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

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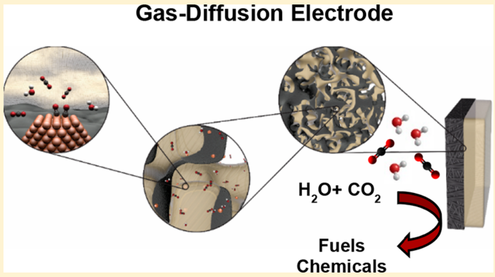
ABSTRACT: Significant advances have been made in recent years discovering new electrocatalysts and developing a fundamental understanding of electrochemical CO_2 reduction processes. This field has progressed to the point that efforts can now focus on translating this knowledge toward the development of practical CO_2 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_2 reduction catalysts into practical device architectures that operate using vapor-phase CO_2 reactants, thereby overcoming intrinsic limitations of aqueous-based systems. Performance comparison is made between state-of-the-art CO_2 electrolyzers and commercial H_2O 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 toward the development of practical CO_2 electrolyzers.



The development of new technologies that reduce greenhouse gas emissions while producing fuels and commodity chemicals has the potential to mitigate the devastating impacts of climate change by transforming the petrochemical sector toward sustainability. Electrochemical CO_2 reduction (CO_2R) coupled with renewably generated electricity (wind, solar, hydro) provides an attractive approach for the carbon-neutral production of valuable hydrocarbon, alcohol, and carbonyl products that find widespread use in the energy and chemical sectors. For this artificial photosynthesis process to be implemented at scale, highly active and selective CO_2R catalysts must be developed and ultimately integrated into devices that can achieve high conversion rates and energy-conversion efficiencies to the desired product(s). Vapor-fed CO_2 devices represent a promising platform for such a technology.

On a fundamental level, there has been much progress understanding electrochemical CO_2R in the liquid phase, where CO_2 molecules are solubilized in an aqueous electrolyte and reduced on the surface of a catalyst (Figure 1a). The unprecedented level of synergy between theoretical and experimental research toward aqueous-phase CO_2R has led to improved understanding regarding the impact of electrolyte ions,[1−3] pH,[4] mass transport,[5−7] temperature,[8] and pressure[8,9] on activity and selectivity. As a result, activity descriptors[10,11] and mechanistic insight into reaction pathways[12,13] have guided catalyst design efforts, leading to the discovery of new compositions[14−16] and morphologies that are more active and selective to desired CO_2R products. A succinct overview of these advances has been provided in a recently published perspective piece.[17] It is furthermore expected these efforts will be accelerated with the implementation of machine learning processes for catalyst discovery.[18,19]

While the above referenced studies have been critical in establishing a deeper understanding of CO_2R, they have traditionally relied upon aqueous-phase CO_2R reactors designed for fundamental investigations (Figure 1a). From an applied standpoint, however, these test reactors have many practical limitations that must be addressed. Most notably, the poor solubility (ca. 34 mM) of CO_2 in aqueous electrolytes,

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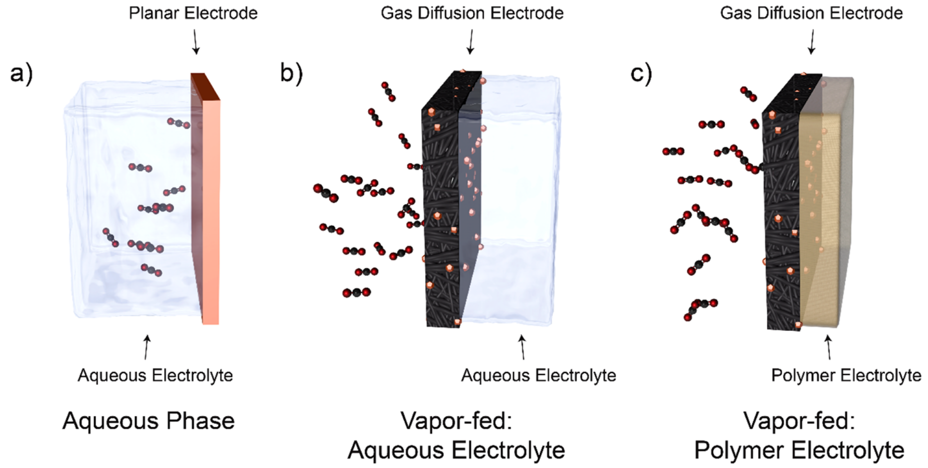

Figure 1. Different electrochemical CO_2R reactor schemes. (a) Aqueous-phase CO_2R, where CO_2 is first solubilized in an aqueous electrolyte and then reduced at a catalyst surface. Vapor-fed CO_2R employing an (b) aqueous or (c) polymer electrolyte.

