

## Perspective

**Gas-Diffusion Electrodes for Carbon-Dioxide Reduction: A New Paradigm**

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## Gas-Diffusion Electrodes for Carbon-Dioxide Reduction: A New Paradigm

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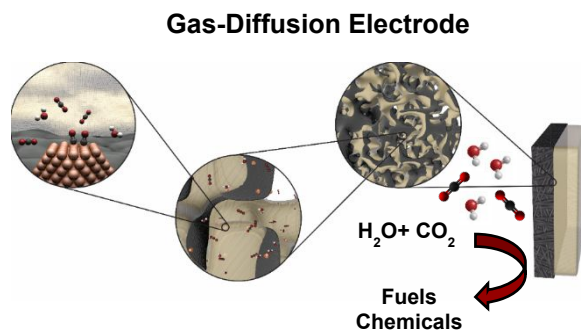
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### Abstract

Significant advances have been made in recent years discovering new electrocatalysis and developing a fundamental understanding of electrochemical CO<sub>2</sub> reduction processes. This field has progressed to the point that efforts can now focus on translating this knowledge towards the development of practical CO<sub>2</sub> electrolyzers, which have the potential to replace conventional petrochemical processes as a sustainable route to produce fuels and chemicals. In this perspective, we take a critical look at the progress in incorporating electrochemical CO<sub>2</sub> reduction catalysts into practical device architectures that operate using vapor-phase CO<sub>2</sub> reactants, thereby overcoming intrinsic limitations of aqueous-based systems. Performance comparison is made between state-of-the-art CO<sub>2</sub> electrolyzers and commercial H<sub>2</sub>O electrolyzers—a well-established technology that provides realistic performance targets. Beyond just higher rates, vapor-fed reactors represent new paradigms for unprecedented control of local reaction conditions, and we provide a perspective on the challenges and opportunities for generating fundamental knowledge and achieving technological progress towards the development of practical CO<sub>2</sub> electrolyzers.

