Investigation and Optimisation of Operating Conditions for Low-Temperature CO₂ Reduction to CO in a Forward-Bias Bipolar-Membrane Electrolyser

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The most recent investigations of operating conditions in a forward-bias bipolar-membrane zero-gap electrolyser using a silver cathode catalyst for the reduction of CO₂ to CO at low temperatures and near-ambient pressures are reported. First, the CO₂ electrolyser performance was investigated as a function of cathode feed humidification and composition. The highest CO partial current density was 127 mA cm⁻², which was obtained at an iR-corrected cell voltage of 2.9 V, a cathode feed humidification of 50%RH, CO₂ feed concentration of 90% and a CO Faradaic efficiency of 93%. The cells were tested continuously for 12 h at 3 V and 8 h at 3.4 V cell voltage to investigate system stability. While Faradaic efficiencies were maintained during the measurements at 3.0 V, a shift in selectivity was observed at 3.4 V, while a deterioration in current densities occurred in both cases. Using a specially designed electrochemical cell with an integrated reversible hydrogen reference electrode, it was found that the cathode catalyst is the main responsible for the observed loss in performance. It was furthermore determined via post-mortem SEM and EDX investigations that cathode deterioration is caused by catalyst agglomeration and surface poisoning.

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Rapid industrialisation and the consequent economic growth of humankind has led to ever faster rising atmospheric CO₂ levels over the last centuries, further contributing to an acceleration of climate change. While many nations have started phasing out electricity generation from fossil fuels and replacing them with renewable energy, challenges remain to be solved in the sectors of transportation, agriculture and heating.¹ Besides the efforts to reduce additional greenhouse gas emissions via technological change and efficiency improvements as well as implementation of carbon capture technologies at large point sources,² it has been forecast that reclaiming and upcycling atmospheric CO₂ through carbon capture and storage (CCS) as well as utilisation (CCU) technologies will be an important building block in the global efforts to reduce CO₂ levels and returning to more stable planetary conditions.^{1–4} One of the remaining challenges is to develop both economically as well as technologically feasible ways to capture and transform CO₂ into valuable chemical compounds.^{5–11}

Once CO₂ has been captured, it can be processed and transformed in low- or high-temperature electrolyzers, which have recently been compared by Küngas.¹² While low-temperature CO₂ reduction was initially performed in liquid-phase cells,^{13,14} more interest has recently been placed on the gas-phase CO₂ reduction reaction (CO₂RR) in order to overcome the limitations caused by the low solubility of CO₂ in aqueous solutions.^{15,16} Multiple different cell architectures for gas-phase CO₂RR have thus been developed, which can broadly be categorised into flow cells and zero-gap membrane-electrode assembly (MEA) cells.^{16–18} Recent advances in CO₂RR as well as the economic and environmental impact of cell design choice have recently been analysed comprehensively in literature.^{14,19}

Flow cells require a separation of the catholyte and anolyte flows by an ion exchange membrane, with the CO₂ being supplied in gaseous form and delivered to the active sites through gas diffusion electrodes (GDEs).^{17,20–38} The microfluidic cell, which is a special type of flow cell originally developed by the Kenis group, operates

with a single electrolyte flow between the electrodes.^{39–57} This design can optionally include an ion exchange membrane within the electrolyte flow to avoid product cross-over from cathode to anode and vice-versa.¹⁶ While flow cell designs allow for a good control of the pH environment at the active sites, stability concerns caused by flooding of the employed GDEs remain to be solved.^{14,16}

For this reason, some work has been conducted in MEA cell assemblies, which do not require electrolyte flows on the cathode at all and thus, the risk of GDE flooding is mitigated. In addition to this advantage, these systems furthermore exhibit lower overall ohmic resistances.¹⁴ Since acidic environments are not favourable for CO production,^{58,59} all-alkaline systems employing anionic exchange membranes (AEMs) are used, with silver being the preferred cathode catalyst.^{59–69} One significant disadvantage of these systems however is the diffusion of carbonate and bicarbonate species to the anode, resulting in a previously described CO₂-pumping effect, which diminishes the efficiency of the electrolyser and necessitates additional gas treatment steps on the anode.^{19,70,71}

One possibility to solve this issue is to employ a bipolar or bipolar-like membrane (BPM) to block the CO₂ transport to the anode.^{70,72} These membranes can be either used in the forward-bias or reverse-bias mode, with the alkaline or acid side facing the cathode, respectively.⁷³ BPMs have so far mostly been used in the reverse-bias orientation in flow cell-like electrolyser configurations for CO₂RR.^{53,72,74–76} The main purpose of the membrane in these applications is to increase stability of the pH and electrolyte concentrations on the respective electrodes.⁷⁵ The best results so far in terms of partial current density were reported by Salvatore et al., who employed an additional solid-supported aqueous electrolyte layer containing either NaHCO₃ or H₂O on the cathodic side to reach maximum current densities for CO production (*i*_{CO}) of roughly 110 mA cm⁻² at a moderate Faradaic efficiency for CO production (FE_{CO}) of 60%.⁵³ However, the reverse-bias operation is unlikely to be employed in a zero-gap MEA cell configuration considering that the acidic conditions are unfavourable for CO₂RR. Thus, in order to investigate CO₂ reduction using a zero-gap BPM electrolyser, the forward-bias operation appears to be more advantageous and should be further studied.

While it has been previously argued that this operation mode may lead to H₂O and CO₂ accumulation at the interface between the

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membrane layers, potentially causing membrane delamination over longer operating periods.⁷⁷ Shen et al. were able to show that these issues can be mitigated by using electrospun BPMs exhibiting a 3D junction.⁷⁸ However—as of now—research on the utilisation of forward-bias BPMs for CO₂RR has been limited to our own previous work.⁷⁰

With the presented investigations, we aim at increasing the understanding of zero-gap forward-bias BPM electrolyser operation for efficient CO₂ reduction to CO by analysing the impact of different process parameters on the electrochemical performance. The relationship between current density and cell voltage is identified for different cathodic feed gas relative humidities as well as gas compositions. Furthermore, stability measurements were conducted to study system behaviour over time. Additional measurements employing a reversible hydrogen electrode (RHE) were used to study the individual electrode potentials and their stability.

