



The inhibition of the proton donor ability of bicarbonate promotes the electrochemical conversion of CO₂ in bicarbonate solutions

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ABSTRACT

Gaseous CO₂ solutions are widely used for CO₂ electrochemical conversion to various valuable products. However, capture, liberation and storage of gaseous CO₂ prior to reduction is cumbersome and costly. CO₂ electrocatalytic reduction from captured CO₂ (in the form of concentrated bicarbonate solution) offers an option to optimize CO₂ reduction processes. Using concentrated bicarbonate solutions from captured CO₂ as large carbon feedstock and reducing CO₂ directly from bicarbonate electrolyte remain a challenge. Indeed, current efficiency is too low (i.e. low selectivity and/or activity) as a consequence of the strong competition with the hydrogen evolution reaction, which bicarbonate promotes to a great extent. In this study, up to 2 M bicarbonate solution is used as electrolyte (mimicking a captured CO₂ solution from an alkaline media) for a CO₂ electrochemical reduction system, which potentially pretends to be a 2 M carbon source, compared to 0.033 M present in a saturated gaseous CO₂ solution. In order to improve the Faradaic efficiency of the process and thereby making the CO₂ electrocatalytic reduction from a bicarbonate feedstock an efficient system and attractive alternative for the reduction starting from gaseous CO₂, a reaction mechanism where bicarbonate acts as a CO₂ donor instead of as a proton donor is proposed. To achieve such property, we inhibit the proton donor ability of bicarbonate and water by covering the surface of the electrode with cationic surfactants, allowing non-polar molecules, like the CO₂ derived from the equilibrium with bicarbonate, to diffuse to the surface of the electrode while avoiding bicarbonate and water to promote the hydrogen evolution reaction. To the best of our knowledge, the Faradaic Efficiency to formate obtained in this study (>70 %) sets a new benchmark in systems involving unsaturated and saturated bicarbonate solutions without previously purging CO₂.

1. Introduction

Climate change and global warming pose a significant threat to our society and are linked to the rising CO₂ levels in the Earth's atmosphere. Carbon Capture and Utilization (CCU) can offer an economic-driven pathway to valorise the transformation of CO₂ into different chemicals, fuels and mineralized products by using renewable energy such as wind and solar. In this context, the electrocatalytic CO₂ reduction (CO₂R) has commonly been postulated as a promising strategy [1–4].

Typical CO₂ electrochemical reactors require gaseous CO₂ feeds or CO₂ pre-saturated electrolytes to be able to efficiently convert it [5]. This CO₂ is currently captured, stored and liberated from highly alkaline solutions to achieve pure and pressurized CO₂. Since the liberation step

requires a significant amount of energy, there is industrial interest in avoiding it [6]. An option could be to integrate the CO₂ capture and conversion processes via the direct electrochemical conversion of captured CO₂ in the form of bicarbonate (HCO₃⁻) solutions. This option would offer a large carbon feedstock where CO₂ can be processed without cumbersome gas storage and manipulation. However, despite the fact that electrocatalytic CO₂R has received increasing attention, little research has focused on electrochemical bicarbonate conversion. Conversion towards CO₂R products is observed in bicarbonate electrolytes that have not been purged or saturated with gaseous CO₂, but the concept has not been studied in depth due to the low efficiency observed and the difficulty to accurately distinguish between CO₂R and direct bicarbonate reduction experimentally [7].

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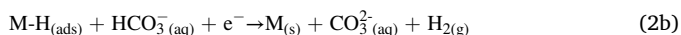
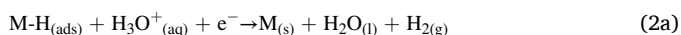
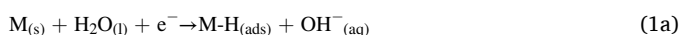
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It was observed that most electrocatalysts able to reduce CO₂ can reduce bicarbonate electrolytes as well with similar products and product distribution. For instance, Cu and Au based electrocatalysts reduce both species to CO and Sn-based materials reduce them to formate (HCOO⁻), as major product [8–10]. However, systems involving saturated CO₂ electrolytes appear to be much more active.

