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Elucidating key mechanistic processes during acidic CO₂ electroreduction on gas diffusion electrodes towards stable production of formic acid



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ABSTRACT

The electrochemical reduction of CO_2 using renewable electricity could be a sustainable alternative to produce formic acid. Although using bulk acidic electrolyte offers system and downstream processing benefits, neutral to alkaline electrolyte systems prevail due to challenge suppressing hydrogen evolution in acidic environment. In recent years, it has been shown that HER could be mitigated by confining the OH^- being generated and constraining the movement of H_3O^+ towards reaction surface, thereby producing an alkaline reaction environment within the electrode. Herein, we have demonstrated how a porous and highly hydrophobic Bi-based gas diffusion electrode enables remarkably efficient bulk acidic electrolysis. Importantly, the local alkaline reaction environment has been proven via electrochemical impedance spectroscopy and pH visualization. Furthermore, optical monitoring of electrolyte conditions through a transparent cell sheds light on the CO₂ recovery process in the acidic system, promoting a better technical practice in handling with electrochemical cells and CO₂ recirculation. Finally, HCOOH accumulation as the key degradation reason is unveiled through investigation into the impact of operating modes on the stability at high current density, where earlier studies failed to adequately address. It is believed that this valuable insight could facilitate stable and efficient formic acid production in future work.

1. Introduction

Achieving a fast and thorough reduction of CO_2 emissions which is the most important greenhouse gas, is of paramount importance for climate protection. This can be accomplished by substituting fossil resources in fuels and chemical feedstocks with renewable energy carriers [1,2]. For a climate-neutral chemical industry, CO_2 from flue gas of certain industrial and biogenic processes or via direct air capture can be valorized as carbon source for the production of a variety of carbonbased materials and chemicals, thereby closing the carbon cycle. Electrochemical reduction of CO_2 has gained significant interest in the last years [3–5] as it has the potential to integrate renewable electricity and produce a wide range of products, including formic acid, CO, and C_{2+} products at ambient pressure and mild temperatures from renewable power [6,7]. Among those, formic acid is an attractive product as it is has a relatively high market price, can be produced at high selectivity and is used in various applications, e.g., as tanning agent in the production of leather, as coagulant for rubber or as an intermediate or ingredient in the pharmaceutical industry [8]. Besides, it is also argued to have great potential as sustainable feedstock in biotechnological processes [9] or as energy and hydrogen carrier [10].

Commonly, gas diffusion electrodes (GDEs) can be applied in the CO₂ electrolysis process to intensify the mass-transport of gaseous CO₂ to the electrocatalyst surface which enables a high partial current operation to the reduced products. This is due to its ability to facilitate intimate contact between gas, solid, and liquid through a porous partially wetted structure [11–14]. Typically, the following electrocatalytic reactions take place in alkaline solutions during CO₂ reduction to formate [15]: $CO_2 + H_2O + 2e^- \Rightarrow HCOO^- + OH^-; CO_2 + H_2O + 2e^- \Rightarrow CO + 2OH^-; 2H_2O + 2e^- \Rightarrow H_2 + 2OH^-$. Although promising performance has been demonstrated when choosing the right catalyst and reaction conditions, multiple intrinsic issues arise when using alkaline electrolyte

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for industrial production which negatively influences process economics and long-term stability. Under alkaline conditions, formate salt is mainly produced which needs to be further protonated to yield the desired formic acid product; a process which is both costly and environmentally problematic due to the generation of large amounts of salts during acidification. At the same time, CO2 dissolution and subsequent reactions with the alkaline electrolyte and generated OH⁻ leads to the accumulation of large amounts of (bi-)carbonate which needs to be regenerated to allow the economically favored recirculation of the electrolyte. If it precipitates within the GDE, the carbonate salt can block diffusion paths for CO₂, as well as deteriorate the GDE structure via nonuniform volume expansion [16-18]. Finally, anionic reduction products can migrate to the anode side when an anion exchange membrane (AEM) is used, causing an increase of overpotential for the oxygen evolution reaction (OER) and the loss of valuable product in the case of formate production [19].

Lately, a few publications have proposed strategies to suppress HER which is commonly favored in acidic environment. Gu et al. and Monteiro et al. conducted both experiments and theoretical modelling on commonly applied GDEs (based on tin oxide, gold, and copper) and demonstrated the possibility of suppressing HER via the introduction of alkali cations in acidic electrolyte. As a matter of fact, the outward migration force of anions from the cathode shrinks when alkali cations gather at the electric field shielded by outer Helmholtz plane. Similarly, it works by hindering the movement of hydronium ions towards the electrode surface for subsequent HER, while ensuring the stable existence of critical reaction intermediates through the altering of the electric field distribution in the double layer [20,21]. Importantly, Osskopp et al. demonstrated the possibility of using acidic electrolyte to produce formic acid at low pH on tin-based GDE, revealing the effect induced by different cell set-ups, while performing numerical simulations to elucidate the reaction environment within the GDEs. They hypothesize that the local generation of OH- and its accumulation within the GDE leads to locally alkaline conditions which are known to favor CO2RR over HER [22]. However, long-term stability of tin-based GDEs is problematic because of the reduction of its native oxide layer at negative potentials encountered in CO2RR leading to tin dissolution and redistribution within the GDEs as described by Bienen et al. In contrary, bismuth is active in both its oxide or metallic state which together with its high selectivity makes it a promising catalyst for this reaction, while fulfilling the requirement as to separate catalyst-, GDE- and systemspecific reasons for deactivation as it provides a stable catalyst in the evaluated time frame [15].