Experimental

Materials.—All CO₂RR experiments were conducted using silver nanoparticles (Ag-NPs, APS 20–40 nm from Alfa Aesar, CAS: 7440–22–4) as the cathodic catalyst material. The particle size distribution of this material was analysed using scanning electron microscopy (SEM) and the obtained results are summarised in Fig. S1 in the Supplementary Information (available online at stacks.iop.org/JES/168/043506/mmedia). H₂O electrolysis experiments were performed using Pt/C 47 wt% from Tanaka® (TEC10E50E) as the cathodic catalyst material. IrO₂-TiO₂ produced by Umicore® was utilised as the catalyst for the oxygen evolution reaction (OER) on the anode. Commercially available Pt/C coated gas diffusion electrodes (GDEs) were used for the operation of the reference electrode (0.4 mg_{Pt/C} cm^{−2} on Sigracet® 25BC GDE, Johnson Matthey®). The investigated BPMs were supplied by Fumatech® (FBM-PK, thickness of 130 μm) and rinsed with deionised (DI) water before electrochemical testing, without any additional treatment steps being required.

Different ionomer solution binders were prepared for the fabrication of acidic and alkaline catalyst layer inks, respectively.

Commercially available 5 wt% Nafion® solution from Sigma Aldrich® was used as acidic ionomer solution for the preparation of the anodic catalyst ink, while Fumion FAA-3 polymer from Fumatech® was employed as alkaline binder for the cathode catalyst ink. The alkaline polymer was exchanged from bromine to carbonate form before use by soaking it in a 0.5 M KHCO₃ solution for 12 h at ambient conditions. It was consequently rinsed with ultrapure water multiple times, filtered, and dried under vacuum before being used to prepare a 2.5 wt% ionomer solution in ethanol.

Electrode and membrane preparation.—In total three separate catalyst inks were prepared for cathode and anode. The first cathode catalyst ink comprised Ag-NPs and 8 wt% of FAA-3 ionomer, diluted in a 50–50 vol.% mixture of MilliQ® water and isopropanol and was used for the CO₂RR experiments. The second cathodic ink, which was utilised for the performed H₂O electrolysis experiments, contained Pt/C as the catalyst and 30 wt% of FAA-3 ionomer, diluted in an 80–20 wt% mixture of MilliQ® water and isopropanol as solvent. The anode catalyst ink consisted of IrTiO₂ and 10 wt% Nafion®, using a 80–20 wt% mixture of MilliQ® water and isopropanol as solvent.⁷⁹ The ink viscosities were optimised for the use in a fully automated Sono-Tek® ExactaCoat® machine, which was used to apply both cathode and anode catalyst layers.

The cathode catalyst layers were spray-coated onto commercial Sigracet® 29BC gas diffusion layers (GDLs) from SGL Carbon®, targeting catalyst loadings of 2 mg_{Ag} cm^{−2} for CO₂RR and 0.85 mg_{Pt} cm^{−2} for H₂O electrolysis, respectively. The anodic catalyst layer was directly applied onto the acidic side of the BPM and the catalyst loading in this case was 2.5 mg_{Ir} cm^{−2}. This was necessary since carbon-supported electrodes could not be employed due to the high anodic potentials, requiring the use of more stable titanium porous transport layers (PTLs), which could not be spray-coated directly. Schuler et al. recently developed a new multilayer PTL material to solve the issue of limited catalyst utilisation due to the coarse surface structure of currently available commercial PTLs.⁸⁰ It is based on sintering a titanium microporous layer (MPL) on top of a conventional PTL backbone structure. The resulting multilayer MPL-PTLs were used on the anodic side during all experiments presented here (Fig. 1(4b)).

Figure 1. Cross-section of the new in-house designed electrochemical differential cell, showing all critical cell components. (1a) Reversible hydrogen electrode (RHE); (1b) Swagelok fixing mechanism of the RHE; (2a) Movable flow field; (2b) Connection rod between movable flow field and spring-mechanism; (2c) Compression spring; (2d) Spring compression mechanism and housing; (3a) & (3b) Electric heating rods mounted in the steel end plates; (3c) Centring pins facilitating cell assembly; (4a) RHE-side flow plate with fixed liquid-phase flow field; (4b) Micro-porous titanium transport layer (MPL-PTL) for liquid environment; (4c) MPL-PTL spacer; (5a) Flow plate accommodating the movable flow field; (5b) Sealing backplate for the movable flow field.

CO₂ electrolyser cell design.—The employed CO₂ electrolyser single cell comprises an active area of 4 cm², was designed in-house as detailed in Fig. 1 and is based on a spring compression design previously described by Suermann et al.⁸¹ It consists of two gold-coated flow plates with machined flow fields and is heated by two electrical heating units (Figs. 1(3a) and 1(3b)), which are integrated into the two steel end plates of the cell. The flow field geometry for gas-phase operation was designed to ensure gas speeds high enough to remove potential liquid droplets, which may form during operation (flow speeds ≥ 10 m s⁻¹). The resulting design relies on a single serpentine flow field with a cross-section of 0.24 mm², while the flow fields for liquid-phase operation consist of five parallel channels with a cross-section of 2 mm² each (Fig. 1(4a)). A comparison of the different flow field geometries is shown in Fig. S2 in the Supplementary Information.

One of the flow fields was originally designed to be movable (Fig. 1(2a)) and connected to a spring-loaded mechanism (Fig. 1(2c)) via a gold-coated steel rod (Fig. 1(2b)), additionally acting as the electrical connector during experiments. The spring allows fixing the internal cell pressure, compensating for height differences caused by manufacturing deviations of the employed cell components, such as the MPL-PTLs. This feature has mainly been included for future tests requiring MPL-PTLs on both sides of a dual-side catalyst coated membrane (CCM) as well as thinner membranes, for which those deviations are more critical. As the GDE, which is employed on the cathode in the presented work, is compressible and can compensate minor height differences by itself, a fixed flow plate was used instead.

The cell is furthermore capable of employing an RHE reference electrode, allowing the deconvolution of cathodic and anodic electrode potentials. It consists of a 3D-printed body (Fig. 1(1a)), which is inserted into a corresponding chamber in the cell as shown in Fig. 1, and fixed in position as well as gas-tightened via a Swagelok connection (Fig. 1(1b)). A circular, commercially available Pt/C GDE is used as the reference electrode of the system and the electrical connection of the RHE is realised via two gold-coated wires with spring-loaded tips, which guarantee a reliable contact with the backside of the employed GDE. The wires are inserted into the 3D-printed body from the backside and glued into place during the initial assembly of the reference electrode.

