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# Bifunctional Artificial Carbonic Anhydrase for the Integrated Capture and Electrochemical Conversion of CO<sub>2</sub>

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# Abstract

To valorise waste and atmospheric CO<sub>2</sub>, Carbon Capture and Utilization (CCU) technologies are currently receiving a lot of attention. Alkali base solutions have shown to be efficient capture solutions and the electrochemical CO<sub>2</sub> conversion (eCO<sub>2</sub>R) is a promising approach to convert CO<sub>2</sub> by using renewable energy. However, the capture and conversion have been investigated almost exclusively as separate processes to date. This strategy has the disadvantage that CO<sub>2</sub> must be desorbed and compressed after capture, which increases the capital and operational costs of the technology significantly. To improve the valorisation potential of CCU technologies, integrating both the capture and electrochemical conversion steps by directly utilizing the post-capture solution as an electrolyte (in the form of bicarbonate) for the eCO<sub>2</sub>R is a highly promising approach. However, bicarbonate electrolysis cannot compete yet in terms of energy efficiency with analogous CO<sub>2</sub>-fed electrolysers. Nevertheless, given its huge potential, there is interest in optimizing the overall technology by, for instance, decreasing the costs of capturing the CO<sub>2</sub> by shortening the operational time or promoting the electrochemical conversion of  $CO_2$  in bicarbonate solutions. In this study, we have synthesized and optimized for the first time ever bio-inspired catalysts that were able to fulfil and improve steps in a combined CO<sub>2</sub> capture and conversion system. In the bestcase scenario, the rate of the conversion of  $CO_2$  to bicarbonate (mimicking the capture step in CCU) increased by 84% when the biomimetic catalyst  $[Zn(cyclen)]^{2+}$  was present in the capture solution. On the other hand, the same catalyst promoted the electrochemical conversion of  $CO_2$  to formate from a bicarbonate post-capture solution by inhibiting the competing Hydrogen Evolution Reaction (HER). The partial current density towards HER decreased from 18 mA cm<sup>-2</sup> in control experiments to 0.7 mA cm<sup>-2</sup> in the presence of  $[Zn(cyclen)]^{2+}$ .

# Keywords

Carbon Capture & Utilization, carbonic anhydrase, biomimetic catalysis, hydrogen evolution reaction inhibition, bicarbonate electrolysis

## Introduction

The level of CO<sub>2</sub> in the atmosphere is increasing year after year to unprecedented levels with current and future generations facing serious climate changes as a result.<sup>1</sup> Climate change is already seriously affecting society due to the huge impact on nature including the rise of ocean levels, global warming, the increased frequency of natural disasters and the alteration of several ecosystems.<sup>2-4</sup> CO<sub>2</sub> is mostly released by anthropogenic activities such as industrial processes or energy production.<sup>5,6</sup> As a consequence, reducing the amount of CO<sub>2</sub> from the atmosphere is becoming more and more crucial to decrease the effects of climate change and eventually revert the threatening situation our society is currently facing.<sup>7</sup> In this context, Carbon Capture and Utilization (CCU) technologies are looking to capture the CO<sub>2</sub> directly from the air or industrial gas and valorise it by using it as a building block within the chemical industry.<sup>8–10</sup> One of the most promising strategies in CCU is to use the captured CO<sub>2</sub> as a substrate in an electrochemical CO<sub>2</sub> reduction (eCO<sub>2</sub>R) cell.<sup>11–13</sup> CO<sub>2</sub> can be converted to several bulk or high valued carbon products such as formic acid, CO, methanol and other C2 products (i.e., ethanol and ethane) by means of an electrocatalyst, which is the main factor influencing the product of the reaction.<sup>14–16</sup> Nowadays, most of the research in the eCO<sub>2</sub>R uses pure CO<sub>2</sub> gas as carbon feed,<sup>17-19</sup> which requires an expensive and energy-demanding posttreatment step after capture, including a compression and regeneration step.<sup>20</sup>

Different media were proposed to capture CO<sub>2</sub> and have been studied such as highly concentrated alkali solutions and amine solutions, which respectively lead to solid carbonate and carbamate solutions after capture.<sup>21</sup> After the CO<sub>2</sub> is captured, there are challenges in extracting and delivering pure CO<sub>2</sub> to the electrochemical cell, as high purity CO<sub>2</sub> (>99%) is preferred to obtain high conversion rates,<sup>22</sup> thus blocking the CCU technology from scaling up. On the one hand, to recover the CO<sub>2</sub> from carbonate salts in a highly concentrated, pure form, the salt must be calcined and then compressed, requiring a high amount of energy and several gas treatment steps, which are cumbersome and inefficient when considered as a precursor of the utilization step.<sup>23</sup> Nevertheless, this is the process followed by the industrial state-of-the-art for carbon capture (i.e., Carbon Engineering and Heirloom),<sup>24,25</sup> as it is still one of the most efficient ways to obtain pure CO<sub>2</sub> gas solutions from the air (Direct Air Capture) or flue gas. On the other hand, desorbing the CO<sub>2</sub> from carbamate requires less temperature than from carbonate (90-120 °C), but the regeneration and compression steps are still needed to provide high purity CO<sub>2</sub> to the conversion step, which are equally energetically and economically expensive.<sup>26,27</sup> Due to the cost and complexity of CO<sub>2</sub> recovery from the capture solutions, there is increasing industrial interest in using the captured CO<sub>2</sub> solution in the form of bicarbonate or carbamate as a carbon substrate instead of pure CO<sub>2</sub> for eCO<sub>2</sub>R.<sup>28,29</sup> Using bicarbonate as carbon feed is especially of high interest because it can also play the role of electrolyte in the eCO<sub>2</sub>R thus avoiding the need to add additional salts to provide conductivity. In addition, after conversion, the alkalinity of the solution is regenerated such that it can be reused as a capture solution.<sup>30</sup> However, bicarbonate electrolysers are still far from being optimized and cannot yet compete in terms of energy efficiency with pure CO<sub>2</sub> electrolysers.<sup>31,32</sup> The main reason is the high proton donor ability of bicarbonate leading to undesired co-reactions like the Hydrogen Evolution Reaction (HER) and the mass transfer limitations in the electrode-electrolyte interface since CO<sub>2</sub> needs to be delivered from the equilibrium of bicarbonate with water.<sup>33,34</sup> In this context, there is increasing interest in optimizing this combined capture and conversion process to make it more feasible.<sup>35</sup> For instance, a promising option to optimize the capture step is to decrease the operational time to capture a certain amount of  $CO_2$  (g  $CO_2$  h<sup>-1</sup>) in the form of bicarbonate.<sup>36</sup> On the other hand, a strategy to increase the energy efficiency of the bicarbonate electrolyser is to inhibit the proton donor ability of bicarbonate and the undesired HER.<sup>37</sup> However, these two strategies have only been investigated as separate processes. Studies showed how the CO<sub>2</sub> capture is catalysed by using certain bio-inspired strategies, while the HER inhibition in  $eCO_2R$  has been investigated continuously in the last decade.<sup>33,38</sup>