Yet, so far little work has been done to characterize mechanistic processes of CO2 reduction and stability performance on a bismuthbased GDE in acidic electrolyte up to industrial relevant currents and how it compares to alkaline conditions. Following the work and hypothesis postulated by Osskopp et al. mentioned above, this work aims to systematically reveal the similarities and differences via experimental evidences in an acidic and an alkaline bulk system. To this end, we combine product analysis and comprehensive electrochemical impedance spectroscopy (EIS) with process visualization through a transparent electrochemical reactor to get a better insight into the local reaction environment, CO2 utilization and recovery process in a well-functioning bulk acidic system. This comparison further includes the assessment of a wide range of aspects crucial for industrial application, particularly the product distribution and long-term stability of the electrolysis, the effect of local catalyst environment on macroscopic behavior, mitigation of non-faradaic CO₂ sequestration and the use of diluted CO₂ feed. Importantly, we performed a systematic analysis of degradation phenomena to show how to enable long-term stability and how it is challenged under typical process conditions encountered in laboratory studies.

2. Material and methods

2.1. Preparation of gas-diffusion electrodes

The same recipe to synthesis a type of carbon-supported bismuthbased catalyst was used as described in the past publications via an aqueous precipitation method [23,24]: 22.5 mL conc. HCl was first added to a slurry mixture made of acetylene black (13.6 g; Alfa Aesar, 100% compressed, 99.9+%), sodium dodecyl sulfate and water to create an acidic environment. Afterwards, the precursor Bi(NO₃)₃•5 H₂O (3.0 g; ≥98.0%, Carl Roth GmbH & Co. KG) was added. Then, pH value of the slurry mixture was adjusted slowly to alkaline environment by pouring in 1.0 M KOH and stirred continuously for 3 h at 90 °C. The final slurry was filtered, washed with 2 L of 18.2 M Ω ·cm milli-Q water and dried in an oven at 90 °C overnight. The catalyst powder was then mixed with 45% percentage of PTFE (Dyneon, TF 2053Z) and pressed into electrodes in a cylindrical mask with subsequent sintering process at 340 $^\circ C$ for 1 h to enhance the mechanical strength of the GDEs [25]. Further characterization details about the catalysts and GDEs can be referred in our past literatures [15,26].

2.2. Electrochemical measurements

All electrochemical measurements were conducted in a homemade plexiglass cell that consists of three electrodes, namely a platinum foil as anode, a gas diffusion electrode (GDE) as cathode and a reversible hydrogen electrode (RHE) as reference electrode (RE). At the anode oxygen evolution reaction was conducted and at the GDE CO₂ reduction reaction occurred with a geometric surface area of 3.14 cm^{-2} . For the alkaline electrolysis system, 1.0 M KOH was used on both the anode and the cathode side separated by an anion exchange membrane (AEM, fumasep® FAB-PK-130), whereas in the acidic electrolysis system 0.5 M H₂SO₄ and acidified 0.5 M K₂SO₄ (pH will be adjusted accordingly) were used on the anode and the cathode side, respectively, separated by a cation exchange membrane (PEM, Nafion[™] 211). All the electrolytes were prepared with 18.2 MΩ·cm milli-Q water. Unless otherwise stated, the inlet temperature was regulated at roughly 20 °C with a water bath through corrosion-resistance heat-exchangers, while anolyte and catholyte were pumped out of reservoirs with certain amount of electrolyte thorough the anode and cathode compartment in single-pass mode at a volumetric flow rate of 5 mL/min by an ICC digital pump (Ismatec Reglo ICC Digital Pump, 3-Channel, 8-Roller) as illustrated in Fig. 1a). In the meantime, the passing electrolyte was directly pumped out of the system and disposed after the reaction. During the measurements, the liquid product was extracted manually via three-neck valves and analyzed subsequently via an offline high-performance liquid chromatograph (HPLC, Agilent Technologies: 1260 Infinity II LC System, Column: Hi-Plex H, 7.7 \times 300 mm, 8 μ m) (cf. Eq. (S2)) if needed. The pH value at the electrolyte outlet on the cathode side was measured after each experiment in the acidic system with a pH-meter (LUTRON, YK). In the mode of electrolyte recirculation as stated in Fig. 1b), a 1 L reservoir is prepared for each side of the electrode with continuous pumping, while all the other settings remain the same. It is worth mentioning that samples need to be extracted at both the electrolyte inlet and outlet to determine the faradic efficiency of formate/formic acid (cf. Eqs. (S3,4)). The gas feed CO₂ (4.5, Linde) was supplied at a flow rate of 50.0 mL • min⁻¹by mass-flow controllers (Bronkhorst® EL-Flow Select) with a negligible pressure drop of a few mbars. Moreover, a 4.5 cm water column was equipped at the end of the pipelines to establish a back pressure towards the GDEs for a better performance. The outlet gas flow rate of the cell was measured with a bubble-meter which allowed a determination of the converted CO2 and formed product gases by an online gas chromatograph (µ-GC, Varian) (cf. Eq S1). N2 (5.0, Linde) was used as a joined flow to bring out all product gas remaining in the setup for a precise analysis. As for the electrochemical measurements, an electrochemical workstation (ZAHNER-Elektrik GmbH & Co. KG



Fig. 1. Sketch of the experimental set-up including electrolysis cell, separate anode (anolyte) and cathode (catholyte) electrolyte reservoirs, gas chromatography analysis of the outlet gas stream and HPLC analysis of the electrolyte product stream. Experiments were conducted in a) single-pass mode electrolyte feed passes through the cathode chamber once without re-circulation, b) electrolyte re-circulation mode: the electrolyte flows back to the operating system, and c) semi-batch mode: a fixed volume of electrolyte is provided in the beginning of the experiment. In all cases the anolyte is re-circulated, CO₂ is continuously fed to the back of the GDE.

