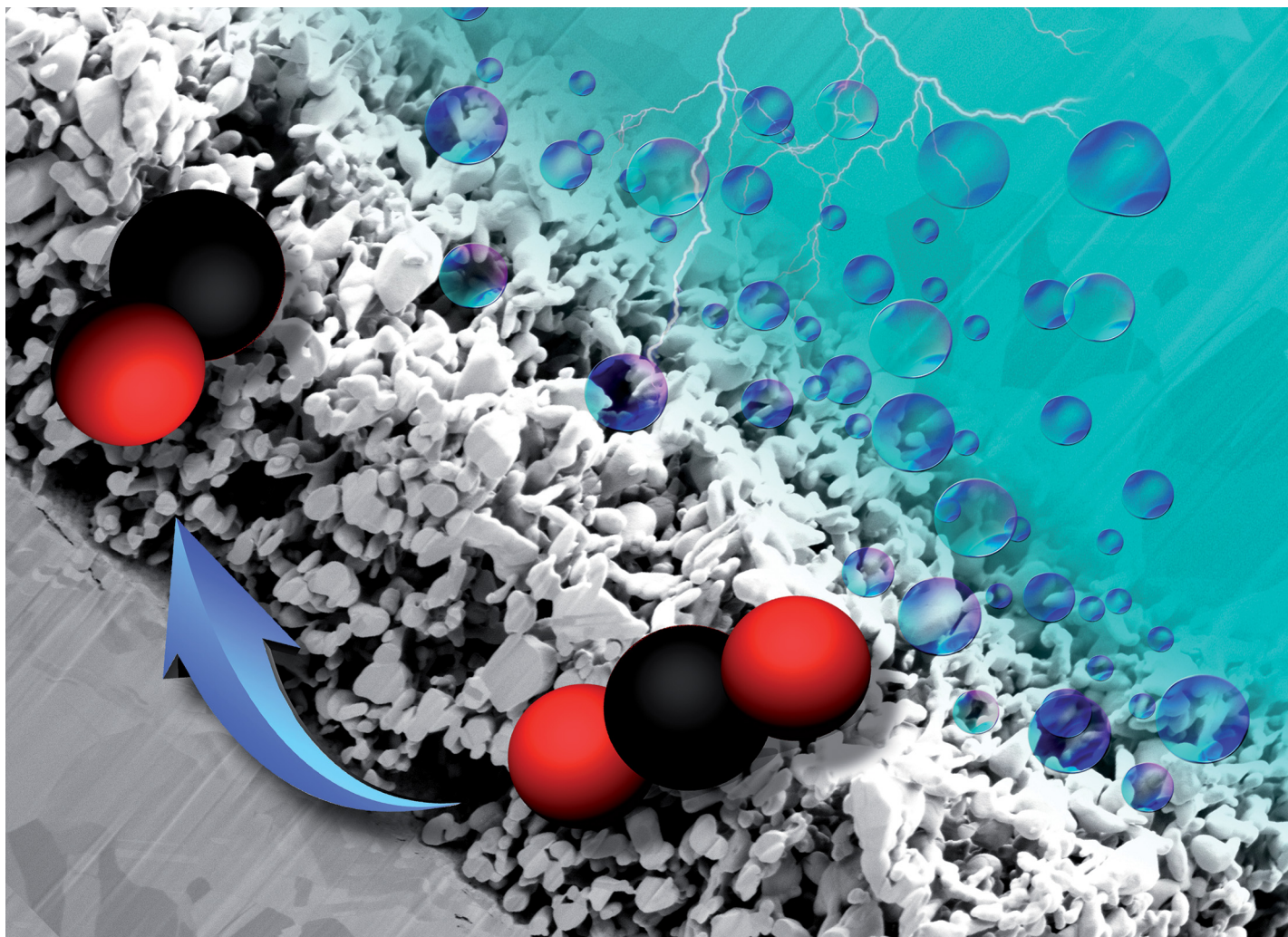




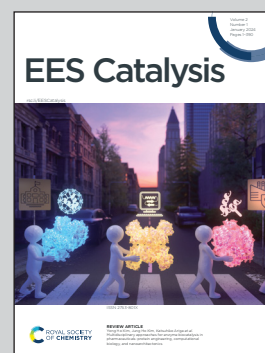
Showcasing research from Professor Roth's laboratory, University of Bayreuth, Germany, and Professor Turek's laboratory, Clausthal University of Technology, Germany

Highly selective Ag foam gas diffusion electrodes for CO₂ electroreduction by pulsed hydrogen bubble templation

The new method generated polymer-based Ag-DHBT-GDEs through electrochemical Ag catalyst deposition on a sputtered Ag-GDL. Coating an insulating polymer fabric with a conductive layer maintained the crucial porous structure for CO₂ electrolysis. Pulsed Dynamic Hydrogen Bubble Templatation (PC) outperformed galvanostatic deposition (DC), exhibiting higher mass loading and ECSA values, surpassing DC-DHBT-GDEs at relevant current densities. Furthermore, perfluorosulfonic acid ionomer infiltration enhanced CO₂ transport without causing flooding, contributing to performance improvement.

Image designed and illustrated by Jens Osiewacz.

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Highly selective Ag foam gas diffusion electrodes for CO₂ electroreduction by pulsed hydrogen bubble templation†

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The electrochemical reduction of carbon dioxide to valuable fossil-free products opens up a way to close the carbon cycle, if based solely on renewable energy sources. Making the process industrially viable, however, needs high CO₂ conversion rates, efficient electrodes, and high selectivity for desired products. To reach this goal, highly catalytically active porous electrodes with maximized surface areas are required. We combined pulsed electrochemical deposition of the Ag foam catalyst with ionomer infiltration of the electrode to produce Ag-based gas diffusion electrodes (GDEs) in a facile and fast production process. Using the dynamic hydrogen bubble templation method (DHBT), we utilized the parasitic hydrogen evolution reaction (HER) to aid the solvent free structuring of the 3D catalyst network and directly manufacture a GDE. Different deposition parameters and in particular pulse-to-pause ratios increased the amount of deposited catalyst and successfully reduced the overpotential during CO₂RR operation. To inhibit electrode flooding and decrease CO₂ mass transport limitations during CO₂RR, we further infiltrated the electrode with a suitable perfluorosulfonic acid ionomer. SEM and EDS analyses showed a homogeneous Ag/F distribution along the cross section of the electrodes. These electrodes catalyzed the conversion of CO₂ to CO at industrially viable current densities of 500 mA cm⁻² with an unprecedented faradaic efficiency up to 76% in 1 M KHCO₃.