In nature there are certain enzymes called carbonic anhydrase (CA) that promotes the conversion of CO<sub>2</sub> to bicarbonate (1), and often considered as an ultra-fast enzyme for the catalysis of this reaction.<sup>39</sup> The active site of the enzyme is formed by a Zn<sup>2+</sup> co-factor coordinated to three histidine residues in a tetrahedral geometry, leaving a forth coordination site vacant (Figure 1) to coordinate and fixate H<sub>2</sub>O (2). The electro-positivity of the metal center draws electro-negativity away from the oxygen atom of the aqua ligand, and in turn greatly decreasing the pK<sub>a</sub> of aqua ligand from 14 to  $\approx$ 7, i.e., becoming more acidic (3). In the presence of CO<sub>2</sub>, the aqua ligand deprotonates and binds CO<sub>2</sub> to forms a bicarbonate ligand (4), which ligand exchanges with a new H<sub>2</sub>O molecule (5  $\rightarrow$  2).<sup>40,41</sup>



Figure 1: Schematic representation of the catalytic mechanism of the conversion of  $CO_2$  to bicarbonate in the metal co-factor of carbonic anhydrase (hydrogen atoms are not displayed). a) H<sub>2</sub>O coordination to the unoccupied position of the tetrahedral structure; b) Reaction between  $CO_2$  and coordinated  $OH^-$  and; c) formation of bicarbonate and substitution with a new H<sub>2</sub>O molecule. Adapted with permission from PDB-101 (Molecule of the Month series, 2004).<sup>42</sup>

$$\mathrm{CO}_2 + \mathrm{H}_2\mathrm{O} \rightleftharpoons \mathrm{HCO}_3^- + \mathrm{H}^+ \tag{1}$$

$$[Zn(His)_3]^{2+} + H_2 0 \rightleftharpoons [Zn(His)_3(H_2 0)]^{2+}$$
(2)

$$[Zn(His)_3(H_2O)]^{2+} \rightleftharpoons [Zn(His)_3(OH)]^+ + H^+$$
 (3)

$$[\operatorname{Zn}(\operatorname{His})_3(\operatorname{OH})]^+ + \operatorname{CO}_2 \rightleftharpoons [\operatorname{Zn}(\operatorname{His})_3(\operatorname{HCO}_3)]^+$$
(4)

$$[\operatorname{Zn}(\operatorname{His})_3(\operatorname{HCO}_3)]^+ \rightleftharpoons \operatorname{HCO}_3^- + [\operatorname{Zn}(\operatorname{His})_3]^{2+}$$
(5)

Because of the above-mentioned properties to convert CO<sub>2</sub> to bicarbonate, CA has been studied for several years in the field of carbon sequestration.<sup>43–45</sup> However, the high price and the low stability of the enzyme in the harsh conditions (very alkaline media and high temperature) of CO<sub>2</sub> capture technologies made it difficult to implement it in the currently available integrated capture and electrochemical conversion strategies. Nevertheless, promising advances in improving the enzyme stability have been achieved.<sup>46</sup> To overcome these drawbacks, the catalytic reaction of the CA can also be achived without the incorporation of the enzyme if the active site is mimicked synthetically, yielding an artificial enzyme.<sup>47</sup> In some cases, artificial enzymes can outperform natural enzymes in their role as catalysts.<sup>48</sup> Different ligands and metals have been used to synthesize artificial CA to study the kinetic properties of the enzyme CA or to immobilize it on a surface for carbon sequestration. Most of these ligands are similar to the ones found in CA and are ligands that typically form tetrahedral geometries with metal cations after coordination.<sup>49,50</sup> However, there are no studies on using these artificial CA enzymes to study the CO<sub>2</sub> capture for integrated CCU technologies as no artifical CA has yet been found to be compatible with the integrated CO<sub>2</sub> capture and conversion strategy. To be compatible, 1) it must be stable in highly alkaline conditions (pH > 14); 2) it must increase the rate of the conversion of  $CO_2$  to bicarbonate; and 3) it must be inert under the electrochemical conditions of eCO<sub>2</sub>R. Additionally to these functions, since in an integrated CCU strategy the artificial CA will still be part of the electrolyte in the eCO<sub>2</sub>R step, it is interesting to investigate if there could be a role for the artificial CA during the electrolysis step, specifically in promoting the efficiency of the reaction.

As mentioned earlier, the efficiency of the bicarbonate electrochemical reduction is low compared to conventional gas-fed CO<sub>2</sub> electrolysers, mainly due to the high proton donor ability of bicarbonate, promoting HER. There are studies focused on how to inhibit HER in CO<sub>2</sub>

reduction and bicarbonate reduction systems to limit this undesirable trait of bicarbonate. Certain agents added to the electrolyte or on the electrode can form a hydrophobic layer onto the surface of the electrode which avoids polar molecules such as H<sub>2</sub>O and bicarbonate (proton donors) to cross the electrochemical double layer (EDL) and react easily, thus inhibiting HER and are of interest for this study as well.<sup>51–53</sup> This concept for promoting the eCO<sub>2</sub>R is inspired by phenomena found in nature, such as the cell membrane interface, the lotus effect found in leaves or the structure of gas-trapping cuticles on subaquatic spiders, as has been recently discribed by Wakerley et al. during their study on HER inhibition using superhydrophobic surfaces for eCO<sub>2</sub>R systems.<sup>54</sup> Similar effects can be achieved using cationic surfactants.<sup>51</sup> Cationic surfactants consists of a hydrophilic cationic head (for instance tetramethylamine in cetrimonium bromide) and a long alkyl hydrophobic chain (for instance the 16-C chain in cetrimonium bromide) or a hydrophobic functional group (such as the aryl group in cetalkonium chloride). During the eCO<sub>2</sub>R, the hydrophilic head faces towards the surface of the cathode (where CO<sub>2</sub> is reduced) and the hydrophobic tail faces towards the bulk electrolyte (limiting the amount of polar molecules that can enter the EDL). Serendipitously, this amphiphilic structure is found in certain artificial CA's, where the Zn<sup>2+</sup> acts as the hydrophilic head and the ligands (usually heterocycles or aliphatic chains) act as the hydrophobic tail. Thus if a proper ligand could be chosen it might not only speed up the conversion of CO<sub>2</sub> to bicarbonate but it could also form a coordination complex able to inhibit HER and promote the eCO<sub>2</sub>R in bicarbonate systems.