It is hypothesized that the products come from the CO₂ present in solution via the equilibrium between bicarbonate and water instead of from bicarbonate directly [11]. The evidence for this hypothesis is two-fold. Firstly, one of the most favoured mechanisms for carbon-metal adsorption in the electrocatalytic reduction of CO₂ requires the bending of the CO₂ molecule from linear to roughly 120° to activate the carbon atom in CO₂, which is impeded for bicarbonate ions [12,13]. Secondly, in nature, CO₂ is the substrate in many enzymatic pathways instead of bicarbonate [14]. The amount of diluted CO₂ in aqueous bicarbonate solutions is determined by the equilibrium between bicarbonate with CO₂ and carbonate in water. The pH determines their ratio. At atmospheric conditions, the pH with maximum amount of dissolved bicarbonate is 8.3. At this pH, a small percentage, around 1.2 %, of diluted CO₂ is present (see Fig. S1, Eqs. S1–3 [15,16]).

Recent studies where bicarbonate was used as electrolyte in zero-gap flow cell reactors with bipolar membrane (BPM) showed an increase in the overall efficiency of the electrolysis compared to the previous benchmark result, which was ≈54 % Faradaic Efficiency using a Pd electrocatalyst [17]. Indeed, Li et al. used a Bi/C catalyst to produce formate from 3 M KHCO₃ achieving up to 64 % Faradaic Efficiency (FE) at 100 mA cm⁻². On the other hand, Zhang et al. produced CO through a similar setup using an Ag-based electrocatalyst reaching up to 19 % at 500 mA cm⁻² [18,19]. While these recent results are quite promising, there is still room for improvement in terms of performance (i.e. FE) and especially in terms of understanding the reaction mechanism. It is for example still unclear and subject of debate within the community whether bicarbonate is directly converted to products or indirectly through CO₂, since the maximum solubility of KHCO₃ is 2.2 M. The cited authors presented evidence for a CO₂-mediated reaction pathway since a BPM was used to acidify the catholyte and shift the equilibrium from bicarbonate to CO₂ and, thus, increase the FE of the process.

Even though the relative abundance of CO₂ in bicarbonate solutions is low, in concentrated bicarbonate solutions the concentration of CO₂ should be high enough to be comparable to saturated CO₂ solutions (0.024 and 0.033 M respectively) and should thus allow for a successful competition with the hydrogen evolution reaction (HER). Unfortunately, the FE towards carbon products of electrolysis in a saturated CO₂ solution is substantially higher compared to a bicarbonate solution, where most of the FE goes to HER. This must mean that other parameters are at play impeding the CO₂R in concentrated bicarbonate electrolytes. An explanation for the high HER obtained in bicarbonate electrolytes can be given by studies done on HER. It is reported that bicarbonate has a role as proton donor similar to water (2a) in the catalytic mechanism of HER via supplying H⁺ to a previously electrochemically reduced weak acid like water (1a) or carbonic acid (1b) in a Volmer-Heyrovsky reaction pathway (2b) [20,21]. However, Dunwell et al. presented evidence that in CO₂ saturated electrolytes, at a controlled acidic pH, low concentrations of bicarbonate act as a CO₂ donor instead of as a proton donor [11]. It appears that the pH and the concentration of bicarbonate are key parameters to determine the role of bicarbonate in certain systems.



The main cause of the inefficiency of the bicarbonate electrolysis

thus might be the strong competition with the HER, the main side reaction, leading to a significant decrease of the FE towards carbon products. In CO₂-saturated electrolytes, the inhibition of HER has been studied by using cationic surfactants either in the electrolyte or on the surface of the electrode. For example, Banerjee et al. used cetyltrimethylammonium ammonium bromide (CTAB) to modify the Outer Helmholtz Plane by displacing the cations during electrolysis, inhibiting HER [22]. Zhong et al. studied the interfacial interactions of different cationic surfactants in CO₂R proposing a mechanism where CO₂ reduction to formate is promoted while HER is inhibited by a CO₂-permeable coating [23]. On the other hand, Wakerley et al. made a hydrophobic electrode by treating Cu dendrites with 1-octadecanethiol, avoiding the penetration of water molecules while allowing CO₂ to reach the surface of the electrode, increasing its local concentration [24]. However, this strategy was never applied to concentrated bicarbonate electrolytes, enabling the desired combination of CO₂ capture and (electro)conversion in one and the same medium which remains a rather unexplored domain and is the main topic of this paper.