### TOC Image



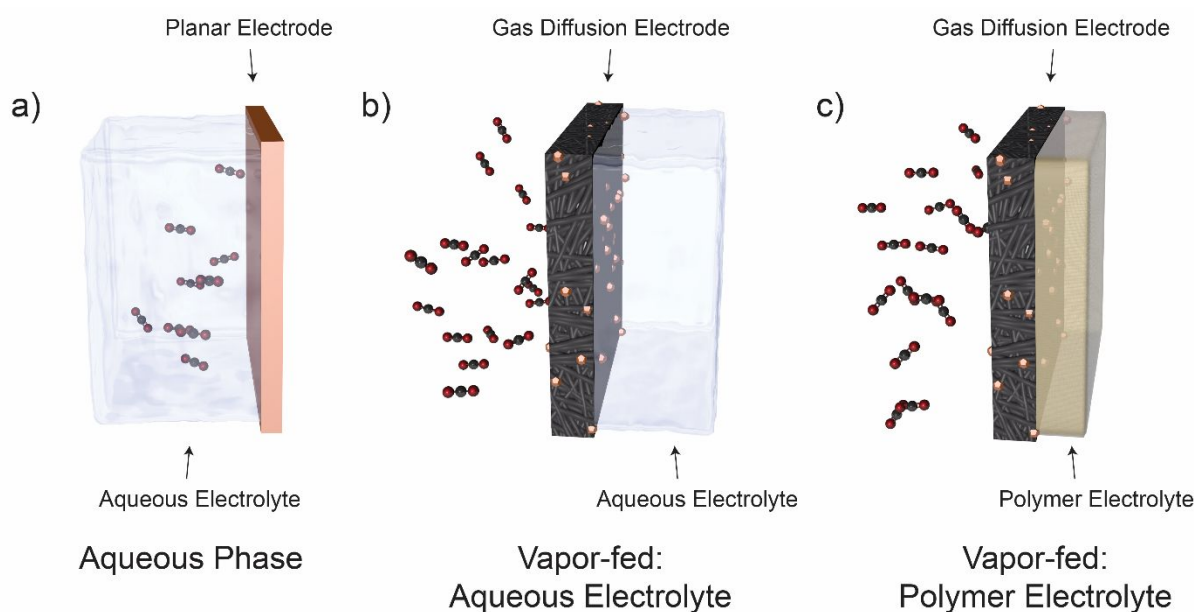
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5 The development of new technologies that reduce greenhouse gas emissions while producing fuels and  
6 commodity chemicals has the potential to mitigate the devastating impacts of climate change by  
7 transforming the petrochemical sector towards sustainability. Electrochemical CO<sub>2</sub> reduction (CO<sub>2</sub>R)  
8 coupled with renewably generated electricity (wind, solar, hydro) provides an attractive approach for the  
9 carbon-neutral production of valuable hydrocarbon, alcohol, and carbonyl products that find widespread  
10 use in the energy and chemical sectors. For this artificial photosynthesis process to be implemented at  
11 scale, highly active and selective CO<sub>2</sub>R catalysts must be developed and ultimately integrated into devices  
12 that can achieve high conversion rates and energy-conversion efficiencies to the desired product(s).  
13 Vapor-fed CO<sub>2</sub> devices represent a promising platform for such a technology.  
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17 On a fundamental level, there has been much progress understanding electrochemical CO<sub>2</sub>R in the liquid  
18 phase, where CO<sub>2</sub> molecules are solubilized in an aqueous electrolyte and reduced on the surface of a  
19 catalyst (Figure 1a). The unprecedented level of synergy between theoretical and experimental research  
20 towards aqueous-phase CO<sub>2</sub>R has led to improved understanding regarding the impact of electrolyte  
21 ions,<sup>1-3</sup> pH,<sup>4</sup> mass transport,<sup>5-7</sup> temperature,<sup>8</sup> and pressure<sup>8-9</sup> on activity and selectivity. As a result, activity  
22 descriptors<sup>10-11</sup> and mechanistic insight into reaction pathways<sup>12-13</sup> has guided catalyst design efforts,  
23 leading to the discovery of new compositions<sup>14-16</sup> and morphologies that are more active and selective to  
24 desired CO<sub>2</sub>R products. A succinct overview of these advances has been provided in a recently published  
25 perspective piece.<sup>17</sup> It is furthermore expected these efforts will be accelerated with the implementation  
26 of machine learning processes for catalyst discovery.<sup>18-19</sup>  
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30 While these referenced studies have been critical in establishing a deeper understanding of CO<sub>2</sub>R, they  
31 have traditionally relied upon aqueous-phase CO<sub>2</sub>R reactors designed for fundamental investigations  
32 (Figure 1a). From an applied standpoint, however, these test reactors have many practical limitations that  
33 must be addressed. Most notably, the poor solubility (ca. 34 mM) of CO<sub>2</sub> in aqueous electrolytes, along  
34 with acid/base buffer (CO<sub>2</sub>/HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>-2</sup>) equilibria lead to intrinsic challenges towards achieving high  
35 conversion rates and energy efficiencies.<sup>20</sup> Moving towards practical reactor designs that operate using  
36 CO<sub>2</sub> delivered to the cathode in the vapor phase (Figure 1b,c) can help to overcome these performance  
37 and solubility challenges. Such gas-diffusion electrodes (GDEs) can achieve this by employing a porous  
38 catalyst layer along with diffusion media to facilitate reactant transport and distribution. GDEs have been  
39 used in other electrochemical energy-conversion devices such as fuel cells and electrolyzers, where the  
40 architecture has been optimized for high current density and low transport losses. However, the  
41 adaptation to CO<sub>2</sub>R will require further advancement, as different operating strategies and  
42 understandings are needed to address product selectivity considerations, which is important to avoid the  
43 need for costly downstream separations.<sup>21</sup> Furthermore, the actual electrolyte can either be aqueous to  
44 form a catalyst/liquid electrolyte interface (Figure 1b), or ideally an ion-conducting polymer that can  
45 transport charged species (e.g., H<sup>+</sup> or OH<sup>-</sup>) and form a catalyst/polymer electrolyte interface (Figure 1c).  
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50 A recently published article<sup>22</sup> provides a critical overview of various electrolyzer designs that can be  
51 considered, along with a review of the technological achievements made in recent years on  
52 electrochemical CO<sub>2</sub>R reactor designs. In this perspective, we discuss the challenges and opportunities  
53 facing GDE development for electrochemical CO<sub>2</sub>R. We provide context in terms of CO<sub>2</sub>R electrocatalysis,  
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3 and include a discussion of the intrinsic advantages and unexpected opportunities of GDEs in an effort to  
4 motivate researchers to translate current understanding towards new GDE designs. The purpose of this  
5 perspective is not to provide a comprehensive review on the topic of electrochemical CO<sub>2</sub>R or GDE  
6 development. Instead, the goal is to provide a forward-looking perspective to inspire and provide  
7 direction for these fields of research, using the technology maturation process of commercial water  
8 electrolyzers as realistic performance targets. We identify areas deemed important for developing a  
9 fundamental understanding of the underlying chemistry, processes, and phenomena occurring in GDEs.  
10 This insight is essential for advancing the state of electrochemical CO<sub>2</sub>R technologies towards commercial  
11 viability.  
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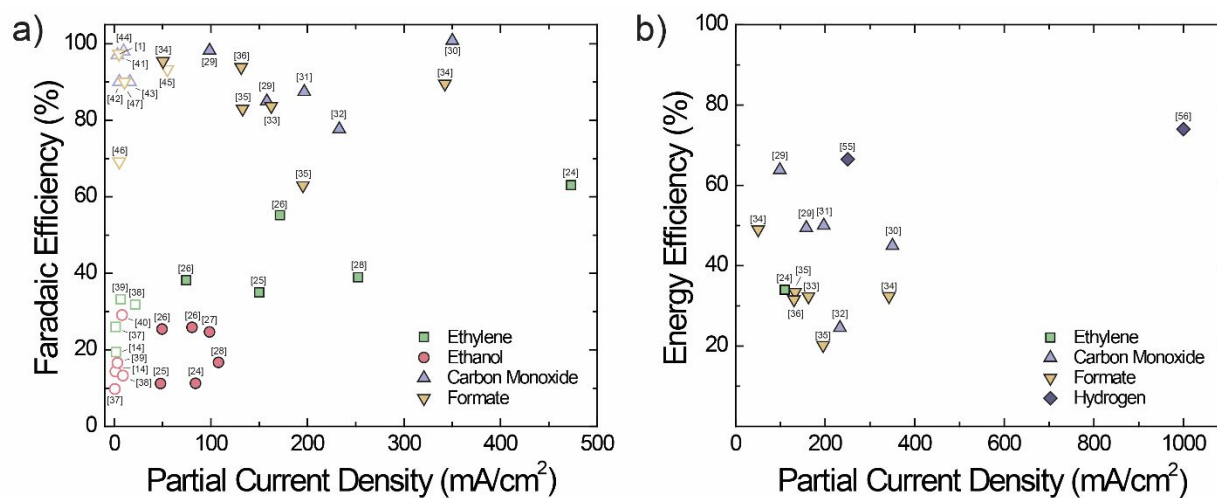
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**Figure 1:** Different electrochemical CO<sub>2</sub>R reactor schemes. **(a)** Aqueous-phase CO<sub>2</sub>R, where CO<sub>2</sub> is first solubilized in an aqueous electrolyte and then reduced at a catalyst surface. Vapor-fed CO<sub>2</sub>R employing an **(b)** aqueous or **(c)** polymer electrolyte.