For this reason, we selected three potential ligands that led to the desired artificial CA being able to fulfil both bio-inspired functions and could thus make the integrated capture and conversion more efficient. Histidine was selected because it is the amino acid coordinated to the Zn<sup>2+</sup> centre in CA. Imidazole was selected as a simplified version of histidine as it only contains the nitrogen donor heterocycle of the amino acid. Finally, 1,4,7,10-tetraazacyclododecane (cyclen) was selected because it is an tetradentate chelator that offers extra ligand-metal binding affinity (Figure 2). Indeed, the [Zn(cyclen)]<sup>2+</sup> complex has preformed favourably in previous CA activity kinetics studies,<sup>55</sup> therefore it was suitable for being tested in present work. Other parameters such as the effect of the concentration of artificial CA and the temperature of the capture solution were studied here as well in order to optimize the capture step. As a result, we could identify the optimal conditions for

capturing CO<sub>2</sub> with artifical CA's. The most optimal ligand (being cyclen), in terms of catalytic performance and stability was selected and further evaluated as HER inhibitor during eCO<sub>2</sub>R using the capture solution directly as carbon substrate. In summary, we propose a biomimetic homogeneous catalyst that is both able to catalyze the capture of CO<sub>2</sub> in a 2 M KOH solution and then promote the electrochemical conversion of CO<sub>2</sub> to formate in a 2 M bicarbonate solution, thus outperforming both catalyst that can only be used to speed up the capture of CO<sub>2</sub> or that inhibit HER during eCO<sub>2</sub>R. The artificial CA [Zn(cyclen)]<sup>2+</sup> increased the rate of capturing CO<sub>2</sub> by 84% compared to control experiments and inhibited the HER (partial current density is disminished from 18 mA cm<sup>-2</sup> in control experiments to 0.7 mA cm<sup>-2</sup>) during the eCO<sub>2</sub>R step. To the best of our knowledge this is the first ever report of a strategy using an artificial CA for integrated capture and conversion of CO<sub>2</sub>.

# Experimental

## Materials and solutions

All the chemicals were obtained from commercial sources and used without purification unless stated otherwise. Every solution was prepared in Ultra-Pure water (MilliQ, 18.2 MΩcm). Each solution was sonicated for 10 minutes at room temperature to ensure homogeneity before experimentation. The potassium hydroxide pellets were purchased from Chem-Lab. The ligands imidazole 99+%, L-histidine 98+% and cyclen 99+% were obtained from Chem-Lab, Alfa Aesar and Chematech, respectively. ZnBr<sub>2</sub> anhydrous 98+% was obtained from Chem-Lab.  $CO_2$ (99.998%) was purchased from Nippon Gas. Benzyltrimethylhexadecylammonium chloride 95+% (CKC) was obtained from Alfa Aesar. The Pt mesh (99.9%) and the Sn wire (99.9985%, 2 mm dia.) were obtained from Goodfellow and Alfa Aesar, respectively. The reference electrode Ag/AgCl 3 M KCl and the pH-electrode were purchased from Metrohm. The Nafion 117<sup>®</sup> proton exchange membrane (PEM) was obtained from FuelCell store. The PEM was pre-treated as follows: 1 h in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 80 °C, followed by 1 h in MilliQ water at 80 °C, then 1 h in 0.5 M H<sub>2</sub>O<sub>2</sub> at 80 °C and finally 1 h in MilliQ water at 80 °C.





L=Imidazole log  $k_b = 2.53$  $pK_a ([Zn(L)_3(H_2O)]^{2+}) = 7.13$ 

L=Histidine log  $k_b$  = 9.30 pK<sub>a</sub>([Zn(L)<sub>3</sub>(H<sub>2</sub>O)]<sup>2+</sup>) = 6.90, 7.40



L=Cyclen log  $k_b$  = 15.3  $pK_a ([Zn(L)(H_2O)]^{2+}) = 8.10$ 

Figure 2: Potential ligands chosen to form the artificial CA. Log  $k_b$  refer to the binding constant  $Zn^{2+}$ -L. The pK<sub>a</sub> corresponds to the H<sub>2</sub>O after being fixated to the complex.<sup>55–59</sup>

# CO<sub>2</sub> capture set-up and procedure

The set-up used for the CO<sub>2</sub> capture experiments is shown in Figure S1. A sealed jacketed electrochemical half-cell was filled with 70 mL of the capture solution: 2 M KOH. The concentration of KOH was chosen based on the solubility of bicarbonate (2.2 M). The solution was thermostated at 25 °C (unless stated otherwise) with a Julabo thermostat. A gas sparger connected to a gas flow controller was used to flush pure CO<sub>2</sub> from the gas bottle to the solution at a fixed flow rate of 10 mL min<sup>-1</sup>. The solution was homogenized at all times with a magnetic stirrer rotating at 300 rpm. The pH of the solution was digitally monitored and registered using the Adafruit IO pH meter. The upper limit of detection of the digital pH-meter was 14, thus the first seconds of reaction (pH>14) were not monitored. This did not affect the outcome of the experiment since this range of pH was not used in this study. The

concentration of the  $[Zn(L)_x]^{2+}$  used as artificial CA for the CO<sub>2</sub> capture catalysis was benchmarked to 2 mM (unless stated otherwise). To properly synthesize the coordination complex in situ, 140 µL of a 1 M ZnBr<sub>2</sub> solution and 150 µL of a 3 M (histidine or imidazole) or 1 M (cyclen) solution were added drop-wise at the same time to the 2 M KOH capture solution while homogenizing the solution at all time with a magnetic stirrer (6). The amount of ligand added was stochiometrically slightly higher than needed to ensure at least a 3:1 ratio (histidine or imidazole) or a 1:1 ratio (cyclen) of coordination. This was crucial to avoid the formation of unsoluble Zn(OH)<sub>2</sub> and thus the loss of catalyst.

$$\operatorname{ZnBr}_2 + \operatorname{xL} \rightleftharpoons [\operatorname{Zn}(L)_x]^{2+} + 2\operatorname{Br}^-$$
 (6)