During operation, the cell is fed with humidified gases on the cathodic, and liquid DI water on the anodic side, using a Bronkhorst® mass flow controller (MFC) and a Verder® gear pump, respectively. The cathodic outlet is connected to a Peltier-cooled water separator, reducing the humidity content in the gas mixture before it is sent to the detection systems. The anodic exhaust liquid-gas mixture is recirculated through a water storage tank, which allows for gas-water separation. The system is pressurised through Bronkhorst® back-pressure controllers, which are installed behind the gas detection systems on the cathode, and at the gas outlet of the water storage tank on the anode. The piping and instrumentation diagram (PID) of the employed test bench is depicted in Fig. S3 in the Supplementary Information.

Operation and conditions.—*Electrochemical measurements.*—Potentiostatic cell measurements were performed for cell voltages between 2.4–3.4 V, using a Biologic® SP-300 potentiostat. The high frequency resistance (HFR), which was recorded through electrochemical impedance spectroscopy (EIS) was used to determine the ohmic overpotentials of the analysed systems.

Another series of measurements was conducted employing the RHE described above. In this case, galvanostatic measurements were recorded with consecutive current steps between 10–400 mA cm⁻².

The cathode was fed with varying mixtures of CO₂/Ar at a flow rate of 20 ml_n min⁻¹ between 2.4–2.6 V and 50 ml_n min⁻¹ above 2.6 V. At the same time, the closed DI water loop was circulated on the anode with a flow rate of 25 ml_n min⁻¹. Humidification of the cathodic gas supply was realised by passing it through a water-bubbler, with the humidity level being fixed via temperature

Figure 2. Overview of the utilised experimental protocol for CO₂ reduction experiments. An initial humidification phase was used to ensure good membrane conductivity, while a conditioning phase at 10 mA cm⁻² was required to activate the system. Electrochemical impedance spectroscopy (EIS) was used to measure the high frequency resistance (HFR) of the system before, during and after the experiment.

differences between the bubbler and the electrochemical cell. The system pressure was kept constant at 1.1 bara and the operating cell temperature was 40 °C. The reference electrode was fed with 10 ml_n min⁻¹ of fully humidified pure H₂ at ambient pressure.

Measurement Protocol.—In order to ensure comparability between the different conducted measurements, a new cell was prepared for each investigated potential at each relative humidity and each CO₂ gas concentration on the cathode. A uniform experimental protocol was followed, as detailed in Fig. 2. The humidification phase including humidified gas and water flow through the system in the beginning of each measurement was required to improve the membrane conductivity. Next, the cell was conditioned for one hour at a low current density of 10 mA cm⁻² to activate the system. The subsequent continuous operation of the system lasted for four hours. The first data point, which is considered as the beginning of life, was recorded after 30 min and the last data point was recorded after four hours. In-between these phases, electrochemical impedance spectroscopy (EIS) was performed to obtain the high frequency resistance (HFR) and hence the ohmic resistance of the system.

Stability measurements.—Stability measurements were conducted at cell voltages of 3.0 V and 3.4 V for different CO₂ concentrations of the cathode gas feed. These experiments lasted between 8–12 h, while the initial humidification and conditioning phases detailed in Fig. 2 remained unchanged. Similar to the electrochemical measurements, the cells were operated at 1.1 bara, 40 °C and a constant cathode feed gas humidification of 50%RH.

To test the stability of the BPM as well as verify the calibration of the gas detection systems, long-term H₂O electrolysis experiments were performed for 18 h in addition to the CO₂RR investigations. The cathode was fed with 50–100 ml_n min⁻¹ of pure Ar and a humidification of 100%RH for this purpose, while liquid DI water was circulated on the anode as in all other experiments.

Gas analysis.—An Omnistar™ GSD 320 mass spectrometer (MS) from Pfeiffer Vacuum® was used for continuous gas detection on the cathodic side of the cell system. Previously, a multivariate calibration method was presented, which was used in all conducted experiments. It allows for signal deconvolution in the MS, which enables the simultaneous detection of CO₂, CO as well as N₂.⁸² Due to the well-studied selectivity of the employed Ag catalyst, the main products of interest were CO and H₂, which were measured in addition to the Ar background, residual CO₂ and N₂. A gas chromatograph (GC) from SRI Instruments® was employed in parallel to measure the produced CO and H₂ at an interval of 30 min, acting as an additional and continuous verification of the MS measurements. More details about the test bench PID can be found in Fig. S3 in the Supplementary Information.

Since both the MS and GC measure relative gas compositions, the aforementioned Ar background was crucial in quantifying the reaction products in the outlet gas stream, as it is not consumed

during the reaction. The inflow of the CO₂/Ar mixture was thus carefully calibrated for the different cathode gas supply compositions to allow a precise quantification of the primary product CO as well as the secondary product H₂. Based on this, the Faradaic efficiency (FE) for each product was defined according to the following expression:⁷⁰

$$FE_k = \frac{n_k \cdot (x_k/x_{Ar}) \cdot v_{Ar} \cdot F}{I} \quad [1]$$

where n_k denotes the number of electrons required to produce one mole of product k , x_k and x_{Ar} are the molar fractions (mol%) of the product and Ar background, respectively, while v_{Ar} is the known molar flow rate (mol s⁻¹) of the background, F is the Faraday constant (96485 C mol⁻¹) and I the total passed current (A).

The measured CO and H₂ concentrations within the product gas stream were between 0–7 mol% and 0–1 mol% during the CO₂RR experiments, respectively, with the analysed gas mixture being further composed of CO₂, Ar, and negligible traces of N₂. The measured H₂ concentrations during the conducted H₂O electrolysis stability tests ranged from 5–22 mol%.

Scanning electron microscopy (SEM) analysis.—The GDE surfaces were analysed using a Carl Zeiss® Ultra55 scanning electron microscope (SEM), which was used with an in-lens detector and employed a voltage of 3 kV for imaging. Additionally, an Apollo XV-SDD energy-dispersive X-ray (EDX) detector manufactured by EDAX® was employed at a voltage of 15 kV to determine the composition of the probed surfaces.

X-Ray diffraction (XRD) analysis.—The crystallographic structures of the GDE before and after CO₂RR were analysed via X-ray diffraction (XRD) measurements in a Smartlab Rigaku® system to determine possible changes occurring during cell operation. The measurements were performed in the Bragg Brentano mode with the source operating at 200 mA and 45 kV. The peak information for the detected Ag-NPs was taken from PDF card number 9008459, while the information on carbon was retrieved from PDF card number 9011577.

