

## Perspective

Perspective and challenges in electrochemical approaches for reactive CO<sub>2</sub> separations

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## SUMMARY

The desire toward decarbonization and renewable energy has sparked research interests in reactive CO<sub>2</sub> separations, such as direct air capture that utilize electricity as opposed to conventional thermal and pressure swing processes, which are energy-intensive, cost-prohibitive, and fossil-fuel dependent. Although the electrochemical approaches in CO<sub>2</sub> capture that support negative emissions technologies are promising in terms of modularity, smaller footprint, mild reaction conditions, and possibility to integrate into conversion processes, their practice depends on the wider availability of renewable electricity. This perspective discusses key advances made in electrolytes and electrodes with redox-active moieties that reversibly capture CO<sub>2</sub> or facilitate its transport from a CO<sub>2</sub>-rich side to a CO<sub>2</sub>-lean side within the last decade. In support of the discovery of new heterogeneous electrode materials and electrolytes with redox carriers, the role of computational chemistry is also discussed.

## INTRODUCTION

The atmospheric concentration of CO<sub>2</sub> has been recorded to fluctuate for 800,000 years between 200 and 300 ppm, oscillating with the glacial and interglacial periods of the planet. In recent years, the concentration had a sharp increase to 415 ppm (Dlugokencky and Tans, 2021). The International Panel on Climate Change released its sixth Assessment Report in the summer of 2021, in which they review the unequivocal evidence that human activity, particularly anthropogenic greenhouse gas (GHG) emission, is the main contributor to global climate change (IPCC, 2021). The report indicates that the 1.5°C increase in average global temperature, established by the Paris Agreement, is approaching much faster than initially thought. The likely hood of surpassing 2°C of average global temperature warming within the next two decades is virtually certain unless significant GHG emission reduction efforts are implemented. One of the most effective ways of combatting this temperature increase is by achieving net-zero emissions of the GHGs, especially from large emitters such as fossil fuel burning power plants. CO<sub>2</sub> is responsible for more than half of the warming imbalance and thus has been a common target of GHG capture research for the past few decades (Tans et al., 2020).

CO<sub>2</sub> can be captured in a number of ways depending on its source. Many of these processes involve feeding CO<sub>2</sub>-rich gas to an absorbent or adsorbent material that selectively captures CO<sub>2</sub>, followed by the regeneration of the sorbent via thermal or pressure swing. The regeneration step is often the most energy-intensive step in the process, and aging of capture materials or solvents under the long-term swing conditions is another challenge. Although more than 70 years of research and some examples of implementation have been focused on technologies that capture CO<sub>2</sub> from post-combustion flue gas, capturing CO<sub>2</sub> from atmospheric air has recently gained more interest. Direct air capture (DAC) technology aims to separate CO<sub>2</sub> from the atmosphere, where the CO<sub>2</sub> concentration is much lower compared to point sources. However, DAC is currently a high-cost technology with 5–10 GJ energy requirements to capture a ton of atmospheric CO<sub>2</sub>. For DAC to be truly a negative emission technology (NET), the energy requirement should be lowered with alternative resources to fossil fuels and the captured CO<sub>2</sub> should be geologically stored. Therefore, materials with high selectivity, significant CO<sub>2</sub> capture capacity, and stability under a wide range of temperatures and humidities are needed for DAC. Furthermore, it would be highly desirable to regenerate DAC materials with low-cost zero-carbon energy. Currently, 28% of the electricity generated globally comes from renewables which is a limiting factor to electrify carbon capture technologies.