Zennium) was used. All the galvanostatic electrochemical impedance spectra were taken from 10 mHz to 300 kHz with an excitation current of 10 mA.

During the measurement of general electrochemical performance, the polarization curves were recorded via a step-wise increase of current density in a 20-min interval from -50 up to -500 mAcm⁻². The faradic efficiencies (FEs) of gas products were measured on-line via GC based on the actual volumetric flow rate, whereas samples were taken from the electrolyte at both anode and cathode outlet (alkaline system) or only at cathode outlet (acidic system) for subsequent tests on HPLC. The EIS spectra were fitted with an equivalent electric circuit reported by Bienen et al. via the RelaxIS 3 software (rhd instruments GmbH & Co. KG) [26]. In the investigation of CO₂ conversion processes, a plexiglass cell equipped with a microscopic camera was used to monitor the gas formation, phase distribution, as well as the color trace in the electrolyte chamber. To further investigate the process of CO₂ recovery process, phenolphthalein solution (0.5 wt% in ethanol, Sigma-Aldrich) as pH indicator was added in a separate experiment under batch mode where all the inlets and outlets of electrolytes were blocked and the electrolyte not stirred as illustrated in Fig. 1c). In the part of elucidating the impact made by feed dilution, the flow rate of the total gas feed remains at 50.0 mL•min⁻¹ with the variation of volumetric fractions of CO₂ at 10, 20, 30, 50, 70, 100 vol% was applied during CP measurements. Among those, EIS spectra at 10, 30, 50, vol% of CO2 were taken and analyzed via the RelaxIS 3 software. During the assessment of stability performance, an industrial relevant current density at $-200 \text{ mA} \cdot \text{cm}^{-2}$ was applied to both systems. To further accelerate the degradation of GDEs, both the alkaline as well as the acidic electrochemical systems were supplied with

a CO_2 flow rate at 10 mL•min⁻¹ and an electrolyte flow rate of 2.5 mL/ min on both sides in the mode of electrolyte recirculation. The gaseous products were analyzed every 30 min till the end of the experiments, whereas liquid product was taken in vials for HPLC measurement at the beginning and the end of the measurement to close the FE balance, i.e., to prove that sole GC measurements on the bismuth-based GDEs can be performed assuming that the missing FE is only formic acid or formate salt.

The purpose of employing different measurement set-ups is to get a better understanding on how the electrolyte conditions affect the experimental outcome which as will be described later has a decisive role in mitigating degradation. Specifically, we used set-up a (singlepass mode) to exclude the impacts made by product accumulation on the experiments and particularly on long-term operation while set-up b (electrolyte re-circulation) aims to include the effect of product accumulation in the system. As for the measurement set-up c (semi-batch mode and unstirred), the motivation is to better visualize the product stream and pH regime flowing out of the GDE.

2.3. Physical characterization

Post-mortem characterization was carried out after the stability measurements to elucidate the structure and component changes of the GDEs via the scanning electron microscopy (SEM, Zeiss Crossbeam 350) equipped with an energy dispersive X-ray microscopy device (EDX, Oxford Ultim Max 100). The acceleration voltages were applied ranging from 15.0 to 20.0 kV. Ahead of taking images, a selection of GDEs was pre-treated through a nitrogen freezing procedure to fix the position of corresponding cations or anions within the electrode with subsequent sublimation of the frozen water under vacuum conditions [15].

To investigate the possible scenario of catalyst leaching into the bulk electrolyte during long-term electrolysis, measurements of bismuth in the electrolytes were conducted for catholyte at the beginning and the end of the experiments via inductively coupled plasma mass spectroscopy (ICP-MS). These measurements were carried out using the device XSeries2 from Thermo Fisher Scientific that is equipped with an argon plasma and a quadrupole for separation of elements by mass-to-charge. During sample preparation, the electrolytes were diluted by the factor of 10. Then, samples were acidified with concentrated nitric acid to reach a final acid concentration of 2 vol% (Rotipuran®Sup, Carl Roth). The internal standard lutetium was added with a final concentration of 1 mg L⁻¹ (ICP Lu standard solution, 1000 mg L⁻¹, Carl Roth, Germany). Calibration included Bi concentrations of 0.5, 1, 5, 7 and 10 μ g L⁻¹ (ICP Bi standard solutions, 1000 mg L⁻¹, Carl Roth, Germany) and ensured a correlation coefficient of at least 0.999.