> Moving toward practical reactor designs that operate using CO_2 delivered to the cathode in the vapor phase can help to overcome these performance and solubility challenges.

along with acid/base buffer ($CO_2/HCO_3^-/CO_3^{-2}$) equilibria lead to intrinsic challenges toward achieving high conversion rates and energy efficiencies.[20] Moving toward practical reactor designs that operate using CO_2 delivered to the cathode in the vapor phase (Figure 1b,c) can help to overcome these performance and solubility challenges. Such gas-diffusion electrodes (GDEs) can achieve this by employing a porous catalyst layer along with diffusion media to facilitate reactant transport and distribution. GDEs have been used in other electrochemical energy-conversion devices such as fuel cells and electrolyzers, where the architecture has been optimized for high current density and low transport losses. However, the adaptation to CO_2R will require further advancement, as different operating strategies and understandings are needed to address product selectivity considerations, which is important to avoid the need for costly downstream separations.[21] Furthermore, the actual electrolyte can either be aqueous to form a catalyst/liquid electrolyte interface (Figure 1b), or ideally an ion-conducting polymer that can transport charged species (e.g., H^+ or OH^-) and form a catalyst/polymer-electrolyte interface (Figure 1c).

A recently published article[22] provides a critical overview of various electrolyzer designs that can be considered, along with a review of the technological achievements made in recent years on electrochemical CO_2R reactor designs. In this Perspective, we discuss the challenges and opportunities facing GDE development for electrochemical CO_2R. We provide context in terms of CO_2R electrocatalysis, and include a discussion of the intrinsic advantages and unexpected opportunities of GDEs in an effort to motivate researchers to translate current understanding toward new GDE designs. The purpose of this Perspective is not to provide a comprehensive review on the topic of electrochemical CO_2R or GDE development. Instead, the goal is to provide a forward-looking perspective to inspire and provide direction for these fields of research, using the technology maturation process of

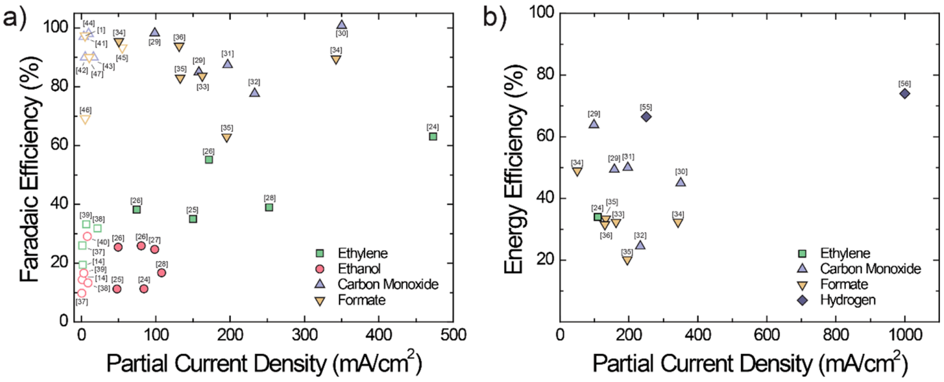

Figure 2. State-of-the-art performance of vapor-fed CO_2 devices. (a) Faradaic efficiencies versus partial current densities to ethylene, ethanol, carbon monoxide, and formate. (b) Energy efficiencies versus partial current densities to ethylene, carbon monoxide, formate, and hydrogen. Performances obtained for vapor-fed CO_2R electrodes are shown in solid symbols, while performance for electrodes in aqueous-phase CO_2R reactors are shown in hollow symbols. All energy efficiencies were calculated as voltage efficiencies using the formula: $\text{energy efficiency} = \frac{(E^0_{\text{anode}} - E^0_{\text{cathode}}) \times \text{FE}}{V_{\text{cell}}}$, **where E^0_{anode} and E^0_{cathode} are the reversible potentials, FE is the faradaic efficiency for the CO_2R product, and V_{cell} is the uncompensated cell voltage.**

commercial water electrolyzers as realistic performance targets. We identify areas deemed important for developing a fundamental understanding of the underlying chemistry, processes, and phenomena occurring in GDEs. This insight is essential for advancing the state of electrochemical CO_2R technologies toward commercial viability.