Results and Discussion

CO₂ electrolysis in bipolar systems.—When the BPM is employed in the forward-bias way, CO₂RR occurs at the cathode in alkaline conditions in competition with the hydrogen evolution reaction (HER), while oxygen is evolved in an acidic environment on the anodic side (OER) as shown in Fig. 3 and summarised in Eqs. 2–4.

Additional chemical side reactions happen in the presence of excess CO₂ on the cathode, leading to bicarbonate and carbonate formation:

The formed anionic species migrate through the alkaline layer of the BPM to the interface, where they are recombined with H⁺ from

Figure 3. The bipolar membrane (BPM) cell is fed with CO₂ and H₂O on the cathode and liquid H₂O on the anode. CO₂ is reduced to CO, with H₂ being evolved in competition in the alkaline cathode environment, while O₂ evolution occurs on the acidic anode. OH⁻, bicarbonate and carbonate species react with protons at the pH interface in between the layers of the BPM and form H₂O as well as CO₂.

the anode and form CO₂ as well as H₂O:

The typical cell performance of the zero-gap BPM CO₂ electrolyser at 50%RH and 50% CO₂ concentration of the cathode feed gas is shown in Fig. 4, with each of the displayed setpoints representing one or multiple individual cells that were tested. While the FE_{CO} is relatively low at 50% below 2.6 V, a plateau of high FE_{CO} is observed between 2.8–3.2 V with values ranging between 80%–85%. It then slightly drops to 73% at a cell voltage of 3.4 V as the HER starts taking over. Investigating the iV-curves, it can be seen that a maximum of 119 mA cm⁻² was reached at 3.4 V, with an i_{CO} of 88 mA cm⁻².

Comparing these benchmark results of the system to previously reported literature, it can be summarised that the obtained FE_{CO} at these cell voltages exceed most previously reported values.^{53,75,76} Current densities are in the same range of comparable studies employing BPMs in a flow-cell like configuration,⁷⁴ but still fall short of the highest reported i_{CO} of 110 mA cm⁻² by Salvatore et al.⁵³ Comparing these results to the limited literature on zero-gap BPM CO₂ electrolysers, it becomes evident that significant improvements were possible both in attainable FE_{CO} and partial current densities for CO production.⁷⁰

The dynamic operation of a CO₂ electrolyser is complex, resulting in many parameters having to be carefully investigated and optimised to maximise CO production efficiency. Following these promising first results, the investigations aimed at determining the influence of relative humidity and composition of the cathodic feed gas on the electrochemical performance as well as identifying the optimal operation point for the zero-gap BPM CO₂ electrolyser.

Relative humidity investigations.—The presence of H₂O in the electrochemical system is of great importance both for proper humidification of the BPM as well as for the CO₂RR itself, according to Eq. 2. For this reason, a closer investigation of the H₂O influence on performance is needed with some first experimental results about the impact of cathode flooding on CO₂RR in an all-alkaline MEA cell having recently been published by Reyes et al.⁶⁷ Since the

Figure 4. Performance overview of the zero-gap bipolar membrane CO₂ electrolyser. (A) illustrates the dependence of Faradaic efficiencies (FEs) for CO and H₂ on the cell voltage. (B) shows the total current density of the system against the cell voltage as well as the iR-corrected cell voltage.

BPM system is more complex, some initial conceptual considerations are required before investigating this phenomenon experimentally.

Conceptual description of the system H₂O balances.—All H₂O flows that potentially contribute to a complete H₂O balance of the system are illustrated in Fig. 5 with all relevant processes labelled as [A]–[L]. On the cathodic side, H₂O is supplied in gas-phase to the system via the inlet [A], while it leaves the cathode via the outlet [B] either in a gas or in a mixed gas-liquid stream, depending on consumption, production, and H₂O flows within the cell. The anode side is fed via a closed H₂O loop [C], which also includes a reservoir tank. H₂O is consumed during the OER on the anode [D], and in the CO₂RR as well as in the HER on the cathode [E]. We have previously shown that most OH[−] ions form bicarbonate in the presence of excess CO₂ and most, if not all bicarbonate species further react to form carbonate, releasing H₂O in the process, according to Eq. 6.⁷⁰ This process thus constitutes a significant source of H₂O formation on the cathode [F]. The remaining

bicarbonate and OH[−] ions are transported together with the carbonate species through the AEM to the internal interface of the BPM, where they react with H⁺ from the anode and form additional H₂O [G]. Protonic drag [H], which is more pronounced at higher current densities may be experienced in this process as well, transporting additional H₂O from the anode to the BPM interface. Some of the gaseous H₂O on the cathode can enter cell cavities [I], such as gaps around the optional movable flow field, condensate and be removed from the process. Additionally, H₂O can directly diffuse to and through the BPM membrane from both cathode and anode sides [J]. H₂O can leave the interface between the BPM layers through diffusion to either the cathode, the anode or in plane out of the system [K]. Due to the liquid environment on the anode and the resulting concentration gradient, it is likely that a net flux of H₂O to the cathode will be observed, further contributing to potential flooding of the active sites there. Finally, since the RHE reference electrode is placed closely to the MPL-PTL on the anode, H₂O can migrate in plane into the RHE chamber and leave the system [L]. Considering all these flows, simplified molar flow H₂O balances can be formulated according to the following expressions:

$$\text{Cathode: } \dot{n}_A + \dot{n}_F + \dot{n}_{K_Cath} = \dot{n}_B + \dot{n}_E + \dot{n}_I + \dot{n}_{J_Cath} \quad [10]$$

$$\text{BPM interface: } \dot{n}_G + \dot{n}_H + \dot{n}_{J_Cath} + \dot{n}_{J_An} = \dot{n}_{K_Cath} + \dot{n}_{K_An} + \dot{n}_{K_InPlane} \quad [11]$$

$$\text{Anode: } \dot{n}_{C_In} + \dot{n}_{K_An} = \dot{n}_{C_Out} + \dot{n}_D + \dot{n}_H + \dot{n}_{J_An} + \dot{n}_L \quad [12]$$

The used notations are listed and further explained in Table S1 in the Supplementary Information. Mathematical modelling combined with additional experimental work will be required to increase understanding on how to better control and optimise humidity levels within the BPM electrolyser and improve overall CO₂RR performance. A mathematical model investigating transport effects in gap-cells was recently published by Reinisch et al.⁸³

Relative humidity of cathode gas feed.—Following the conceptual considerations of the H₂O influence on cell performance, it becomes apparent that the relative humidity of the cathode feed gas is one of the key operating parameters and its influence was thus investigated first. For this purpose, a sensitivity study was performed at 0, 50 and 100%RH, respectively, and the obtained results are summarised in Fig. 6.