3. Results and discussion

3.1. Revealing the reaction environment by electrochemical methods

The average faradaic efficiencies (FE) as function of current density obtained during CO₂ electrolysis with acidified $0.5 \text{ M} \text{ K}_2 \text{SO}_4$ (pH = 2.94) and 1 M KOH electrolytes (pH \sim 14) were measured on electrodes of the same manufacturing batch (cf. Fig. 2a). As can be seen, the overall formic acid or formate selectivity, respectively, is comparable in both cases ranging from 90 to 95 % over the entire current density region up to $-500 \text{ mA} \cdot \text{cm}^{-2}$, whereas CO starts to evolve up from $-100 \text{ mA} \cdot \text{cm}^{-1}$ and accounts for approximately 7% to 10% of the total current applied. These results are comparable with the ones obtained from earlier studies using the same type of GDE with tin-based catalysts [25] in moderately alkaline and bismuth-based catalysts [15] conducted in highly alkaline conditions, as well as measurements with tin-based catalysts [22] in bulk acidic electrolyte. It is important to note that the final product received from the acidic system is formic acid (pKa = 3.75) [22], with the outlet stream having a pH ranging from 2 to 3 measured at the cathode outlet. The remarkable selectivity towards formic acid in acidic environment is ascribed to locally alkaline conditions induced by OH accumulation (Eqs. (1), (2)) generated during the electrochemical reaction and its hindered transport from the reaction zone into the bulk electrolyte. The latter could be ascribed to the local confinement of OHand sufficient gas-liquid interface provided by the porous and highly hydrophobic GDE structure as can be seem from the SEM images (cf.

Fig. S1) [27]. As a matter of fact, Bi-based GDEs manufactured by drypressing process without solvent (refer to section 2.1) largely increase their hydrophobicity via melting of PTFE particles during subsequent heat treatment into homogenous network, which could not be achieved by other solvent-based methods [25]. Meanwhile, the introduction of alkali cation (K^+) might additionally facilitate the CO2R and suppress HER as suggested by the literature [20,21]. By the combination of the optimized GDE, the catalyst and the process conditions, highly efficient bulk acidic electrolyte is simultaneously achieved at high current density.

To assess mechanistic aspects of the GDE in the respective system, we start with an evaluation of the Tafel slope in both acidic and alkaline conditions. The potential of CO₂ electroreduction were recorded versus a reversible hydrogen electrode (RHE) at pre-defined current densities and converted subsequently to the SHE scales via Eq. (1) [28] with the standard hydrogen electrode potential E_{SHE}^0 , the gas constant R, temperature Т and the faraday constant F: $E_{\rm RHE} = E_{\rm SHE}^0 - 2.303 \bullet R \bullet T \bullet p H_{\rm Chamber} / F$ (Eq. (1)). As can be seen in Fig. 2b, the current voltage curves (vs. SHE) exhibit very similar behavior and are just slightly shifted in potential with comparable Tafel slope values of 97 mV/dec and 91 mV/dec in the acidic and alkaline electrolyte, respectively. Meanwhile, both values of Tafel Slope indicate an active Bi-based GDE for fast initial electron transfer to CO₂⁻ intermediates among previous studies [29].

To further investigate the mechanistic processes taking place during CO2 reduction, Electrochemical Impedance Spectroscopy (EIS) was applied to compare the alkaline and acidic conditions. Based on the work of Bienen et al. [26,30] who assessed the same type of GDE but with tin catalyst under alkaline bulk conditions, an equivalent circuit model (ECM) can be constructed that consists of an inductance, an ionic resistance, and a series of two constant phase element and resistance in parallel representing the charge transfer reaction ($CO_2 + e^- \Rightarrow CO_2^{\bullet-}$) and presumably the preceding chemical equilibrium of bicarbonate anion formation (CO₂ + OH⁻ \rightleftharpoons HCO₃⁻). In our case, the configuration of the impedance spectra recorded in the identical bulk alkaline condition agrees well with the work from Bienen et al. on Sn-based GDEs [26] indicating that despite the different catalyst, the same ECM can be used for its analysis. As a matter of fact, an identical EIS also implies that the second process exists during bulk acidic electrolyte (CO_2 + $OH^- \Rightarrow HCO_3^-$), indicating the prescence of OH^- within the GDEs. The characteristic frequency at 54 Hz during CO₂ electroreduction (100 vol % CO₂ as feed), which differs from the one at 2 Hz in the absence of CO₂ (100 vol% N2 as feed) and sole HER indicates a lower time-constant and more facile kinetics for CO2RR on bismuth as expected in light of it



Fig. 2. Left side: Faradaic efficiency (FE) of H₂, CO, formate/formic acid measured from -10 to -500 mA/cm^2 for 20 min with corresponding error bars; Right side: Tafel slopes retrieved from the polarization curves. (Cathodic potentials recorded at -500 mA/cm^{-2} have large errors due to strong bubble formation disturbing the *iR*-correction.).

being a good catalyst for this reaction. EIS measurements with the same conditions have been conducted in the system with acidified K₂SO₄. As results show, comparable EIS spectra, characteristic frequency, and trends with increasing current density in 100 vol% CO2 can be observed (cf. Fig. 3c,d). The impedance data is further analyzed by calculating the polarization capacitance as well as the distribution of relaxation times (DRT) (cf. Fig. S2.3) that gives an additional way of representing the almost complete alignment of the impedance results between alkaline and acidic conditions. By applying the Kirchhoff's law $Z_{\mathrm{total}}(\omega) =$ $R_{el} + j \bullet L \bullet \omega + \frac{1}{\frac{1}{R_{cl}} + Q_{cl} \bullet (j \bullet \omega)^{a_{cl}}} + \frac{1}{\frac{1}{R_{ch}} + Q_{ch} \bullet (j \bullet \omega)^{a_{ch}}}$ (Eq. (2)), the charge transfer resistance of CO2RR R_{ct} can be retrieved via fitting with the ohmic resistance R_{el} , the resistance of the preceding chemical equilibrium R_{ch} , the corresponding constant phase elements $Q_i \bullet (j \bullet \omega)^{\alpha_i}$, and the inductive element $j \bullet L \bullet \omega$. Based on the similar results obtained for both systems and minor deviations among three repetitions $\Delta \overline{R_{ct}}$ listed in Table 1, the same ECM as proposed for the alkaline electrolyte can be used for further analysis and the existing knowledge transferred to the bulk acidic system at hand.