In this study, we propose for the first time a method to obtain high FE from the conversion of CO₂ to formate from saturated bicarbonate electrolytes by inhibiting the proton donor ability of bicarbonate and water and, thus, inhibiting HER. To the best of our knowledge, the FE to formate obtained in this study (>70 %) sets a new benchmark in systems involving unsaturated and saturated bicarbonate solutions without previously purging CO₂. This study also confirms the previously mentioned but unconfirmed CO₂-mediated mechanism behind bicarbonate electrocatalytic conversion. Additionally, the proposed method renders the process feasible and promising to be competitive with gas-fed CO₂ electrolyzers and gives an alternative pathway that does not involve oversaturated bicarbonate electrolytes (unstable) or the use of BPM (high ohmic resistance) in zero-gap reactors to increase the concentration of CO₂, which are currently used in the studies mentioned before [18,25]. This allows broader amount of strategies to be considered when reducing CO₂ from bicarbonate solutions. However, the pathway proposed can also be complementary to the strategies previously mentioned to even reach higher performance.

2. Experimental

2.1. Reagents preparation

All the chemicals were obtained from commercial sources and used without purification unless stated otherwise. KHCO₃ solutions used as catholyte were prepared by dissolving the corresponding amount of 0.1, 0.5, 1 and 2 M of potassium hydrogen carbonate 99.5 % (Chem-Lab) in Ultra-Pure water (MilliQ, 18.2 MΩcm). The saturated CO₂ solution was prepared by bubbling a 0.5 M KHCO₃ solution with gaseous CO₂ for 45 min prior to the corresponding electrochemical experiment. A pH-meter was used to control and identify saturation. The anolyte was prepared by dissolving the corresponding amount of 1 M of potassium hydroxide pellets (Chem-Lab) in Ultra-Pure water. Each surfactant solution was prepared by dissolving the corresponding amount of hexadecyl trimethylammonium bromide, 98 %+ (Chem-Lab); benzyl dimethyl hexadecyl ammonium chloride, 95 %+ (Alfa Aesar); sodium dodecyl sulphate, 98 %+ (Chem-Lab); or hexadecyl trimethylammonium chloride, 98 % (Sigma Aldrich) in a previously prepared KHCO₃ solution. The solutions were sonicated for 10 min at room temperature. See the structure and the abbreviation of the surfactants in Table S1. Metallic Sn 99.9985 % (2.0 mm dia., Alfa Aesar); Sn rotating disc electrode, RDE, (Good Fellow, polycrystalline, 99.999+%) and Cu RDE (Good Fellow, polycrystalline, 99.99+%) were used as working electrode. The surface was polished with alumina (particle size: 1 μm) and then sonicated in HPLC-grade acetonitrile (Chem-Lab) and Ultra-Pure water separately for 10 min. Nafion 117 proton exchange membrane (PEM) was used in the electrochemical H-Cell for chronoamperometric studies. The pre-treatment procedure of the Nafion 117 membranes was:

1 h in 0.5 M H₂SO₄ at 80 °C, followed by 1 h in MilliQ water at 80 °C, then 1 h in 0.5 M H₂O₂ at 80 °C and finally 1 h in MilliQ water at 80 °C.

2.2. Instruments

The chronoamperometric experiments were performed with a Biologic potentiostat and the Linear Sweep Voltammetry (LSV) experiments with an Autolab potentiostat. The software EC-Lab (Biologic) and Nova (Autolab) were used for setting the electrochemical conditions up. For product analysis, Waters 2695 Separation module High-Performance Liquid Chromatography (HPLC) and RSpak KC-811 8 × 300 column was used to separate the products and Waters 2996 Photodiode Array Detector to detect and quantify formate in the form of formic acid. The samples were previously acidified with HClO₄ and filtered to avoid bubble formation and obstruction in the column. HClO₄ 0.1 % was used as mobile phase.