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Removal of CO<sub>2</sub> as a means of revitalizing breathing air has been an active research area since the 1940s (i.e., submarines and spacecraft, and more recently for sustainability in space) (Kammermeyer, 1966; Knox, July 2018; Blum et al., 1952). The concept of DAC to mitigate the rise in CO<sub>2</sub> levels in the atmosphere was introduced by Lackner in 1999 (Lackner et al., 1999). Approaches to DAC include aqueous alkaline bases (Stolaroff et al., 2008), humidity-swing quaternary ammonium-based anion-exchange resins (Shi et al., 2020a; Wang et al., 2011), and solid-supported amines (Bali et al., 2015; Didas et al., 2015; Sujan et al., 2019) with fewer technologies based on electrochemical and membrane separations (Sanz-Pérez et al., 2016). Causticization with aqueous alkaline bases requires regeneration temperatures of 800–900°C, which constitutes the majority of the energy required for CO<sub>2</sub> removal (6–9 GJ per ton of CO<sub>2</sub>). On a purely thermodynamic basis, the conversion of CO<sub>2</sub> to calcium carbonate salt has a reaction enthalpy of approximately –109 kJ/mol, but the intermediate regeneration step of converting calcium carbonate to calcium oxide has a reaction enthalpy of +179 kJ/mol, resulting in an unavoidable energy penalty of at least 70 kJ/mol of CO<sub>2</sub> before factoring in system inefficiencies. Aqueous amines (El Hadri et al., 2017; Yu et al., 2012; Nguyen et al., 2010) have milder regeneration temperatures (~120°C); however, their reaction enthalpies, on the order of –80 kJ/mol of CO<sub>2</sub> (Kim and Svendsen, 2007), are still demanding, especially when coupled with the evaporation of both the amine and water. The resulting vapor must be recondensed to prevent the loss of active material, leading to an even greater energy penalty (Nguyen et al., 2010). The volatility and toxicity of amines further eliminate their use in open systems. Solid-supported amines are, therefore, more promising, but these systems present slow transport of CO<sub>2</sub> and performance degradation over time owing to oxidation and moisture, similar to metal-organic frameworks (MOFs) and zeolites. The current state of the field necessitates improved solvents/sorbents with high CO<sub>2</sub> selectivities and capacities, fast transport, new regeneration mechanisms or improved energy requirements for thermal regeneration, and long-term stability, as underscored by the 2018 National Academy of Sciences report on Negative Emission Technologies and Reliable Sequestration (National Academies of Sciences et al., 2018).

Humidity swing (Shi et al., 2020b), dielectric heating by electromagnetic field (Tsubaki et al., 2020), and electrochemically mediated separations (Liu et al., 2020b) are some of the more recent examples of alternative regeneration processes. The use of moisture or humidity is an attractive mechanism to drive the absorption–desorption cycle of CO<sub>2</sub>, specifically in comparison to the requirement of heat in thermal-swing and mechanical work in pressure-swing. Humidity-swing processes involve the absorption of CO<sub>2</sub> with the hydroxide ion resin to form bicarbonate. As the resin uptakes CO<sub>2</sub> under low humidity conditions (10–40% RH), some water is released owing to the difference in the hydration of the ions present. The flow of moist air (>70% RH) over the CO<sub>2</sub>-saturated resin during desorption results in the hydration of the ions which provides the free energy for CO<sub>2</sub> release. To maximize energy efficiency, humidity-swing could be coupled with other driving forces such as thermal boost as increasing the temperature of a feed with a certain water content lowers the relative humidity (Lackner et al., 2020). CO<sub>2</sub> regeneration by dielectric heating via electromagnetic field stimulation and Joule heating via electric-current stimulation are relatively new concepts with very few studies demonstrated to date for aqueous amines (McGurk et al., 2017; Tsubaki et al., 2020) and carbonaceous adsorbents (Sevanthi et al., 2016), respectively. On the other hand, electric stimuli for CO<sub>2</sub> separations have been studied in a number of systems by Hatton and co-workers. One of the electrochemically mediated CO<sub>2</sub> capture systems involves the use of redox-active carriers and another involves the use of amine absorbers that release CO<sub>2</sub> in the presence of cupric ions. In these isothermal systems, the need for thermal energy is eliminated and the energy requirement is dependent on the overpotentials; additional voltage is required to perform the redox reaction resulting from kinetic and mass transport limitations. Design of the electrochemical cell and materials can help to minimize these overpotentials and the associated energy penalty. Furthermore, steam is not needed, thus enabling modularity in CO<sub>2</sub> capture. Using renewable energy sources for these processes supports the distributed nature of electrochemical processes. In this perspective, we discuss the recent electrochemical approaches in CO<sub>2</sub> separations (Table 1) with a specific focus on multifunctional electrolytes, modified electrodes, and the role of quantum chemistry in the design space of active materials, as summarized in Figure 1.

## ELECTROCHEMICAL GAS SEPARATION

Electrochemical gas separations involve the selective reduction of the target gas, followed by the transport of the gas in ion form from one electrode to the other. In the counter electrode, the ion gets selectively oxidized, releasing the gas. This process can be envisioned as pumping the target gas from the catholyte

**Table 1. Examples of electrochemical approaches to reactive CO<sub>2</sub> separations with reported current densities (*i*) and faradaic efficiencies ( $\eta$ )**