### State-of-the-art

In comparison to electrodes studied in aqueous-phase electrochemical reactors, various types of vapor-fed CO<sub>2</sub>R electrodes have been shown successful in improving the partial current densities and energy efficiencies for CO<sub>2</sub>R.<sup>23</sup> This has been achieved by taking the most selective catalysts identified through fundamental aqueous-phase reactor investigations, and integrating them into vapor-fed device designs. This research translation trend is depicted in Figure 2a, which summarizes state-of-the-art Faradaic efficiencies versus partial current densities achieved for CO, formate, ethylene, and ethanol production.

Performance obtained from vapor-fed GDEs<sup>24-36</sup> (solid symbols) are shown in comparison to similar catalyst compositions tested in aqueous-phase reactors<sup>1, 14, 37-47</sup> (hollow symbols). While different reactor designs and catalyst configurations were used throughout these studies, this comparison shows the general trend of vapor-fed GDE research successfully improving partial current densities beyond those achievable in aqueous-phase investigations, while retaining similar selectivity. Amongst these major products shown, the highest Faradaic efficiencies and partial current densities are generally reported for CO and formate, as there are a number of different catalyst types that are intrinsically selective to these 2e<sup>-</sup> reduction products.<sup>36, 48-52</sup> On the other hand, data for the further reduced (>2e<sup>-</sup>) products, ethylene and ethanol, demonstrates that selectivity is still a major challenge. This selectivity challenge is largely because ethylene and ethanol are competitively co-produced on Cu-based catalysts through very similar mechanistic reaction pathways. However, improvements in ethylene selectivity have been observed by implementing Cu-based catalysts in vapor-fed GDEs for electrochemical CO<sub>2</sub>R,<sup>24, 26</sup> along with similar results demonstrated for electrochemical carbon monoxide reduction.<sup>53-54</sup> This observation suggests that vapor-fed conditions are a promising avenue for tuning the local environment and reaction conditions that control CO<sub>2</sub>R selectivity (*vide infra*), while simultaneously achieving higher partial current densities. However, altering the local CO<sub>2</sub> environment is largely underexplored for GDEs and presents an opportunity for increased understanding compared to solely aqueous-phase reactor investigations.