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Broader context

A new direct fabrication method for polymer-based Ag-DHBT-GDEs was developed, combining pulsed electrochemical deposition of Ag catalysts with ionomer infiltration of a sputtered Ag-GDL. The sputtering process prepared the insulating polymer fabric by depositing a conductive thin layer. This allowed for the electrochemical deposition of Ag catalysts, resulting in a conductive GDL that maintained its porous structure essential for gas transport during CO₂ electrolysis. The DHBT method utilized the parasitic HER to structure the 3D catalyst network and directly fabricate a future benchmark GDE. While galvanostatic deposition (DC) produced Ag foam structures, they did not show improved performance compared to sputtered Ag electrodes. To address this, a pulsed DHBT process (PC) was introduced, resulting in efficient Ag deposition with high mass loading and ECSA values. Linear sweep voltammetry tests demonstrated improved performance for PC-DHBT electrodes compared to DC-DHBT-GDEs at industrially relevant current densities. To further enhance CO₂ electrolysis, the Ag foam GDE was infiltrated with a perfluorosulfonic acid ionomer. This prevented flooding and improved CO₂ mass transport. SEM and EDS analysis confirmed a homogeneous Ag/F distribution. The infiltrated electrode enabled CO₂ electrolysis at higher current densities while maintaining its CO selectivity. Overall, this chapter presents a novel approach for fabricating polymer-based Ag-DHBT-GDEs using a combination of sputtering, electrochemical deposition and ionomer infiltration. The developed GDE allows for efficient CO₂ electrolysis with unprecedented performance and selectivity.

1. Introduction

Electrochemical carbon dioxide reduction reaction (CO₂RR) can contribute decisively to overcoming the challenge of rising greenhouse gas emissions on our planet. Combining renewable energy sources like wind and solar power with the CO₂RR, the carbon cycle can be closed and fossil-free chemicals like syngas (CO + H₂), formic and acetic acid, or hydrocarbons, such as ethylene, can be produced, depending on the catalyst material

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On top of the GDLs, a coating of the active catalytic layer needs to be airbrushed,³³ doctor-bladed,^{34,35} sputtered^{32,36,37} or electrochemically deposited^{38–40} to achieve a porous 3D composite structure. Luo *et al.*⁴¹ reported a manufacturing strategy to enhance the CO₂RR activity by electrochemical

A hydrophobic treatment of the GDEs was carried out by dropcasting a perfluorosulfonic acid (PFSA) suspension onto the electrodes. The suspension contained 1-propanol, water

and 12–18 wt% (7–11 mg) of a short side chain ionomer with an equivalent weight of 800 g mol⁻¹ (3 M-800EW, 3 M, USA). For the dropcasting process a planar position of the GDE was necessary to guarantee a uniform distribution of the ionomer suspension. After the dropcasting process the GDEs were dried in air for 24 h.

Electrode performance and product analysis

Performance tests and CO₂RR experiments of the GDEs with a geometric surface area of 3.14 cm² were performed in three-electrode set-ups at room temperature in the same custom-built gas-tight polymer flow-cell (SI-2, ESI[†]) in two testing facilities (Bayreuth and Clausthal). In Bayreuth testing was performed using a potentiostat (Gamry Reference 3000, Gamry Instruments, USA). While testing, Ag-based GDEs, a platinum mesh ($A_{\text{geo}} = 3.14 \text{ cm}^2$, 99.95%, Biologic) and a HydroFlex[®] (Gaskatel GmbH, Germany) reversible hydrogen electrode (RHE) functioned as working electrode (WE), counter electrode (CE) and reference electrode (RE), respectively. Electrolyte containing compartments were separated by a Selemin anion exchange membrane (AGC Chemicals Europe, England). The gas compartment of the cell was continuously supplied with CO₂ ($\geq 99.995\%$, Air Liquide, France), at a flow rate of 20 N mL min⁻¹, using a calibrated mass flow controller (Bronkhorst, Netherlands), while a backpressure of 30 mbar was maintained by a backpressure controller (Bronkhorst, Netherlands). The electrolyte utilized for the CO₂RR (1 M KHCO₃ solution) was prepared of powder ($>99.7\%$ KHCO₃, Carl Roth, Germany) and ultrapure water (Barnstead GenPure Pro, Thermo Scientific, USA) respectively. The electrolyte was supplied and pumped using peristaltic pumps (DOSAFlex, Dosatron GmbH, Germany) with a constant pump rate of 3 L h⁻¹. Linear sweep voltammetry measurements (LSV) were accomplished applying the current interrupt (CI) mode to correct for the inner ohmic resistance (iR). The potential range was scanned with a constant rate of 10 mV s⁻¹ up to -1.5 V vs. RHE. CO₂RR chronopotentiometric measurements (CP) lasted up to 100 hours. For the CO₂RR, different current densities (10, 30, 50, 100, 200, 300, 400 and 500 mA cm⁻²) were tested. The gas outlet of the cell was in-line connected to a gas chromatograph (GC) (GC-2014, Shimadzu, Japan) to detect and quantify the gaseous products of the CO₂RR. The product gases H₂, CO, and CO₂ were analyzed every 5 min of electrolysis and separated in HayeSep capillary columns connected in series (HayeSep Q + HayeSep R, 80/100 mesh, 2 + 2 m × 1/8 in.). The GC was equipped with a thermal conductivity detector (TCD) for the detection of H₂. A flame ionization detector (FID) was used to detect CO (in the form of CH₄ after passing through a methanation unit before passing the FID, carrier gas = Ar 5.0).

In Clausthal, the 1 M KHCO₃ solution prepared from KHCO₃ ($>99 \text{ wt}\%$, Carl Roth) was cycled through the catholyte and anolyte chambers at a flow rate of 480 mL min⁻¹ each in isolated cycles. The electrolyte chambers were separated by an anion exchange membrane (fumasep[®] FAA-3-130-PK, fumatech). CO₂ (99.995%, Linde) was supplied to the gas chamber at a flow rate of 50 N mL min⁻¹. The experiments were conducted at ambient temperature (25 °C), with a catholyte pressure of

1000 mbar and a gas pressure of 1030 mbar, corresponding to a 30 mbar differential pressure over the GDE. Measurements were performed using an electrochemical workstation (Zahner ZenniumPro, Zahner GmbH) in a three-electrode configuration, with the GDE as WE, a nickel mesh as CE and a RHE (HydroFlex, Gaskatel) as reference. Each current density was applied galvanostatically for 30 min, starting from lowest to highest. At the 15 min and 30 min mark for each current density, gas products from gas and electrolyte chamber were analyzed using gas chromatography (Trace1310, ThermoFischer) in a two channel setup with column stripper (Hayesep Q and 5 Å molecular sieve), equipped with two TCDs.

