

# Reactive Carbon Capture Enables CO<sub>2</sub> Electrolysis with Liquid Feedstocks

Published as part of the Accounts of Chemical Research special issue “Opportunities and Challenges of Nanomaterials in Sustainability: Pursuing Carbon Neutrality”.

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Cite This: *Acc. Chem. Res.* 2024, 57, 1007–1018



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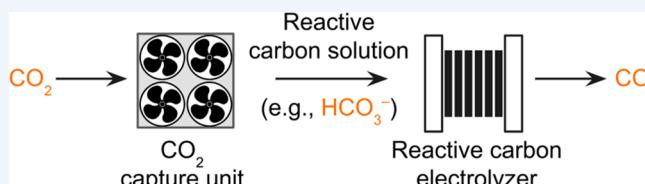
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**CONSPPECTUS:** The electrochemical reduction of carbon dioxide (CO<sub>2</sub>RR) is a promising strategy for mitigating global CO<sub>2</sub> emissions while simultaneously yielding valuable chemicals and fuels, such as CO, HCOO<sup>-</sup>, and C<sub>2</sub>H<sub>4</sub>. This approach becomes especially appealing when integrated with surplus renewable electricity, as the ensuing production of fuels could facilitate the closure of the carbon cycle. Despite these advantages, the realization of industrial-scale electrolyzers fed with CO<sub>2</sub> will be challenged by the substantial energy inputs required to isolate, pressurize, and purify CO<sub>2</sub> prior to electrolysis.

To address these challenges, we devised an electrolyzer capable of directly converting reactive carbon solutions (e.g., a bicarbonate-rich eluent that exits a carbon capture unit) into higher value products. This “reactive carbon electrolyzer” operates by reacting (bi)carbonate with acid generated within the electrolyzer to produce CO<sub>2</sub> *in situ*, thereby facilitating CO<sub>2</sub>RR at the cathode. This approach eliminates the need for expensive CO<sub>2</sub> recovery and compression steps, as the electrolyzer can then be coupled directly to the CO<sub>2</sub> capture unit.

This Account outlines our endeavors in developing this type of electrolyzer, focusing on the design and implementation of materials for electrocatalytic (bi)carbonate conversion. We highlight the necessity for a permeable cathode that allows the efficient transport of (bi)carbonate ions while maintaining a sufficiently high catalytic surface area. We address the importance of the supporting electrolyte, detailing how (bi)carbonate concentration, counter cations, and ionic impurities impact selectivity for products formed in the electrolyzer. We also catalog state-of-the-art performance metrics for reactive carbon electrolyzers (i.e., Faradaic efficiency, full cell voltage, CO<sub>2</sub> utilization efficiency) and outline strategies to bridge the gap between these values and those required for commercial operation. Collectively, these findings contribute to the ongoing efforts to realize industrial-scale electrochemical reactors for CO<sub>2</sub> conversion, bringing us closer to a sustainable and closed-loop carbon cycle.



## KEY REFERENCES

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- Pimlott, D. J. D.; Jewlal, A.; Mowbray, B. A. W.; Berlinguette, C. P. Impurity-Resistant CO<sub>2</sub> Reduction Using Reactive Carbon Solutions. *ACS Energy Lett.* 2023, 8, 1779–1784.<sup>4</sup> Demonstration of how dissolved nitrogen and sulfur impurities affect a reactive carbon electrolyzer.

## INTRODUCTION

Carbon capture and utilization (CCU) upgrades waste CO<sub>2</sub> into valuable chemical feedstocks such as CO, HCOO<sup>-</sup>, and

Received: September 9, 2023

Revised: January 18, 2024

Accepted: January 19, 2024

Published: March 25, 2024

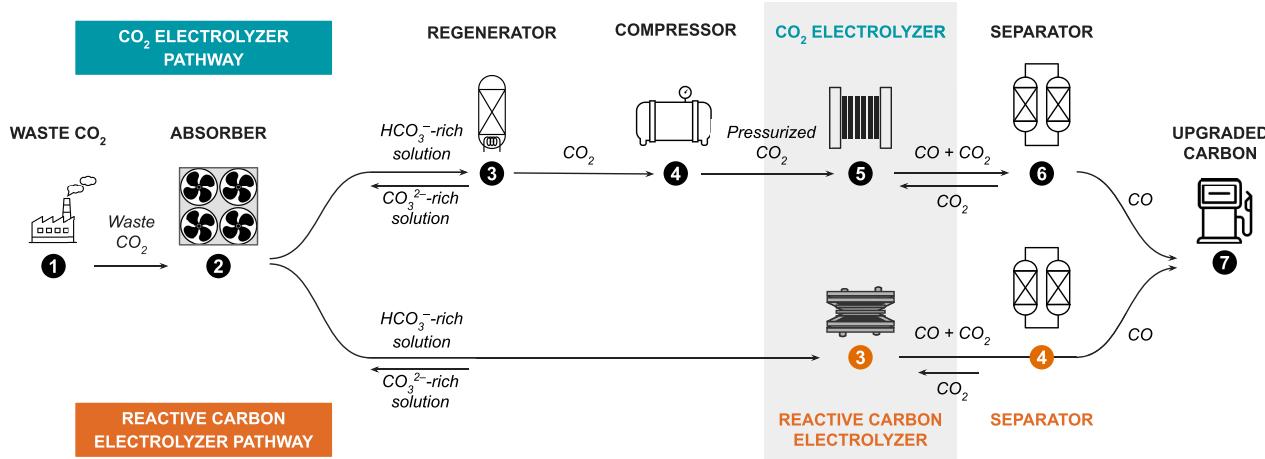


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<https://doi.org/10.1021/acs.accounts.3c00571>  
*Acc. Chem. Res.* 2024, 57, 1007–1018



**Figure 1.** Pathways for CO<sub>2</sub> capture and utilization using CO<sub>2</sub> and reactive carbon electrolyzers. In both cases, an aqueous sorbent reacts with CO<sub>2</sub> to form a “reactive carbon solution” enriched with bicarbonate. The top pathway thermally liberates gaseous CO<sub>2</sub> from bicarbonate prior to upgrading in a CO<sub>2</sub> electrolyzer. The bottom pathway feeds the reactive carbon *liquid* solution directly to the reactive carbon electrolyzer.

C<sub>2</sub>H<sub>4</sub>.<sup>5–8</sup> To be put into practice, this conversion of CO<sub>2</sub> will likely occur in a continuous flow electrochemical reactor, or an “electrolyzer”.<sup>5</sup> Electrolyzers are widely used in industry today to electrolytically drive the production of chemicals such as hydrogen, chlorine, and sodium hydroxide.<sup>9,10</sup> All of these commercial electrolyzers use *liquid* feedstocks.