As EIS is a very sensitive method to study deviations in mechanistic processes and their time constants as function of the environmental conditions or catalytic properties, along with the Tafel slope and iden-

Table 1

Average fitting values of charge transfer resistances $\overline{R_{\text{ct}}}$ and corresponding error bars $\Delta \overline{R_{\text{ct}}}$ based on the equivalent circuit at different currents in acidic and alkaline systems.

Bulk electrolyte	imA • cm ⁻²	$V_{{ m CO}_2}$ vol%	$\overline{\mathbf{R}_{\mathrm{ct}}} \mathbf{\Omega} \bullet \mathbf{cm}^2$	$\Delta \overline{R_{ct}}\%$
$pH = 2.94, 0.5 \text{ M K}_2 \text{SO}_4$	50	100	0.83	1.19
рН = 14, 1 М КОН	50	100	0.78	2.80
$pH = 2.94, 0.5 \ M \ K_2 SO_4$	100	100	0.59	0.53
рН = 14, 1 М КОН	100	100	0.62	6.18
$pH = 2.94, 0.5 \ M \ K_2 SO_4$	50	0	1.90	0.70
pH = 14, 1 M KOH	50	0	1.79	1.62

tical product distribution, they all strongly support the argument above that in both cases the same reaction conditions prevail at the catalyst surface. As for the existing subtle potential difference and shift observed in the impedance spectra and DRT analysis, anion species of the electrolyte (OH⁻, SO₄²⁻) [31] or differences in the double layer and the concentration profiles between the reaction zone and the bulk electrolyte could play a role.



Fig. 3. Impedance spectra recorded on bismuth-based GDE obtained with a) pure CO_2 (100 vol% CO_2) or pure N_2 (100 vol% N_2) as feed in bulk acidic (orange) and alkaline (blue) system and c) at different current densities, as well was their corresponding imaginary part vs. frequency plots b), d). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.2. CO₂ utilization

As discussed in the previous chapter, comparable pH conditions are expected in the reaction zone inside the GDE during operation in both systems. This means that despite the acidic bulk electrolyte, CO2 will still be sequestered in significant amounts due to the carbonate equilibrium reaction in the alkaline environmental zone of the GDE. As a consequence, it could substantially reduce CO₂ utilization in the bulk acidic system due to its chemical reaction to carbonate. However, according to the literature [22], CO₂ was found to be partly recovered in a bulk acidic system with zero-gap anode by the calculation of entire mass balance considering the electrochemically converted CO₂, the amount in the feed and the total amount of CO₂ on the gas outlet. The author suspected that the neutralization of the carbonate stream under acidic conditions takes place in the reaction system. In this study, experiments were additionally conducted to close the CO2 mass balance during CO2 electroreduction by quantifying the amount of CO₂ at the gas inlet, outlet, the amount of CO₂ converted to CO and formic acid (faradaic), as well as the dissolution or reaction of CO₂ with the electrolyte (non-faradaic). In the end, the derived non-faradaic utilization rate of CO₂ according to Eq. (S6) are significant lower in the bulk acidic case (0 \sim 10%) than the alkaline case (around 50 %) as can be seen in Fig. S4.

To further enhance the understanding of CO₂ recovery by this effect, the pH distribution during electrolysis and its local transition between alkaline and acidic within the electrolyte chamber is monitored by an optical microscope and by adding a few drops of phenolphthalein solution which changes its color from transparent to pink at a pH > 8.3 [32]. Please note that the cell was maintained in unstirred condition to clearly reveal the alkaline flow and its interface with the acidic electrolyte. As can be seen in Fig. 3a at an operating current density of -50 mA·cm⁻², a pink-colored thin film grows gradually upon the GDE/ electrolyte interface within the first 7 s, verifying the formation of an alkaline reaction environment within the GDE which is consequently transported out of the electrode. As time proceeds, the alkaline stream is slowly flowing towards the membrane where it is neutralized with

protons and releases gaseous CO₂ bubbles. Moreover, it is interesting to note that the alkaline stream flows primarily to the bottom owing to the highly concentrated and dense carbonate solution transporting out of the GDE compared to the far lower density of the bulk electrolyte (0.5 M K₂SO₄). As a matter of fact, bubble accumulation could be much more severe at a higher operating current owing to the enhanced production of hydroxide and carbonate, as well as the transfer of protons from the anode side (cf. Fig. 4b). To get a better understanding of how the pH evolves in the catholyte chamber and at which location CO2 is regenerated, a simplified stationary diffusion model is established at various current densities. The concept of the model is adapted from Du et al.'s work [33] as outlined in the Supporting Information. The corresponding pH gradient along the bottom of the catholyte chamber is plotted in Fig. 4b). As can be seen, the transition region from alkaline to acidic locates near to the membrane where excess protons coming from the proton-exchange-membrane react with the carbonate stream. This is an important finding as it gives information about the available buffer between the alkaline and acidic regions and, thus, has direct consequences on the cell design, particularly gap thickness and flow regime to protect the GDE from the acidic conditions. Moreover, an increasing current density leads to a more concentrated alkaline flow with higher pH and a lower pH at the membrane interface with enhanced proton transfer and CO₂ recovery as can be visualized by the video-recording. The accumulation of gas bubbles in the electrolyte environment leads to a discontinuous CO2 recovery in the system, i.e., the CO2 recovered that could be detected at the gas outlet is only observable after certain time of operation. This is the reason why the dissolution rate at the late stage of continuous CO2 mass balance experiment is calculated in negative values proving the delayed detection of recovered CO2 in the system (cf. Fig. S4).