State-of-the-Art. In comparison to electrodes studied in aqueous-phase electrochemical reactors, various types of vapor-fed CO_2R electrodes have been successful in improving the partial current densities and energy efficiencies for CO_2R.[23] 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[24−36] (solid symbols) are shown in comparison to similar catalyst compositions tested in aqueous-phase reactors[1,14,37−47] (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. Among 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 $2e^-$ reduction products.[36,48−52] On the other hand, data for the further reduced ($>2e^-$) products, ethylene and ethanol, demonstrates that selectivity is still a major challenge. This selectivity challenge is largely because ethylene and ethanol are competitively coproduced 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_2R,[24,26] along with similar results demonstrated for electrochemical carbon-monoxide reduction.[53,54] This observation suggests that vapor-fed conditions are a promising avenue for tuning the local environment and reaction conditions that control CO_2R selectivity (vide infra), while simultaneously achieving higher partial current densities. However, altering the local CO_2 environment is largely underexplored for GDEs and presents an opportunity for increased understanding compared to solely aqueous-phase reactor investigations.

On a system level, Figure 2b shows a summary of state-of-the-art energy efficiencies versus partial current densities, which takes into account transport resistances (ionic and electronic), along with kinetic losses from both the anode and cathode.[55] A comparison is also provided to the performance of representative alkaline[55] and proton-exchange membrane[56] (PEM) H_2O electrolyzers. It is interesting to note that all of the vapor-fed CO_2R cells incorporate an aqueous electrolyte (Figure 1b), in part because alkaline electrolytes can improve energy efficiencies by reducing cathodic overpotentials. Thus, a traditional commercial H_2O electrolyzer with an aqueous alkaline electrolyte[55] likely provides the most appropriate comparison. While the representative alkaline H_2O electrolyzer performance is superior to that of the vapor-fed CO_2 cells shown in Figure 2b, the performance of CO_2R to CO cells has been recently closing the gap. Comparing CO_2R cell data to the representative PEM H_2O electrolyzer shows the intrinsic advantages of the PEM configuration (Figure 1c) for high current-density applications (Figure 2b) due to their more efficient reactant management, high reaction area, and minimal distances for ion transport. Clearly, there are opportunities to develop vapor-fed CO_2 devices in this configuration as there is currently a dearth of such studies. Moving forward, it is necessary to understand and optimize transport properties and reaction kinetics in vapor-fed CO_2R devices to advance the

> The challenges and opportunities facing vapor-fed CO_2R electrode development relate to understanding and optimizing the multitude of processes occurring in three-dimensional GDEs. These processes span different length and time scales, with the complex interplay between phenomena ultimately having a governing effect on the CO_2 reaction selectivity and the energy-conversion efficiencies and rates.

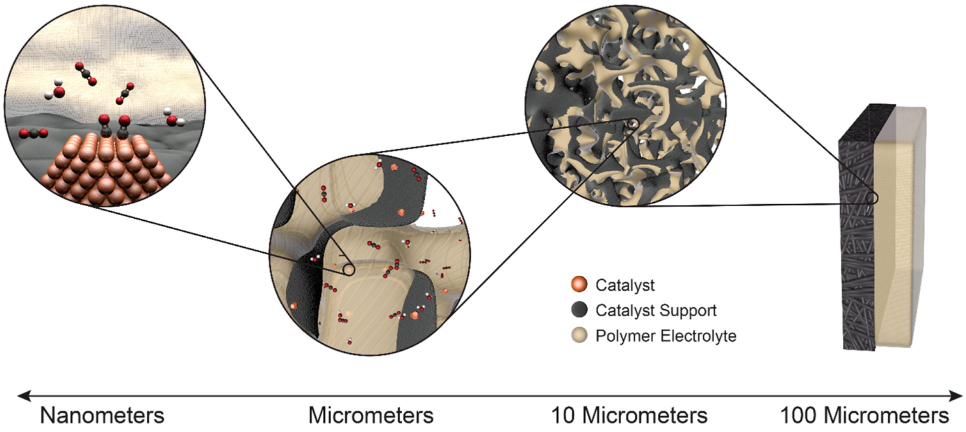

Figure 3. Schematic of a three-dimensional GDE depicting the multiple length scales where phenomena are occurring during electrochemical CO_2R.

performance toward practical viability. While we have focused on partial current density, Faradaic efficiency, and energy efficiency as immediately important performance figures of merit, we note that other parameters such as CO_2 utilization and component stability will also become increasingly important.