When CO<sub>2</sub> started flushing the capture solution, a titration-like curve was obtained from monitoring the pH (Figure 3). In the beginning, the pH decreased gradually. This was because the capture solution was acting as a buffer (7-8):

$$[OH^{-}] = 2 M$$

$$CO_{2} + OH^{-} \rightleftharpoons HCO_{3}^{-}$$

$$HCO_{3}^{-} + OH^{-} \rightleftharpoons CO_{3}^{2-} + H_{2}O$$
(8)

This continued until the supplied amount of acid (i.e., CO<sub>2</sub>) became larger than the buffer capacity could support, upon which the base was fully converted to carbonate (9):

$$CO_2 + 2OH^- \rightleftharpoons CO_3^{2-} + H_2O$$
 (9)  
 $[CO_3^{2-}] = 2 M$ 

Afterwards, the pH continued decreasing due to the continued introduction of  $CO_2$  and interaction with the solvent (i.e., water) (10-11) until the point where half of the carbonate is converted to bicarbonate (i.e., point of half-neutralization):

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$
(10)

$$\mathrm{CO_3}^{2-} + \mathrm{H^+} \rightleftharpoons \mathrm{HCO_3}^{-} \tag{11}$$

$$[\text{HCO}_3^{-}] = [\text{CO}_3^{2^{-}}] = 1 \text{ M}$$

After this point the pH decreased gradually again due to the buffering effect of the solution. Finally, at pH 8, the solution was saturated. All the carbonate was fully converted to bicarbonate but some free CO<sub>2</sub> remains in solution as the maximum solubility of bicarbonate (i.e., 2.2 M) was reached at pH 8.3 (or the pH at which the maximum relative abundance of bicarbonate is found, see Bjerrum plot as Figure S2).

$$[HCO_3^{-}] = 2 M$$

This small portion of dissolved CO<sub>2</sub> goes at the cost of a portion of bicarbonate, therefore, to obtain the maximum amount of bicarbonate and maximize CO<sub>2</sub> capture efficiency, either the capture experiment is stopped at pH 8.3 or the initial concentration of KOH is increased to 2.2 M. To avoid precipitation of salts due to concentration gradients within the solution and the reactor, the first option was more appropriate for the experiments and was therefore selected.

As explained, several equilibria and buffer reactions were occurring during the titration of KOH with CO<sub>2</sub>. These reactions are compiled in Figure 3 The concentration of each species at a given time is described by their rate equation (Eq. 1-5).<sup>60</sup>

$$\frac{d[CO_2]}{dt} = k_{c-1}[H^+][HCO_3^-] + k_{c-2}[HCO_3^-] - k_{c+1}[CO_2] - k_{c+2}[OH^-]$$
Eq. 1

$$\frac{d[HCO_3^-]}{dt} = k_{c+1}[CO_2] + k_{c+2}[CO_2][OH^-] + k_{c+3}[CO_3^{2-}][H^+] + k_{c-4}[CO_3^{2-}] - k_{c-1}[HCO_3^-][H^+] - k_{c-2}[HCO_3^-]$$
Eq. 2  
-  $k_{c-3}[HCO_3^-] - k_{c+4}[HCO_3^-][OH^-]$ 

$$\frac{d[CO_3^{2-}]}{dt} = k_{c-3}[HCO_3^{-}] + k_{c+4}[CO_2][OH^{-}] - k_{c+3}[CO_3^{2-}][H^{+}] - k_{c-4}[CO_3^{2-}]$$
Eq. 3

$$\frac{d[H^+]}{dt} = k_{c+1}[CO_2] + k_{c-3}[HCO_3^-] + k_{c+5} - k_{c-1}[HCO_3^-][H^+] - k_{c+3}[CO_3^{2-}][H^+] - k_{c-5}[OH^-][H^+]$$
Eq. 4

$$\frac{d[OH^{-}]}{dt} = k_{c-2}[HCO_{3}^{-}] + k_{c-4}[CO_{3}^{2-}] + k_{c+5} - k_{c+2}[CO_{2}][OH^{-}] - k_{c+4}[CO_{2}][OH^{-}] - k_{c-5}[OH^{-}][H^{+}]$$
Eq. 5



Figure 3: Evolution of pH and equilibrium reactions of the species present when saturating a 2 M KOH solution with gaseous CO<sub>2</sub>.

To elaborate a detailed kinetic model and determine the accurate, independent, rate constant  $(k_c)$  of the capture of CO<sub>2</sub>, every differential equation had to be taken into consideration. However, we could elaborate a model based on the evolution of pH over time, which is directly related to the consumption of CO<sub>2</sub> and thus the CO<sub>2</sub> capture rate. As observed in Figure 3, the pH decreases during the CO<sub>2</sub> capture, thus the concentration of H<sup>+</sup> increases over time, allowing us to calculate a (pseudo)rate constant (K<sub>c</sub><sup>\*</sup>) based on the (pseudo)first-order rate equation of the production of H<sup>+</sup> (Eq. 6).

$$\frac{+d[H^+]}{dt} = K_c^*[H^+]$$
 Eq. 6

As such, we obtain a rate equation that only depends on the concentration of  $H^+$  at a given time, which is calculated from the measured pH of the solution. This approximation is experimentally proven by using the linear regression fitting method. In a (pseudo)first-order kinetic equation, ln[X] has linear regression with time (R>0.95). This is indeed observed in our system. For instance, when evaluating the pH evolution during the step where carbonate is converted to bicarbonate in a CO<sub>2</sub> capture experiment using 2 M KOH as capture solution, a linear regression was obtained (Figure 4). We can then confirm that this rate equation and model is valid for studying the evolution of H<sup>+</sup> overtime during the CO<sub>2</sub> capture and thus to calculate  $K_c^*$  for each case scenario (ligand, concentration and temperature screening). The  $K_c^*$  is directly related to the efficiency of the capture solution (KOH + artificial CA) to convert CO<sub>2</sub> to bicarbonate, the larger the faster the capture step.





The procedure to evaluate each artificial CA and system is displayed in Figure S5. The capture solution (2 M KOH) was purged with CO<sub>2</sub> in the presence and the absence of the artificial CA. The nature of the ligand, the concentration of the catalyst and the temperature of the solution varied throughout the study. The pH was measured from the starting point (pH > 14) to the saturation point (when pH remains constant). For conventional systems, the experiment finished at pH = 8. The K<sub>c</sub><sup>\*</sup> was calculated using the data that belonged to the conversion of carbonate to bicarbonate (pH 10  $\rightarrow$  pH 8.3) to avoid the lack of data at the beginning of the experiment (pH > 14) and the half-neutralization point (pH 13  $\rightarrow$  10). The pH range of the study varied  $\pm$  0.3 depending on the variables of the study. A higher K<sub>c</sub><sup>\*</sup> determined a faster rate of the conversion of CO<sub>2</sub> to bicarbonate (Reaction 10). Three tests per set of experiments were performed and are displayed as average. The error bars correspond to the standard deviation.