High FEs for CO production are observed at the beginning of life between 2.8–3.4 V, with the 50%RH cell at 3.2 V exhibiting the highest measured FE_{CO} of 85%. Both 0%RH and 100%RH showed significantly lower FEs below 3.0 V as well as slightly inferior values at higher cell voltages compared to the benchmark system described above. The total current densities at 50 and 100%RH and

Figure 5. H₂O flows to consider in a complete H₂O balance of the bipolar membrane (BPM) electrolyser system are shown and described. [A] Cathodic inlet; [B] Cathodic outlet stream; [C] Anodic liquid circulation loop; [D] H₂O consumed in OER; [E] H₂O consumed in CO₂RR and HER; [F] H₂O formed during carbonate formation; [G] Diffusion of OH[−], bicarbonate and carbonate to the BPM interface and subsequent formation of H₂O; [H] Protonic drag causing H₂O transport from the anode to the BPM interface; [I] H₂O diffusion into cell cavities; [J] Diffusion of H₂O to the BPM interface; [K] Diffusion of H₂O formed at BPM interface to cathode, anode or in plane; [L] In plane migration of H₂O to the reference electrode chamber.

Figure 6. Overview of relative humidity and cell voltage influence on current density as well as Faradaic efficiencies (FEs) for CO and H₂ production in a bipolar CO₂ electrolyser. (A) shows the influence of cathode feed humidification and fixed cell voltage on the FEs of the target products CO and H₂. (B) illustrates the corresponding current densities vs the iR-corrected cell voltages. (C) shows the development of FEs after four hours of operation. While FEs remain high for lower relative humidities, a decrease in CO selectivity is observed at 100%RH. (D) illustrates a drastic decline in current densities after four hours.

3.4 V cell voltage were 119 and 117 mA cm⁻², respectively, which is twice as much as the only 54 mA cm⁻² recorded at 0%RH. This is due to the fact that sufficient humidity is needed at the cathode for both the CO₂RR as well as for proper membrane humidification. When the cathodic side is fed with dry gas, the required H₂O must first diffuse through the membrane, hindering efficient operation. Investigating the iR-corrected cell voltages, it can be seen that the 50%RH cell at 3.4 V achieves slightly higher current densities at an almost 0.1 V lower iR-corrected cell voltage than the cell operated at 100%RH.

Comparing these results with the ones obtained after four hours of operation, major changes were observed in both FEs and current densities as illustrated in Figs. 6(C) and 6(D). While the FE_{CO} remained more or less constant between 2.8–3.4 V for 0%RH and 50%RH and even increased to 90% at 3.2 V for the 50%RH cell, a significant drop was observed in the cells operated at 100%RH.

As discussed in the previous section, almost all OH⁻ ions are transformed into CO₃²⁻ in the presence of excess CO₂ on the cathode, releasing significant amounts of H₂O according to Reaction (6), which results in excess humidity, liquid droplet formation and ultimately cathode flooding in the case of a fully humidified cathode gas feed. Because of this, all H₂O previously consumed in the CO₂RR is effectively recovered on the cathode. Additionally, the formed CO₃²⁻ and the remaining minor amounts of OH⁻ and HCO₃⁻ are transported to the interface of the BPM (Fig. 5[G]), forming significant amounts of H₂O there as well (Reactions (7)–(9)). The amount of the produced H₂O in these reactions is directly proportional to the current passed through the system and thus H₂O management becomes more important at higher current densities. Due to the concentration gradient between the liquid anode and the gas-phase cathode, this interfacial H₂O is likely to diffuse to the cathode, further contributing to the abundance of H₂O there. The only true consumption of H₂O at the

cathode occurs during the HER reaction (Fig. 5[E]), which is minor compared to CO₂RR at higher cell voltages as shown in Fig. 6. The cathodic outflow (Fig. 5[B]) remains the only practical option for humidity removal from the cathode side of the system. Because of the continuous additional H₂O production and H₂O diffusion to the cathode, the maximum vapor pressure is exceeded, liquid droplets form, and ultimately flooding effects occur, facilitating HER over CO₂RR.

The measured HFR of the analysed systems were between 4.5–10.1 Ω cm² at 0%RH, 2.0–8.0 Ω cm² at 50%RH and 2.2–5 Ω cm² at 100%RH, with the lower values being observed at higher cell voltages. As discussed above, higher current densities are observed at higher potentials, leading to an increased amount of H₂O formation at the BPM interface as well as on the cathodic side. Consequently, the resistance of the system is reduced because the additional humidity improves the conductivity of the membrane. Detailed HFR values depending on the cathode gas supply humidity are shown in Fig. S4 in the Supplementary Information.

Another observed effect was a decrease in current densities over time at all investigated relative humidities as detailed in Fig. 6(D). This could either be caused by catalyst deactivation, membrane deterioration or combined effects. Among the compared cells, the 50%RH cells exhibit the highest remaining current densities, with a maximum of 49 mA cm⁻² at 3.4 V, compared to 38 mA cm⁻² at the other humidity set points. The FEs at 2.4 V and 2.6 V could not be determined reliably after four hours of operation as the decline in current density was too great, causing only minor CO and H₂ production and hindering the precise measurement via MS and GC. Consequently, all further investigations were conducted between 2.8–3.4 V.

These experiments have shown that a cathodic feed gas humidity of 50%RH allows balancing the different requirements of the cell

Figure 7. Overview of the dependence of Faradaic efficiencies (FEs) and current density on the CO₂ concentration in the cathode feed gas stream with a constant relative humidity of 50% for all cells. (A) shows that FE_{CO} increases with higher CO₂ concentration, and (B) current densities increase at the same time as well. Graph (C) illustrates that no significant change in the FEs is observed after four hours of operations, however a drastic decline in current densities is observed (D).

system. First it ensures sufficient H₂O availability for the electrochemical reactions as well as for a good membrane conductivity through proper humidification. Second it makes sure that any additional H₂O on the cathode can be transported out of the system in gas phase rather than as liquid droplets, which would cause flooding of the active sites on the cathode. For these reasons, 50% RH was chosen as the fixed relative humidity for all further experiments.