The WE potential was continuously measured against the reference electrode and averaged for each current density after steady-state was reached. iR compensation was conducted for each point of measurement using the high frequency response method (HFR) to accurately account for the changing ohmic resistance caused by bubble formation.^{42,43} For this, an alternating current with an amplitude of 20 mA and a frequency of 15 kHz was superimposed over the direct current. The impedance response at this frequency was determined beforehand by impedance spectroscopy to be free of capacitive and inductive features at the measured current densities for the given setup. The faradaic efficiencies (FE) of the specific products i were determined by dividing their partial currents I_i by the total current I_t using eqn (1), where x_i , z_i , F , and $\dot{n}$ are the volume fractions of the detected gaseous product, the number of electrons involved for a given reduction product, the Faraday constant, and the molar flow rate, respectively.

$$\text{FE}_i = \frac{I_i}{I_t} = \frac{x_i \cdot z_i \cdot F \cdot \dot{n}}{I_t} \quad (1)$$

Electrochemical surface area

The electrochemical surface area (ECSA) of the GDEs was measured in alkaline electrolyte (1 M KHCO₃), in a three-electrode set-up, using an in-house built H-cell. After conditioning the electrodes at the starting potential of 0.07 V vs. RHE for 30 s, the cyclic voltammograms (CVs) were recorded in the non-faradaic region between 0.03–0.07 V vs. RHE. The electrochemical double layer capacitance (C_{DL}) was calculated according to eqn (2), where I was the average value of the charging current from the anodic and cathodic sweep, and V , the scan rate used to calculate the ECSA from eqn (3). Ten different scan rates were applied (10 to 100 mV s⁻¹) and the step size was set to 2 mV. The double layer capacitance of the reference ($C_{\text{ref}} = 1.5 \times 10^{-4} \text{ F} \pm 7.6 \times 10^{-8} \text{ F}$) was determined experimentally from multiple CVs at ten different scan rates with the protocol described above, using a Ag sputtered polymer substrate, as described in the section about the preparation of the Ag foam GDEs.

$$C_{\text{DL}} = \frac{I}{v} \quad (2)$$

$$\text{ECSA} = \frac{C_{\text{DL}}}{C_{\text{Ref}}} \cdot A_{\text{geo}} \quad (3)$$



Gravimetric measurements

A high precision balance (Kern ABT 220-5DM, resolution of 0.01 mg) was used to weigh the Ag catalysts before and after electrodeposition and the corresponding mass differences (Δm) were calculated with respect to the total masses of the sputtered substrate.

Contact angle measurements

To evaluate the hydrophobic properties of the GDEs, contact angle measurements were conducted using an aqueous 1 M KHCO_3 solution. A drop of liquid (10 μL) was dispensed onto the centre of the tested electrode, using the dispensing option of the SCA 20 software (DataPhysics Instruments, Germany).

Microstructure analysis

High resolution images were recorded using the secondary electron detector (SED) of a scanning electron microscope (SEM) (Zeiss Ultra plus, Carl Zeiss, Germany). To analyse the cross-section of electrodes at high resolution a Zeiss Crossbeam 340 Gallium-Focused Ion Beam-SEM (FIB-SEM) was applied. Pieces of 5 mm $\times$ 10 mm were cut out from the centre of the electrode with a scalpel and were mounted on a sample holder using a carbon pad. For the microstructural investigation, the sample surfaces and the cutting surfaces were analysed. FIB cuts were performed by applying an acceleration voltage of 3 keV and a current of 30 nA. Images were taken at an acceleration voltage of 1 keV. For chemical analyses a Bruker XFlash 6–100 energy-dispersive X-ray spectroscopy (EDS) detector was used. For these measurements an acceleration voltage of 5 keV was applied.

X-ray diffraction

The Ag phase in the samples was analyzed by X-ray diffraction (Philips X'Pert-MPD PW 3040/00) in Bragg–Brentano geometry using unfiltered CuK_α radiation (PW3373/00 Cu LFF at 40 kV and 40 mA). The 10 mm $\times$ 20 mm samples were placed on a sample holder steel disc and the sample height was adjusted using a dial gauge (Käfer GmbH, Germany). Diffractograms were recorded with a proportional point detector (WP3011) at a step size of $0.02^\circ 2\theta$ and a scan rate of $0.12^\circ 2\theta \text{ min}^{-1}$ between 10° and $90^\circ 2\theta$. $\text{Cu K}_{\alpha 2}$ reflections were removed post measurement with Highscore software.

Physisorption measurements

The IUPAC recommendations for gas physisorption were taken into account to conduct the gas physisorption measurements.⁴⁴ Therefore, the measurements were performed with Krypton as adsorptive gas at 77.15 K. Krypton physisorption data were collected in the p/p_0 range of 0.09–0.2 (fixed p_0 : 0.35 kPa) by using an Anton Paar QuantaTec ASiQ-MP-MP-AG setup. The data were evaluated *via* Brunauer–Emmett–Teller (BET) method.⁴⁵ Prior to the measurements the samples were cut in pieces and degassed at 120 $^\circ\text{C}$ for 12 h.

Capillary flow porometry

Flow-through pores and bubble point pressure were determined using capillary flow porometry (Porometer 3Gzh, Quantachrome). A high-wetting liquid, with contact angle of zero, (Porofil, Quantachrome) was applied to the probe of 18 mm diameter, which was adjusted in the device. Afterwards, the fluid was driven out of the pores with a pressure gradient. The resulting air flow was detected on top of the probe. The bubble point pressure was determined at a flow rate of 0.1 L min^{-1} . The flow-through pore distribution was finally determined by comparing the air flow through the wet and dry sample.

3. Results and discussion

Modification of the polymer substrate for electrodeposition

To turn the insulating polymer fabric into a suitable substrate for electrodeposition, it was necessary to apply a conductive layer that retains its porous character to enable gas permeability in the GDE application. Fig. 1a shows the substrate that consists of a bipolymeric fibre fabric, made of a thin PTFE fibre layer (thickness $\sim 20 \mu\text{m}$) on top of a larger PET fibre layer (thickness $\sim 105 \mu\text{m}$), functioning as backing layer to increase its mechanical stability. Fig. 1b shows the thin Ag layer, which was sputtered on top of the polymer fibres and served as the contact layer for the later GDE structure.