# Bicarbonate electrolysis: set-up and procedure

The set-up for electrochemically converting bicarbonate (i.e., the capture solution) to formate is shown in Figure S4. A tailored jacketed H-cell was filled with 140 mL of electrolyte: 70 mL of catholyte and 70 mL of anolyte. The catholyte was the 2 M potassium bicarbonate solution obtained from the CO<sub>2</sub> capture step (in the presence or the absence of additives) and the anolyte was a 1 M KOH solution. To obtain a 2 M bicarbonate solution, the CO<sub>2</sub> capture step had to be stopped at pH 8.3. Both half-cells were separated by a PEM to ensure ionic conductivity (charge balance) and avoid product crossover. The system was thermostatic at 25 °C. A Sn wire (0.2 cm<sup>2</sup>) was used as an electrocatalyst to convert CO<sub>2</sub> to formate, an Ag/AgCl 3 M KCl electrode was used as a reference electrode and a Pt mesh was used as a counter electrode in the three-electrode system. A Sn electrocatalyst was selected due to its high selectivity towards formate, which we could quantify by liquid analysis and thus allowed a proper evaluation of our model.<sup>61,62</sup> With a Biologic potentiostat (model VMP3), one-hour chronoamperometry experiments at the fixed potential of -0.9 V<sub>RHE</sub> was performed to electrochemically convert the bicarbonate solution. The working potential was chosen based on the bicarbonate electrolysis potential screening performed in our previous work.<sup>63</sup> The preconditioning of the working electrode followed the same procedure as in our previous work (i.e. cleaning and electrochemical surface stabilization). The solution was homogenized with a magnetic stirrer at 300 rpm throughout the experiment. After electrolysis, 0.5 mL of the solution was sampled and analyzed in an Agilent 1200 High-Performance Liquid Chromatography (HPLC) using an Agilent Hi-Plex H 7.7×300 mm column. The samples were previously diluted in MilliQ water and acidified with H<sub>2</sub>SO<sub>4</sub> to avoid bubble formation and obstruction in the column.  $H_2SO_4$  0.01 M was used as the mobile phase. The results of the electrolysis are presented in the form of the Faradaic Efficiency (FE, Eq. S1). The FE towards formate is quantified by liquid analysis while the rest of the FE is considered to go towards HER, although this is an approximation based on the high selectivity of Sn electrocatalyst towards formate. Gas analysis was performed in preliminary studies where saturated CO<sub>2</sub> solutions were used instead of bicarbonate solutions in the same conditions as this study and a negligible fraction of FE went to CO (less than 1%), allowing this approximation. Three tests per set of experiments were performed and displayed as average. The error bars correspond to the standard deviation.

To study the effects of the additives on the electrochemical performance of the electrolyte, Linear Sweep Voltammetry (LSV) and Electrochemical Impedance Spectroscopy (EIS) were performed on an Autolab potentiostat (model PGSTAT302N). For LSV experiments, the current density (CD) was measured in the potential range of -0.3 to -1.3 V<sub>RHE</sub> at 5 mV s<sup>-1</sup>. For EIS experiments, the impedance was measured at the fixed potential of -0.9 V<sub>RHE</sub> from 1 to 20000 Hz. The details on the equivalent circuit model and the Nyquist plot fitting are shown in the supporting information (Figure S6). The results are displayed in the form of Double-Layer Capacitance (DL-Capacitance, Eq. S2).

# **Results and discussion**

# Biomimetic catalysis of the CO<sub>2</sub> capture

#### Effect of the nature of the ligand

The first investigated parameter was the nature of the ligands. The ligand(s) determines the stability of the [Zn(L)<sub>x</sub>]<sup>2+</sup> complex, and how well it competed with the formation of insoluble  $Zn(OH)_2$  and  $ZnCO_3$ . The ligand(s) also modulates the electronic properties of the  $Zn^{2+}$  center. A more electro-positive Zn<sup>2+</sup> center results in a stronger Zn-OH<sub>2</sub> bond, making the aqua ligand more acidic and thus increasing K<sub>c</sub><sup>\*</sup>. As shown in Figure 5, the K<sub>c</sub><sup>\*</sup> increased in the presence of the artificial CA,  $[Zn(L)_x]^{2+}$ , independently of the ligand used. In the absence of the catalyst (No ligand), the value of the  $K_c^*$  was 7.7 × 10<sup>-3</sup> s<sup>-1</sup> while in the presence of histidine, imidazole and cyclen the value was  $8.9 \times 10^{-3}$ ,  $10.6 \times 10^{-3}$  and  $11.1 \times 10^{-3}$  s<sup>-1</sup>, respectively. The best performance was thus obtained by using imidazole and cyclen as the ligand(s), the latter being slightly more effective (+37 and +41%, respectively). Although histidine is the amino acid that forms the coordination complex in the enzyme CA, in this set of experiments it was the least effective catalyst (+15%). We can attribute this effect to the amine and carboxylic acid groups of histidine, which in the enzyme are not present because they form the peptidic bonds, are interfering with the formation of the tetrahedral Zn<sup>2+</sup> complexes and/or the binding of H<sub>2</sub>O and consequently also the annexing of CO<sub>2</sub>. Coordination complexes with simpler ligands (imidazole) and ligands with a fixed structure (cyclen) appeared to be more efficient in binding and fixing  $H_2O$  for the catalysis of the reaction of  $CO_2$  to bicarbonate.



Figure 5: a) Evolution of  $In[H]^+$  over time and b)  $K_c^*$  calculated from the corresponding linear regression equation (Figure S7) of a CO<sub>2</sub> capture solution in the presence and in the absence of  $[Zn(L)_x]^{2+}$ , where L are different ligands tested (histidine, imidazole and cyclen).