2.3. Experimental set-up and procedure

Two types of working electrodes were used depending on the performed electrochemical experiment. For LSV experiments, a Sn RDE of 0.22 cm² and a Cu RDE of 0.28 cm² were used to provide better electroanalytical control while for chronoamperometric experiments a Sn wire electrode of 2 cm² (immersed length: 3.15 cm) was used in order to obtain higher concentrations of formate and ensure analytical detection. A Pt mesh was used as counter electrode and Ag/AgCl 3 M was used as reference electrode (Picture S1). A voltammetry cell in a Faradaic cage was used for LSV experiments and a jacketed H-Cell was used for chronoamperometric experiments (Picture S2). To separate the anolyte and the catholyte in the H-Cell and avoid product re-oxidation but ensure conductivity, a Nafion 117 membrane was used. For LSV experiments, 50 mL of electrolyte were previously purged with N₂ for 10 min to remove the diluted O₂ and the air-liquid interface was gassed with N₂ during the experiment to avoid diffusion of O₂ from the air. However, in experiments involving diluted CO₂, the solution was purged with CO₂ instead. The Sn RDE working electrode was electrochemically preconditioned by cycling from -0.5 V to -1.5 V vs Reversible Hydrogen Electrode (RHE) 10 times at 100 mV s⁻¹ prior to the experiment. To perform LSV experiments, the current was measured from -0.55 V to -1.3 V_{RHE} at 1 mV s⁻¹. For chronoamperometric experiments the Sn wire working electrode was electrochemically preconditioned by cycling from -0.5 V to -1.5 V_{RHE} 10 times at 100 mV s⁻¹ prior to the experiment, too. However, in addition to the previous treatment, the electrode was finally cycled up to -2 V vs RHE to completely reduce the surface of the electrode. After the electrochemical precondition, 140 mL of electrolyte (70 mL of catholyte and 70 mL of anolyte) were electrolyzed at a fixed potential for one hour. The solution was continuously stirred with a magnetic stirrer at 300 rpm. After one hour, 0.5 mL of the solution is sampled and analysed in the HPLC. After analysis, the concentration of

formate in the electrolyte was obtained and the FE and partial current densities were calculated (Equation S5–8). Since we only performed liquid analysis (formate), we can only quantify the FE towards formate. Thus, in this study, we consider that the rest of the current goes towards HER. Each CA experiment with cetalkonium chloride (CKC) was repeated three times. The FE shown in the manuscript belongs to the average value of three experiments and the error bars correspond to the standard error. For control bicarbonate solutions (blank), only one experiment was performed.

3. Results and discussion

We studied the role of bicarbonate by performing LSV and chronoamperometric experiments in different concentrations of bicarbonate (Fig. 1). Within the reduction current, CO₂R and HER occur simultaneously [21]. Current density and FE should increase with the concentration of bicarbonate, since more ionic species are present and the concentration of CO₂ is therefore higher. Results show that the current density corresponding to HER/CO₂R increases significantly with the concentration of bicarbonate, as expected, but the FE to formate barely improves. Instead, even though the concentration of CO₂ is higher as the concentration of bicarbonate increases, most of the FE, and therefore the current, goes to HER (≈90 %). This indicates that a high concentration of bicarbonate must promote HER over CO₂R and confirms the role of bicarbonate in highly concentrated bicarbonate solutions as a proton donor specie, inevitably giving high HER rates and low CO₂R FE's, in accordance with previous literature [21]. As a consequence, the process becomes highly inefficient.

Unlike in CO₂-saturated systems, in concentrated bicarbonate electrolytes, the addition of cationic surfactants does not only impact the inhibition of HER by inhibiting the reaction step between an adsorbed hydrogen and water (Eq. 2a), but also interrupts the proton donation of bicarbonate (Eq. 2b) in a similar way it does this for water molecules. This effect is achieved after negatively polarizing the electrode and covering the surface of the electrode by a hydrophobic layer where charged and polar molecules (bicarbonate and water) are partially repelled and non-polar and small molecules/ions (CO₂, H⁺) can trespass, allowing CO₂ hydrogenation and inhibiting HER. This may sound contradictory since the trespassing of H⁺ should thus promote HER. The exact HER inhibition may then be more complex than just the hydrophobic effect of cationic surfactants and it is, then, an interesting objective of research in future studies. The composition of the surfactant can also influence the overall effectiveness of this HER inhibition. It has been reported that cationic surfactants with aromatic groups in the polar head give higher hydrophobic properties to the surface compared to those without such groups. While the aromatic group plays a similar role as the long non-polar alkyl chain in forming a branched hydrophobic layer [23], its aromatic amines additionally form an optimized CO₂-amine complex, further promoting the CO₂R over the HER [26]. Thereby,