	<i>E</i> (kJ/mol CO <sub>2</sub> )	<i>i</i> (mA/cm <sup>2</sup> )	$\eta$	Advantages	Disadvantages	Ref
<b>Amine-Based Systems</b>						
EMAR <sup>a</sup>	45	2.5	0.42	Suppressed solvent volatility (compared to thermal swing amines)	Electrode dissolution and plating causes material imbalance in electrolytes	(Stern et al., 2013) (Wang et al., 2020)
CRAB <sup>b</sup>	−8.2 <sup>h</sup>	3	0.45	Harvests binding energy of CO <sub>2</sub> -sorbent complex	Requires thermal amine regeneration with low-pressure steam	(Li et al., 2020)
<b>Redox-Active CO<sub>2</sub> Carriers</b>						
Quinones	43	0.5	0.95	Natural compounds with a large structural design space	Unstable in aqueous media; Highly susceptible to protonation in reduced form Slow diffusion in non-aqueous solvents	(Gurkan et al., 2015; Scovazzo et al., 2003)
Disulfides	200	3.03 <sup>c</sup>	.9934 <sup>c</sup>	Less basic/susceptible to protonation than quinones	Sluggish oxidation kinetics Large potential difference between reduction (CO <sub>2</sub> capture) and oxidation (CO <sub>2</sub> release) leading to inefficiencies	(Singh et al., 2017a, 2017b)
<b>Biomimetic Proton Carriers for PCET<sup>d</sup></b>						
Phenazine derivatives	21.6	10	0.958	Moisture stable High faradaic efficiency	Vulnerable to oxidizing gases (e.g., O <sub>2</sub> in DAC)	(Xie et al., 2020b)
Tiron	105.6	18	0.55 <sup>e</sup>	High diffusion coefficient in aqueous media	Poor cycle performance owing to loss of alkalinity over multiple cycles	(Huang et al., 2019)
FMN <sup>f</sup>	9.8	10	0.943	Low cost redox-active species	Slow and consistent capacity fade over multiple cycles	(Xie et al., 2020a)
<b>Membrane-Based Processes (pH swing)</b>						
KOH Absorption/K <sub>2</sub> CO <sub>3</sub> Electrolysis	290–350	100	0.908	CO <sub>2</sub> and H <sub>2</sub> produced, can be coupled with utilization technology	Large overpotentials at high pH gradients	(Stucki et al., 1995)
Electro-dialysis membrane stacks coupled with synthesis of Methionine	1109	30	0.864	CO <sub>2</sub> product recycled into amino acid synthesis	Difficult to integrate with existing power plant infrastructure	(Jiang et al., 2017)
Hydroxide exchange membrane cell	350	20	0.95 <sup>g</sup>	Can be coupled with fuel cell technology O <sub>2</sub> presence improves efficiency	Low CO <sub>2</sub> product purity	(Eisaman et al., 2009; Landon and Kitchin, 2010; Matz et al., 2021)

Energy consumptions (*E*) in kJ per mole of CO<sub>2</sub> desorbed were theoretically estimated using the experimental cell voltages via the formulation  $FV/\eta_e$  where *F* is the Faraday's constant, *V* is the cell voltage required to release CO<sub>2</sub> and  $\eta_e$  is the electron utilization term. It was assumed that the electron utilization term is 0.9 although this may depend on the actual temperature, pressure and the active material concentration of the system.

<sup>a</sup>Electrochemically mediated amine regeneration.

<sup>b</sup>CO<sub>2</sub>-regenerative amine-based battery.

<sup>c</sup>obtained from the computer model.

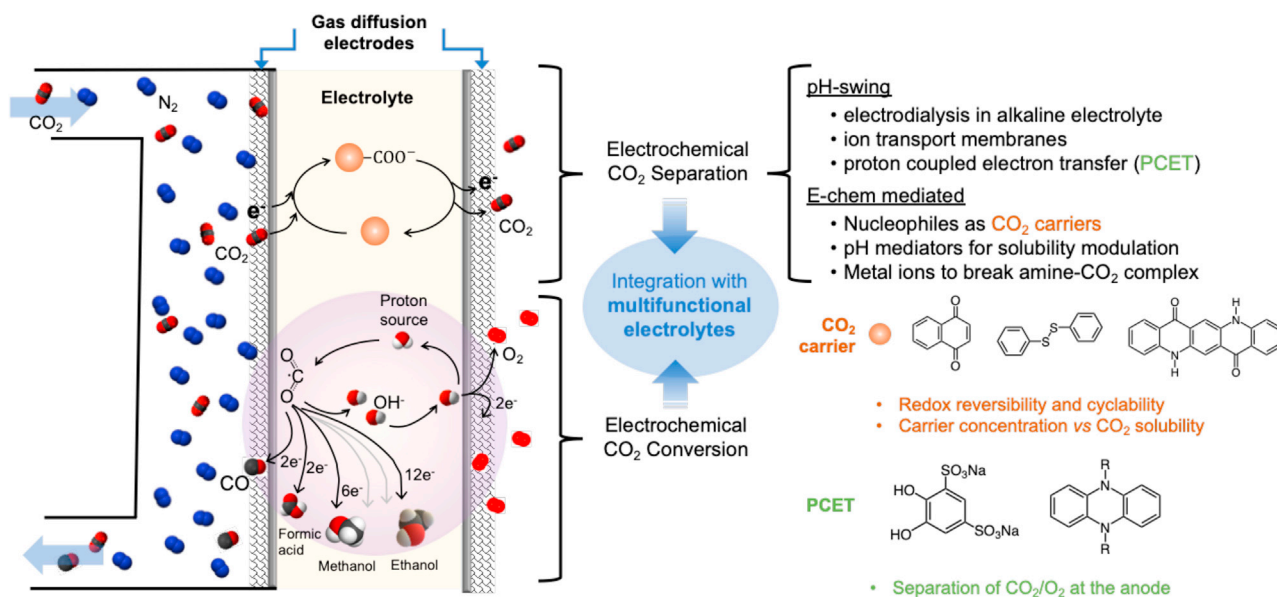
<sup>d</sup>PCET = proton-coupled electron transfer.