Based on the calculation of  $K_c^*$ , it can then be assumed that both imidazole and cyclen were almost equally effective as ligands in  $[Zn(L)_x]^{2+}$  for the catalytic capture of CO<sub>2</sub>. However, during the experiment, we observed that in the presence of imidazole, the solution became colloidal and finally a sediment was formed, which was not observed when histidine and cyclen were used as ligands. After further evaluation, we reached the conclusion that the sediment formed was ZnCO<sub>3</sub> and Zn(OH)<sub>2</sub> based on the fact that imidazole has a significantly lower binding constant ( $k_b$ ) to Zn<sup>2+</sup> (2.53) as compared to those of histidine (9.30) and cyclen (15.3). Therefore, since the  $k_b$  of imidazole to form  $[Zn(imidazole)_3]^{2+}$  is low, the coordination complex was easily dissociated to the metal cation and the ligands (12). In the first steps of the experiment (pH >14  $\rightarrow$  pH 10.5) the concentration of OH<sup>-</sup> was high (starting at 2 M) and the CO<sub>2</sub> was captured mostly in the form of carbonate (7-8). Since the  $Zn^{2+}$  was easily dissociated from [Zn(imidazole)<sub>3</sub>]<sup>2+</sup>, it reacted with OH<sup>-</sup> and the carbonate, leading to the water-insoluble compounds  $ZnCO_3$  and  $ZnOH_2$  (13-14). Since  $Zn^{2+}$  is lost in the presence of imidazole, this means that less amount of [Zn(imidazole)<sub>3</sub>]<sup>2+</sup> is necessary to achieve a catalytic activity similar to that of [Zn(cyclen)]<sup>2+</sup>. Therefore, it can be considered that [Zn(imidazole)<sub>3</sub>]<sup>2+</sup> has slightly higher catalytic activity than [Zn(cyclen)]<sup>2+</sup>. Nevertheless, the loss of catalyst in the capture step is a stronger reason to stop considering imidazole as ligand and thus exclude it from further study.

$$\operatorname{Zn}^{2+}_{(aq)} + 3 \operatorname{Imidazole}_{(aq)} \quad \rightleftharpoons \quad [\operatorname{Zn}(\operatorname{Imidazole})_3]^{2+}_{(aq)}$$
(12)

$$\operatorname{Zn}^{2+}_{(aq)} + \operatorname{CO}_{3}^{2-}_{(aq)} \to \operatorname{ZnCO}_{3(s)} ; K_{s(ZnCO_3)} = 1.3 \times 10^{-11}$$
 (13)

$$\operatorname{Zn}^{2+}_{(sq)} + 20\mathrm{H}^{-}_{(aq)} \rightarrow \operatorname{Zn}(0\mathrm{H})_{2(s)}$$
;  $K_{s(Zn(0H)_2)} = 3.0 \times 10^{-16}$  (14)

Cyclen showed the best effectiveness as a ligand in coordinating  $Zn^{2+}$  to form an artificial CA for capturing CO<sub>2</sub>. It outperformed histidine in terms of catalytic activity ( $K_c^*$ =11.1 1 × 10<sup>-3</sup> s<sup>-1</sup>) and imidazole in terms of stability. Therefore, for the following two sets of experiments (effects of the concentration of catalyst and temperature of the solution), cyclen was benchmarked as the ligand for the synthesis of artificial CA.

# Effect of the concentration of catalyst

The next parameter to study was the effect of the concentration of the artificial CA present in the capture solution. We expected that by increasing the concentration, the performance of the catalyst would increase due to the presence of a higher number of catalytic sites in the capture solution. The concentration of [Zn(cyclen)]<sup>2+</sup> was increased from 0 to 50 mM and the K<sub>c</sub><sup>\*</sup> was calculated for each concentration (Figure 6). As expected, the catalytic performance did indeed increase with the concentration of [Zn(cyclen)]<sup>2+</sup>. The most significant increase in  $K_c^*$  was from 7.7 × 10<sup>-3</sup> to 11.1 × 10<sup>-3</sup> s<sup>-1</sup> (+41%) with a change in concentration from 0 to 2 mM. Upon further increases in concentration, the value of the  $K_c^*$  increased to  $12 \times 10^{-3}$  (+56%) at 10 mM, 12.9 × 10<sup>-3</sup> (+68%) at 20 mM and 14.7 × 10<sup>-3</sup> s<sup>-1</sup> (+91%) at 50 mM. We attributed the abrupt increase of the catalytic performance from 0 to 2 mM to the effect of the addition of the homogeneous catalyst. At higher concentrations, the increase of the K<sub>c</sub><sup>\*</sup> is less pronounced since the concentration of CO<sub>2</sub> is not high enough to occupy all the active sites present in the solution. We must take into account that although the kinetic study relates to the conversion of carbonate to bicarbonate, CO<sub>2</sub> must first be dissolved in the solution (CO<sub>2</sub>  $\rightarrow$  CO<sub>2(aq)</sub>) to start the catalytic reaction. The solubility of CO<sub>2</sub> is very low in aqueous (g) solutions (33 mM). Very fast conversion to bicarbonate due to the presence of the artificial CA is thus limited by the concentration of diluted CO2. In this scenario, where the concentration of catalyst is high and that of the substrate (CO<sub>2</sub>) is low, the effect of adding additional artificial CA is further diminished since it also catalyses the reverse reaction (conversion of bicarbonate back to CO<sub>2</sub>).

Further increasing the concentration above 50 mM was not considered since the solution became slightly colloidal during the experiment with 50 mM CA. This is likely attributed to the solubility limit of the metal complex in water. As was the case for imidazole in chapter 3.1.1, we cannot assume that the  $K_c^*$  obtained at 50 mM is valid (most likely overestimation). Therefore, 20 mM is chosen as the optimal concentration of  $[Zn(cyclen)]^{2+}$  to capture  $CO_2$  using 2 M KOH as capture solution (a +68% faster capture is achieved). This concentration of artificial CA was used in the following studies, both for the evaluation of the impact of temperature on the capture step and for the bicarbonate electrolysis experiments.



Figure 6: a) Evolution of  $In[H]^+$  over time and b)  $K_c^*$  calculated from the corresponding linear regression equation (Figure S8) of a CO<sub>2</sub> capture solution in the presence and the absence of  $[Zn(cyclen)]^{2+}$  at different concentrations.

# Effect of the temperature of the capture solution

Finally, the last studied parameter was the temperature of the capture solution. As with any catalytic system, temperature plays an important role. Rate and catalytic constants are temperature dependent, as defined by the Arrhenius equation, and thus  $K_c^*$  will also change with temperature. Nevertheless, given the Arrhenius equation and enzymes natural working temperature, we can assume that  $K_c^*$  will increase with temperature. However, we must also take into account that as the temperature of the solution changes, the solubility and

equilibrium constants of the species and reactions involved in the catalytic route ( $CO_2$ , bicarbonate and carbonate equilibrium and coordination stability) are affected, as well. An increase in temperature decreases the solubility of  $CO_2$ , which is undesirable, while on the other hand the solubility of bicarbonate and carbonate increases, which is desirable. Thus, several factors play a role and were taken into consideration when evaluating each system.