Challenges and Opportunities. A crucial first step in the development of vapor-fed CO_2R devices relates to engineering the GDE structures. Despite decades of studies, GDEs continue to be an active area of research in the fuel-cell sector, and performance improvements are still being realized through GDE optimization strategies that aim to address the many open questions that remain. GDEs in fuel cells may represent a simplified case in comparison to those in CO_2R cells, as reaction selectivity and different product phases (vapor versus liquid) are not as crucial considerations for fuel cells. The challenges and opportunities facing vapor-fed CO_2R electrode development relate to understanding and optimizing the multitude of processes occurring in three-dimensional GDEs. These processes span different length and time scales (Figure 3), with the complex interplay between phenomena ultimately having a governing effect on the CO_2 reaction selectivity and the energy-conversion efficiencies and rates. As these research efforts are accelerated, it will be necessary to translate fundamental knowledge from aqueous-phase CO_2R studies to vapor-fed systems and identify gaps and emergent phenomena. The vapor-fed systems are inherently more complex, due to the presence of a myriad of heterogeneous interfaces on the micro- and nanometer scales. Future research and scientific challenges must be addressed by closely coupled experimental and theoretical investigations. Areas deemed important for knowledge generation and technological process are outlined herein.

Transport of Reactants. In vapor-phase CO_2R electrodes, the delivery of relevant reaction species (CO_2, electrons, and H^+) can be readily optimized to achieve improved conversion rates. Most notably, vapor-fed cells overcome the intrinsic solubility challenges of CO_2 in aqueous electrolytes (ca. 34 mM). At these low concentrations, mass-transport limitations significantly hinder CO_2 conversion rates in aqueous-phase devices when current densities exceed ca. 10 mA/cm^2.[20] 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_2, ion, and product transport simultaneously.[57] If present, the properties of the diffusion media, including porosity, pore structure, hydrophilicity, and thickness also play significant roles in governing electrode performance. These parameters have been explored and optimized in the case of fuel cells,[58] whereby H_2/O_2 fuel cells are able to reliably achieve current densities in excess of 1 A/cm^2. This provides a good basis for comparison, yet very limited understanding exists toward the design and development of high current density CO_2R electrodes, which must be established through concerted experimental and theoretical efforts.

The relative humidity and concentration of water in vapor-fed CO_2R reactors can be carefully controlled to overcome the intrinsic challenges associated with aqueous-phase CO_2R, where the concentration of water at the catalyst surface is ca. 55 M, whereas in a typical ion-exchange membrane, water concentrations on the order of 1−25 M or so are obtainable via humidity control although there is trade-off in ionic conductivity at low water contents.[59−61] Water can be a proton source for CO_2R as well as for the undesirable HER. As the reversible potentials for most electrochemical CO_2 reactions lie within 200 mV of the HER,[37] the HER provides competition to CO_2R by occupying electrocatalytically active sites and consuming electrons as well as the proton source, resulting in reduced CO_2 conversion rates and energy efficiencies toward the desired product(s). By delivering CO_2 to the cathode in the vapor-phase, the local partial pressure of CO_2 can be decoupled from the concentration of water (provided an ionic transport pathway remains), enabling strategies to steer selectivity by controlling reactant transport to tune the coverage of intermediates on the catalyst surface. The impact of CO_2 partial pressure on vapor-fed device performance is, however, not well understood and should be the focus of future studies. Parametric investigations on well-characterized GDEs should be conducted and closely coupled to the development of continuum mathematical models to understand transport processes throughout these 3-dimensional porous electrodes and identify their impact on performance.