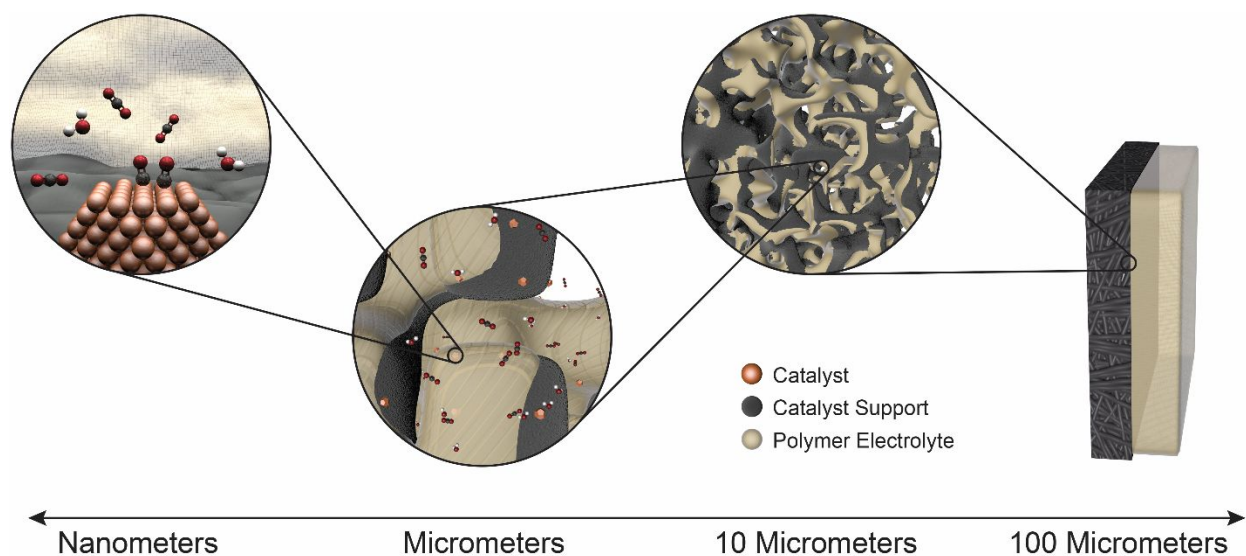
**Figure 2:** State-of-the-art performance of vapor-fed CO<sub>2</sub> devices. **(a)** Faradaic efficiencies versus partial current densities to ethylene, ethanol, carbon monoxide, and formate. **(b)** Energy efficiencies versus partial current densities to ethylene, carbon monoxide, formate, and hydrogen. Performances obtained for vapor-fed CO<sub>2</sub>R electrodes are shown in solid symbols, while performance for electrodes in aqueous-phase CO<sub>2</sub>R reactors are shown in hollow symbols. All energy efficiencies were calculated as voltage efficiencies using the formula:

$$\text{Energy Efficiency} = \frac{(E_{anode}^0 - E_{cathode}^0) \cdot FE}{V_{cell}}; \text{ where } E_{anode}^0 \text{ and } E_{cathode}^0 \text{ are the reversible potentials, } FE \text{ is the Faradaic efficiency for the CO}_2\text{R product, and } V_{cell} \text{ is the uncompensated cell voltage.}$$

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3 On a system level, Figure 2b shows a summary of state-of-the-art energy efficiencies versus partial current  
4 densities, which takes into account transport resistances (ionic and electronic), along with kinetic losses  
5 from both the anode and cathode.<sup>55</sup> A comparison is also provided to the performance of representative  
6 alkaline<sup>55</sup> and proton-exchange membrane<sup>56</sup> (PEM) H<sub>2</sub>O electrolyzers. It is interesting to note that all of  
7 the vapor-fed CO<sub>2</sub>R cells incorporate an aqueous electrolyte (Figure 1b), in part because alkaline  
8 electrolytes can improve energy efficiencies by reducing cathodic overpotentials. Thus, a traditional  
9 commercial H<sub>2</sub>O electrolyzer with an aqueous alkaline electrolyte<sup>55</sup> likely provides the most appropriate  
10 comparison. While the representative alkaline H<sub>2</sub>O electrolyzer performance is superior to that of the  
11 vapor-fed CO<sub>2</sub> cells shown in Figure 2b, the performance of CO<sub>2</sub>R to CO cells has been recently closing the  
12 gap. Comparing CO<sub>2</sub>R cell data to the representative PEM H<sub>2</sub>O electrolyzer shows the intrinsic advantages  
13 of the PEM configuration (Figure 1c) for high current-density applications (Figure 2b) due to their more  
14 efficient reactant management, high reaction area, and minimal distances for ion transport. Clearly, there  
15 are opportunities to develop vapor-fed CO<sub>2</sub> devices in this configuration as there is currently a dearth of  
16 such studies. Moving forward, it is necessary to understand and optimize transport properties and  
17 reaction kinetics in vapor-fed CO<sub>2</sub>R devices to advance the performance towards practical viability. While  
18 we have focused on partial current density, Faradaic efficiency, and energy efficiency as immediately  
19 important performance figures of merit, we note that other parameters such as CO<sub>2</sub> utilization and  
20 component stability will also become increasingly important.  
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### 29 **Challenges and Opportunities**