Influence of CO₂ concentration.—Higher CO₂ concentrations are hypothesised to increase reactant availability on the catalyst surface and thus boost the attainable current densities for CO production. To verify this assumption, the influence of the cathodic gas stream composition was evaluated by varying the CO₂ concentration between 25–90 vol% in Ar and the results are summarised in Fig. 7. Since the inert Ar does not participate in the cathodic reactions, its molar flow rate remains constant, which is used to calculate the molar flow of the product gas streams needed for the calculation of the FE_{CO} and FE_{H₂} according to Eq. 1, respectively.^{70,82} A minimal Ar background was thus required and no experiments were performed using a pure CO₂ cathode feed. Following the hypothesis mentioned above however, CO₂RR performance is expected to be higher at 100% CO₂ compared to the tested 90%.

The results at the beginning of life show that an increased CO₂ concentration on the cathode side enables both higher FEs for CO production (Fig. 7(A)) as well as increased attainable current densities (Fig. 7(B)). A maximum FE_{CO} of 96% was obtained at a cell voltage of 3.0 V and a CO₂ concentration of 90%, while the maximum i_{CO} was 127 mA cm⁻² with a FE_{CO} of 93% at 3.4 V cell voltage (2.9 V iR-corrected) and the same cathode feed concentration. While literature on all-alkaline MEA CO₂ electrolyzers report

similar^{64,65,67} and even higher^{61–63,66} partial current densities for CO production, these systems suffer from CO₂ formation on the anode, leading to decreased efficiency as well as increased operational and investment costs of the overall system.^{19,70} As discussed above, BPMs have so far only been employed in flow-cell type configurations for CO₂ reduction. Comparing the obtained results to literature on these systems, improvements in both maximum i_{CO} as well as FE_{CO} were achieved.^{53,70,72,74–76} A lower CO₂ concentration not only leads to a decreased selectivity towards CO production with a maximum FE_{CO} of only 83% at 3.0 V, but also reduces the attainable current densities to 91 mA cm⁻² at 3.4 V and an i_{CO} of 63 mA cm⁻².

Investigating the resistance of the system, similar values were observed for all different CO₂ concentration between 2.0–8.0 Ω cm², with the lower values again being recorded at higher cell voltages. Further details can be found in Fig. S4 in the Supplementary Information.

After four hours of operation, FEs for CO are maintained for all tested systems, with the 90% CO₂ feed gas concentration cells continuing to exhibit superior values at all tested cell voltages (Fig. 7(C)), while the observed current densities were significantly reduced once more (Fig. 7(D)). While a clear correlation could be seen between concentration and attainable current density in the beginning of the cell experiments, the current densities after four hours of operation appear to be independent of the cathode feed gas composition. This is another indicator that either electrocatalytic activity is lost or the membrane stability is compromised, which leads to the partial pressure of CO₂ at the cathode no longer being the determining factor for the reachable current density. Additionally, the obtained results show that the performance deterioration is more pronounced at higher cell voltages compared to the lower ones.

Figure 8. Stability measurements were performed at fixed cell potentials of 3.0 V and 3.4 V for different cathode feed gas concentrations. (A) While Faradaic efficiencies (FEs) for CO stayed constant at the lower cell voltage, (B) shows that current densities for all systems converged towards 20 mA cm⁻². (C) FE_{CO} decreased significantly at the higher cell voltage, which was coupled with an increase in FE_{H₂}. (D) illustrates a more rapid deterioration of measured current densities at the higher cell voltage for all tested systems and a convergence towards 17 mA cm⁻².

CO₂ electrolyser stability measurements.—In order to understand the deterioration effects discussed in the previous sections and investigate the cell performance more closely over a longer time, stability measurements were conducted at 3.0 V and 3.4 V for the same three cathodic feed gas concentrations described above. The cells were continuously operated for 12 and 8.5 h, respectively, and the results are summarised in Fig. 8.

The FE_{CO} remained stable during the entire operation at 3.0 V for all different cathode feed concentrations with values between 85–98%, while a drastic decline from 70–95% to around 50% was observed over time for all tested cells at 3.4 V. In the latter case, FE_{H₂} increased at the same time, indicating a shift in product selectivity. Investigating the total current densities, it can be concluded that, while initially higher CO₂ concentrations allow higher current densities at 3.0 V, all tested cells converge towards 20 mA cm⁻² after 12 h of operation. A similar trend was observed for the 3.4 V stability measurements, however here a much steeper decline from values between 150–90 mA cm⁻² to current densities around 17 mA cm⁻² was observed. These results further confirm that the extent of deactivation is proportional to the applied potential, explaining the more pronounced performance loss at 3.4 V.

Membrane stability and detection system verification.—As previously mentioned, either membrane stability or catalyst deactivation could be causing the observed deterioration. In order to first verify the membrane stability in the utilised orientation, H₂O electrolysis stability measurements were conducted for 18 h at constant cell voltages of 2.7 V, 3.0 V and 3.4 V, respectively. The obtained current densities as well as the HFRs of the systems are shown in Fig. 9 and compared to the corresponding CO₂RR stability measurements with a 90% CO₂ feed at 3.0 V and 3.4 V, respectively. The calibration and proper operation of the gas detection systems

were furthermore verified during H₂O electrolysis and the obtained FEs for the only expected product H₂ are shown in Fig. 9(C). The current density increased from below 250 mA cm⁻² after one hour of operation to roughly 385 mA cm⁻² after nine hours at an applied cell voltage of 2.7 V, presumably due to an improved conductivity of the membrane through proper membrane humidification. It then declined to a stable performance of 345 mA cm⁻² after 18 h, as some potential deterioration effects started appearing. A maximum current density of about 1000 mA cm⁻² was reached after 4.5 h at a cell voltage of 3.0 V, with the current density continuously declining for the remaining measurement duration towards roughly 700 mA cm⁻² after 18 h. The maximum recorded current density at 3.4 V finally was 1470 mA cm⁻², which was reached after 2 h and it then continuously declined to values around 950 mA cm⁻² in the end of the stability measurement. The current densities were thus reduced from the respective highest values by 11% at 2.7 V, 30% at 3.0 V and 35% at 3.4 V upon completion of the 18 h stability measurements. The current densities observed during CO₂RR stability testing in contrast were reduced from the maximum currents by 51% at 3.0 V and 89% at 3.4 V after much shorter operating times of 12 and 8.5 h, respectively. Investigating the HFRs shown in Fig. 9(B) revealed a slight increase in resistances for all three operating cell voltages in the case of H₂O electrolysis, while HFRs tended to decrease or remain relatively constant for CO₂RR. As the higher current densities observed in the former case led to more H₂O being evolved at the bipolar interface, improved membrane conductivity is hypothesised to cause the significantly lower overall HFRs observed in the H₂O electrolysis systems. However, as these products accumulate at the interface and struggle to diffuse towards cathode and anode, gradual delamination of the membrane is hypothesised to cause a slight increase in the HFRs over time. Nevertheless no abrupt drop in performance was observed during the

Figure 9. Membrane stability was tested via potentiostatic H₂O electrolysis measurements at cell voltages of 2.7 V, 3.0 V and 3.4 V over continuous operation of 18 h. (A) shows the obtained current densities as well as the results of the corresponding CO₂RR experiments. (B) illustrates the trends in the HFRs over time for both H₂O and CO₂ electrolysis, while (C) depicts the obtained Faradaic efficiencies (FE) for H₂ production over time, which stayed within a 5% margin around 100%.