Polymer Electrolyte and Ionomer: Charge Carrier Transport and Catalyst/Electrolyte Interfaces. As previously mentioned, a key challenge of aqueous-phase CO_2R is the CO_2/carbonate/bicarbonate buffering equilibria that limits the range of operational pH values for CO_2R, and convolutes an accurate depiction of the boundary-layer properties at the catalyst surface.[20] This leads to inflexibility in tuning the chemical properties of the catalyst/electrolyte interface, despite the importance of these chemical properties in dictating surface reaction kinetics, mechanisms, and charge-transport processes. For example, electrolyte pH is known significantly impact CO_2R activity and selectivity. In particular, increased activity toward valuable C−C coupled products are favored at high pH values,[4,62] which cannot be reliably achieved for aqueous-phase CO_2R due to the above-mentioned equilibria. This presents a valuable opportunity to develop and utilize polymer electrolytes that can operate in different pH regimes and may exhibit very different ion concentrations due to their thinness as well as background charge. Furthermore, advances in polymer electrolytes must be translated to the development of ionomers for incorporation throughout the three-dimensional structure of a GDE to create an interconnected thin-film network needed for ionic species transport. Despite similar structures, the behavior of ionomer thin films in an electrode can vary quite significantly from the bulk polymer,[60] and advances in their development and understanding are needed.

Solid-state polymer electrolytes (Figure 1c) pose many intrinsic advantages over liquid-phase electrolytes (Figure 1b). Particularly, simplified device designs requiring fewer auxiliary components for electrolyte circulation and replenishment, and the elimination of any mobile counterions other than protons and hydroxyls are ideal from a sustainability and CO_2 utilization standpoint. Vapor-fed GDE based devices employing polymer electrolytes also provide additional transport advantages versus aqueous electrolytes as they enable shorter distances between the anode and cathode,[63] thereby minimizing ohmic resistances through a “zero-gap” complete solid-state configuration. Avoiding the use of corrosive liquid electrolytes also poses several safety advantages, including avoiding the risk of leaking or heat-induced pressure buildup. Polymer electrolytes furthermore enable operation at higher pressures and potentially allow for differential pressures to be used between the two electrodes, as reactant crossover can be suppressed.[63] Finally, they provide an opportunity for separation of volatile liquid-phase CO_2R products directly at the site of generation. For example, when targeting alcohol products, in comparison to aqueous-phase CO_2R, vapor-fed devices will avoid the formation of azeotropic alcohol/water mixtures that would require energy intensive downstream separation processes.[21] Clearly there is an immense opportunity for the development of solid polymer electrolytes and their integration with vapor-fed CO_2R GDEs. Key challenges include designing and integrating new polymer electrolytes that simultaneously satisfy the requirements of low cost, high ionic conductivity and selectivity, resistance to reactant/product crossover, CO_2 tolerance, and long-term chemical and mechanical stability under operating conditions.

On the electrode level, the ionomer properties, including type (i.e., anionic, cationic), structure and catalyst/ionomer interactions strongly influence CO_2R activity and selectivity, where the tethering of the ionic groups hinder movement of their counterions as well as influence the reactivity of the ionic group themselves relative to their behavior in liquid electrolytes. Ionic species (e.g., H^+, OH^-, HCO_3^-) transport in the ionomer phase is a crucial consideration, in addition to the distribution of the ionomer phase throughout the three-dimensional GDE structure. Particularly, optimized ionomer distributions can enable good charge species transport and active site utilization, while nonideal distributions can adversely affect performance through catalytic or transport resistances.[64] There also exist enticing opportunities to modify ionomer structures to accommodate functional or ionic species that can provide promotional CO_2R effects, such as increasing the local CO_2 concentration, decreasing selective site poisoning through blocky architectures,[15] or impacting reaction mechanisms and routes through chemical modification[65] and field effects, where the local ion concentrations and distances can be more precisely controlled.[2]

While recent advances have enabled understanding of how different parameters (i.e., pH, electrolyte concentrations, catalyst functionalization) fundamentally affect aqueous-phase CO_2R catalysis, it is an opportune time to translate and validate this current state of understanding to highly porous vapor-fed GDEs. For example, polymer electrolytes exhibit different acid/base equilibria time constants than aqueous electrolytes due to the existence of the polymer backbone.[66] Furthermore, while one may obtain the desired high pH in aqueous electrolytes using high flow rates, this provides challenges from a practicality standpoint;[24] a similar effect may perhaps be obtained with polymer electrolytes since their thinness and possibility for high current-density operation result in large hydroxide fluxes and amounts in the electrode ionomer. Targeted approaches to understand polymer electrolyte effects, ionomer distributions, ionomer/catalyst interactions and charge-carrier transport properties must be carried out on model and/or prototype vapor-fed CO_2R systems, where the use of new polymer electrolytes and ionomers provide an increased ability to control and manipulate the local reaction environment at the catalyst surface. It is suggested that researchers leverage previous efforts on these topics reported in the fuel cell or electrolyzer literature, especially as anion-exchange membranes and ionomers become more prevalent and understood.