30 A crucial first step in the development of vapor-fed CO<sub>2</sub>R devices relates to engineering the GDE  
31 structures. Despite decades of studies, GDEs continue to be an active area of research in the fuel-cell  
32 sector, and performance improvements are still being realized through GDE optimization strategies that  
33 aim to address the many open questions that remain. GDEs in fuel cells may represent a simplified case  
34 in comparison to those in CO<sub>2</sub>R cells, as reaction selectivity and different product phases (vapor versus  
35 liquid) are not as crucial considerations for fuel cells. The challenges and opportunities facing vapor-fed  
36 CO<sub>2</sub>R electrode development relate to understanding and optimizing the multitude of processes occurring  
37 in 3-dimensional GDEs. These processes span different length- and time-scales (Figure 3), with the  
38 complex interplay between phenomena ultimately having a governing effect on the CO<sub>2</sub> reaction  
39 selectivity and the energy-conversion efficiencies and rates. As these research efforts are accelerated, it  
40 will be necessary to translate fundamental knowledge from aqueous-phase CO<sub>2</sub>R studies to vapor-fed  
41 systems and identify gaps and emergent phenomena. The vapor-fed systems are inherently more  
42 complex, due to the presence of a myriad of heterogeneous interfaces on the micro- and nanometer  
43 scales. Future research and scientific challenges must be addressed by closely coupled experimental and  
44 theoretical investigations. Areas deemed important for knowledge generation and technological process  
45 are outlined herein.  
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**Figure 3:** Schematic of a 3-dimensional GDE depicting the multiple length scales where phenomena are occurring during electrochemical CO<sub>2</sub>R.

### *Transport of Reactants*

In vapor-phase CO<sub>2</sub>R electrodes, the delivery of relevant reaction species (CO<sub>2</sub>, electrons and H<sup>+</sup>) can be readily optimized to achieve improved conversion rates. Most notably, vapor-fed cells overcome the intrinsic solubility challenges of CO<sub>2</sub> in aqueous electrolytes (ca. 34 mM). At these low concentrations, mass-transport limitations significantly hinder CO<sub>2</sub> conversion rates in aqueous-phase devices when current densities exceed ca. 10 mA/cm<sup>2</sup>.<sup>20</sup> The type of catalyst and GDE fabrication process must be carefully selected to maximize the catalytically active surface area available, and micro- and nanoscale electrode architectures must be designed to optimize CO<sub>2</sub>, ion, and product transport simultaneously.<sup>57</sup> If present, the properties of the diffusion media, including porosity, pore structure, hydrophilicity, and thickness also play a significant role governing electrode performance. These parameters have been explored and optimized in the case of fuel cells,<sup>58</sup> whereby H<sub>2</sub>/O<sub>2</sub> fuel cells are able to reliably achieve current densities in excess of 1 A/cm<sup>2</sup>. This provides a good basis for comparison, yet very limited understanding exists towards the design and development of high current density CO<sub>2</sub>R electrodes, which must be established through concerted experimental and theoretical efforts.

The relative humidity and concentration of water in vapor-fed CO<sub>2</sub>R reactors can be carefully controlled to overcome the intrinsic challenges associated with aqueous-phase CO<sub>2</sub>R, where the concentration of water at the catalyst surface is ca. 55M, whereas in a typical ion-exchange membrane, water concentrations on the order of 1 to 25 M or so are obtainable via humidity control although there is tradeoff in ionic conductivity at low water contents.<sup>59-61</sup> Water can be a proton source for CO<sub>2</sub>R as well as for the undesirable HER. As the reversible potentials for most electrochemical CO<sub>2</sub> reactions lie within 200 mV of the HER,<sup>37</sup> the HER provides competition to CO<sub>2</sub>R by occupying electrocatalytically active sites and consuming electrons as well as the proton source, resulting in reduced CO<sub>2</sub> conversion rates and energy

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3 efficiencies towards the desired product(s). By delivering CO<sub>2</sub> to the cathode in the vapor-phase, the local  
4 partial pressure of CO<sub>2</sub> can be decoupled from the concentration of water (provided an ionic transport  
5 pathway remains), enabling strategies to steer selectivity by controlling reactant transport to tune the  
6 coverage of intermediates on the catalyst surface. The impact of CO<sub>2</sub> partial pressure on vapor-fed device  
7 performance is, however, not well understood and should be the focus of future studies. Parametric  
8 investigations on well-characterized GDEs should be conducted and closely coupled to the development  
9 of continuum mathematical models to understand transport processes throughout these 3-dimensional  
10 porous electrodes and identify their impact on performance.  
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#### 14 *Polymer Electrolyte and Ionomer - Charge Carrier Transport and Catalyst/Electrolyte Interfaces*

