] Researchers like Senocrate *et al.*^[24] (in the group of Corsin Battaglia at Empa) emphasize in their works that the *first line of defense* (a phrase we owe to Kenis^[25]) 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.*^[22,23] (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*-CO₂RR.

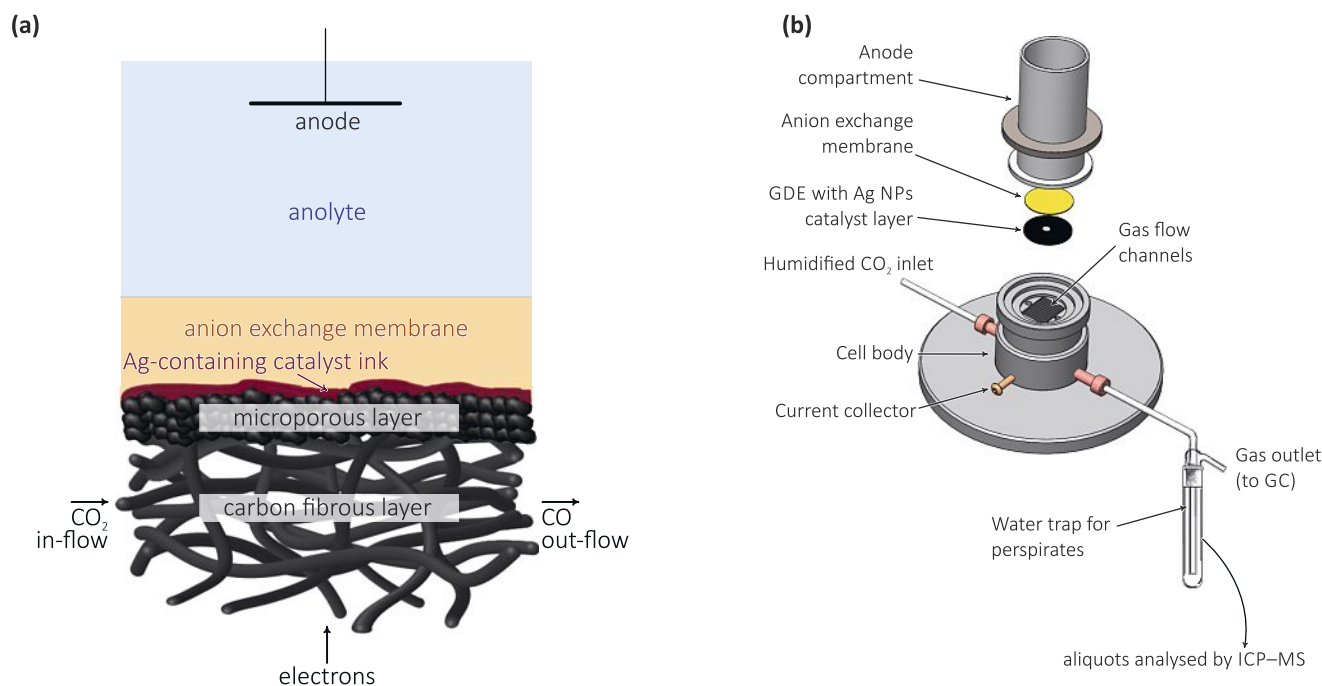


Fig. 1. (a) Scheme (figure not to scale) of a carbon-based bilayer gas diffusion layer (GDL) composed of a carbon fibrous layer (CFL) and a microporous layer (MPL). The GDL supports Ag nanoparticle catalysts and is in direct contact with an anion exchange membrane to form a so-called ‘zero-gap’ membrane-electrode 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 CO₂-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^[20,21] (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.*^[22,23]

The absence of a catholyte phase in this configuration will not be problematic if (like in the case of CO₂-to-CO conversion with Ag catalysts) *ec*-CO₂RR yields gaseous products only.^[20,22] 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.^[23–29]

If instead of large industrial-scale electrolyzers, 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^[26] – 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.^[20–23,27–29]

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.