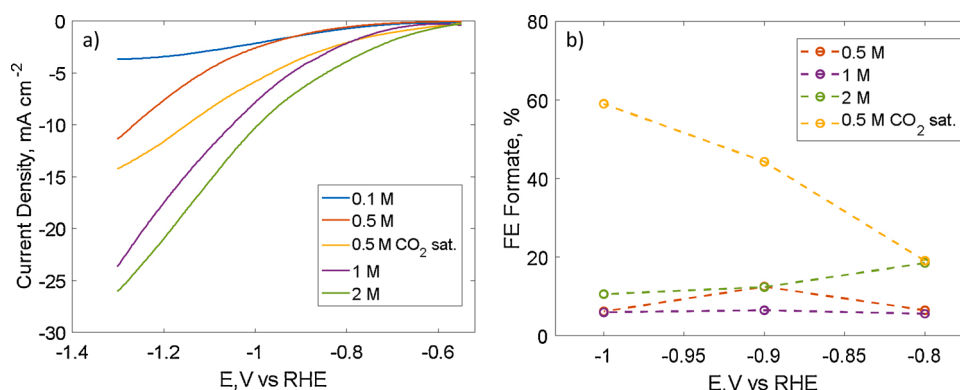


Fig. 1. a) LSV voltammograms of a Sn electrode in different KHCO₃ solutions. b) FE_{formate} at different potentials in various KHCO₃ solutions.

the overall performance should further improve as confirmed hereafter.

Based on the observations above, cetalkonium chloride (CKC) was proposed as the most promising functional cationic surfactant to inhibit HER in bicarbonate electrolytes. CKC is a cationic surfactant that has a 16-carbon alkyl chain and a tertiary amine as polar head functionalized with a benzyl group (Table S1). We expect HER to be inhibited when CKC is present following a similar mechanism as CTAB was reported to do in CO₂ saturated electrolytes. However, we expect a higher inhibition with CKC compared to CTAB because of the presence of the aromatic group, increasing the hydrophobicity and CO₂-philicity of the surfactant layer. In order to see the effect of

CKC and identify HER we briefly looked at the electrochemical behaviour of the working electrode when it is negatively polarized in a 2 M bicarbonate solution in presence and in the absence of CKC. LSV showed that a reduction peak, starting at $-0.7 V_{RHE}$, appeared only in presence of CKC (Fig. 2a). At more negative potentials ($< -0.9 V_{RHE}$), lower currents are achieved than in the absence of CKC, indicating that the HER is inhibited as it generally takes up the most significant fraction of the current at these more negative potentials. The reduction peak might correspond to the adsorption of CKC to the Sn surface, forming an ad-layer, which acts as the hydrophobic layer mentioned. Although the exact mechanism of reduction and adsorption of CKC to the Sn surface is not clear and not reported up to day, there are hints indicating that the interaction between the amine of the surfactant and the metastable oxide layer of Sn at cathodic currents might play a role since such reduction peak is not observed in electrodes of different nature like Cu (Fig. S2). Other cationic surfactants like CTAB presented a similar behaviour when adsorbing to O⁻ charged surfaces [27]. For instance, it can be observed in Fig. 2a how, in presence of CTAB and CTAC, a reduction shoulder appears at similar reduction potential. The difference in behaviour between CKC and CTAB/CTAC might thus come from the interaction of the metastable oxide layer with the benzyl group present in CKC as well as the different electronic properties of the amine compared to the other species mentioned (Fig. 2b). However, a deep electrochemical study is needed in order to define and confirm the precise mechanism and the electrochemical reduction process of the phenomena observed when a cathodic current is applied to Sn surfaces in presence of cationic surfactants, which is now our target as future approach.

Other parameters like the charge of the surfactant and the nature of the counter ion have been already studied in other electrochemical studies involving CO₂ and surfactants [23]. To confirm that the mentioned parameters have a similar effect on bicarbonate electrolytes, we briefly evaluated the impact on the decrease of the current, which is directly related to HER inhibition, of surfactants of different nature on bicarbonate electrolytes (Fig. 2a). LSV experiments showed that only cationic surfactants inhibit HER. Anionic surfactants (SDS) had little effect compared to control experiments (blank). In presence of CTAB and

CTAC a shoulder is observed as mentioned before, although the HER inhibition is lower than CKC, confirming previous work and our hypothesis that the presence of the aromatic group amine group is beneficial for the performance. Looking at CTAB and CTAC voltammograms, we can say that the difference when using Cl⁻ or Br⁻ as counter ions of the surfactants is not significant in this system.