<sup>e</sup>in mol CO<sub>2</sub> per mole e<sup>−</sup>.

<sup>f</sup>riboflavin 5'-monophosphate sodium salt hydrate.

<sup>g</sup>CO<sub>2</sub> removal efficiency from 1000 sccm air containing 400 ppm CO<sub>2</sub>.

<sup>h</sup>Theoretical energy created by the battery; the calculation did not account for the energy use associated with the low-pressure steam and the overpotentials.



**Figure 1.** Summary of electrochemical approaches to CO<sub>2</sub> separations discussed in this perspective with an outlook of possible integration with conversion processes through multifunctional electrolytes that can maintain high CO<sub>2</sub> solubility at the electrode surface.

side to the anolyte side in an electrochemical cell with gas diffusion electrodes. In an alkaline solution, CO<sub>2</sub>, being an acidic gas, is absorbed from the feed gas in contact with the catholyte. It then reacts with the hydroxide ion to form bicarbonate (CO<sub>2</sub> + OH<sup>-</sup> → HCO<sub>3</sub><sup>-</sup>). Bicarbonate can then further react with another hydroxide to form a carbonate ion and water in pH's higher than 8 (HCO<sub>3</sub><sup>-</sup> + OH<sup>-</sup> → CO<sub>3</sub><sup>2-</sup> + H<sub>2</sub>O). In an electric field, the anions move toward the anode where the pH is lowered owing to the oxygen evolution reaction (4OH<sup>-</sup> → O<sub>2</sub> + 2H<sub>2</sub>O + 4e<sup>-</sup>), thus reversing the catholyte reactions and releasing CO<sub>2</sub>. The large dependence of the solubility of CO<sub>2</sub> on pH enables the reversible capture and release of CO<sub>2</sub> even with a small pH swing between pH 6 and 8 (Datta et al., 2013).

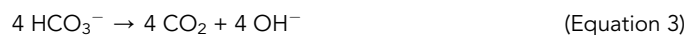
### pH-swing by electrodialysis and membranes

A variety of electrochemical pH-swing methodologies was devised to enable CO<sub>2</sub> separation under ambient temperature and pressure, such as direct electrolysis (Mehmood et al., 2016; Datta et al., 2013), bipolar membrane electrodialysis (Eisaman et al., 2011a), and membrane capacitive deionization (Legrand et al., 2020; Sharifian et al., 2021). In 1996 (Xiao and Li, 1997), an electrodialysis system was reported for pH-swing CO<sub>2</sub> separation by an electrochemical membrane module with polyamide soaked with aqueous potassium carbonate for air revitalization in confined spaces. Increased CO<sub>2</sub> removal rate by achieved by increasing current density, which was obtained at high voltages (i.e., 3 V). However, at voltages above 1.23 V, water splitting occurs and the efficiency of CO<sub>2</sub> removal is significantly reduced. In an effort to reduce voltage requirements, another study in 2010 (Landon and Kitchin, 2010), utilized an anion exchange membrane which reduced the ohmic resistance compared to the previous studies with thick separators. The anion exchange membrane transports CO<sub>2</sub> in the form of bicarbonate. Bicarbonate forms as a result of CO<sub>2</sub> reacting with the hydroxide ions that are released during oxygen reduction reaction (ORR) at the cathode (Equations 1 and 2). The reactions are reversed at the anode releasing CO<sub>2</sub> and O<sub>2</sub> (Equations 3 and 4).