We chose Ag as contact layer material to avoid any influence or contamination by an additional metal on the CO_2RR . Next to the electrical conductivity, which enables high-quality electrodeposition and high CO_2RR activity at the later stages, another requirement for an efficient GDE is the facile and even supply of CO_2 gas to the final catalyst layer. Therefore, the Ag sputter layer needed to be as thick as possible for electrical conductivity without losing its porosity as caused by a completely closed Ag surface layer on top of the PTFE fibres. The optimum parameters for the sputtered layer are shown in Table 1.

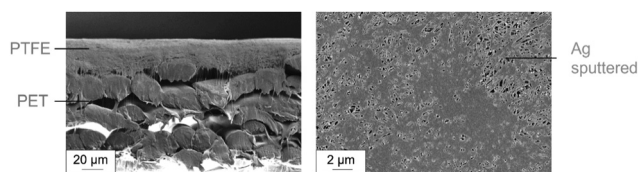


Fig. 1 Analysis of electrode microstructure by scanning electron microscopy. (a) Cross-section of a pristine polymer fibre fabric and (b) top-down view of the polymer substrate, which was sputtered with Ag for 360 s.

Table 1 Parameters (time, current) used for sputtering and the deposited mass, specific mass and thickness of the thin Ag layer on the polymer substrate to obtain a conductive GDL for electrodeposition

Parameter	Value
Time, t [s]	360–420
Current, I [A]	0.016
Δm [mg]	1.09 ± 0.12
Specific mass, m_{spec} [mg cm^{-2}]	0.13
Thickness, d [nm]	123.68 ± 13.95



Preparation and characterization of the DHBT microstructure

The sputtered Ag/polymer fibre substrate was used as WE in the electrochemical DHBT process as described in the experimental section above. Fig. 2a shows a graphical representation of the DHBT process, which makes use of the HER taking place on the conductive substrate, with its bubbles as the negative template responsible for the final porous foam structure. SEM images in Fig. 2b show the characteristic DHBT foam structure, consisting of microporous craters formed by hydrogen bubbles and the nanoporous foam walls consisting of Ag nano needles. An EDS analysis of the cross-section of a GDE after DHBT can be seen in the ESI†(SI-5), where the porous Ag foam forms the top layer of the GDE, with the hydrophobic PTFE layer underneath. This PTFE coating should prevent the electrolyte from entering the pores and prevent electrolyte flooding during

CO₂RR operation. Fig. 2c shows the XRD patterns of the stainless steel sample holder, the polymer substrate and the two Ag samples. Five small reflections can be attributed to the sample holder itself. XRD measurement of the polymer substrate revealed a decrease in intensity of the background signal. Additionally, amorphous reflections of the semi-crystalline structure of the PET (reflex at 22° and 26° 2θ) and the sharp crystalline peak of the PTFE and PET at 18° 2θ can be detected.^{46,47} Adding a very thin Ag sputter layer of approx. 130 nm on top results in five small reflections at 38°, 44°, 64°, 77° and 81° 2θ, representing the (111), (200), (220), (311) and (222) plane of the sputtered Ag. The XRD pattern of the electrodeposited Ag foam shows an increase in intensity of all characteristic fcc Ag reflections, accompanied by a decrease in intensity of the crystalline PTFE and amorphous PET reflections, indicating the successful preparation of a ready-to-use metallic GDE.

Parameter selection for dynamic hydrogen bubble templation

To analyse the successful implementation of the DHBT process, the electrodeposited Ag mass was measured and the Ag deposition Efficiency (DE_{Ag}) was calculated (eqn (S1), ESI†). Fig. 3a demonstrates an increase in deposited Ag mass with increasing charge densities under galvanostatic deposition mode. By DC deposition, the highest Ag catalyst loading with ~26 mg Ag at 50 A s cm⁻² can be reached. For each electrode, the DE_{Ag} stays approximately on the same level for every deposition charge density (SI-1, ESI†). This result indicates that the increase in Ag loading is a consequence of increasing deposition time during DC deposition rather than of increased coulombic efficiency during the DHBT process. Based on the measurements of the double-layer capacitance, the calculated ECSA also increased with increasing deposition time under DC mode, compared to the sputtered electrode (300 s) (Fig. 3a). Similar results have been shown and reported for model electrodes for H-cell applications in an earlier study.⁴⁸

The sputtered electrode (sputter time = 300 s) and the DC electrode with the highest ECSA and Δ*m*, respectively (DC-50 A s cm⁻²), were tested and compared for their electrochemical performance in testing conditions identical to the CO₂RR (Fig. 3b). In comparison to the sputtered electrode, the DC-50 A s cm⁻² electrode exhibits slightly elevated current densities within the potential range of -0.6 to 1.0 V vs. RHE. This most certainly represents the onset potential for CO₂RR at approximately -0.65 V vs. RHE, equating to an approximate current density of -10 mA cm⁻². Below -1.0 V vs. RHE, the current densities of both electrodes increase steeply, with the sputtered electrode showing slightly higher values. The desirable value of 200 mA cm⁻² can be reached for both electrodes at the tested potential of -1.2 V vs. RHE. Consequently, the intricate foam structure does not appear to lead to beneficial effects and higher performance.

As the DHBT electrode shows similar behaviour in the LSV sweep compared to the sputtered GDE at the target value of 200 mA cm⁻², we focused on reducing the electrode overpotential by increasing the catalyst loading and hence, the electrode performance. A similar strategy of reduced overpotentials