Considering the technical realization of the process, CO_2 release and bubble accumulation between the electrodes needs to be avoided under all circumstances as ionic movement is hindered which leads to high ohmic losses and voltage oscillation. This could be realized, for instance, by adjusting the flow speed, the outlet and inlet position of the catholyte



Fig. 4. a) Screenshots of the real-time video recording on the catholyte chamber with the addition of phenolphthalein solution at $-50 \text{ mA} \cdot \text{cm}^{-2}$ (Bottom) and graphic illustration of suggested mechanism of CO₂ recovery (Top); b) Bubble accumulation in the single-pass mode at 300 s (Top) as well as simulated profiles of pH gradient along the bottom of electrolyte chamber at various current densities with zooming (yellow rectangle) at membrane interface (Bottom). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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and ensuring a laminar flow regime preferably pushing CO_2 release to outside of the cell. Computational fluid dynamics, i.e. numerical optimization of the flow regime coupled with the diffusion characteristics and chemical equilibria will help in finding a suitable solution for that issue.

3.3. Feed dilution

Another important factor that needs to be considered is the volume fraction of CO_2 in the feed stream. On the one hand, lower CO_2 concentrations can be preferable as it decreases purification requirements [34]. On the other hand, as it is the case herein, investigating the

electrochemical behavior of the GDE at low concentrations can reveal subtle differences regarding transport phenomena where their influence becomes more pronounced. Here we investigated diluted CO_2 streams by mixing with N_2 . To this end, impedance spectroscopy as well as voltage oscillations were analyzed as function of CO_2 concentration and electrolyte conditions.

As shown in Figs. 5a and S5, for both acidic and alkaline bulk conditions, the reaction resistance increases as the volume fraction of CO_2 drops in the feed gas which is ascribed to lower concentration of dissolved CO_2 according to Henry's Law (with characteristic frequency shifting from around 20 Hz to 1 Hz for 50 % and 10 %, respectively, cf. Fig. 5b). Accordingly, the reaction resistance reaches its highest value at



Fig. 5. a) Impedance spectra recorded on bismuth-based GDE with different levels of CO₂ dilution in the feed. b) Characteristic frequency of the measured impedance spectra. c) Impedance spectra and d) optical microscope images at different electrolyte flow rates in bulk acidic and alkaline electrolysis system after 20 min operation time.

20 vol% for both the alkaline and acidic conditions indicating the occurrence of a limiting case where CO₂ is not easily accessible to catalytic sites [26]. This applies until there is a notable shift in the product distribution to H₂ happening at 10 vol% CO₂ (cf. Fig. S6), where the total reaction resistance decreases owing to the fact that HER is not limited to any mass transport difficulties. However, a deviation between alkaline and acidic conditions arises regarding the reaction resistance with 20 vol % and 30 vol% CO₂ in the feed, the GDE retains favorable capability to reduce CO₂ in bulk acidic conditions, especially at an intermediate CO₂ concentration of 30% compared to the alkaline system. Since the local alkaline reaction environment in bulk acidic electrolyte during the reaction has been proven in the previous sections, it is generally assumed that similar reaction resistances should be observed with same feed conditions. Therefore, further investigations in the following are needed to reveal the impact of CO₂ recovery made on impedance results. By recording the electrolyte chamber with an optical microscope (cf. Fig. 5c) under the chosen experimental conditions of electrolyte flow rate (5 ml min^{-1}) , significant CO₂ recovery can be observed in the catholyte chamber owning to the continuous contact between alkaline stream and bulk acidic electrolyte. Note that for each EIS measurement, the duration is 20 min in total with 10 min of stabilization and two times of repetition, which allows one to observe bubble accumulation in the entire system compared to the one with less operation time (5 min) presented in Fig. 4 in the batch mode. Due to the fact that CO₂ recovery also happens in very close proximity to the GDE surface after sometime, we hypothesized that the observed effect in the EIS spectra can be ascribed to a simultaneous enrichment of dissolved CO2, while low flow rate of electrolyte detains the gas bubbles from leaving the electrode surface to growth and nucleation. This facilitates CO₂ reduction close to the GDE/electrolyte interface which decreases the overall resistance that can be observed in the spectra and the working potentials (cf. Fig. S7e). To verify the validity of this hypothesis, the electrolyte flow rate was increased to 35 ml min⁻¹ which leads to a much shorter residence time of electrolyte in the cathode chamber and sole recovery of CO₂ at the membrane (cf. Fig. 5d). As a consequence, this leads to the absence of the observed difference in the EIS spectra at 30% CO₂ between alkaline and acidic conditions as suggested.