H₂O electrolysis experiments, which would have been an indication for severe membrane delamination effects. Fig. 9(B) furthermore shows that the measured HFRs as well as their trends over time are more or less the same during the last 10 h of the H₂O electrolysis experiments, indicating that they are independent of the measured current densities as well as the applied cell voltages.

The obtained FEs for H₂ remained within a variation margin of ± 5% around 100% during the entire stability investigations. These results confirm that both membrane stability as well as detection accuracy are adequate for the conducted and reported experiments, since both the duration as well as the sustained current densities far exceeded what was observed and tested during the CO₂RR experiments. It can thus be concluded that membrane deterioration or delamination is not the cause of the observed loss in cell performance.

Electrode stability.—Reference electrode measurements.—To investigate the potential catalytic deactivation of the respective electrodes, an additional set of measurements was performed, utilising the RHE reference electrode in the acidic environment close to the anode to measure the electrode potentials separately during galvanostatic operation. The cathodic and anodic electrode stabilities were investigated at multiple different current density steps between 10–400 mA cm⁻², which were consecutively measured without building a new cell for each setpoint. Most of the current steps were held for 30 min, with the exception of the first and fifth steps at 10 and 125 mA cm⁻², respectively. While the former was extended to one hour to allow for proper stabilisation of the system after the initial activation phase, the latter was when the cathodic potential drift was first observed, and thus longer operation was chosen to study this initial deterioration phase before moving to

higher current densities. The obtained electrode potentials, the corresponding FEs for CO and H₂ as well as the electrode iV-curves are shown in Fig. 10.

The cathodic electrode potential has been corrected for the pH difference between the alkaline and acidic layers of the BPM. Considering the pH stability of the BPM material itself, as provided by the manufacturer (stability range pH 1–14), the acidic layer pH is estimated to be 1, while the pH of the alkaline layer is 9 due to the excess of CO₂ during operation, resulting in a pH difference of about 8 between the layers. The resulting remaining potential drop occurs at the interface between the BPM layers and is also shown in Fig. 10. The calculations involved in the pH-correction are discussed in chapter S6 in the Supplementary Information.

The obtained results indicate a deterioration of the cathode performance, as its potential started to drift at a current density of 125 mA cm⁻², while the anodic potential only marginally increased between current steps and otherwise remained stable as shown in Fig. 10(A). The FE_{CO} remained high up to 100 mA cm⁻² as shown in Fig. 10(B), confirming the results shown before. Above this point, a rapid decline in CO selectivity was observed, with H₂ already taking over slightly above 125 mA cm⁻². This indicates that the deterioration of the cathode had already started to influence the results, as the previously reported *i*_{CO} could not be reached anymore. Comparing the iV-curves of the two electrodes in Fig. 10(C) shows that a much larger increase in cathodic potential is required to increase current density, compared to the necessary increase in anodic potential. This further confirms the finding that the cathode is the limiting electrode of the overall process.

Summarising these results, it can be concluded with confidence that the deterioration in cell performance is caused by a loss of

Figure 10. A reversible hydrogen electrode (RHE) was employed to measure the cathodic and anodic potentials and study their behaviour during operation. (A) illustrates the electrode potentials over time and at different current densities, with a clear increase in cathodic potential observable from 125 mA cm⁻² onwards. (B) Faradaic efficiencies (FEs) for CO and H₂ are shown depending on cathodic potential as well as the corresponding current density. (C) shows the cathodic and anodic iV-curves as well as the potential drop at the interface of the two bipolar layers and the overall cell voltage.

catalytic activity on the cathode, while the anode exhibited a stable operation at all tested current densities.

SEM/EDX analyses.—To further investigate the identified cathode degradation, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were used to analyse and compare the surface structure of the cathode GDE before and after cell operation. The newly coated GDE exhibited the same surface structure as the utilised Ag-NPs themselves and remained unchanged and stable during compression of the cell components as illustrated in detail in Fig. S5 in the Supplementary Information.

The surface of the cathode GDE exhibited a fine nano-structure before electrochemical operation as is depicted in Fig. 11(A). 2D EDX mapping measurements were performed on a newly prepared GDE to confirm that this structure was composed of Ag-NPs, which are evenly distributed on the surface of the GDL backbone. The obtained mapping results are shown in Fig. S6 as well as Fig. S7 in the Supplementary Information. The morphology of the surface shown in Fig. 11(A) mainly results from the GDL itself, which was analysed using SEM/EDX as well and is illustrated in Fig. S8 in the Supplementary information. Large particles covered with an

adsorbed surface layer were visible at the end of the stability tests, as shown in Fig. 11(B.1). EDX analysis was used in the attempt to identify the nature of these particles, however, their morphology changed under the electron beam, the surface adsorbates deteriorated, leaving behind large coalesced and agglomerated particles as illustrated in Fig. 11(B.2). The EDX results showed Ag being the main component of these agglomerates after the observed changes, which is further illustrated in Fig. S9 in the Supplementary Information.

Previous literature studies reported Ag poisoning by graphitic carbon, which was attributed to the further reduction of CO as the detachment of adsorbed CO from the two-phase interfaces would be quite difficult and the reduction of CO to C is thermodynamically possible.^{84–87} In the present case, however, other reaction intermediaries appear to be involved in the Ag poisoning since they are vanishing under the electron beam, which would not be the case for graphitic carbon. Carbonate species precipitation has also been reported to block flow channels and active sites on the cathode during CO₂RR.^{68,88} This phenomenon is mostly observed in flow cells as the carbonate present in such systems can interact with potassium cations from the electrolyte and consequently form salt

Figure 11. Comparison of cathodic catalyst layer before and after stability measurement. (A) shows a SEM picture of a newly prepared, spray-coated silver nanoparticle (Ag-NP) catalyst gas diffusion electrode (GDE) with the Ag-NPs evenly covering the gas diffusion layer (GDL) in a fine-grained structure and the morphology resulting from the GDL itself. (B.1) illustrates the surface changes occurring during operation with large particles (diameters on the order of $1\ \mu\text{m}$) being visible, indicating coalescence and growth of larger catalyst particle agglomerates. Furthermore, surface poisoning of the agglomerates is visible as a white covering of the agglomerated particles, which deteriorates under the electron beam, only leaving behind the agglomerates themselves shown in (B.2).