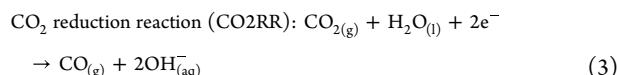
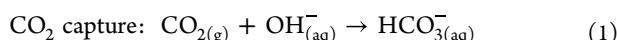
Electrolyzers being developed to reduce CO<sub>2</sub> are typically fed with *gaseous* CO<sub>2</sub>. We submit that electrolyzers fed with gaseous CO<sub>2</sub> (“CO<sub>2</sub> electrolyzers”) will face greater performance, engineering, and maintenance issues than those fed with liquids to the anode and cathode compartments: The performance of CO<sub>2</sub> electrolyzers is compromised by inherently low CO<sub>2</sub> utilization efficiencies and (bi)carbonate crossover through the membrane, and it is more challenging to maintain the physical integrity of seals, membranes, and components of CO<sub>2</sub> electrolyzers when managing a pressurized gas feed.

Another significant issue is that a CO<sub>2</sub> electrolyzer requires a pure and concentrated supply of CO<sub>2</sub>.<sup>2</sup> When CO<sub>2</sub> is derived from air, the CO<sub>2</sub> concentrations are too low (0.04% v/v) to achieve sufficient concentrations at the cathode for meaningful product formation.<sup>11</sup> Industrial flue gases contain higher concentrations of CO<sub>2</sub> (5–15% v/v), but even these concentrations are insufficient to enable highly selective CO<sub>2</sub> conversion.<sup>12</sup> Consequently, CO<sub>2</sub> streams must be concentrated, purified, and delivered to the electrolyzer as a pressurized feedstock in order to reach sufficiently high current densities. The isolation, purification, and pressurization of CO<sub>2</sub> is expensive.<sup>13</sup>

These collective factors prompted our program to find ways to directly couple upstream CO<sub>2</sub> capture to an electrolyzer, where the electrolyzer is able to convert the CO<sub>2</sub>-enriched *liquid* eluent (“reactive carbon solution”) from the capture unit into an upgraded carbon product (Figure 1).<sup>1</sup> This form of CCU is labeled “reactive carbon capture”, and eliminates the expensive steps of desorbing and concentrating gaseous CO<sub>2</sub> prior to entering the electrolyzer, and provides the opportunity to supply electrolyzers with a *liquid* reactive carbon solution.<sup>14</sup>

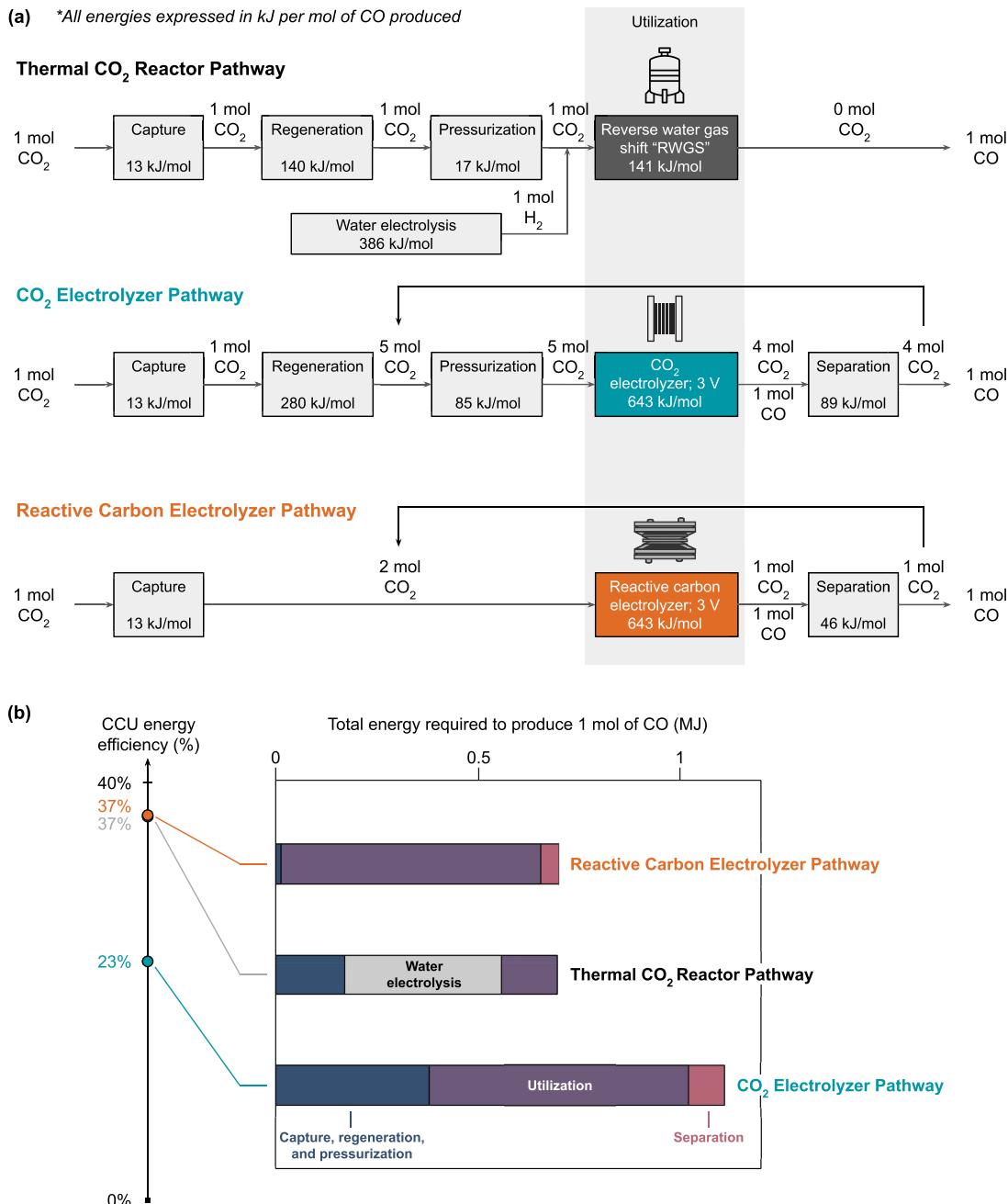
To realize this goal, we used a “reactive carbon electrolyzer” to upgrade bicarbonate-rich reactive carbon solutions.<sup>1</sup> We later coupled a reactive carbon electrolyzer to a capture unit<sup>3</sup> inspired by the design reported by Keith et al.<sup>13</sup> To perform reactive carbon capture, CO<sub>2</sub> is captured using a liquid KOH sorbent

that passes over a high-surface-area manifold to generate a bicarbonate-enriched eluent (eq 1). This eluent, a “reactive carbon solution”, enters the cathode compartment of the reactive carbon electrolyzer. During electrolysis, the reactive carbon electrolyzer produces H<sup>+</sup> sourced either from the membrane or from the anodic reaction, and delivers this acid to the cathode compartment. This acid then reacts with reactive carbon solution near the cathode to produce CO<sub>2</sub>. This *in situ* generated CO<sub>2</sub> (*i*-CO<sub>2</sub>; eq 2) then proceeds through the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) at the cathode (eq 3).<sup>1,15,16</sup> The byproduct of this reaction is KOH, which can then be returned to the capture unit to react with CO<sub>2</sub>.