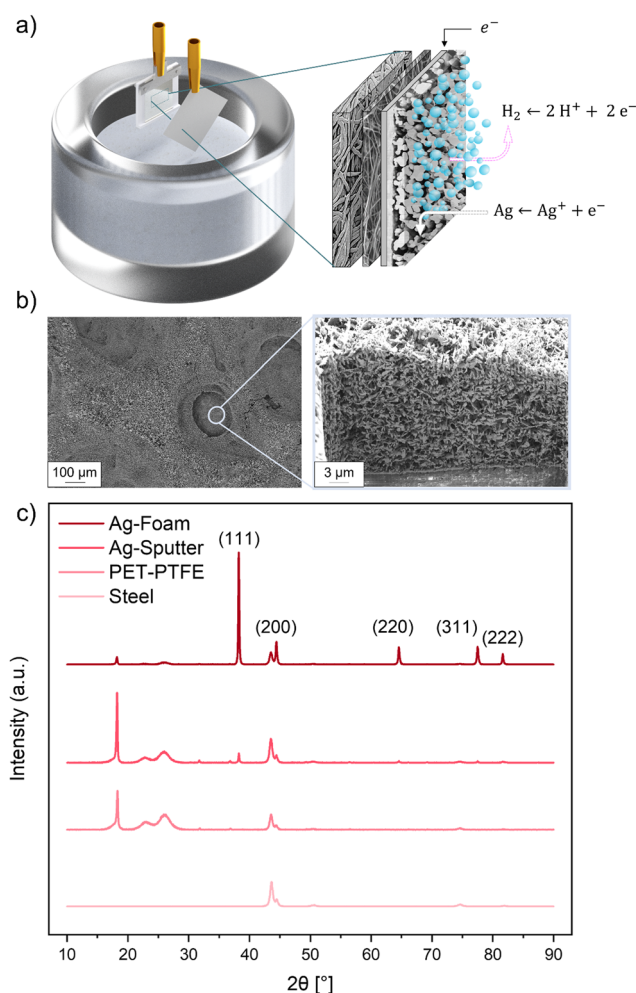


Fig. 2 Analysis of the dynamic hydrogen bubble templation process. (a) Graphical representation of the working principle of the DHBT method. (b) SEM images of the Ag foam pores by HER occurring during DHBT method and high resolution image of a Ag pore with agglomerated Ag nanoparticles on top of the porous sputter layer, (c) XRD pattern of the reference steel plate (ICDD: 04-006-1881), PTFE-PET substrate (ICDD: 00-054-1595, 00-050-2275), the Ag sputter layer (ICDD: 04-001-2617) and the Ag DHBT foam (04-006-1881).

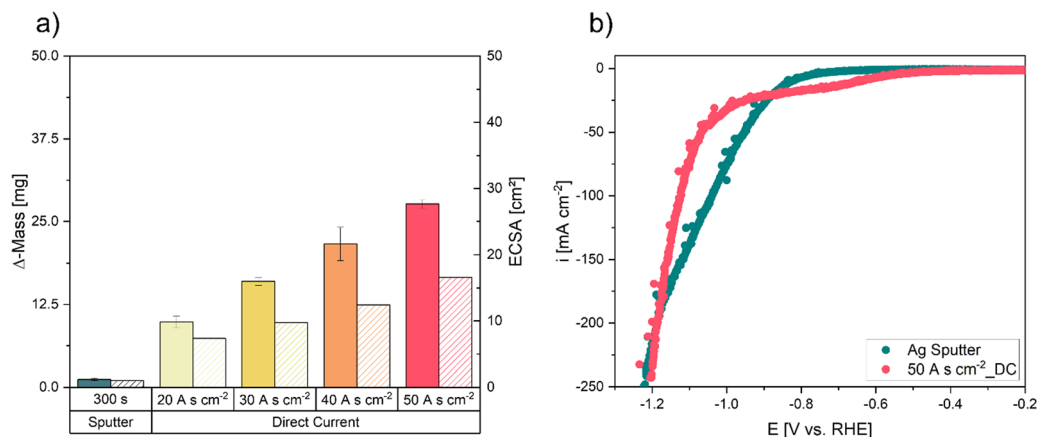


Fig. 3 Characterization of the Ag-sputtered electrode compared to the DHBT electrodes manufactured in DC mode. (a) Deposited Ag mass and ECSA values of Ag-sputtered electrode and DHBT foam electrodes with increasing charge densities during DC mode, (b) linear sweep voltammetry curves for the Ag sputter electrode and the DC-50 A s cm⁻² electrode to test their electrochemical performance (IR corrected potentials by applied CI method).

to increase the electrodes flooding resistance by inhibiting electro-wetting, has been reported by Yang *et al.*^{49,50} Hence, we went from DC to PC electrodeposition, to realize a higher metal deposition efficiency by limiting HER during electrodeposition.⁵¹ By interrupting the direct current a quasi-stationary state of the reduction products during electrodeposition is obtained, while the depletion of the metal ions close to the surface area can be reduced and the competing HER should be limited. Nikolić *et al.*⁵² demonstrated that inhibiting electrolyte stirring by less pronounced HER bubble formation resulted in the formation of dendrites and small metal

agglomerates, due to decreasing pulse-to-pause ratios in PC deposition. This effect should result in an increased surface area which we intended for optimized activity.

Fig. 4 illustrates the results of deposited Ag mass, the DE_{Ag} and the resulting total ECSA values as well as the specific ECSA in dependence of the applied pulse-to-pause ratios. Higher charge densities as well as lower pulse-to-pause ratios show an increase in Ag mass loadings (Fig. 4a). Electrodes deposited with the lowest pulse-to-pause ratio (1:4) show the highest increase in Ag loading, which results in the highest