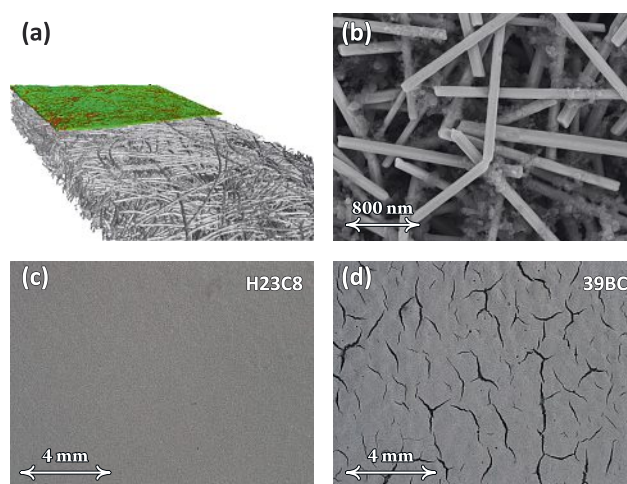


Fig. 2. Ag nanowires-containing GDEs prepared for electrolysis stress tests. (a) X-ray micro tomography image of a H23C8 GDL support with a compact (crack-free) MPL. (b) Scanning electron microscopy (SEM) image of the prepared GDE, with Ag nanowires visible on top of the MPL. (c) and (d) Optical microscopy 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.*^[23] 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 CO₂ 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 electrolyzers. Thus, the EDX-based mapping of the surface and

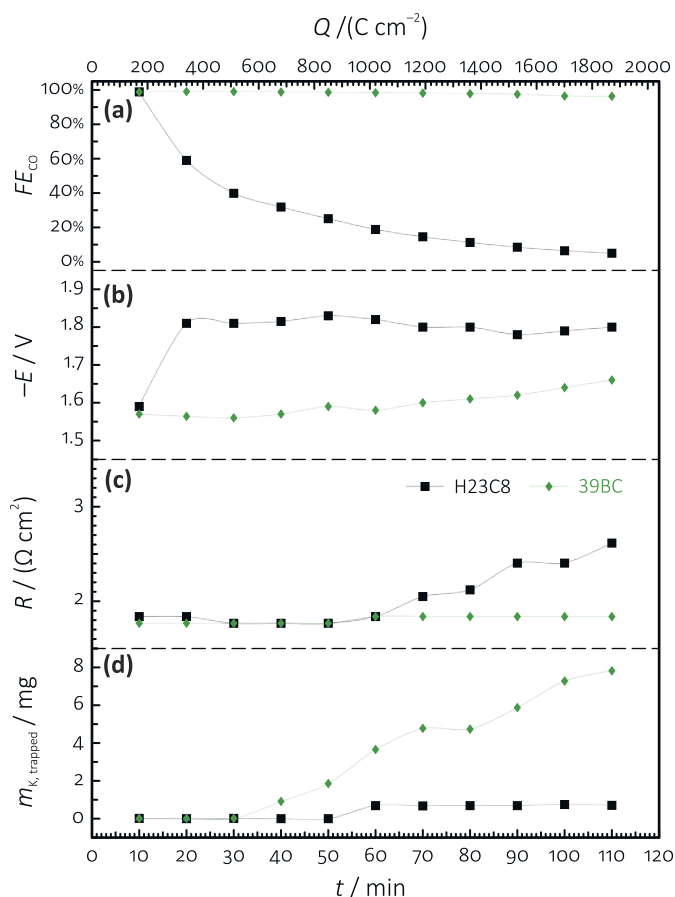


Fig. 3. Results of electrolysis stress tests on Ag nanowire catalyst containing GDEs prepared with crack-free (H23C8) and cracked (39BC) GDL substrates (cf. Fig. 2). The Faradaic efficiency of CO production (a), the measured cathode potential (b), the cell resistance (c) and the total amount of perspired K^+ (d) are shown as a function of time for galvanostatic electrolyses conducted at -283 mA cm^{-2} current density employing aqueous 2 mol dm^{-3} KOH as anolyte. A humidified 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).^[22,23]

It has to be emphasized here that the emergence of K_2CO_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.*^[23] 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 CO_2 gas flow, and its quantity can be determined by inductively coupled plasma mass spectrometry (ICP–MS) measurements.^[22,23] 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 CO_2 , blocking the access of this reactant to the catalyst layer (Fig. 5).