This coupling of a capture unit to the reactive carbon electrolyzer led to the first reported closed-loop experimental demonstration of CCU (“Reactive Carbon Electrolyzer Pathway”; Figure 1).<sup>3</sup> More importantly, we calculated the CCU energy efficiency for making CO with the Reactive Carbon Electrolyzer Pathway to be much higher (37%) than a pathway where a CO<sub>2</sub> electrolyzer is used (“CO<sub>2</sub> Electrolyzer Pathway”; CCU energy efficiency = 23%; Figure 2). The lower CCU energy efficiency for the CO<sub>2</sub> Electrolyzer Pathway is due to the energies required to isolate, purify, and pressurize CO<sub>2</sub> from the capture unit prior to delivery to the CO<sub>2</sub> electrolyzer. The Reactive Carbon Electrolyzer Pathway bypasses these steps to yield CCU energy efficiencies comparable to the reverse water gas shift pathway (“Thermal CO<sub>2</sub> Reactor Pathway”; Figure 2). Similar calculations were performed for the production of syngas; see Supporting Information (SI). The reactive carbon electrolyzer can also produce methane with much higher yields than CO<sub>2</sub> electrolyzers fed with gaseous CO<sub>2</sub>,<sup>17</sup> and the formation of C<sub>2+</sub> products such as ethylene have been documented.<sup>18–20</sup>

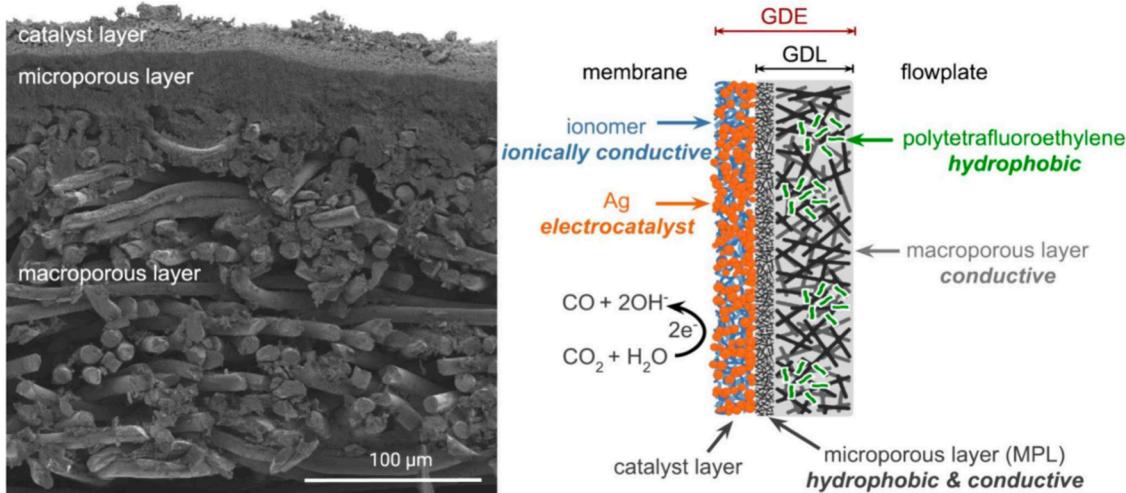
These findings make a case for the further development of reactive carbon electrolyzers for CCU. This Account is intended



**Figure 2.** Energy assessment of three different carbon capture and utilization (CCU) pathways. (a) CCU pathway flow diagrams. The differentiating feature of each pathway is the utilization step where CO<sub>2</sub> is converted into CO thermochemically (Thermal CO<sub>2</sub> Reactor Pathway) or electrochemically (CO<sub>2</sub> Electrolyzer and Reactive Carbon Electrolyzer Pathways). (b) CCU energy efficiency and total energy consumption for each CCU pathway. The total energy consumption is divided into four different categories: capture, regeneration, and pressurization; water electrolysis for H<sub>2</sub> production; utilization; and separation. CCU energy efficiency is defined as the ratio of the minimum theoretical energy required to convert CO<sub>2</sub> into 1 mol of CO, to the total energy actually required to capture and convert CO<sub>2</sub> into 1 mol of CO. This metric is not ideal; it is intended to provide a benchmark accessible to a general audience. For example, the maximum CCU energy efficiency is different for each pathway and in each case is less than 100%.

to teach how reactive carbon electrolyzers are differentiated from CO<sub>2</sub> electrolyzers, and to highlight the value propositions offered by both. We note that three related classes of reactive carbon capture are now known: direct amine conversion, molten salt carbonate electrolysis, and dilute CO<sub>2</sub> electrolysis. Direct amine conversion uses amine absorbers to capture CO<sub>2</sub> from flue gases, and the eluent is then delivered into an electrolyzer (“amine electrolyzer”) to upgrade CO<sub>2</sub>.<sup>21–24</sup> A “molten carbonate electrolyzer”, which operates at high temperatures

(650–900 °C), directly captures CO<sub>2</sub> from ambient air, and converts the captured CO<sub>2</sub> into solid carbon at the cathode and oxygen at the anode.<sup>25</sup> Finally, dilute CO<sub>2</sub> streams from air or point sources could in principle be electrolyzed directly.<sup>26–28</sup> A comparison of these pathways to the CO<sub>2</sub> and reactive carbon electrolyzer pathways is outside of the scope of this Account.



**Figure 3.** Cross-sectional scanning electron microscopy (SEM) image of a gas diffusion electrode (GDE) common to CO<sub>2</sub> electrolyzers. The schematic on the right highlights the various components that constitute the GDE. (GDL = gas diffusion layer.) Adapted with permission from ref 37. Copyright 2020, The American Chemical Society.

## ■ CO<sub>2</sub> AND REACTIVE CARBON ELECTROLYZER CONFIGURATIONS

We limit our discussion here to “zero-gap” electrolyzers because they show the highest performance to date.<sup>5,29,30</sup> These electrolyzers contain an ion-conducting membrane sandwiched tightly between a porous anode and cathode. The electrolyzer uses flow plates to pass the feedstocks to the anode and cathode. All of these components are pressed together within a metal housing, which is easier to seal for a liquid feedstock than a gaseous feedstock. The lack of a gap between the active layers of the flow cell serves to minimize voltage losses relative to other cell designs where fluid is passed between an electrode and the membrane.<sup>31</sup>

CO<sub>2</sub> electrolyzers can be made with cation exchange membranes (CEMs), anion exchange membranes (AEMs), or bipolar membranes (BPMs) to permit the flow of cations and anions between the anode and cathode compartments.<sup>5</sup> The choice of metals used for the cathode and anode in a CO<sub>2</sub> electrolyzer is dictated by the choice of membrane, which governs the pH in each compartment. The choice of metal cathode governs which CO<sub>2</sub>RR product is favored; for example, silver favors CO formation, and copper can form C<sub>2+</sub> products.<sup>6</sup> CEMs require iridium to be used as the anode, while a range of metal anodes can be used with AEMs and BPMs. Electrolyzers containing AEMs generally produce higher conversion efficiencies and energy efficiencies than CEMs and BPMs,<sup>30,32–34</sup> but CEMs and BPMs deliver acid to the cathode compartment to avoid the formation of parasitic bicarbonate.<sup>2,35,36</sup>