Figure 12. (A) shows the scanning electron microscopy (SEM) investigations of a gas diffusion electrode (GDE) employed in CO_2RR , which was soaked in deionised water and subsequently dried before the performed analysis. Large particles similar to the ones shown in Fig. 11(B) are present, with their surfaces being covered once more by surface adsorbates, which are not stable under the electron beam. (B) shows the SEM image of a post-mortem Pt/C GDE employed in a performed H_2O electrolysis experiment. Neither catalyst agglomeration nor surface poisonous species could be detected in this case.

precipitation. This is however less likely to occur in a zero-gap cell since the abundance of these cations is much lower in this case due to the absence of a liquid electrolyte on the cathode. While this might still be a suitable explanation for the observed effects, it is currently unclear whether such precipitates could be analysed using the employed techniques or if they would deteriorate as it has been observed in the presented investigations.^{89–91} SEM analyses of a post-mortem Pt/C GDE employed during H_2O electrolysis showed some presence of potassium resulting from the ionomer binder in the cathodic catalyst layer, as illustrated in Fig. S10 in the Supplementary Information. This could be a potential source of positive counter ions required for the formation of potassium carbonate precipitation in the case of CO_2RR .

Additional SEM analyses were performed on a post-mortem GDE employed in CO_2RR , which was soaked in DI water and subsequently dried to determine whether the surface adsorbates were soluble in water, which would be the case for potassium carbonate species. The surface of a post-mortem Pt/C GDE, which had been used for the performed H_2O electrolysis experiments at 3.4 V, was furthermore probed to determine if the same surface changes would be present as in the case of CO_2RR . The obtained results from these two SEM investigations are illustrated in Fig. 12.

Figure 12(A) shows that surface poisonous species are still present after the pre-treatment described above, while no surface adsorbates are present on the Pt/C catalyst surface depicted in Fig. 12(B) at all. The adsorbates thus do not appear to be soluble in water, which would be the case if potassium carbonate precipitation were responsible for the degradation effects, while chemical membrane degradation was once again shown not to significantly impact the performed experiments as no surface adsorbates were visible on the GDE after H_2O electrolysis.

XRD analyses.—XRD measurements were consequently performed to understand potential crystallographic surface changes caused by CO_2RR operation and the obtained results are depicted in Fig. 13.

Neither structural crystallographic changes could be determined between the analysed fresh and post-mortem GDEs, nor any additional phases could be observed in the material bulk, which could have formed during cell operation. The crystallite size of Ag (111) was evaluated using the Scherrer equation and it was estimated to increase from 31 nm in the pristine GDE to 39 nm in the post-mortem GDE, representing a growth of around 25% during operation of the cell.

Figure 13. (A) X-ray diffraction (XRD) analysis of a newly prepared gas diffusion electrode (GDE) as well as for a post-mortem GDE (B), which was employed for CO₂RR, are shown. Silver was detected resulting from the employed catalyst (Ag-NPs), while carbon results from the gas diffusion layer (GDL) backbone itself. (B) shows the overlay of the first two Ag peaks and the slight difference in their broadness, which is caused by crystallite size changes from 31 nm to 39 nm during operation. These results are consistent with the average particle size of 35 nm, which was determined using scanning electron microscopy (SEM) as illustrated in detail in Fig. S1 in the Supplementary Information.

While additional studies are necessary to better understand the mechanism behind these effects, the performed surface characterisations clearly showed that the decline in cell performance is caused by the deactivation of the cathode catalyst layer through coalescence and agglomeration of the Ag-NPs as well as poisoning of the surface by adsorbed reduction intermediaries, which have yet to be identified.

Conclusions

The influence of the relative humidity and composition of the cathode feed gas on the current-potential relationship of a zero-gap BPM CO₂ electrolyser has been investigated alongside an evaluation of the Faradaic efficiencies for CO and H₂. While both too high and too little humidity on the cathode result in reduced performances due to insufficient humidification and flooding effects, respectively, it was shown that a relative humidity of 50%RH allows for optimal performance, ensuring proper humidification, while at the same time avoiding liquid droplet formation, which would lead to GDE flooding effects. A conceptual discussion on the importance of proper water management in the electrolyser was presented, identifying carbonate formation in presence of excess CO₂ on the cathode as well as diffusion of H₂O from the BPM interface to the cathode as the most important potential causes for cathode flooding.

Increased CO₂ concentrations on the cathode led to both increased FEs for CO as well as higher achievable current densities. The maximum recorded FE_{CO} was 96% at a cell voltage of 3.0 V and the maximum i_{CO} was 127 mA cm⁻² at a FE_{CO} of 93%. The utilised approach of using a forward-bias BPM system for CO₂RR is unique in the field and the obtained results are encouraging for the further development of this technology.

However, some challenges remain to be solved. Stability issues were identified within the employed system, which mainly resulted from instability of the employed commercial Ag cathode catalyst material. Long-term H₂O electrolysis experiments showed stable operation of the bipolar membrane in the forward-bias operation mode, while the employment of a 3D printed reference electrode confirmed the stable operation of the anode as well. Complementary SEM and EDX analysis confirmed microstructural changes, coalescence, agglomeration, and subsequent poisoning of the silver cathode catalyst layer. It was furthermore determined that these surface species were not soluble in water and not stemming from

chemical decomposition of the employed bipolar membrane material. Additional XRD investigations neither showed changes in the crystallographic structure, nor the appearance of new phases during cell operation. However, the crystallite size of the Ag-NPs was shown to increase from 31 nm to 39 nm during operation, constituting an increase of around 25%.

Additional research is encouraged to investigate the conceptually discussed H₂O management of the cathode and its effect on electrochemical performance in more depth. The uncovered stability issues should be further studied, understood, and overcome to bring this technology closer to implementation. As they are potentially caused by the cathode catalyst material itself, exchanging the commercial Ag with more stable alternatives should be considered as a first step. Additional X-ray tomographic microscopy analysis of cathodic flooding might in this context provide further insights into more rational MEA designs.

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