A similar effect can be observed in galvanostatic experiments in which it was observed that at a certain low level of volume fraction, voltage oscillation occurs in the acidic and alkaline system (cf. Fig. S7ab in 200 s, S7cd in 40 s for a better illustration). The resulting potential change could probably be attributed to non-uniform reactant concentration distributed within the electrodes due to the temporal feed consumption and local N2 filling that can be similarly found with fuel cell operating at low air stoichiometric factor on the anode side [35,36]. The calculated potential variances ($\sigma_E^2 = \sum_{s=1}^n \frac{(\bar{v}-v_s)^2}{n}$, where σ_E^2 states for the potential variance [V²] with the sum of averaged potential deviation $\frac{(\bar{\nu}-\nu_s)^2}{r}$ from the averaged potential $\bar{\nu}$ counting from data point 1 to the end (n).) on the cathode side at different feed conditions during the last 200 s operation period after it reaches the steady-state are plotted (cf. Fig. S7e). As can be indicated, the turning point of the voltage oscillation can be recognized when the potential variance is of multiple magnitudes larger, which is at the condition with a feed of 20 vol% and 30 vol% in the acidic and alkaline systems, respectively. Although the turning point in the acidic system occurs at higher dilution, the potential variance becomes larger owing to intensified concentration change of CO2. In case of 10 vol% CO2 feed, the oscillation should be related to the reaction shift to hydrogen production reduced from the electrolyte which accounts a lot of the total current (approx. 25 % H₂ in both electrolysis systems). However, this phenomenon needs further investigation, e.g. coupling with measurements of pressure drop or volumetric flow at gas outlet.

3.4. Long-term stability and degradation mechanism

To become relevant for technical realization, any electrode system needs to exhibit long-term stability on the order of 1000 h and more. To understand how the stability is affected by switching from alkaline to acidic conditions, we conducted long-term experiments with different modes of operation at an industrially relevant current density of -200 mA cm⁻² in both systems. For that purpose, we have chosen specifically harsh conditions, i.e., a high current density, a low electrolyte and CO₂ flow rate which can be considered as an accelerated stress protocol.

As shown in Fig. 6a, the FE towards H₂ in alkaline conditions remains largely stable at around 5% with only a slight increase throughout the 20 h experiment. In contrary, the H₂ FE continuously rises in the acidic case. To study the reason behind this, we first excluded the factors that could be the direct reasons of performance degradation in the bulk acidic system, such as binder dissolution and mechanical failure that are not observed based on the element mapping of fluorine (cf. Fig. S10), where the Teflon network remains largely unchanged. To evaluate the possibility of catalyst leaching into the bulk electrolyte, the electrolyte composition was examined via ICP-MS after the electrolysis to check for dissolved bismuth species. Yet, in both acidic and alkaline conditions, the bismuth concentration remained below the detection limit (0.01 µgL ¹). However, a significant difference in the bismuth distribution within the GDE after electrolysis could be observed in the cross-sectional EDXmapping shown in Fig. 7. Clearly, a substantial loss of bismuth was found inside the wetted electrode volume (indicated by the presence of potassium) in the acidic case, while the dispersion remains homogeneous under bulk alkaline conditions after the electrolysis. In addition, a large amount of bismuth agglomerates (see EDX spectrum in Fig. 7, white dots in the material contrast images) can be detected on the surface of the GDE after the acidic electrolysis, indicating catalyst loss from GDE inside and redeposition on its surface (cf. Fig. 7; cf. Fig. S9; cf. Table S1,2).

Since we have shown that the local reaction environment inside the GDE is comparable in both systems, the bulk composition and how it evolves with time has to play an important role in the observed behavior. Aiming for a better insight, we decided to investigate the mode of operation in more detail and what effect the accumulation of product has on stability. Interestingly, by changing from circulation to single-pass mode, where fresh electrolyte is continuously passing through the catholyte chamber, the acidic system becomes fully stable during the operation (cf. Fig. 6b). Therefore, it is suspected that the change of electrolyte composition, i.e. either formic acid accumulation itself or the corresponding pH drop in the bulk electrolyte has caused the observed degradation. Indeed, when the initial HCOOH concentration is adjusted to 0.17 M (pH = 2.35) (the same value as measured at the end of the experiment in circulation mode), hydrogen evolution starts to increase instantly after the start of the electrolysis. In contrary, adjusting the bulk acidic catholyte to a comparably low pH value (pH = 2.22) with sulfuric acid does not have a measurable effect on the stability of the system (cf. Fig. 6b). Therefore, we conclude that HCOOH accumulation is responsible for the performance degradation. Although the experimental data clearly suggests that formic acid is responsible for the performance decay, it is not fully clear why this is the case. It is suspected that relatively high concentration of formic acid (HCOOH) in the bulk acid electrolyte changes the composition of the electrochemical double-layer based on the Gouy-Chapman-Stern model [37]: uncharged and undissociated HCOOH molecules [22] without hydration shell are able to diffuse into the inner Helmholtz plane (IHP) and adsorb on the electrode surface unlike the negatively charged anions (e.g. (HCOO⁻) $(H_2O)_n$) which are hydrated and therefore remain in the diffusion layer. In the end, the adsorbed HCOOH can displace CO₂ and H₂O from the active site, acting as hydrogen donor for subsequent HER (small pKa = 3.75 compared to water) which is known from literature [38]. As this process requires a sufficiently low pH value to ensure the presence of undissociated HCOOH taking place at the region close to the GDE/



Fig. 6. a) Stability performance of both systems in the circulation mode. b) Investigation of HCOOH and pH influence on the stability performance. c) The best scenario of stability performance in bulk alkaline and acidic electrolysis systems.