The temperature of the capture solution was increased from room temperature (25 °C) to 40 and 60 °C (Figure 7). From 25 to 40 °C, the K<sub>c</sub><sup>\*</sup> increased significantly from 12.9 × 10<sup>-3</sup> to 14.2 × 10<sup>-3</sup> s<sup>-1</sup> (+68% and +84%, respectively). This behaviour could be explained by the Arrhenius equation, being an exponential function, the rate constant thus increases rapidly with the temperature. However, this equation could not explain why from 40 to 60 °C, the K<sub>c</sub><sup>\*</sup> barely increased to 14.3 × 10<sup>-3</sup> s<sup>-1</sup> (+85%). Therefore, the increase in the temperature, and thus the kinetic rate must have been counteracted by the instability of the artificial CA, which is also observed in natural enzymes.<sup>64</sup> Since the formation of  $[Zn(cyclen)]^{2+}$  is an exothermic reaction, the stability of the coordination complex (and thus k<sub>b</sub>) decreases with the increase in temperature (as described by Van't Hoff equation), weakening the coordination bond and dragging the equilibrium towards the dissociated species Zn<sup>2+</sup> and cyclen, thus deactivating the artificial CA. An additional effect is the weakening of the Zn<sup>2+</sup>-OH bond, key for the CO<sub>2</sub>- HCO<sub>3</sub><sup>-</sup> catalytic interconversion (see reactions 1-5).

To obtain information on the system when it is cooled, we also evaluated it at lower temperatures (i.e. 10°C). As expected, the  $K_c^*$  decreased to  $9.3 \times 10^{-3} \, \text{s}^{-1}$ . Nevertheless, the  $K_c^*$  was still higher than in a capture solution at 25°C in the absence of artificial CA (+20%). In addition, although it took more time to reach saturation, the final pH, 7.4, was lower than at 25 °C , meaning that more CO<sub>2</sub> was captured at the end of the experiment (Figure S10), in accordance with the increase of the solubility of CO<sub>2</sub> at lower temperatures.



Figure 7: a) Evolution of  $In[H]^+$  over time and b) calculated  $K_c^*$  from the corresponding linear regression equation (Figure S9) of a CO<sub>2</sub> capture solution at different temperatures in the presence and the absence of 20 mM of  $[Zn(cyclen)]^{2+}$ .

Based on the results obtained, increasing the temperature up to 40 °C is beneficial for obtaining a faster  $CO_2$  capture rate, however, increasing the temperature further leads to the deactivation of the artificial CA and is, thus, detrimental for the technology. Capturing  $CO_2$  at lower temperatures may be attractive in terms of total DIC captured, but the rate constant is significantly decreased.

# Promoted bicarbonate electrolysis

Here we describe the effect of the presence of the artificial CA during  $eCO_2R$ . The most optimal conditions for capturing  $CO_2$  in a 2 M KOH solution found in the previous section (cyclen as ligand and 20 mM as the concentration of artificial CA) were selected. After the  $CO_2$  capture step, the resulting solution contained 2 M KHCO<sub>3</sub> in the presence of 20 mM of  $[Zn(cyclen)]^{2+}$  and will be the electrolyte of the electrochemical cell in further experiments. The FE obtained from the electrolysis experiments were compared to analogous experiments in the absence of artificial CA (no additive), in presence of 20 mM of cyclen (but in the absence of  $Zn^{2+}$ ) or in the presence of 1 mM of the cationic surfactant CKC (known HER inhibitor).<sup>65</sup> The preliminary capture experiments in presence of 20 mM cyclen (without being coordinated to  $Zn^{2+}$ ) showed little effect of the ligand on the capture kinetics when it's free in the capture solution (0.0069 s<sup>-1</sup> compared to the blank 0.0072 s<sup>-1</sup>, Figure S11). As can be observed in Figure 8, the FE towards formate is very low (4.1%) in pure bicarbonate

electrolytes (no additive), which is in accordance with the literature.<sup>37</sup> In bicarbonate electrolytes in the presence of uncoordinated cyclen, the FE towards formate was in the same range as in pure bicarbonate electrolytes (4.6 %). The presence of cyclen did not affect the selectivity of the reaction. However, it can be observed how the total current density significantly increased (from 19 to 32 mA cm<sup>-2</sup>) compared to the pure bicarbonate electrolyte (Figure 9). It is known that some additives can inhibit the corrosion of a metal surface under an applied potential increasing the effective active surface area, which explains the increase in the total current density.<sup>66</sup> On the other hand, in the presence of [Zn(cyclen)]<sup>2+</sup>, the FE towards formate increased substantially from 4.6 to 55%. Furthermore, the partial current density towards HER is substantially and selectively decreased from 18 to 0.7 mA cm<sup>-2</sup> while the current density towards formate remained similar compared to control experiments (from 0.7 to 0.8 mA cm<sup>-2</sup>), meaning that HER is being inhibited. This effect was also observed when the HER inhibitor CKC is present (FE towards formate of 64% and HER partial current density of 0.8 mA cm<sup>-2</sup>). We thus assume that the artificial CA [Zn(cyclen)]<sup>2+</sup> and the HER inhibitor CKC play a similar role in inhibiting HER in eCO<sub>2</sub>R in bicarbonate electrolytes.



Figure 8: FE towards formate (measured) and H<sub>2</sub> (approximated) of the electrolysis of a 2 M KHCO<sub>3</sub> solution (prepared from a 2 M KOH capture solution) in the presence and the absence of 20 mM of cyclen, 20 mM of [Zn(cyclen)]<sup>2+</sup> or 1 mM of CKC.



Figure 9: Partial CD towards formate and H<sub>2</sub> (approximated) of the electrolysis of a 2 M KHCO<sub>3</sub> solution (prepared from a 2 M KOH capture solution) in the presence and the absence of 20 mM of cyclen, 20 mM of [Zn(cyclen)]<sup>2+</sup> or 1 mM of CKC.