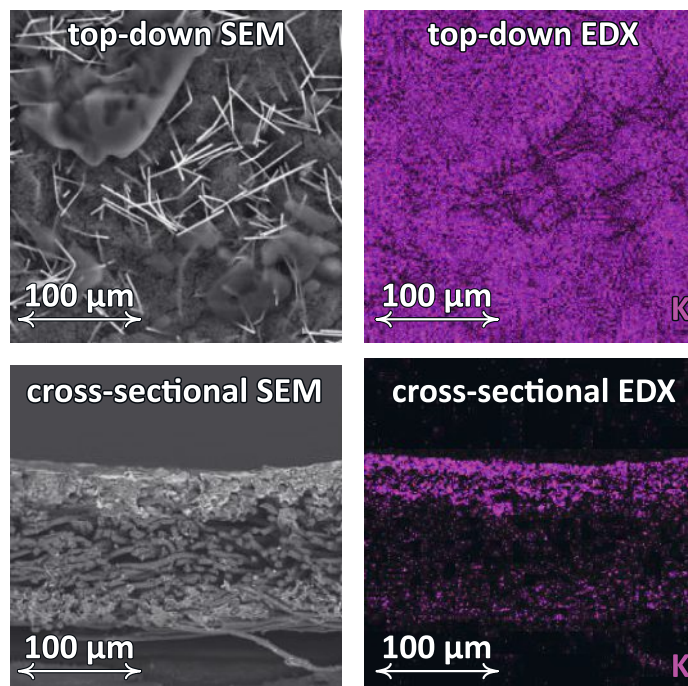


Fig. 4. Post-electrolysis SEM and EDX images of the 39BC substrate-based GDE, following electrolysis. See ref. [23] for details of the measurement.

The main conclusion of Kong *et al.*^[23] 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 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 CO_2 -to-CO-converting zero-gap GDE MEAs was further discussed in two recent publications of Hu *et al.*^[28] and Liu *et al.*^[29]

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.

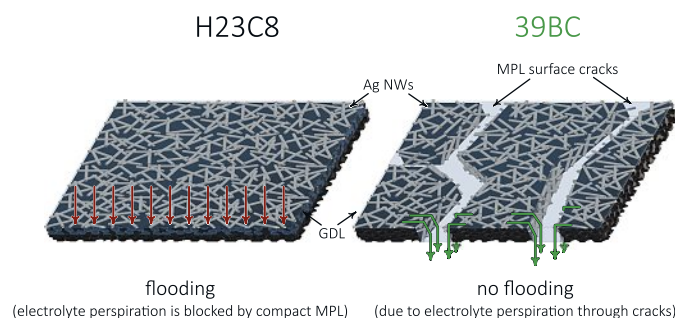


Fig. 5. A scheme illustrating the main findings of Kong *et al.*^[23] effective perspiration pathways (provided, e.g., by surface cracks present in the MPLs of GDL substrates) are essential to uphold the stability of CO_2 -to-CO reducing zero-gap GDE-membrane assembly cathodes.