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16 As previously mentioned, a key challenge of aqueous-phase CO<sub>2</sub>R is the CO<sub>2</sub>/carbonate/bicarbonate  
17 buffering equilibria that limits the range of operational pH values for CO<sub>2</sub>R, and convolutes an accurate  
18 depiction of the boundary-layer properties at the catalyst surface.<sup>20</sup> This leads to inflexibility in tuning the  
19 chemical properties of the catalyst/electrolyte interface, despite the importance of these chemical  
20 properties in dictating surface reaction kinetics, mechanisms, and charge-transport processes. For  
21 example, electrolyte pH is known significantly impact CO<sub>2</sub>R activity and selectivity. In particular, increased  
22 activity towards valuable C-C coupled products are favored at high pH values,<sup>4, 62</sup> which cannot be reliably  
23 achieved for aqueous-phase CO<sub>2</sub>R due to the above-mentioned equilibria. This presents a valuable  
24 opportunity to develop and utilize polymer electrolytes that can operate in different pH regimes and may  
25 exhibit very different ion concentrations due to their thinness as well as background charge. Furthermore,  
26 advances in polymer electrolytes must be translated to the development of ionomers for incorporation  
27 throughout the 3-dimensional structure of a GDE to create an interconnected thin-film network needed  
28 for ionic species transport. Despite similar structures, the behavior of ionomer thin films in an electrode  
29 can vary quite significantly from the bulk polymer,<sup>60</sup> and advances in their development and  
30 understanding are needed.  
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35 Solid-state polymer electrolytes (Figure 1c) pose many intrinsic advantages over liquid-phase electrolytes  
36 (Figure 1b). Particularly, simplified device designs requiring fewer auxiliary components for electrolyte  
37 circulation and replenishment, and the elimination of any mobile counter-ions other than protons and  
38 hydroxyls are ideal from a sustainability and CO<sub>2</sub> utilization standpoint. Vapor-fed GDE based devices  
39 employing polymer electrolytes also provide additional transport advantages versus aqueous electrolytes  
40 as they enable shorter distances between the anode and cathode,<sup>63</sup> thereby minimizing ohmic resistances  
41 through a “zero-gap” complete solid-state configuration. Avoiding the use of corrosive liquid electrolytes  
42 also poses several safety advantages, including avoiding the risk of leaking or heat-induced pressure  
43 buildup. Polymer electrolytes furthermore enable operation at higher pressures and potentially allow for  
44 differential pressures to be used between the two electrodes, as reactant crossover can be suppressed.<sup>63</sup>  
45 Finally, they provide an opportunity for separation of volatile liquid-phase CO<sub>2</sub>R products directly at the  
46 site of generation. For example, when targeting alcohol products, in comparison to aqueous-phase CO<sub>2</sub>R,  
47 vapor-fed devices will avoid the formation of azeotropic alcohol/water mixtures that would require  
48 energy intensive downstream separation processes.<sup>21</sup> Clearly there is an immense opportunity for the  
49 development of solid polymer electrolytes and their integration with vapor-fed CO<sub>2</sub>R GDEs. Key challenges  
50 include designing and integrating new polymer electrolytes that simultaneously satisfy the requirements  
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3 of low cost, high ionic conductivity and selectivity, resistance to reactant/product crossover, CO<sub>2</sub>  
4 tolerance, and long-term chemical and mechanical stability under operating conditions.  
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6 On the electrode level, the ionomer properties, including type (i.e., anionic, cationic), structure and  
7 catalyst/ionomer interactions strongly influence CO<sub>2</sub>R activity and selectivity, where the tethering of the  
8 ionic groups hinder movement of their counterions as well as influence the reactivity of the ionic group  
9 themselves relative to their behavior in liquid electrolytes. Ionic species (e.g., H<sup>+</sup>, OH<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>) transport in  
10 the ionomer phase is a crucial consideration, in addition to the distribution of the ionomer phase  
11 throughout the 3-dimensional GDE structure. Particularly, optimized ionomer distributions can enable  
12 good charge species transport and active site utilization, while nonideal distributions can adversely affect  
13 performance through catalytic or transport resistances.<sup>64</sup> There also exists enticing opportunities to  
14 modify ionomer structures to accommodate functional or ionic species that can provide promotional CO<sub>2</sub>R  
15 effects, such as increasing the local CO<sub>2</sub> concentration, decreasing selective site poisoning through blocky  
16 architectures,<sup>15</sup> or impacting reaction mechanisms and routes through chemical modification<sup>65</sup> and field  
17 effects, where the local ion concentrations and distances can be more precisely controlled.<sup>2</sup>  
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22 While recent advances have enabled understanding of how different parameters (i.e., pH, electrolyte  
23 concentrations, catalyst functionalization) fundamentally affect aqueous-phase CO<sub>2</sub>R catalysis, it is an  
24 opportune time to translate and validate this current state of understanding to highly porous vapor-fed  
25 GDEs. For example, polymer electrolytes exhibit different acid/base equilibria time constants than  
26 aqueous electrolytes due to the existence of the polymer backbone.<sup>66</sup> Furthermore, while one may obtain  
27 the desired high pH in aqueous electrolytes using high flowrates, that may provide challenges from a  
28 practicality standpoint, and thin electrodes,<sup>24</sup> a similar effect may perhaps be obtained with polymer  
29 electrolytes since their thinness and possibility for high current-density operation result in large hydroxide  
30 fluxes and amounts in the electrode ionomer. Targeted approaches to understand polymer electrolyte  
31 effects, ionomer distributions, ionomer/catalyst interactions and charge-carrier transport properties must  
32 be carried out on model and/or prototype vapor-fed CO<sub>2</sub>R systems, where the use of new polymer  
33 electrolytes and ionomers provide an increased ability to control and manipulate the local reaction  
34 environment at the catalyst surface. It is suggested that researchers leverage previous efforts on these  
35 topics reported in the fuel cell or electrolyzer literature, especially as anion-exchange membranes and  
36 ionomers become more prevalent and understood.  
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#### 42 *Opportunities for Fundamental Understanding*