We evaluated the performance of CKC on inhibiting HER by electrolyzing a 2 M bicarbonate solution for one hour with a Sn electrode in presence of 1000 μM of CKC at different potentials and comparing the results to analogous control experiments in the absence of a cationic surfactant. In Fig. 3a it is observed how the FE towards formate increases substantially upon addition of CKC. For instance, 66 % FE is obtained in presence of CKC compared to 12 % in surfactant-free electrolyte at $-0.9 V_{RHE}$, an increase of 54 %. Analogous experiments involving CTAB (Fig. S3) confirmed that CKC has higher impact than CTAB on HER inhibition ($\approx 20\%$ addition in FE) due to the presence of aromatic groups. In agreement with previous literature on CO₂-saturated electrolytes, the presence of a cationic surfactant results in a decrease of the total current density in proportion with the increase of FE towards CO₂R products and a decrease of FE towards HER [22]. This decrease in the total current density is related to HER as the partial current density of HER is diminished while the CO₂R remains almost unaffected (Fig. 3c,d). Then, the overall decrease of the current density is not negatively affecting the performance when reducing CO₂, since it only affects the HER (Fig. 3b). The FE remained rather constant when increasing the concentration of CKC proving that once a critical micellar concentration is reached (CMC, 500 μM) further increasing the concentration doesn't result in further increase in performance (Fig. 4a). We observed closer this effect by performing LSV experiments with different concentrations of CKC (Fig. S4). By comparing the total current density, from the CMC, the efficiency of HER inhibition does not differ much when the concentration of CKC is increased ($6-9 \text{ mA cm}^{-2}$ at $-1.1 V_{RHE}$). This may indicate that once the surfactant starts forming micelles, HER inhibition is not further improved. On the other hand, when the concentration of CKC is below CMC (100 μM), HER inhibition is decreased substantially since the current density is much closer to control values (33 mA cm^{-2} and 43 mA cm^{-2} respectively at $-1.1 V_{RHE}$).

Additional experiments were carried out varying the concentration of bicarbonate and fixing the applied potential to $-0.9 V_{RHE}$ (Fig. 4b). In contrast with the results shown in Fig. 1b, where the FE barely changes with the concentration of bicarbonate, in presence of CKC the FE increases considerably when the concentration of bicarbonate goes from 0.5 M to 1 and 2 M. Between 1 and 2 M, FE lies within the same range (71 and 66 %, respectively). The FE in 0.5 M bicarbonate with CKC slightly increases compared to the control test (19 and 13 %, respectively), which is believed to be due to the very low CO₂ concentration (6 mM). The concentration of bicarbonate thus clearly matters as higher concentrations result in more CO₂ being transported to the surface of the

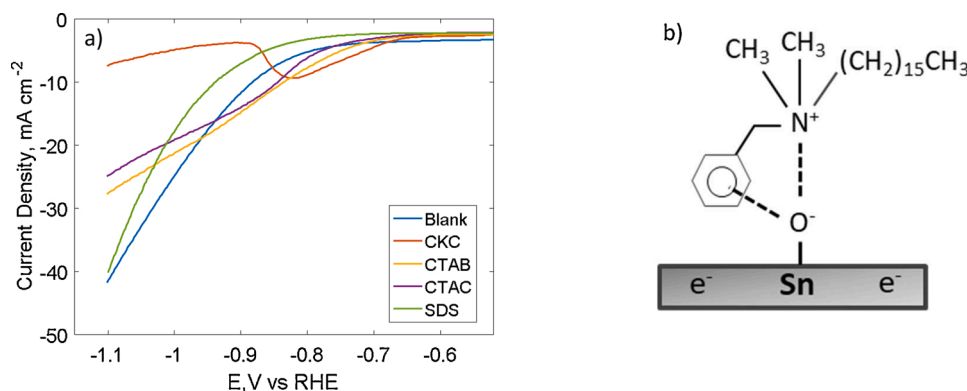


Fig. 2. a) LSV voltammograms of a Sn electrode in KHCO₃ 2 M electrolytes in presence and in the absence of 1000 μM of surfactants of different nature. b) Proposed interaction between CKC and the metastable Sn oxide layer.