Reactive carbon electrolyzers follow a similar design configuration, but require an acid source to activate the *i*-CO<sub>2</sub> from bicarbonate in the cathode compartment. As a result, reactive carbon electrolyzers need to work with BPMs or CEMs between the anodic and cathodic compartments (although membrane-free configurations are possible). Catalysts used in gaseous CO<sub>2</sub> electrolyzers work effectively in reactive carbon electrolyzers; e.g., silver cathodes produce CO<sub>1,15,37,38</sub> and tin and bismuth cathodes produce formate.<sup>16,39,40</sup> It is currently more challenging to generate C<sub>2+</sub> products at a copper cathode in a reactive carbon electrolyzer, but rapid progress is being made.<sup>20</sup> Notably, the acidity of the cathodelmembrane interface

enables significantly higher methane yields than what has been achieved to date with CO<sub>2</sub> electrolyzers.<sup>17</sup>

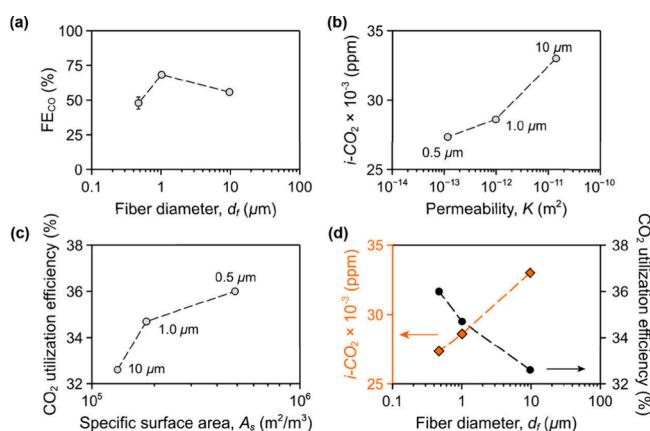
### Cathode Design

In a reactive carbon electrolyzer, the key carbon reagent is a charged species (HCO<sub>3</sub><sup>-</sup>). A CO<sub>2</sub> electrolyzer uses a neutral reagent (CO<sub>2</sub>). The cathode of a reactive carbon electrolyzer therefore needs to be designed differently than that for a CO<sub>2</sub> electrolyzer.

Cathodes for CO<sub>2</sub> electrolyzers draw heavily from the fuel cell community, and typically contain porous carbon to support the electrocatalyst (Figure 3). The fabrication of these gas diffusion electrodes involves depositing thin, porous catalyst layers containing catalyst nanoparticles and ionomers onto fibrous gas diffusion layers coated with a microporous layer.<sup>1,37</sup> These components are often made hydrophobic with polytetrafluoroethylene (PTFE) to mitigate electrode flooding and to regulate membrane and ionomer hydration.<sup>41,42</sup> The labor-intensive fabrication of these gas diffusion electrodes requires training to achieve reproducible results.<sup>42,43</sup>

A widely accepted dogma in the community is that cathodes should be designed with higher surface areas to increase electrolyzer current densities. However, there is a trade-off with permeability, which impacts mass transport of cathodes (Figure 4).<sup>38</sup> To demonstrate this point in a reactive carbon electrolyzer, we tested a series of electrospun fibrous carbon-based cathodes with different fiber sizes, coated with silver nanoparticles, and found that electrodes with higher permeabilities increased *i*-CO<sub>2</sub> generation through more effective transport of bicarbonate ions from the flow plate to the membranelcathode interface (Figure 4). However, these highly permeable electrodes yielded lower CO<sub>2</sub> utilization due to lower surface areas. Consequently, the most effective electrodes we tested had an intermediate fiber size (Figure 4).

Reactive carbon electrolyzers operate effectively with porous carbon supports, so long as they are hydrophilic.<sup>37</sup> This hydrophilicity is actually a major advantage of a reactive carbon electrolyzer, because it enables metal cathodes to also be used without carbon supports. The metallic surface of metal foam electrodes provides sufficient hydrophilicity to facilitate efficient transport of aqueous bicarbonate feedstock through the electrode. Metal foams are also known for their high



**Figure 4.** Electrolysis data recorded during the galvanostatic electrolysis of 3.0 M KHCO<sub>3</sub> at 100 mA cm<sup>-2</sup> in a reactive carbon electrolyzer. (a)  $FE_{CO}$  plotted as a function of average fiber diameter of carbon fibers that comprise the cathode gas diffusion layer. (b)  $[i\text{-CO}_2]$  measured at the outlet of the electrolyzer with different electrode permeabilities. (c) CO<sub>2</sub> utilization efficiency plotted against the specific surface area of the electrodes. (d)  $i\text{-CO}_2$  generation and CO<sub>2</sub> utilization efficiency shown as a function of fiber diameter for different porous electrodes. Adapted with permission from ref 38. Copyright 2022, The American Chemical Society.

permeability and specific surface area. These electrodes not only simplify the assembly and reproducibility of an electrolyzer, but they are also more durable than carbon-based cathodes and yield high Faradaic efficiencies for CO formation ( $FE_{CO} = 95\%$  at 100 mA cm<sup>-2</sup> and 55% at 400 mA cm<sup>-2</sup> in a reactive carbon electrolyzer).<sup>15</sup>

Another consideration in designing cathodes for reactive carbon electrolyzers is the management of H<sup>+</sup> delivered from the bipolar membrane from the anode. A high concentration of H<sup>+</sup> at the membranelcathode interface can favor the competing hydrogen evolution reaction (HER) over CO<sub>2</sub>RR, resulting in low selectivity toward the desired product. To mitigate the highly acidic environment at the interface of the membrane and cathode, a hydrophilic and uncatalyzed “buffer layer” placed

between the cathode and membrane facilitates the buffering of H<sup>+</sup> by HCO<sub>3</sub><sup>-</sup> and suppresses HER.<sup>2,19,44</sup>

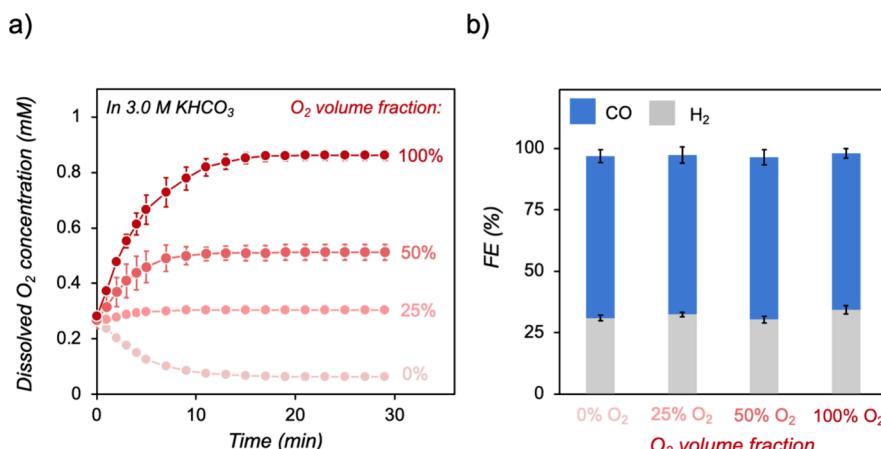
The electrocatalytic activity, hydrophilicity, and the ion conductivity of cathodes used in reactive carbon electrolyzers must be designed differently than those in CO<sub>2</sub> electrolyzers. These studies emphasize that a metal electrode is a significant advance because all commercial electrolyzers use metals and not porous carbon.