To gain further insights into how the [Zn(cyclen)]<sup>2+</sup> inhibits HER, we further evaluated the role of the artificial CA by studying specifically the changes on the surface of the electrode. LSV experiments showed how the total current density increases substantially in the presence of cyclen (reinforcing the previously explained observation), but decreases also substantially in the presence of [Zn(cyclen)]<sup>2+</sup>, which is also in accordance with the electrolysis experiments (Figure 10).

At the electrolysis working potential (i.e., -0.9  $V_{RHE}$ ) a small shoulder was observed in the LSV plots, which can be attributed to the reduction of CO<sub>2</sub> or, on the other hand, to the reduction of Zn<sup>2+</sup> to metallic Zn (E°=-0.76V), which would mean that the coordination complex is not stable under the working potential. We performed an additional analogous experiment involving [Zn(imidazole)<sub>3</sub>]<sup>2+</sup> as artificial CA to verify this. Due to the low k<sub>b</sub>, the coordination complex was easily dissociated and thus Zn<sup>2+</sup> was present more often as a free cation in the electrolyte. For this experiment, 2 mM [Zn(imidazole)<sub>3</sub>]<sup>2+</sup> had to be used instead of 20 mM since the solution became very colloidal at these high concentrations. Even at this low concentration, the FE towards formate was 1.2%, which is low even in comparison with the 4.1% of the control experiment and much lower than the 55% of [Zn(cyclen)]<sup>2+</sup> experiment.

The HER inhibition effect is lost as the coordination complex is unstable but more importantly, the FE dropped by 3% as compared to the control experiment, which was attributed to the current that was spent for the reduction of  $Zn^{2+}$  to metallic Zn. Additionally, after one hour of electrolysis, the surface of the Sn electrode was completely covered with a black coating, corresponding to the metallic Zn, which was not observe when  $[Zn(cyclen)]^{2+}$  was used (Figure S12). We can therefore assume that  $[Zn(cyclen)]^{2+}$  is stable in the working conditions (-0.9  $V_{RHE}$ ) and the shoulder can thus most likely be entirely assigned to CO<sub>2</sub> reduction. Even if part of the current of the observed small shoulder in the LSV corresponded to the reduction of  $Zn^{2+}$ , the effect was negligible to be considered as a drawback as no Zn deposits were discovered on the Sn wire in this case.



Figure 10: a) LSV and b) DL-Capacitance of 2 M KHCO<sub>3</sub> solutions in the presence and the absence of cyclen and [Zn(cyclen)]<sup>2+</sup>.

To further evaluate the surface effects due to the presence of  $[Zn(cyclen)]^{2+}$ , we performed EIS and calculated the DL-Capacitance for three scenarios (Figure 10, no additive, cyclen addition only and CA addition). From our previous work it is know that the DL-capacitance of the EDL formed between the working electrode and the electrolyte is typically lower in the presence of HER inhibitors such as CKC, directly linked to an increase in hydrophobicity of the surface.<sup>65</sup> This was observed in our current system as well when  $[Zn(cyclen)]^{2+}$  was added to the electrolyte. Indeed, the DL-Capacitance dropped from 37 to 18 µF cm<sup>-2</sup>. When cyclen alone was present, the DL-Capacitance remained similar (35 µF cm<sup>-2</sup>). Since  $[Zn(cyclen)]^{2+}$  is a cationic species, once the working potential (i.e., -0.9 V<sub>RHE</sub>) is applied, it migrated towards the cathode, taking part of the inner layer of the EDL (Figure 11), similar to the mechanism found

when cationic surfactants were used as HER inhibitors. Without the presence of Zn<sup>2+</sup>, cyclen can't migrate towards the surface of the electrode and take part directly in the EDL, thus the expected hydrophobic layer cannot form and as such the DL-Capacitance did not increase because of a lower surface that would have been available otherwise. With these results, we can confirm that [Zn(cyclen)]<sup>2+</sup> has the function of a HER inhibitor during eCO<sub>2</sub>R and has the same effect on the surface of the electrode as conventional cationic surfactants such as CKC during the inhibition of HER but with the added advantage that it also aids capturing as compared to CKC which does not fulfil this role.



Figure 11: EDL representation for each case scenario (absence of artificial CA, presence of cyclen and presence of [Zn(cyclen)]<sup>2+</sup>) and HER inhibition model proposed.

# Conclusions

Integrating the capture and the electrochemical conversion of CO<sub>2</sub> is a challenging technology that requires the most optimal operational conditions for both the capture and the conversion steps to be proposed as a potential technology in the field of CCU. However, until now the capture and the conversion steps were investigated mostly as separated processes, limiting the up-scalability of the integrated concept. In the field of CO<sub>2</sub> sequestration, artificial CA has been investigated to promote the conversion of CO<sub>2</sub> to bicarbonate and the addition of cationic surfactants to the electrolyte has been investigated to promote bicarbonate

electrolysis. In our work, after an optimization study, we proposed the bio-inspired coordination complex [Zn(cyclen)]<sup>2+</sup> as an additive able to fulfil the two functions. An increase of the rate of the conversion of  $CO_2$  to bicarbonate of 84% was obtained when using 20 mM [Zn(cyclen)]<sup>2+</sup> in a 2 M KOH solution at 40 °C. The resulting bicarbonate solution was further used as an electrolyte in the  $eCO_2R$ , where the coordination complex fulfilled the role of HER inhibitor. After one hour of electrolysis, the FE towards formate increased from 4.1 (in absence of CA) to 55%. We have demonstrated how, by studying at the same time the capture and the conversion steps, new possibilities appear such as the addition of new agents able to have a significant role in each of the two steps. Nevertheless, there is still room for improvement. Although [Zn(cyclen)]<sup>2+</sup> is a promising artificial CA for this application, other metal centers and ligands could outperform it. It is thus further screening of potential artificial CA is ongoing. On the other hand, in the eCO<sub>2</sub>R experiments, a low total CD was obtained since most of the current density belonged to HER and it was inhibited. For upscaling technologies, to reach techno-economic milestones in the field of integrated capture and eCO<sub>2</sub>R, CD in the range of 50-500 mA cm<sup>-2</sup> are needed. Then, for future work, it is interesting to perform the electrolysis experiments at such CD to properly evaluate this system at stateof-the-art conditions. To reach these conditions, upscaling the setup to a flow electrolyser is in progress.

# **Supporting information**

Formulas & equations, experimental setup, EIS model fitting & simulation, regression fitting, etc.

#### **Conflict of interests**

There are no conflicts to declare.

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Integrating the capture and conversion of  $CO_2$  is crucial towards developing a carbon-neutral technology that allows using  $CO_2$  from the air as resource for the energy and chemical industry.