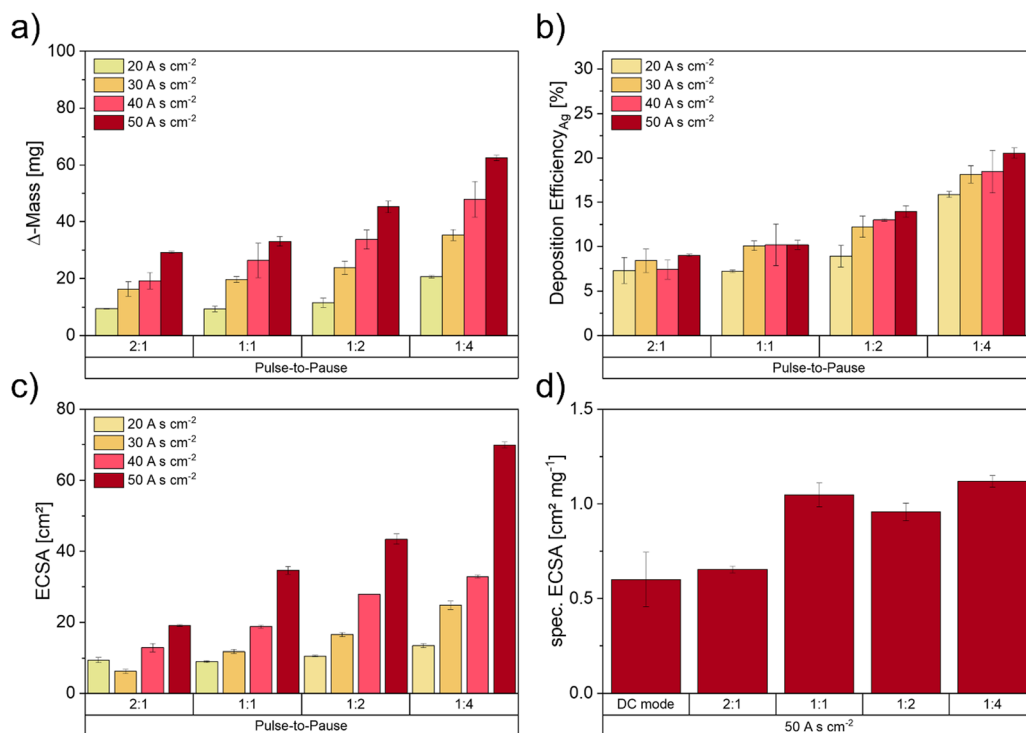
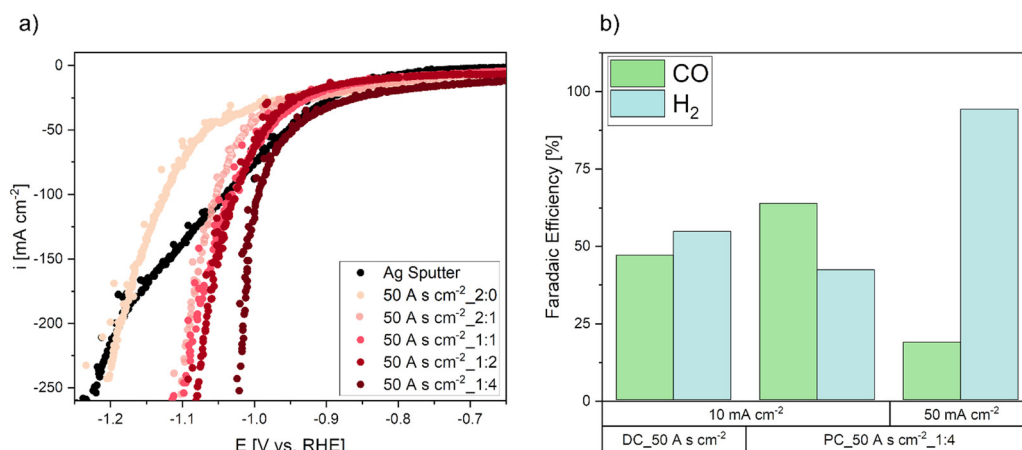


Fig. 4 Electrochemically deposited masses (a) and the calculated FE of the DHBT in dependence of the varied pulse-to-pause ratios (b), calculated ECSA values by measurement of the double layer capacity and specific ECSA (d) of the deposited samples with 50 A s cm⁻² in dependence of the pulse-to-pause ratios.



Since the analysis of the specific ECSA (Fig. 4d) shows an increase for decreasing pulse times, the mass change can not be the only affecting component. The reason for the rise in specific ECSA could be found in the microstructure of the foam, which may change with the pulse duration due to the necessity for the system to build new crystallisation nuclei at the start of each pulse. A quantitative analysis of Ag particles can be done by FIB tomography, which has been proven to be a successful characterisation method for Ag foam model electrodes in an earlier study.⁴⁸

As the CO₂RR performance of the electrodes cannot be evaluated by LSV scans alone, due to parallel CO₂RR and HER, galvanostatic operation at various current densities for 1 h was tested. The results of the galvanostatic CO₂RR experiments are shown in Fig. 5b. At relatively low current densities of 10 mA cm⁻², the DC electrode already shows higher HER selectivity than the PC_50A_s cm⁻²_1:4 electrode. Increasing the galvanostatic operation from 10 to 50 mA cm⁻² shifted the selectivity towards HER even for the PC electrode. This behaviour can be explained by a hydrophilic Ag catalyst layer and therefore significant mass transport limitations for CO₂. As the electrode consists of pure Ag, the surface of the electrode is completely flooded with electrolyte and the reacting CO₂ gas



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requires long pathways to be transported to the three-phase boundary regions.

Without hydrophobic components to reduce diffusion lengths in the GDE, the mass transport limitations are reached quickly by increasing current densities. As a result, the CO₂RR selectivity shifts towards the undesired HER. Therefore, an additional hydrophobic component is needed to improve the performance of the GDE structure.

Perfluorinated ionomer infiltration for higher performance

Several approaches have been reported in the literature over the last few years on how to manage GDE flooding by the electrolyte and control electrode wettability.⁵⁰ Especially incorporating different fluorinated and non-fluorinated polymers, such as PTFE, PFSA (e.g. Nafion) or PSMIM (e.g. Sustanion), can establish a suitable hydrophobic microenvironment.^{29,31,35,53,54} This results in decreased electrode flooding and promotes gas transport in the catalyst layer, which in turn will lead to improved current densities during the CO₂RR.^{23,50,55} Furthermore, functional groups containing ionomers, such as PFSA with its sulfonic acid group, can not only provide hydrophobic regions (PTFE backbone), but also water pathways inside the ionomer structure within the GDE during CO₂RR operation. This beneficial acidic microenvironment results in a higher ion transport, which is sufficient to sustain a proton supply for the complex multistep CO₂ reduction reaction.^{23,56–58} These ionomer properties can be significantly improved by the choice of the ionomer type, the dispersion solvents or drying parameters and will have a strong influence on viscosity, distribution in the catalyst layer, structural conformation, water uptake and

therefore ion conductivity.⁵⁵ García de Arquer *et al.*²³ designed and implemented a catalyst:ionomer bulk heterojunction (CIBH) based on a long-side-chain PFSA into the Ag-GDEs and reported a CO₂RR partial current density as high as 400 mA cm⁻².

To enable the formation of favorable connected three-phase boundaries within the GDE structure, we implemented an infiltration process of a short side-chain perfluorosulfonic acid ionomer (3M-800EW). The beneficial effect of its low equivalent weight and the short-side chain results in a higher proton conductivity than long-side-chain ionomers used in previous studies.^{55,59} Studies by Lees *et al.*⁵⁸ showed that an optimized ionomer loading is needed for the electrodes to perform at a high FE_{CO}. With increasing ionomer loading the FE_{CO} decreases and promotes the HER due to blockage of the pores by the ionomer. Consequently, we studied the influence of different ionomer loadings in our Ag foam GDE on the hydrophobic behaviour of the surface and the resulting ECSA. A graphical representation of the dropcasting infiltration process is shown in Fig. 6a.