Cathode:



Anode:



Although these systems appear economically promising with consideration of potential improvements in cell design such as higher activity electrocatalysts and lower resistance membranes, they may not be ideal end-units in power plants to capture and sequester  $\text{CO}_2$ , as the separated  $\text{CO}_2$  always contains a side gas such as  $\text{O}_2$ . The US Department of Energy's target of a 90%  $\text{CO}_2$  capture rate with less than 35% cost of electricity requires such systems to operate at as small as 0.5 V with at least a 3.5 separation ratio of  $\text{CO}_2:\text{O}_2$ . Therefore, these systems need a valorization process to follow where  $\text{O}_2$  or other impurities are tolerable. Most recently, it was demonstrated (Matz et al., 2021) the removal of  $\text{CO}_2$  from the air upstream of a hydroxide exchange membrane fuel cell. In this electrochemically driven  $\text{CO}_2$  capture process associated with the fuel cell, high purity of  $\text{CO}_2$  could be produced by suppressing the generation of  $\text{O}_2$  at the anode by the flow of hydrogen gas ( $2 \text{OH}^- + \text{H}_2 \rightarrow 2 \text{H}_2\text{O} + 2 \text{e}^-$ ).

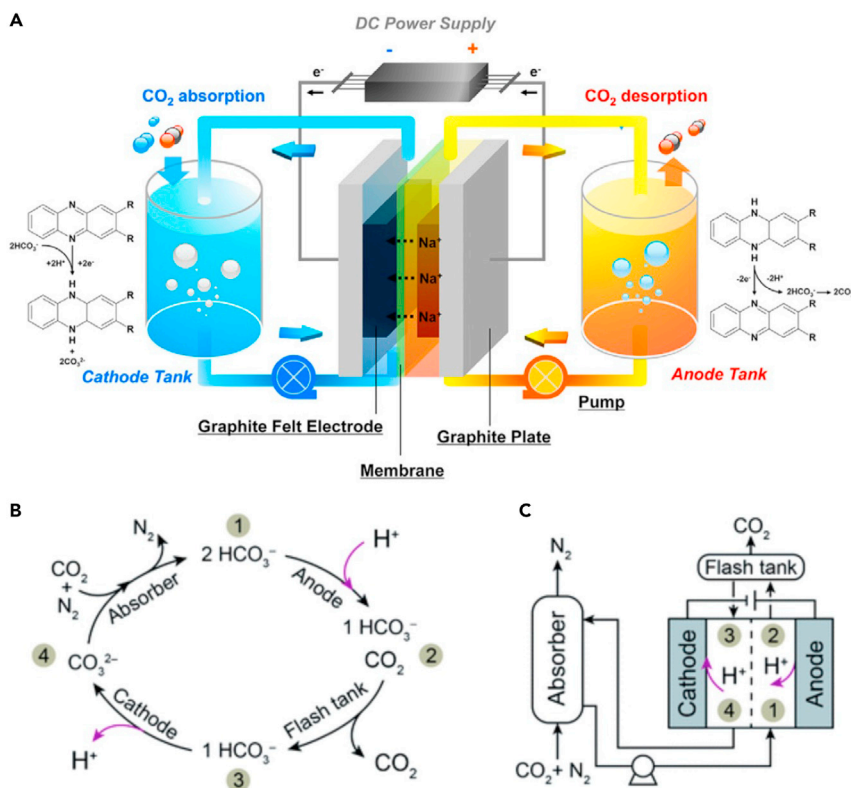
### pH-swing by proton-coupled electron transfer reactions

Different from the previous approaches, proton carriers undergoing redox reactions are also utilized in pH-swing (Xu et al., 2010). It has been reported that the theoretical energy requirement of PCET is small compared to the general electrodialysis mechanism involving water-splitting (Renfrew et al., 2020). Quinone chemistry has been typically used for  $\text{CO}_2$  capture by PCET reactions (Watkins et al., 2015). In 2020, sodium 3,3'-(phenazine-2,3-diylbis(oxy))bis(propane-1-sulfonate) (DSPZ) was studied as a redox-active organic proton carrier (Jin et al., 2020). By utilizing the redox activity of 3,3'-(phenazine-2,3-diylbis(oxy))bis(propane-1-sulfonate) as a pH mediator, it was possible to capture  $\text{CO}_2$  by forming an alkaline solution via the reduction of the redox molecule and to release  $\text{CO}_2$  through acidification by re-oxidation. In another study, biomimetic phenazine derivatives were also used as the proton carrier (Figure 2A) (Xie et al., 2020b). The low solubility of organic proton carriers in aqueous solutions is one of the main obstacles that limit the  $\text{CO}_2$  capture and release rates. To solubilize the phenazine-based molecules, sulfonic group modification was conducted, and the product 7,8-dihydroxyphenazine-2-sulfonic acid exhibited excellent kinetics and cyclability. This sulfonic group modification has also been applied to quinones (i.e., tiron), taking advantage of the reduced quinone's sensitivity to protonation to make a pH mediator (Huang et al., 2019). Loss of alkalinity over time resulted in poor cycle performance for this system. Lower pH and lowered quinone concentration were shown to improve cyclability at the cost of lower  $\text{CO}_2$  capacity (Luo et al., 2021). The water-soluble form of vitamin B2, riboflavin 5'-monophosphate sodium salt, is the most recent example of a biomimetic proton carrier for pH swing by PCET, sporting an extremely low energy requirement for regeneration at 9.8 kJ/mol  $\text{CO}_2$  (Xie et al., 2020a).