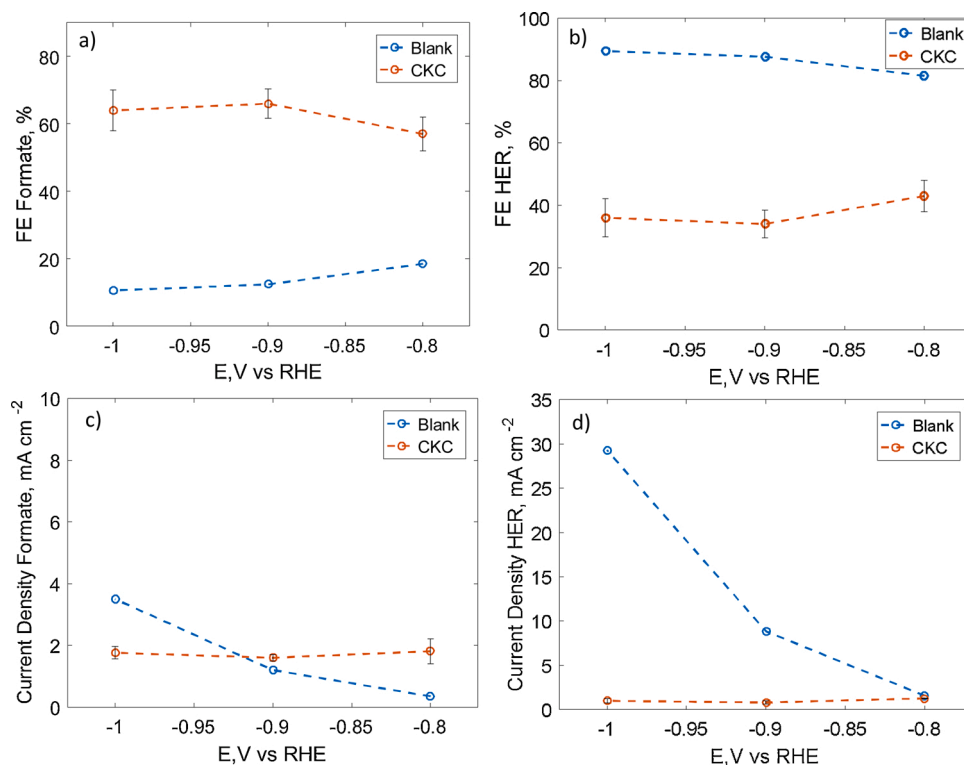


Fig. 3. a) FE_{formate} at different applied potential in KHCO₃ 2 M in presence and in the absence of 1000 μM of CKC. b) Corresponding FE_{HER} c) Partial current density towards formate; d) partial current density towards HER.

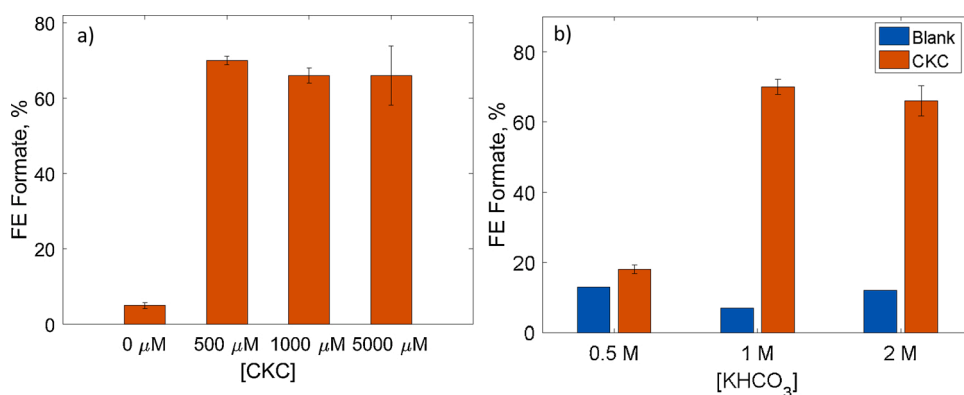


Fig. 4. a) FE_{Formate} at $-0.9 V_{RHE}$ in 2 M KHCO₃ with different concentrations of CKC. b) FE_{Formate} at $-0.9 V_{RHE}$ in KHCO₃ electrolytes of different concentrations in presence and in the absence of 1000 μM of CKC.

electrode and converted. This finding is very significant since one of the main objectives of using bicarbonate as a substrate instead of gaseous CO₂ feeds is to provide a system where CO₂ can be continuously and efficiently converted from a liquid phase. Therefore, future research should be performed with an as high as possible bicarbonate concentration to run an as efficient as possible process from capture to conversion.