### Electrolyte Formulations

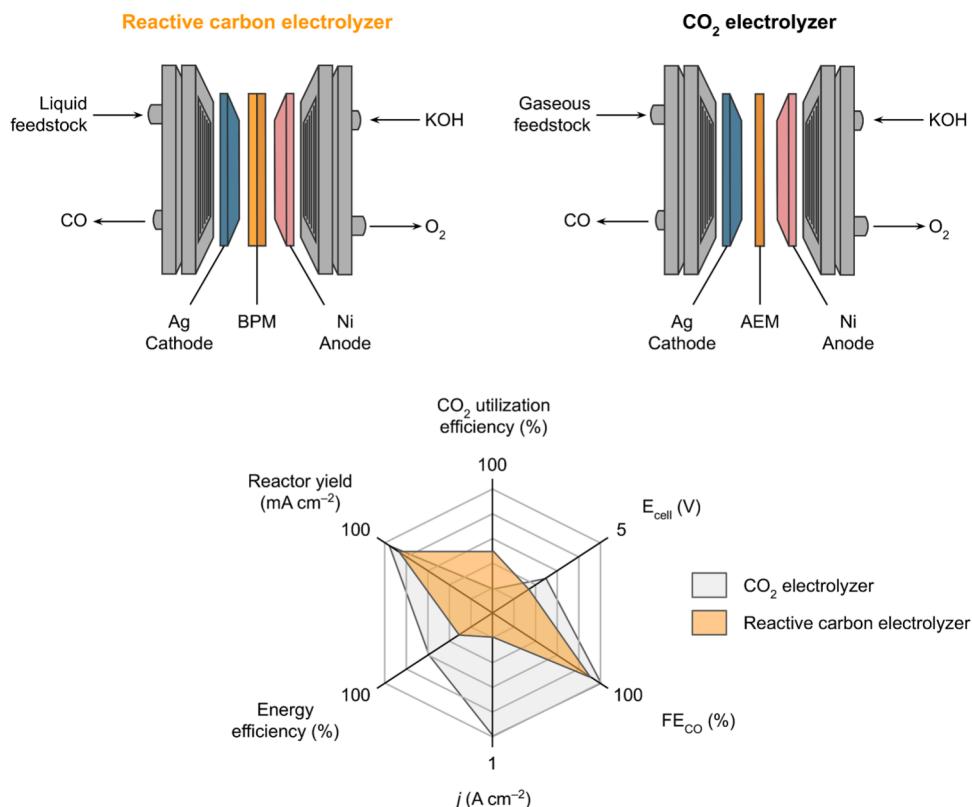
There is far less information known about how supporting electrolytes and additives affect reactive carbon electrolyzers compared to CO<sub>2</sub> electrolyzers. The aqueous medium of a reactive carbon electrolyzer can be modified to affect the reaction environment in ways that are not possible with a gaseous feedstock. Given the impact that bulk and cathode surface pH, electrolyte composition, electrolyte concentration, and additives have on CO<sub>2</sub>RR,<sup>4,17,45–49</sup> we contend that there is a broad parameter space available for exploration to improve both the reactive carbon electrolyzer as well as the coupled CO<sub>2</sub> capture unit.

Electrolytic reactive carbon conversion relies on bicarbonate to serve as both the feedstock and the supporting electrolyte; thus changes in concentration impact metrics such as  $FE_{CO}$ ,  $i\text{-CO}_2$  generation, and cell voltage. Electrolysis performed using a range of bicarbonate ion concentrations (0.5–3.0 M HCO<sub>3</sub><sup>-</sup>) revealed a dose-dependent response in the selectivity for CO, increasing from 14% at 0.5 M to 67% at 3.0 M.<sup>1</sup> This increase is attributed to an increase in the  $i\text{-CO}_2$  concentration near the cathode surface from the reaction of bicarbonate with H<sup>+</sup> supplied by the membrane, and a suppression of HER by increasing the bulk pH of the electrolyte. The change in bicarbonate concentration from 0.5 to 3.0 M was also accompanied by a 0.1 V decrease in total cell voltage due to the higher conductivity of the electrolyte.

The majority of reactive carbon electrolyzer studies use K<sup>+</sup> as the counterion in the catholyte.<sup>1,18,37</sup> Not only is K<sup>+</sup> economical, but larger cations such as K<sup>+</sup> have been linked to higher selectivities for CO<sub>2</sub>RR products in CO<sub>2</sub> electrolyzers (although the underlying mechanism remains a topic of debate).<sup>50</sup> Electrolysis performed in the reactive carbon



**Figure 5.** Electrolysis in a reactive carbon electrolyzer with O<sub>2</sub>-saturated and O<sub>2</sub>-depleted feedstocks. Humidified CO<sub>2</sub> (0–100%) and O<sub>2</sub> (0–100%) were bubbled into a 3.0 M KHCO<sub>3</sub> solution prior to and during electrolysis at a constant flow rate of 200 sccm. (a) Concentration of dissolved O<sub>2</sub> in a 3.0 M KHCO<sub>3</sub> solution as a function of time for 30 min prior to electrolysis. (b) Product distributions from the electrolysis of 3.0 M KHCO<sub>3</sub> bubbled with CO<sub>2</sub> (0–100%) and O<sub>2</sub> (0–100%). Electrolysis was performed for 5 min at a constant applied current density of 100 mA cm<sup>-2</sup>. Adapted with permission from ref 56. Copyright 2023, The American Chemical Society.



**Figure 6.** Product specifications for the best reactive carbon and  $\text{CO}_2$  electrolyzers reported to date.  $\text{CO}_2$  electrolyzers can operate at higher current densities, but at lower  $\text{CO}_2$  utilization efficiencies. Consequently, the liquid-fed reactive carbon electrolyzer is able to operate at comparable reactor yields.

electrolyzer is consistent with these previous reports; the  $\text{FE}_{\text{CO}}$  increased with increasing alkali metal ion size:  $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$ .<sup>51</sup> For example, at a concentration of 1.0 M  $\text{MHCO}_3$  (where M represents an alkali metal), electrolysis at 100 mA  $\text{cm}^{-2}$  in the presence of the larger cesium ions resulted in  $\text{FE}_{\text{CO}}$  values of 60%. When M = Li<sup>+</sup>, the  $\text{FE}_{\text{CO}}$  did not exceed 30% because  $\text{LiHCO}_3$  is a saturated solution at 0.84 M. The cation identity did not impact the formation of *i*- $\text{CO}_2$  in these experiments. Because the formation of *i*- $\text{CO}_2$  depends on pH, we conclude that changing the cation identity does not change the pH at the membrane/electrode interface. This conclusion differs from reports of  $\text{CO}_2$  electrolyzers fed with  $\text{CO}_2$  dissolved in water, where larger cations are claimed to decrease the local pH by polarizing water molecules in the cation hydration shell.<sup>52</sup> In reactive carbon electrolyzers, the availability of  $\text{CO}_2$  at the catalyst seems to be primarily regulated by the transport of  $\text{HCO}_3^-$  and the flux of H<sup>+</sup> from the BPM. The formation of *i*- $\text{CO}_2$  was not dependent on cation identity. We therefore attribute cation-induced increases in  $\text{FE}_{\text{CO}}$  to high charge density near the cathode, which was supported in independent experiments.<sup>51</sup>

### Impurity Management

Impurities from  $\text{CO}_2$  capture units will affect  $\text{CO}_2$  electrolysis.<sup>27,53,54</sup> These impurities need to be managed in order to link upstream  $\text{CO}_2$  capture with downstream  $\text{CO}_2$  conversion.