It was also attempted to modulate pH using electrodes by applying proton intercalating  $\text{MnO}_2$  for  $\text{CO}_2$  capture (Rahimi et al., 2020a).  $\text{MnO}_2$  stored and released protons by the redox reaction of Mn(IV)/Mn(III) and the corresponding intercalation/deintercalation of  $\text{H}^+$ . This work showed not only the effective  $\text{CO}_2$  separation via pH modulation with reversible  $\text{MnO}_2$  protonation, but also the practical feasibility of this system by the development of a thermodynamic model integrating a  $\text{K}_2\text{CO}_3$ -based  $\text{CO}_2$  absorption and electrochemically mediated pH swing (Figures 2B and 2C). Bench-scale experiments with this system were also demonstrated, focusing on the continuous desorption of  $\text{CO}_2$  from a  $\text{K}_2\text{CO}_3$  solution (Rahimi et al., 2020b). Overall, the PCET process is still in the early stages of development, and the low stability of the organic proton carriers or redox electrodes is the current limiting issue. Further works to improve both the conductivity and the cyclability would advance this strategy into a viable and scalable  $\text{CO}_2$  separation system.

### ELECTROCHEMICALLY MEDIATED $\text{CO}_2$ SEPARATION

Slightly different than the electrochemical gas separations discussed above, electrochemically mediated  $\text{CO}_2$  separations involve electrochemically generated nucleophiles that act as  $\text{CO}_2$  carriers or electrochemically generated metal ions which disrupt the  $\text{CO}_2$  binding of the amine absorbers. The carrier molecules have no affinity to  $\text{CO}_2$  at their neutral state but bind with  $\text{CO}_2$  at their reduced state. The redox mechanism facilitates the pumping of  $\text{CO}_2$  from the cathode to the anode side as the carrier compound gets reduced at the cathode and oxidized at the anode. DuBois and coworkers (Bell et al., 1988) in 1988 examined electroactive species in quest of regenerable  $\text{CO}_2$  removal systems for the National Aeronautics and Space Administration's long space missions. Simpson et al. (Comeau Simpson and Durand, 1990) electrochemically



**Figure 2. Proton-coupled electron transfer reactions for  $\text{CO}_2$  capture processes**

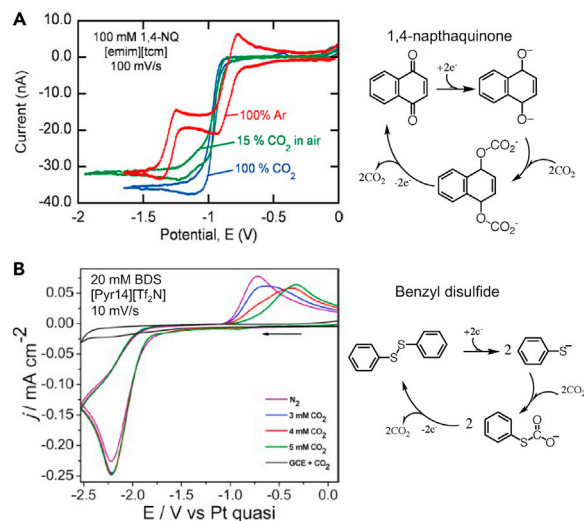
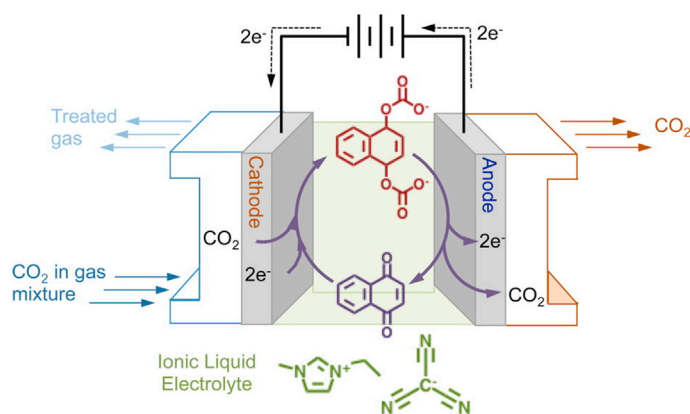
(A–C) (A) Schematics of the system studied by Xie et al. that utilizes phenazine derivatives to drive the  $\text{CO}_2$  absorption by pH modulation in aqueous  $\text{HCO}_3^-/\text{CO}_3^{2-}$ . Reprinted with permission from Ref (Xie et al., 2020b). Copyright 2020, Elsevier; (B)  $\text{CO}_2$  capture with  $\text{K}_2\text{CO}_3$  as the absorbent (cation not shown for simplicity) and (C) a schematic diagram of the process. The proton deintercalation from the electrode shifts the  $\text{CO}_2(\text{aq})/\text{HCO}_3^-(\text{aq})/\text{CO}_3^{2-}(\text{aq})$  equilibrium toward  $\text{CO}_2$  formation at the anode and this is followed by gas separation through a flash tank. Subsequently, the proton intercalation in the cathode aids the regeneration of the absorbent.