Fig. 7. Post-mortem SEM taken on electrodes after the circulation mode. Top: Surface SEM images of GDE facing electrolyte; Bottom: Cross-sectional EDX-Mapping of Bi and K.

electrolyte interface, it could lead to changes in the pH and potential profile as well as non-uniform current distribution induced by blocking of active sites due to gas bubble formation [39]. This in turn could potentially give rise to mechanical disintegration or other forms of catalyst degradation, causing its redistribution within the GDE [40] as can be evidenced in the SEM images of GDE cross-sections (cf. Fig. 7). The above-mentioned hypothesis should be further studied, e.g., via numerical simulation of the pH- and concentration profiles and by thoroughly investigating the correlation between electrolyte composition, stability of the catalyst, and degradation.

Whereas the product distribution stabilizes in the acidic electrolysis in single-pass mode, this is not the case in the alkaline system in circulation mode which continuously degrades during the long-term test although at much lower pace compared to the acidic system under the same conditions (cf. Fig. 6c). In fact, notable non-uniform volume expansion and salt precipitation can be identified after the alkaline electrolysis (cf. Fig. 7) which is consistent with literature findings suggesting this to be one of the main challenges of prolonged alkaline electrolysis. Note that the potassium band in the EDX mapping is the result of electrode wetting with potassium-containing electrolyte during polarization which is immediately frozen and dried under vacuum after the measurement [15]. Carbon precipitation can be observed in the cross-section of GDE from the bulk alkaline system as irregular shaped crystallites with intensified signals shown in the EDX potassium mapping. In contrary, no carbonate precipitation and mechanical disintegration of the electrode can be observed in the acidic system as evidenced by post-mortem analysis which suggests that the much more pronounced concentration gradient (lower bulk concentration) as driving force for the carbonate diffusion out of the pore system is beneficial.

Recently, acidic electrolysis has gained more attention. To put our work in context, key performance metrics of the latest research work regarding acidic CO₂ electroreduction to formic acid are summarized in Table 2 with faradaic efficiencies of all products in our experiments listed in Table S4. As can be seen, a combination of both high current density and long-term stability as done herein, has not been demonstrated. Interestingly, all of the recent reports have been conducted experiments in a circulation mode. In an actual industrial process, partial recirculation would be desired to accumulate the product to a reasonably high value before negative side effects like loss into the anolyte chamber or degradation become more dominant. By revealing that HCOOH accumulation is the main obstacle for long-term operation, the stability performance from previous and future work could be largely enhanced along with the development of novel catalysts and electrode design. To allow for an actual long-term experiment, the electrochemical cell and practical operating parameters need to be thoroughly optimized as the subject for future investigation.

4. Conclusions

By applying various measurement techniques, a thorough understanding of the acidic electrolysis system on the specified GDE to produce formic acid is realized. The selectivity and the activity towards formic acid production has not been influenced by the use of bulk acidic electrolyte as the local reaction environment is alkaline as a consequence of the accumulation of OH^- inside the GDE during the reaction. This is ascribed to the local confinement and sufficient gas–liquid interface within the porous and highly hydrophobic GDE structure and the shielding effect provided by the K⁺, which is further evidenced by the polarization curve, electrochemical impedance spectroscopy, simulation, and real-time video recording of an alkaline stream flowing out of the GDE during the operation.

Meanwhile, CO_2 recovery that takes place in the acidic electrolysis system increases the overall utilization rate of CO_2 in the system and, at the same time, allows operation at less negative potential with lower amount of CO_2 feed compared to the alkaline ones. The complex

Table 2

Recent advances in acidic CO_2 electroreduction to produce HCOOH (FE_{non-FA} is the faradic efficiency of species analyzed other than formic acid.).

Work	pH ₀ [-]	Current density [mA/cm ²]	FE _{non-} _{FA} [%]	Duration [min]	Operation mode of electrolyte
Osskopp et al. [22]	3.4	200	16	120	Circulation
Gu et al.	1.5	200	26	240	Circulation
Tao et al.	2.7	40	20	1500	?
Li et al. [41]	1	100	10	7500	Circulation (based on FE calculation)
Wang et al. [42]	2.5	4	10	1200	Circulation
Qiao et al.	1	120	20	480	Circulation
This work (cf. Table S4)	2.94	200	~100	1050	Circulation
This work (cf. Table S4)	2.94	200	14	1103	Single-Pass
This work (cf. Table S4)	2.22	200	15	1148	Single-Pass

interplay between electrolyte flow rate, feed dilution, current density and chamber structure could largely affect the overall efficiency of bulk acidic electrolysis system. In this respect it is important to ensure that the CO_2 recovery is pushed to outside of the cell by facilitating a laminar flow between the electrodes and optimization of flow rate and in-/outlet position.

As for the long-term stability performance, the bulk alkaline electrolysis system suffers from product cross-over, carbonate accumulation, as well as the deformation of GDE structure that lead to substantial HER in the long-time run. In contrary, the acidic bulk electrolysis system has none of the above-mentioned disadvantages when operating in a singlepass mode, where HCOOH is not accumulating in the bulk electrolyte. When electrolyte is recirculated, HCOOH accumulation can cause severe degradation and catalyst leaching which sheds light to a possible improvement of the past and future work. Understanding this effect in more detail requires additional studies in the future that should include the combination of modelling and operando techniques to better understand what is happening inside the GDE and how transport phenomena influence performance and stability.

While this study focused on formic acid production with Bi-based GDEs, the findings are also valuable for other catalyst systems in which trade-offs between acidic and alkaline environment are expected (e.g. Cu- or Ag-based GDEs).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.cej.2023.146486.

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