4. Conclusions

In summary, we efficiently converted CO₂ to formate from a bicarbonate electrolyte that has not been previously purged with CO₂ by inhibiting the proton donor ability of bicarbonate, and thus the HER, with the cationic surfactant CKC. High FE towards formate from bicarbonate electrolytes (> 70 %) were obtained in this study, setting a benchmark in the field. As shown, with the presence of the cationic

surfactant CKC in the bicarbonate electrolyte, the surface of the electrode becomes hydrophobic enabling non-polar molecules, like the CO₂ derived from the equilibrium with bicarbonate, to diffuse to the surface of the electrode and preventing polar molecules like bicarbonate and water to promote HER. This way, bicarbonate acts as a CO₂ source instead of as a proton donor. Through this mechanism, a bicarbonate solution becomes a highly loaded carbon pool enabling CO₂ to be captured and stored up to saturation levels of bicarbonate (~2 M) and then converted to valuable products in an electrochemical cell, avoiding the necessity of using a pure CO₂ gas inlet and thus the separation and storage costs.

The mechanism proposed in this manuscript and the results shown enable new strategies for the electrochemical conversion of CO₂ from bicarbonate, which in many cases, although industrially very attractive, its practical use has been limited within the community due to high obtained HER rates. Since such disadvantage is tackled in this study and

high FE for formate production is obtained (thereby low HER rates), further fundamentals on the reaction mechanism (such as the buffering effect of bicarbonate, the kinetics or the product selectivity) can be studied in detail and the strategy of electrochemically converting CO₂ from bicarbonate becomes more promising and closer to applicability. Up to day, only the electrocatalytic conversion of CO₂ from bicarbonate to CO and formate has been reported in literature, opening a wide window of research where other CO₂R valued products (like CH₃OH, CH₄ or CH₃CH₂OH) can be targeted by modulating cell parameters such as the catalyst choice. Although the presence of surfactant should affect the selectivity of the reaction (since the electrochemical double layer is altered), the HER inhibition mechanism proposed in this study should behave in a similar way whatever catalyst is used, since it is apparently dependent on the electrolyte.

However, there is still room to improve in order to make the process economically feasible and competitive with scaled-up CO₂ flow electrolyzers. For instance, in this study, low current densities are shown compared to scaled-up CO₂ electrochemical reduction reactors since the research was entirely focused on the fundamental aspects behind the selectivity between formate and hydrogen of the electrocatalytic reduction. However, recent studies, mentioned in this manuscript, showed that high current densities can be achieved from bicarbonate electrolytes (up to 500 mA cm⁻² has been reported recently producing 19 % FE CO from 3 M KHCO₃ in a zero gap flow cell reactor using a Ag catalyst [19]), thereby proving that bicarbonate can be scaled-up to industrially relevant current densities. Combining optimal reactor design models and the HER inhibition strategy as proposed in this article, could provide new research routes towards an electrochemical conversion of bicarbonate that is both highly selective (i.e. high FE) and highly active (i.e. high current density).

CRedit authorship contribution statement

Oriol Gutierrez-Sanchez: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Writing - Original Draft, Visualization. **Nick Daems:** Investigation, Writing - Review & Editing, Visualization. **Willem Offermans:** Writing - Investigation, Writing - Review & Editing, Visualization. **Yuvraj Y. Birdja:** Writing - Investigation, Writing - Review & Editing, Visualization. **Metin Bulut:** Writing - Supervision, Provision of study materials, Project administration. **Deepak Pant:** Resources, Provision of study materials, Writing -Review & Editing. **Tom Breugelmans:** Resources, Provision of study materials, Writing - Supervision, Project administration.

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.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jcou.2021.101521>.

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