To study the influence of different ionomer concentrations on the hydrophobic behaviour of the electrode surface, the resulting contact angles were measured and presented in Fig. 6b. The contact angle increases by increasing ionomer concentration from approximately 3° of the pure Ag foam to 89° and 110° for 12 wt% and 18 wt% PFSA, respectively, which implies an increase in hydrophobicity of the surface. To investigate the quality of the infiltration process within the GDE we performed line scans on cross-sections of the GDEs. The results in Fig. 6c present an almost uniform F distribution across the

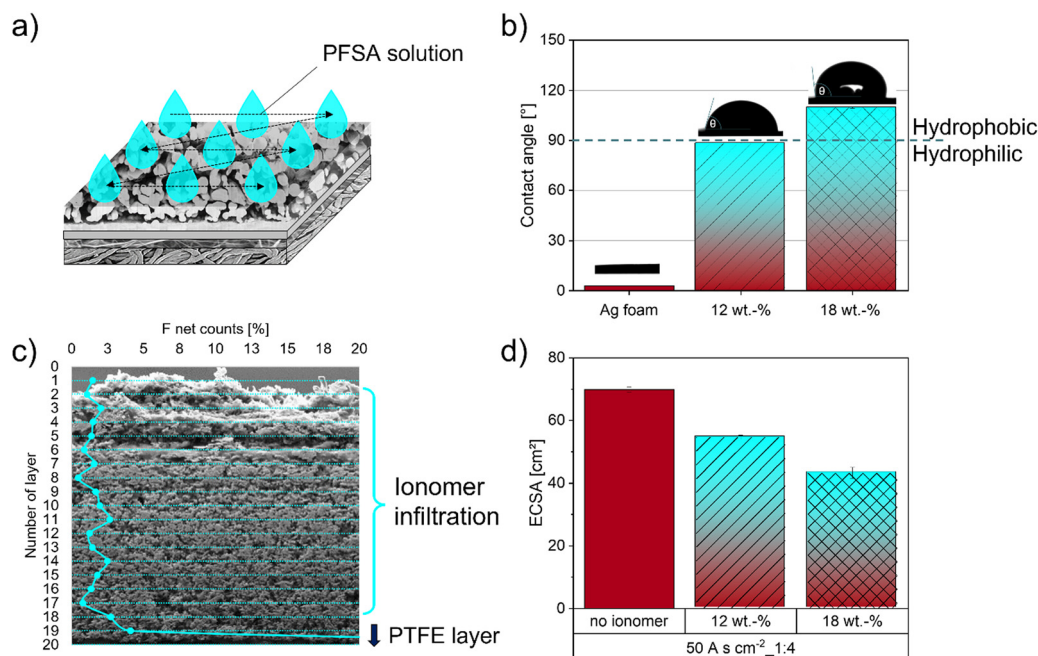


Fig. 6 Graphical representation of the PFSA infiltration and its influence on the Ag electrode. (a) Infiltration routine of the electrodes, (b) surface contact angle of the Ag foam electrodes before and after infiltration with different PFSA contents, (c) F distribution along the thickness of the GDE and (d) effect of different weight percentage of perfluorinated polymer on the ECSA of the GDE.



We believe that the CO conversion performance of our Ag DHBT GDE can be achieved by the interplay of controlled pore sizes, amount of high surface area catalyst and the well distributed phase-separated PFSA. The hydrophobic property plays an important role in preventing the electrode from flooding, whereas the hydrophilic part can control the transport and availability of protons at the catalyst surface. The high number of catalytically active sites, given by the Ag nanostructured GDE reduces the energy barrier of the initial electron transfer step



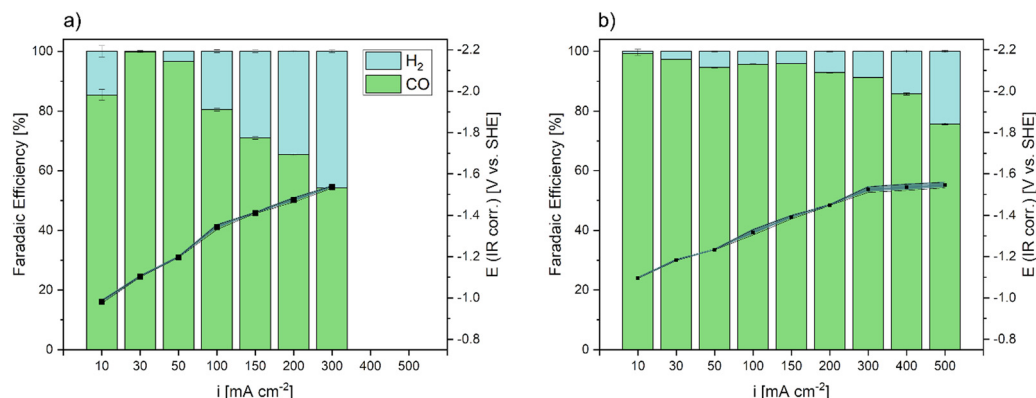


Fig. 8 Normalized faradaic efficiencies of CO and H₂ after galvanostatic operation at current densities up to 500 mA cm⁻² and the recorded WE potential after correction for the inner resistance. (a) CO₂RR results of a commercial Covestro GDE and (b) CO₂RR results of the Ag DHBT GDE. Each curve represents the mean of two replicate measurements with the respective standard deviations indicated by the shaded areas.

and consequently, improves the stabilization of the important COOH_{ads} intermediate.⁶⁸ As already proposed in previous studies on the CO₂RR mechanisms,^{57,69,70} the rate-limiting factor in this reaction is the combined proton and electron donation step (PEDS). We assume that the SO₃⁻ group of PFSA can provide protons for the reaction quickly and efficiently, resulting in a fast conversion rate from COOH_{ads} to CO_{ads}. In addition to that, SO₃⁻ groups can have a decisive effect on OH⁻ inhibition, generating higher pH values, which are required for the successful suppression of the HER, as already stated by Berlinguette *et al.*⁵⁸ and Bell *et al.*^{53,54} We propose that the interplay of the

COOH_{ads} stabilizing nanostructured Ag morphology, the fast PEDS by the highly proton conductive PFSA and the increase of local pH by OH⁻ species provided by the fast cathodic reactions (CO₂RR/HER), are responsible for FE_{CO} of more than 90% at current densities up to 300 mA cm⁻².