The most abundant impurity from  $\text{CO}_2$  capture units is O<sub>2</sub>.<sup>27</sup> Oxygen is present in flue gases at concentrations as high as 15%, and in air at a concentration of 21%. These O<sub>2</sub> concentrations lead to significant (>90%) losses in CO2RR product selectivity in  $\text{CO}_2$  electrolyzers because the oxygen reduction reaction (ORR) occurs at a more thermodynamically favorable potential

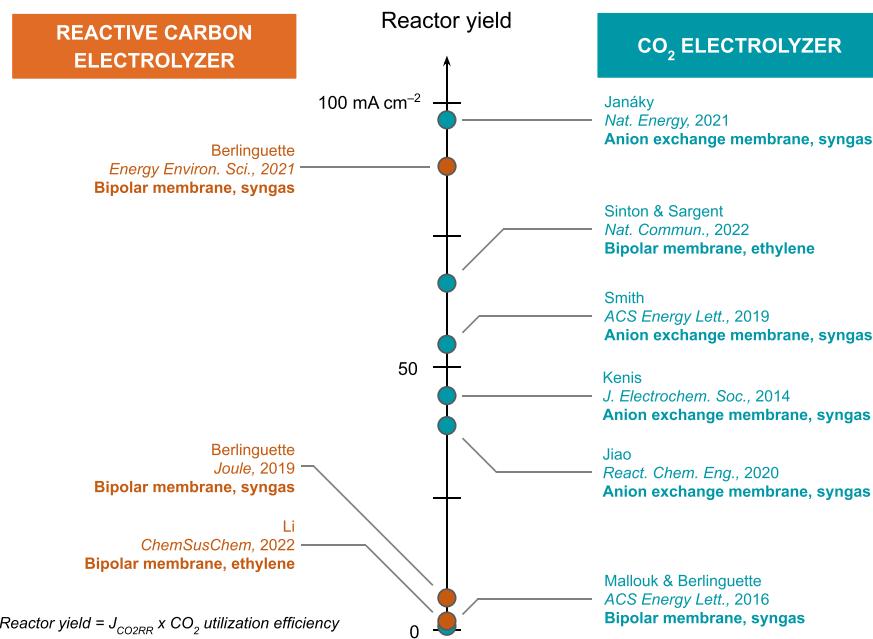
than CO2RR.<sup>27,55</sup> Consequently,  $\text{CO}_2$  streams need to be purified and concentrated prior to entry into a  $\text{CO}_2$  electrolyzer.

The reactive carbon electrolyzer solves this problem because it is not sensitive to the presence of O<sub>2</sub> in the liquid feedstock.<sup>56</sup> The reason is simply because the solubility of O<sub>2</sub> in aqueous media is low, merely 0.0012 M @ 1 atm, 298 K.<sup>56,57</sup> Electrolysis using a liquid aqueous medium inherently avoids O<sub>2</sub> from reacting at the cathode. For example, the same  $\text{FE}_{\text{CO}}$  of 65% at 100 mA  $\text{cm}^{-2}$  was measured using an O<sub>2</sub>-saturated feedstock and an O<sub>2</sub>-depleted feedstock (Figure 5).

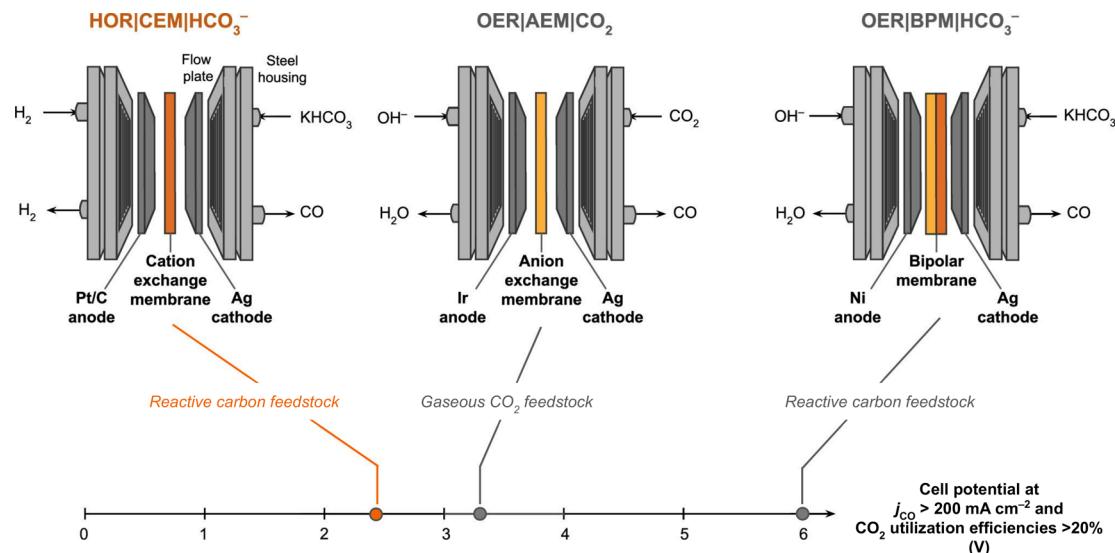
Other impurities can also affect the operation of  $\text{CO}_2$  electrolyzers and reactive carbon electrolyzers.<sup>4</sup> For example, flue gas impurities such as nitrogen oxides (NO<sub>x</sub>) and sulfur oxides (SO<sub>x</sub>) are soluble in alkaline  $\text{CO}_2$  capture solutions. SO<sub>x</sub> reacts in solution to form  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$ , while NO<sub>x</sub> reacts to form  $\text{NO}_2^-$  and  $\text{NO}_3^-$ .<sup>58,59</sup> These contaminants are redox-active and can compete with CO2RR at the cathode. Experimentation revealed that SO<sub>x</sub> impurities do not decrease CO2RR in the reactive carbon electrolyzer as they do in  $\text{CO}_2$  electrolyzers,<sup>53</sup> but ppm-level concentrations of NO<sub>x</sub> anions in the feedstock cause >50% losses in reaction selectivities. Impurity management is thus an important consideration when performing electrolysis in a reactive carbon electrolyzer.