studied several quinone species as redox-active carriers in an organic solvent. Quinones are natural compounds that undergo oxidation and reduction at potentials that depend on the pH of the media. Several studies to date have utilized quinones for energy harvesting and storage, with specific examples including their use in electrode design for Na-ion batteries (Gurkan et al., 2017) and in electrolyte formulation for organic redox flow batteries (Huskinson et al., 2014). In the case of electrochemically generated metal ions, the amine- $\text{CO}_2$  bond is replaced with the interaction with the amine and the metal ions (i.e., cupric ions) thereby regenerating the amine and releasing  $\text{CO}_2$ . We discuss  $\text{CO}_2$  separation by redox carriers studied to date and the metal electroplating/stripping to facilitate absorbent regeneration later in discussion.

### Electrochemically generated nucleophiles as $\text{CO}_2$ carriers

One common example of a  $\text{CO}_2$  carrier is quinones that contain carbonyl groups. Upon reduction, they yield nucleophiles that bind with  $\text{CO}_2$ . The concept of electrochemically mediated  $\text{CO}_2$  separation with the use of a quinone species was demonstrated with an imidazolium hexafluorophosphate ionic liquid (IL) (Scovazzo et al., 2003). However, the solubility of the quinone in the IL was not significant which resulted in low separation capacity. Furthermore, significant overpotentials were present that led to low Faradaic efficiency. In 2015, it was demonstrated (Gurkan et al., 2015) that with the choice of substitution in quinone structure and an IL with high polarity, the net  $\text{CO}_2$  separation capacity can be improved while also improving the efficiency (Figure 3A). The reduction and the consecutive  $\text{CO}_2$ -binding potential of 1,4-naphthaquinone (1,4-NQ) in an imidazolium tricyanomethanide ([emim][tcm]) IL translated to favorable energetics over the amine solvent regeneration by thermal-swing.





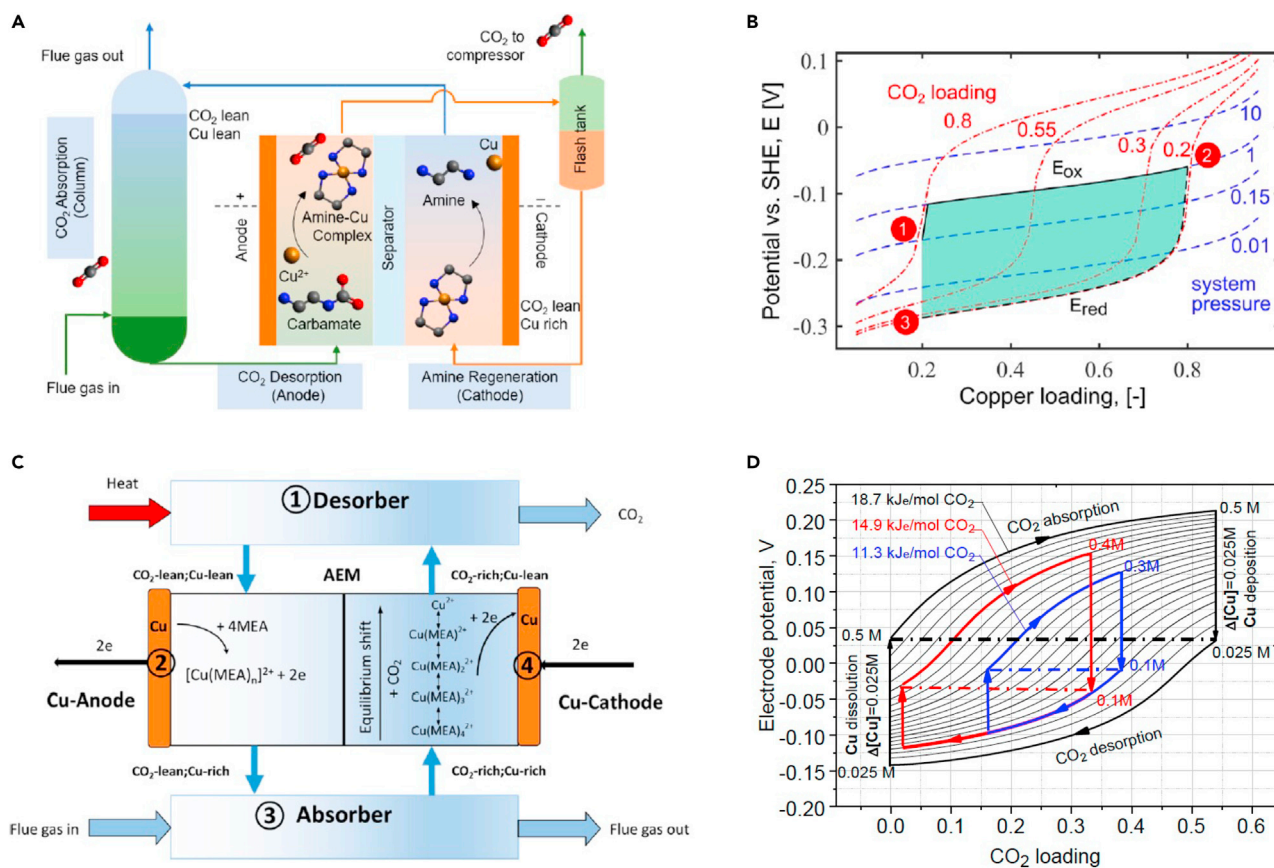
**Figure 3. Redox carriers for electrochemically mediated CO<sub>2</sub> separation**