To investigate the stability of the Ag DHBT GDE under conditions relevant to industrial applications, we performed galvanostatic long-term measurements at 200 mA cm⁻² for a duration of up to 100 h (Fig. 9). Initially, during the initial 42 h, the GDE exhibited remarkably stable operating potentials with minor shifts of approximately 50 mV. In this phase of CO₂RR,

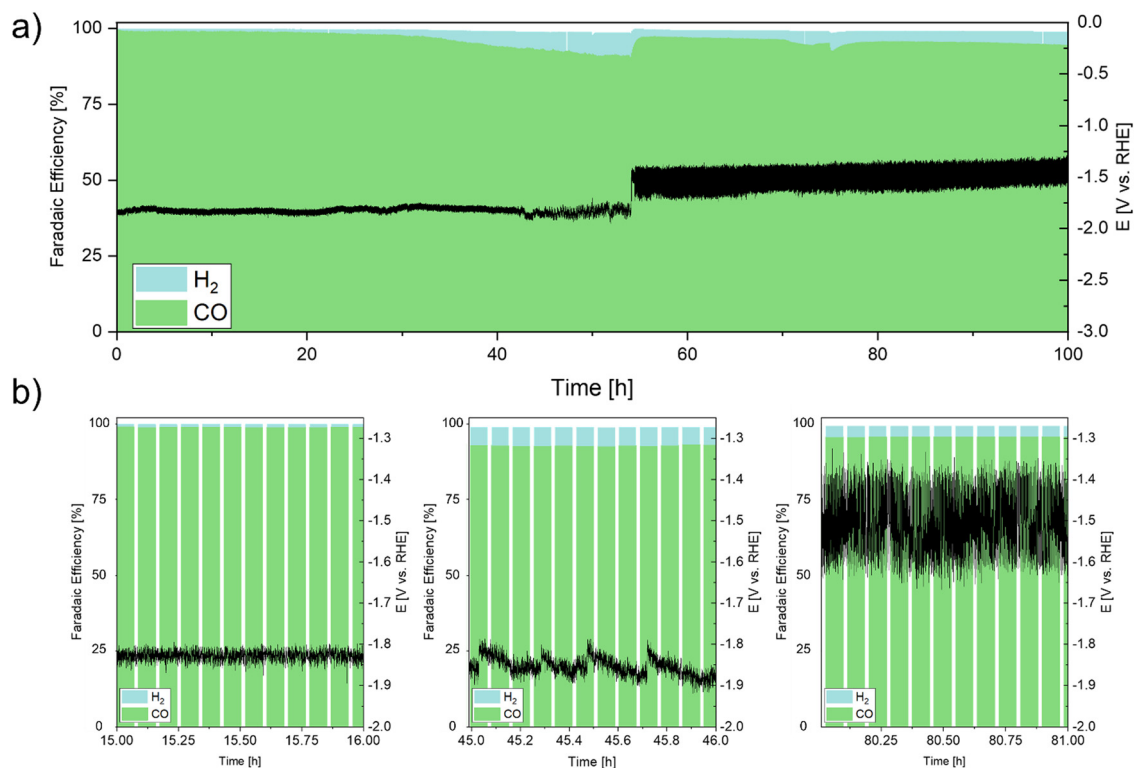


Fig. 9 Long-term stability tests of the DHBT-GDE in galvanostatic mode at 200 mA cm⁻² for 100 h. (a) WE potential without compensation and normalized FE of the only detected products over 100 h, (b) WE potential and FE of 1 h of operation each, during three different operating stages.



by crystallization on the surface of the GDL due to shielding effects that limit the evaporation of water between isolated salt crystals and their porous and hygroscopic nature, which pumps the electrolyte through its structure *via* capillary forces. Consequently, gas diffusion pathways in the electrode pores are blocked by precipitated salts, which consume CO_2 and form bicarbonates through reactions with the carbonate deposits.⁵⁰ Jeanty *et al.*⁷⁴ demonstrated the importance of preventing the gas chamber from flooding and how the degree of turbulence and the amount of gas movement in the gas chamber can be improved, leading to optimised long-term stability of CO_2 electrolysis by avoiding salt deposits.

4. Conclusions

We demonstrated a simple and rapid fabrication process for Ag-based GDEs by combining pulsed DHBT of Ag catalysts with ionomer infiltration. Before DHBT, a sputtering process was necessary to transform the insulating bipolymeric fibre fabric into a conductive substrate. The sputtered layer met the requirements for electrodeposition, leading to a conductive GDL that could withstand deposition currents up to 500 mA cm^{-2} without losing its porous character, which was essential for gas transport and distribution in the Ag foam catalyst structure during CO₂RR.

Galvanostatic deposition of Ag foams showed no advantage in electrode performance over sputtered Ag electrodes. Therefore, we switched from direct current DHBT to pulsed current DHBT and varied the pulse-to-pause ratios. The study revealed an efficient Ag deposition process resulting in high Ag mass deposition and high ECSA values while maintaining the porous foam structure by decreasing pulsing times. Linear sweep voltammetry tests showed a performance enhancement of about 200 mV at industrially viable current densities of PC DHBT electrodes compared to DC DHBT electrodes, resulting in slightly higher CO₂RR selectivity at galvanostatic CO₂RR operation. Increasing the operating current density required further electrode development, as HER became predominant for pure Ag foam electrodes at intermediate current densities. The incorporation of perfluorinated PFSA ionomer into the Ag foam GDE enabled efficient CO₂RR operation at high current densities of up to 500 mA cm⁻², while preserving a remarkable faradaic selectivity of 76% for CO production. This notable accomplishment positions the infiltrated electrode as a benchmark when compared to previous studies (Table S2, ESI†). In order to study the electrolyte distribution and the formation of the three-phase-boundary within the electrodes, operando analysis by synchrotron imaging should become the next step to gain more insights into electrolyte intrusion into the porous structure under operating conditions.^{72,75} These studies can help to improve electrode design by confining the pore structure during the manufacturing process and resulting in even better CO₂RR performance.

Future work will incorporate the study of high current density deposition on the structure-performance relationship

of the DHBT-GDE and the effect on the long term stability due to prevention of salt precipitations at the backside of the electrode, which needs to be improved to enhance the lifetime of the GDE. Additionally, we intend to present an extensive 4D depiction of electrolyte distribution. This will contribute to cultivating a profound comprehension of the exact localization of the three-phase boundary within porous Ag GDEs during CO₂RR operations, thereby enhancing our understanding.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Author contributions

Conceptualization, C. R., T. T. and I. M.; methodology, H. H. and S. L.; validation, H. H. and M. K.; formal analysis, M. K., and H. H.; investigation, H. H., M. K, J. O., S. L., B. E. and A. H.; resources, C. R., T. T. and I. M.; data curation, H. H., M. P.-R.; writing – original draft preparation, H. H., M. K.; writing – review & editing, H. H. and C. R.; visualization, H. H. and M. P.-R.; supervision, C. R.; project administration, C. R. and H. H.; funding acquisition, C. R., T. T. and I. M.

Conflicts of interest

The authors declare that they have no conflict of interest.

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