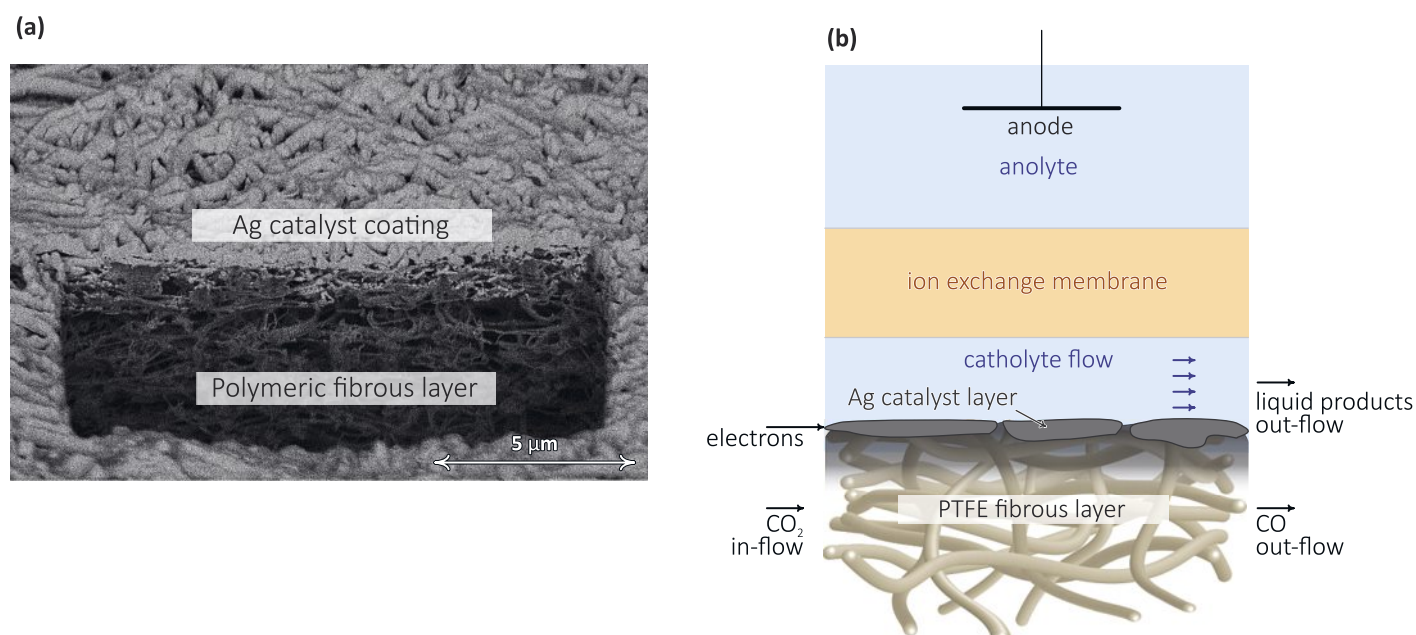


Fig. 6. (a) A fibrous PTFE layer covered by sputtered Ag, used as a GDE for ec -CO₂RR. (b) The cell configuration in which the GDE is used in direct contact with a catholyte flow (figure not to scale). Adopted from the work of Senocrate *et al.*^[24]

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 -CO₂RR was recently emphasized by the works of Li *et al.*^[30] and Kenis *et al.*^[25] 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.*^[31] 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.*^[24] 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 -CO₂RR. 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.*^[24] 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.^[24] 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 CO₂ to the Ag active sites. In addition, also the stability of ec -CO₂RR (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 -CO₂RR to CO, obtained by acting solely on the GDE substrate microstructure.

4. Summary and Outlook

In a recent work,^[24] 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 -CO₂RR 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.*,^[22,23] Hu *et al.*^[28] and Liu *et al.*^[29] 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 -CO₂RR. 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 -CO₂-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 CO₂-to-CO converters.

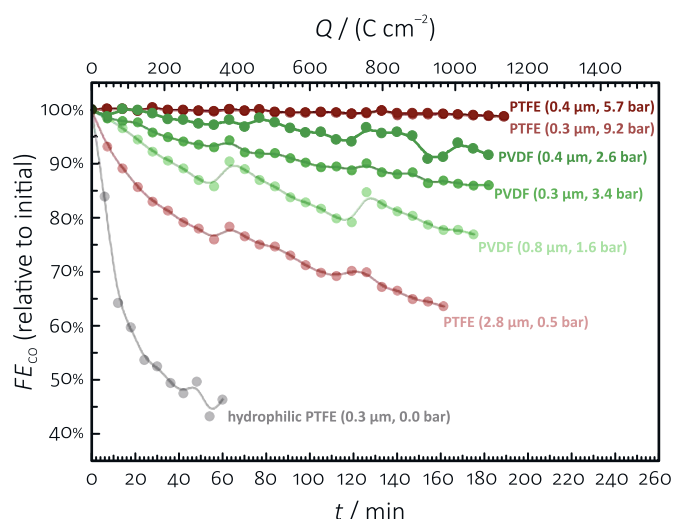


Fig. 7. Results of electrolysis stress tests conducted on polymeric fibrous layer-based GDEs. Fibrous layers of smaller pore size and higher WEP (both values are indicated in the figure) retain their Faradaic efficiency for CO production for longer times. Experiments are carried out at 100 mA cm⁻² current density, with both the catholyte and anolyte compartments filled with 1 mol dm⁻³ CO₂-saturated KHCO₃ solution. See ref. [21] for further details.

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