Opportunities for Fundamental Understanding. With the seemingly overwhelming number of factors that govern the multiscale processes and performance of a GDE, a detailed understanding of these phenomena will require experimental approaches closely coupled with multiscale theoretical modeling and prediction. Comprehensive models do not currently exist that simultaneously capture and bridge quantum- and molecular-level dynamics with continuum models of reactant and product transport. The difficulty lies in the disparate length- and time-scales between these processes that require the combination of nonlinear partial differential equations with complex boundary conditions. Robust numerical techniques that can accomplish this are needed, which will enable the necessary multiprocess understanding and optimization that will be essential for guiding and understanding GDE approaches.

In terms of experimental approaches, the increasing complexity of vapor-fed devices necessitates the development and utilization of operando, in situ, and ex situ probes that probe interfacial phenomena in highly porous electrodes. For this, simplified vapor-fed cells can potentially be designed to deconvolute the influence of common experimental parameters.[67] This could serve to enable facile characterization and CO_2R evaluation of catalyst and electrode structures, which will accelerate the implementation of new GDE formulations in high-performance devices. Additionally, vapor-fed GDEs offer a promising platform for experimentally characterizing the multiscale properties of devices and processes occurring during operation. By minimizing the use of liquids, challenges associated with beam attenuation and refraction are avoided, enabling mechanistic probing of electrode processes using X-ray scattering, absorption, or photoelectron techniques. For example, the electronic or chemical structure of catalytically active surface sites in GDEs under reaction conditions can be probed by in situ X-ray absorption spectroscopy[68−70] or in situ X-ray photoelectron spectroscopy,[71,72] respectively; meanwhile the effects of electrode pore sizes, structures, and surface properties on microscale transport processes can be interrogated by X-ray computed tomography coupled with performance evaluation.[73−77] Developing an improved understanding of the effects of operating conditions and GDE configurations on performance will provide opportunity to engineer devices to provide multivariable optimization for achieving unprecedented knowledge and performance.

Beyond GDE designs to optimize the multiscale processes underlying their operation, electrode integration into vapor-fed reactors provides an ideal opportunity for advanced understanding. The impact of operational parameters such as relative humidity, reactant flow rates, temperature, and device electrical potential on CO_2 conversion rates and efficiency remains largely unexplored, yet provide additional levers to tune performance and selectivity. The type of polymer electrolyte (proton exchange, anion exchange, bipolar) and anode design and materials are essential considerations for incorporating GDEs into working devices,[78,79] and GDE compatibility with electrolytes and anodes must be understood. The stability of GDEs under operating conditions is also an important topic that has not been addressed in detail here or in the literature, because vapor-fed CO_2R electrode design is a relatively early stage field of research. Stable, long-term operation will be essential for achieving practicality of these devices. As these devices will ideally be coupled with renewable sources of power, the question of variability and how it relates to GDE performance and stability must also be understood and addressed. Furthermore, engineering vapor-fed GDEs to be capable of accommodating low-grade or dilute CO_2 feed sources (e.g., atmospheric CO_2) improves the practicality of these devices to different applications and elucidation of these effects is important.

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

Outlook. Recent efforts have demonstrated the potential of translating scientific advances made in electrochemical CO_2 reduction research toward the development of practical CO_2 electrolyzers. Key challenges and opportunities that remain involve the understanding and development of three-dimensional vapor-fed CO_2 reduction electrodes that can achieve high conversion rates and energy efficiencies toward the desired products. Particularly, there is an immense scientific opportunity to develop fundamental understanding of the multiscale processes occurring in three-dimensional GDEs, and to optimize GDE performance through rational engineering approaches. Closely integrated experimental and theoretic investigations are required to progress upon our current state of understanding and perpetuate the advancement of CO_2 electrolyzers toward practical relevance. The knowledge generated and progress made in catalyst integration, electrode engineering, and electrochemical device design will also be directly applicable to other electrochemical conversion devices that could be of technological importance in the near future to replace gigatonne-scale, carbon-intensive industrial processes. These include sustainable electrochemical technologies for the production of fuels and chemicals from carbon-based feedstocks, or the synthesis of ammonia-based fertilizers from ambient N_2.

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