43 With the seemingly overwhelming number of factors that govern the multiscale processes and  
44 performance of a GDE, a detailed understanding of these phenomena will require experimental  
45 approaches closely coupled with multiscale theoretical modeling and prediction. Comprehensive models  
46 do not currently exist that simultaneously capture and bridge quantum- and molecular-level dynamics  
47 with continuum models of reactant and product transport. The difficulty lies in the disparate length- and  
48 time-scales between these processes that require the combination of non-linear partial differential  
49 equations with complex boundary conditions. Robust numerical techniques that can accomplish this are  
50 needed, which will enable the necessary multi-process understanding and optimization that will be  
51 essential for guiding and understanding GDE approaches.  
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3 In terms of experimental approaches, the increasing complexity of vapor-fed devices necessitates the  
4 development and utilization of *operando*, *in-situ*, and *ex-situ* probes that probe interfacial phenomena in  
5 highly porous electrodes. For this, simplified vapor-fed cells can potentially be designed to deconvolute  
6 the influence of common experimental parameters.<sup>67</sup> This could serve to enable facile characterization  
7 and CO<sub>2</sub>R evaluation of catalyst and electrode structures, which will accelerate the implementation of  
8 new GDE formulations in high-performance devices. Additionally, vapor-fed GDEs offer a promising  
9 platform for experimentally characterizing the multi-scale properties of devices and processes occurring  
10 during operation. By minimizing the use of liquids, challenges associated with beam attenuation and  
11 refraction are avoided, enabling mechanistic probing of electrode processes using X-ray scattering,  
12 absorption or photoelectron techniques. For example, the electronic or chemical structure of catalytically  
13 active surface sites in GDEs under reaction conditions can be probed by *in-situ* X-ray absorption  
14 spectroscopy<sup>68-70</sup> or *in-situ* X-ray photoelectron spectroscopy<sup>71-72</sup>, respectively; meanwhile the effects of  
15 electrode pore sizes, structures and surface properties on microscale transport processes can be  
16 interrogated by X-ray computed tomography coupled with performance evaluation.<sup>73-77</sup> Developing an  
17 improved understanding of the effects of operating conditions and GDE configurations on performance  
18 will provide opportunity to engineer devices to provide multi-variable optimization for achieving  
19 unprecedented knowledge and performance.

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21 Beyond GDE designs to optimize the multiscale processes underlying their operation, electrode  
22 integration into vapor-fed reactors provides an ideal opportunity for advanced understanding. The impact  
23 of operational parameters such as relative humidity, reactant flow rates, temperature, and device  
24 electrical potential on CO<sub>2</sub> conversion rates and efficiency remains largely unexplored, yet provide  
25 additional levers to tune performance and selectivity. The type of polymer electrolyte (proton exchange,  
26 anion exchange, bipolar) and anode design and materials are essential considerations for incorporating  
27 GDEs into working devices,<sup>78-79</sup> and GDE compatibility with electrolytes and anodes must be understood.  
28 The stability of GDEs under operating conditions is also an important topic that has not been addressed  
29 in detail here or in the literature, because vapor-fed CO<sub>2</sub>R electrode design is a relatively early stage field  
30 of research. Stable, long-term operation will be essential for achieving practicality of these devices. As  
31 these devices will ideally be coupled with renewable sources of power, the question of variability and how  
32 it relates to GDE performance and stability must also be understood and addressed. Furthermore,  
33 engineering vapor-fed GDEs to be capable of accommodating low-grade or dilute CO<sub>2</sub> feed sources (e.g.,  
34 atmospheric CO<sub>2</sub>) improves the practicality of these devices to different applications and elucidation of  
35 these effects is important.