### ELECTROLYZER PERFORMANCE

To design electrolyzers to upgrade  $\text{CO}_2$ , it is useful to draw information from established industry-scale electrolyzers and techno-economic analyses for guidance on what product specifications reactive carbon and  $\text{CO}_2$  electrolyzers must achieve to make CCU economically viable. We limit our discussion here to  $\text{CO}_2$  utilization efficiency (CU), full cell



**Figure 7.** A summary of reactor yields calculated for zero-gap reactive carbon electrolyzers<sup>1,15,80</sup> and CO<sub>2</sub> electrolyzers.<sup>30,34,35,64–66</sup> This graphic includes studies that report the metrics necessary to calculate reactor yield, which is defined as the product of partial current density and CO<sub>2</sub> utilization efficiency.



**Figure 8.** Schematic diagrams of electrolyzers that convert CO<sub>2</sub> to CO. The HOR|CEM|HCO<sub>3</sub><sup>-</sup> and OER|BPM|HCO<sub>3</sub><sup>-</sup> configurations use a reactive carbon solution as the feedstock. The OER|AEM|CO<sub>2</sub> electrolyzer is a common design that employs gaseous CO<sub>2</sub> as the feedstock. This schematic reports the lowest reported cell voltages for each electrolyzer architecture, when  $j_{\text{CO}} > 200 \text{ mA cm}^{-2}$  and CO<sub>2</sub> utilization efficiency > 20%.<sup>2,15,75</sup> The nomenclature follows the format “anode reaction|membrane|cathode feedstock”. Adapted with permission from ref 2. Copyright 2022, The American Chemical Society.

voltage ( $E_{\text{cell}}$ ), Faradaic efficiency (FE), and current density ( $j$ ), but other factors are important for commercialization (e.g., cost, flow rates, durability, feedstocks). Electrolyzers likely need to satisfy product specifications for all of these metrics in order to be commercially viable. For example, an electrolyzer that operates at a current density of 1000 mA cm<sup>-2</sup> is not effective if the operating voltage is 15 V. The design of a system that meets all product specifications simultaneously is not trivial. The state-of-the-art performance metrics for CO<sub>2</sub> and reactive carbon electrolyzers are shown in Figure 6.

### CO<sub>2</sub> Utilization Efficiency

CO<sub>2</sub> electrolyzers have been demonstrated at higher current densities than reactive carbon electrolyzers (Figure 6). However, high-performance CO<sub>2</sub> electrolyzers use an AEM that maintains a high pH at the cathode. This hydroxide can react with CO<sub>2</sub> reagent to form carbonate before it can be converted into product, thereby limiting the maximum theoretical CU to 50% for CO production (Figure 7). The maximum theoretical CU for C<sub>2</sub>H<sub>4</sub> production is even lower at 25%.<sup>60</sup> This (bi)carbonate can pass from the cathode to the

anode, and thus a substantial amount of carbon is lost to the anode.<sup>60–62</sup> Indeed, the (bi)carbonate ion is the dominant charge carrier that results in decreased CU in CO<sub>2</sub> electrolyzers containing AEMs.<sup>63,64</sup>

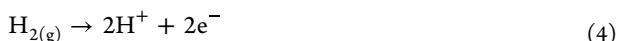
Reactive carbon electrolyzers containing BPMs bypass this issue to yield significantly higher carbon utilization. The BPM provides acid to the cathode, facilitating the conversion of HCO<sub>3</sub><sup>-</sup> into *i*-CO<sub>2</sub>, while maintaining a high pH at the anode to enable the energy efficient oxygen evolution reaction (OER).<sup>1,15,37,38</sup> These membranes prevent ion crossover between the anode and cathode compartments of the reactive carbon electrolyzer and create the necessary isolated acidic and alkaline regions for electrolysis.<sup>67</sup>

To show how important the prevention of ion crossover is for electrolyzer performance, we cataloged the “reactor yield” of high-performance reactive carbon and CO<sub>2</sub> electrolyzers reported in the literature. Reactor yield, a term our program uses for benchmarking, is the product of carbon utilization efficiency and partial current density, and is intended to consider works that optimize for both (Figure 7). While CO partial current densities exceeding 500 mA cm<sup>-2</sup> have been reported with CO<sub>2</sub> electrolyzers in the literature, the reactor yield of these same electrolyzers are typically low due to their insufficient utilization of CO<sub>2</sub> (e.g., <20%).<sup>33–35,64,68,69</sup> In contrast, reactive carbon electrolyzers yield substantially higher reactor yields (90 mA cm<sup>-2</sup>) despite the lower CO partial current densities (220 mA cm<sup>-2</sup>). The higher reactor yield of reactive carbon electrolyzers is attributed to a larger portion of CO<sub>2</sub> being converted into CO (i.e., CO<sub>2</sub> utilization efficiency of >40%).<sup>2,44</sup>

### Operating Voltages

Reactive carbon electrolyzers containing BPMs reported to date are characterized by voltages that are too high for commercial applications. While advances in BPM designs are sure to lower these voltages,<sup>70</sup> we have also proven that CEMs are effective for delivering H<sup>+</sup> to the cathode in reactive carbon electrolyzers.<sup>2</sup> We remain enthusiastic about using BPMs, but we are drawn to CEMs because they are already used in commercial devices. Moreover, CEMs avoid the 0.83 V thermodynamic requirement of dissociating water in BPMs,<sup>71</sup> and they are available with lower thicknesses, which can reduce Ohmic resistance within the electrolyzer.<sup>72</sup>

A reactive carbon electrolyzer with a CEM can use H<sub>2(g)</sub> instead of water as a feedstock for the anode compartment. This modification relies on the hydrogen oxidation reaction (HOR) instead of OER to generate H<sup>+</sup> at the anode (eq 4).<sup>2</sup> Because H<sub>2(g)</sub> ( $E^\circ = 0$  V vs SHE) is more readily oxidized at the anode than water ( $E^\circ = 1.23$  V vs SHE), a lower applied voltage is required to drive electrolysis within the cell (Figure 8). Consequently, a reactive carbon electrolyzer containing a CEM and fed with H<sub>2(g)</sub> to the anode can operate at a low cell voltage of 2.3 V at 500 mA cm<sup>-2</sup>. This cell voltage is among the lowest reported for any electrolyzer that upgrades CO<sub>2</sub>.<sup>73</sup>



Nevertheless, the use of H<sub>2(g)</sub> as the anode feedstock requires additional energy and capital investments for the production of H<sub>2(g)</sub>. Moreover, the gaseous feedstock creates engineering challenges presented at the beginning of this Account. It is possible to use CEMs in reactive carbon electrolyzers that use a dilute sulfuric acid solution as the anolyte to drive acidic water oxidation.<sup>19,44</sup> The H<sup>+</sup> ions generated at the anode migrate through the CEM to the cathode, where they generate *i*-CO<sub>2</sub>.

This acidic water oxidation requires a higher potential ( $E^\circ = 1.23$  V vs SHE) to drive electrolysis compared to OER under alkaline conditions ( $E^\circ = 0.40$  V vs SHE). An acid-stable electrocatalyst is also required, and the options available today are limited to expensive metals such as iridium. Moreover, sustained electrolysis is difficult with a sulfuric acid anolyte due to the concentration of the acid.<sup>74</sup> Consequently, robust reactive carbon electrolyzers using a CEM at high current densities are possible, but have not yet been demonstrated. This goal is a major focus of our program.

### Faradaic Efficiencies

Initial demonstrations of electrolytic conversion of reactive carbon solutions to CO exhibited lower Faradaic efficiencies (e.g., FE<sub>CO</sub> = 32% at 100 mA cm<sup>-2</sup>) than CO<sub>2</sub> electrolyzers (FE<sub>CO</sub> ~ 100% at 100 mA cm<sup>-2</sup>). Recent advances in reactive carbon electrolyzer configurations and cathodes have led to product selectivities that approach those of gas-fed systems. For example, a reactive carbon electrolyzer with a silver catalyst on a more hydrophilic carbon support achieved an FE<sub>CO</sub> of 82% at 100 mA cm<sup>-2</sup>, over double the reported values obtained prior.<sup>37</sup> This increase in FE<sub>CO</sub> was achieved by removing PTFE from the GDL. Free-standing porous electrodes also exhibit a low hydrophobicity and mediate bicarbonate conversion to CO.<sup>15</sup> A later study using a CEM in a reactive carbon electrolyzer achieved a CO selectivity of 89% at 100 mA cm<sup>-2</sup>, with the added caveat that the electrolyzer was pressurized to 3.5 atm.<sup>2</sup>

Despite these advances, further progress is required for commercially viable reactive carbon electrolyzers. Ultimately, more hydrophilic cathodes are required in order to increase the concentration of solvated bicarbonate ions near the metal surface, and, in turn, boost conversion of bicarbonate to CO<sub>2</sub>. Mass transport of CO<sub>2</sub> also remains a central challenge limiting product selectivities. Whereas CO<sub>2</sub> in a gas-fed electrolyzer is available at high concentrations, CO<sub>2</sub> must be generated *in situ* in the reactive carbon electrolyzer. Higher *i*-CO<sub>2</sub> formation is therefore necessary to achieve higher CO<sub>2</sub>RR selectivity.

### Current Densities

Commercial electrolyzers will likely need to operate at current densities in excess of 200 mA cm<sup>-2</sup>.<sup>5</sup> CO<sub>2</sub> electrolyzers meet this requirement, exhibiting high selectivities at high current densities (>99% at 1000 mA cm<sup>-2</sup>).<sup>75,76</sup> Reactive carbon electrolyzers with BPMs have not yet proven sustained operation at >200 mA cm<sup>-2</sup>. At 500 mA cm<sup>-2</sup>, for example, the  $E_{\text{cell}}$  of a reactive carbon electrolyzer with a BPM exceeded 10 V.<sup>2</sup> These high voltages are the result of Ohmic drop, water dissociation occurring in the membrane, and mass transport limitations. While the latter can be addressed by increasing the production of *i*-CO<sub>2</sub> and designing selective cathodes, the former two voltage penalties are inherent to the membrane.

As previously described, the use of a CEM has enabled electrolysis at significantly lower voltages than with BPMs. One of the key outcomes from these lower voltages is that higher current densities can be reached with a CEM electrolyzer operating at 1000 mA cm<sup>-2</sup>, which is commensurate with state-of-the-art gas-fed CO<sub>2</sub> electrolyzers. Further improvement upon membrane design by decreasing thickness and increasing rates of ion exchange can further drive the operation of reactive carbon electrolyzers toward higher current densities.

## CONCLUSIONS AND FUTURE DIRECTIONS

This Account makes a case for studying electrolyzers that can be coupled to CO<sub>2</sub> capture units and fed with liquid reactive carbon

solutions. We focus our discussion on a reactive carbon electrolyzer pathway, which could convert CO<sub>2</sub> into fuels with high energy efficiencies by bypassing the energy-intensive CO<sub>2</sub> purification steps that are required for gas-fed CO<sub>2</sub> electrolyzers.

There remain many opportunities for chemists and materials scientists to further advance reactive carbon electrolyzers. Reactive carbon electrolyzers tend to work more effectively with hydrophilic cathodes. There is limited information available for these types of cathodes, and a larger database of materials is needed that teach how to properly balance mass transport characteristics with electrochemically-active surface areas. This information will help reactive carbon electrolyzers reach higher current densities and Faradaic efficiencies.

Another component that remains wide open for this field is the ion exchange membrane.<sup>77</sup> It is clear that the delivery of acid to the cathode is important for liberating CO<sub>2</sub> from reactive carbon solutions. A more concentrated effort on appropriate membranes is important for reactive carbon electrolyzers, yet the CO<sub>2</sub> electrolysis community has focused heavily on AEMs to date. BPMs that minimize the energy for water dissociation at the bipolar interface will be a particularly powerful contribution to reactive carbon electrolyzers.<sup>78</sup> Reactive carbon electrolyzers also present an opportunity for chemists to modify catholyte compositions in ways that are not possible with a gaseous CO<sub>2</sub> feedstock. The role surfactants and additives have on electrolyzer performance remains underexplored.

The most significant challenge that needs to be addressed for reactive carbon electrolyzers to be put into practice is the identification of a reactive carbon solution capable of efficiently capturing and upgrading CO<sub>2</sub> in a capture unit and reactive carbon electrolyzer, respectively. Capture units require a strongly caustic solution to capture CO<sub>2</sub> effectively, while reactive carbon electrolyzers will likely work more effectively at neutral pH. We sought to address this gap by adding CO<sub>2</sub> capture promoters (e.g., glycine,<sup>3</sup> carbonic anhydrase<sup>79</sup>) to the liquid medium.

Reactive carbon electrolyzers also need to produce higher bicarbonate-to-CO<sub>2</sub> conversion rates. This conversion is particularly important in a closed-loop system, as the amount of *i*-CO<sub>2</sub> released from the reactive carbon solution governs the overall CO<sub>2</sub> capture efficiency.<sup>3</sup> One could increase the bicarbonate-to-CO<sub>2</sub> conversion rate by operating at higher current densities, but membranes with higher water transport rate and lower Ohmic resistances are needed than what is currently available. Higher-permeability electrodes could increase the rate of *i*-CO<sub>2</sub> generation.

These are just a few of the many opportunities available for the chemistry and materials science communities to advance reactive carbon electrolyzers and to enable CO<sub>2</sub> capture and utilization systems.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.accounts.3c00571>.

Example calculations and a summary of input and output parameters for the energy analysis presented in Figure 2; a supplementary figure summarizing the energy analysis for syngas production, as opposed to CO, using the same carbon capture and utilization pathways illustrated in Figure 2 of the main text (PDF)

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<https://pubs.acs.org/10.1021/acs.accounts.3c00571>

### Author Contributions

<sup>†</sup>These authors contributed equally to this work. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare the following competing financial interest(s): We have filed patents around the reactive carbon electrolyzer.

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**Douglas J. D. Pimlott** is a Ph.D. student in the Berlinguette Group at the University of British Columbia (UBC). His research focuses on investigating the impacts of impurities on the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) and conducting techno-economic analyses of CO<sub>2</sub>RR processes.

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## ■ DEDICATION

This Account is dedicated to Dr. Danielle A. Salvatore.

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