## 36 37 38 39 40 41 42 43 44 45 46 47 **Outlook**

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49 Recent efforts have demonstrated the potential of translating scientific advances made in electrochemical  
50 CO<sub>2</sub> reduction research towards the development of practical CO<sub>2</sub> electrolyzers. Key challenges and  
51 opportunities that remain involve the understanding and development of 3-dimensional vapor-fed CO<sub>2</sub>  
52 reduction electrodes that can achieve high conversion rates and energy efficiencies towards the desired  
53 products. Particularly, there is an immense scientific opportunity to develop fundamental understanding  
54 of the multi-scale processes occurring in 3-dimensional GDEs, and to optimize GDE performance through  
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3 rational engineering approaches. Closely integrated experimental and theoretic investigations are  
4 required to progress upon our current state of understanding and perpetuate the advancement of CO<sub>2</sub>  
5 electrolyzers towards practical relevance. The knowledge generated and progress made in catalyst  
6 integration, electrode engineering and electrochemical device design will also be directly applicable to  
7 other electrochemical conversion devices that could be of technological importance in the near future to  
8 replace Gigatonne-scale, carbon intensive industrial processes. These include sustainable electrochemical  
9 technologies for the production of fuels and chemicals from carbon-based feedstocks, or the synthesis of  
10 ammonia-based fertilizers from ambient N<sub>2</sub>.  
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### 16 **Biographies**

17 Drew Higgins has been at Stanford University and SLAC National Laboratory since 2015, first as a Banting  
18 Postdoctoral Fellow and then Associate Staff Scientist working on electrochemical catalyst development,  
19 understanding and device integration. In January 2019, he starts a Faculty position at McMaster  
20 University in the Department of Chemical Engineering. <https://www.higginslab.com/>  
21  
22

23 Christopher Hahn began his current position at SLAC National Accelerator Laboratory in 2015, where he  
24 is conducting research with the Joint Center for Artificial Photosynthesis on catalyst discovery and  
25 understanding reaction mechanisms for electrochemical CO<sub>2</sub> reduction.  
26

27 <https://suncat.stanford.edu/people/christopher-hahn>  
28

29 Chengxiang (“CX”) Xiang and his team is working on development of testbed prototypes for  
30 photoelectrochemical CO<sub>2</sub> reduction and water-splitting. <http://sunlight.caltech.edu/cx/>  
31  
32

33 Thomas Jaramillo is an Associate Professor at Stanford and SLAC National Accelerator Laboratory and is a  
34 Thrust Coordinator in JCAP overseeing electrocatalysis research. His laboratory focuses on fundamental  
35 catalytic processes occurring on solid-state surfaces in both the production and consumption of energy.  
36 <http://jaramillogroup.stanford.edu/>  
37  
38

39 Adam Weber is currently a Staff Scientist at LBNL where he leads the Energy Conversion Group and is a  
40 Thrust Coordinator in JCAP overseeing continuum modeling, multicomponent integration, and test-bed  
41 construction and evaluation. He is a Fellow of the Electrochemical Society for his research on  
42 understanding electrochemical technologies. <https://weberlab.lbl.gov/>  
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## Quotes

Moving towards practical reactor designs that operate using CO<sub>2</sub> delivered to the cathode in the vapor phase can help to overcome these performance and solubility challenges

The challenges and opportunities facing vapor-fed CO<sub>2</sub>R electrode development relate to understanding and optimizing the multitude of processes occurring in 3-dimensional GDEs. These processes span different length- and time-scales, with the complex interplay between phenomena ultimately having a governing effect on the CO<sub>2</sub> reaction selectivity and the energy-conversion efficiencies and rates.

Particularly, there is an immense scientific opportunity to develop fundamental understanding of the multi-scale processes occurring in 3-dimensional GDEs, and to optimize GDE performance through rational engineering approaches.

There also exists enticing opportunities to modify ionomer structures to accommodate functional or ionic species that can provide promotional CO<sub>2</sub>R effects, such as increasing the local CO<sub>2</sub> concentration, decreasing selective site poisoning through blocky architectures, or impacting reaction mechanisms and routes through chemical modification and field effects, where the local ion concentrations and distances can be more precisely controlled.