**Left:** Schematic illustration of electrochemical CO<sub>2</sub> separation using redox carriers. Figure reprinted with permission from Ref (Gurkan et al., 2015). Copyright 2015, American Chemical Society. Electrochemically generated nucleophiles bind with CO<sub>2</sub> at the cathode and diffuse to the anode owing to the concentration gradient and finally release CO<sub>2</sub> upon oxidation at the anode. **Right:** (A) 1,4-NQ reduction on Pt microelectrode and binding with CO<sub>2</sub> in ionic liquid [emim][tcm]. Potentials with respect to internal Fc/Fc<sup>+</sup> (Gurkan et al., 2015), (B) BDS reduction on glassy carbon and binding with CO<sub>2</sub> in [Pyr14][Tf<sub>2</sub>N]; Singh et al. Reprinted with permission from Ref (Singh et al., 2017a). Copyright 2017, American Chemical Society.

In addition to quinones, sulfur-containing redox carriers have been developed by Buttry and colleagues (Singh et al., 2017a). Benzyl disulfide (BDS), upon reduction forms two benzothiolate anions, which can react with CO<sub>2</sub> to form thiocarbonate. Thiolates are less basic than quinone nucleophiles and more stable in the presence of water. Although the electrochemically generated nucleophile is promising for CO<sub>2</sub> scavenging, the oxidation potential of the thiocarbonate to disulfide and simultaneous CO<sub>2</sub> release is far separated from the reduction potential with slow e-transfer rates (Rheinhardt et al., 2017). Furthermore, the highly negative reduction potential of BDS once again requires the use of a nonaqueous electrolyte. Figure 3B shows the microelectrode voltammetry of the CO<sub>2</sub> redox carrier 1,4-NQ in [emim][tcm] from the study by (Gurkan et al., 2015). It is clearly seen that the reduction of quinone (Q) to the dianion (Q<sup>2-</sup>) via the radical anion formation (Q<sup>•-</sup>) under argon occurs by a 2-step single electron transfer reaction (Q → Q<sup>•-</sup> → Q<sup>2-</sup>) whereas, under CO<sub>2</sub> there is a single wave that corresponds to the two-electron reduction and complexation with CO<sub>2</sub>. This concerted mechanism at the same potential is enabled by the solvent media. The bottom panel of Figure 3C from a later study by (Singh et al., 2017a) shows the reduction of another CO<sub>2</sub> redox carrier BDS in 1-butyl-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([Pyr14][Tf<sub>2</sub>N]) IL. In the case of BDS, the reaction is not reversible (too far apart reduction and oxidation); the electron transfer reaction involves a significant reorganization for the creation of the nucleophile. The S-S bond dissociation energy makes up a significant portion of the intrinsic energy barrier. Therefore, unless structural designs of diaryl sulfides that enable improved kinetics of electron injection are demonstrated, this approach will unlikely be practical in consideration of the energetics. Quinones, although having a more robust redox reaction, are not as stable especially in the presence of water.

Bipyridine-based compounds can also be reduced to become nucleophilic as demonstrated in 1994 (Ishida et al., 1994). As these compounds in their reduced form, such as quinones, are susceptible to protonation, an aprotic solvent is required. Later it was shown that owing to the stability of the radical anion CO<sub>2</sub> adduct, a one-electron reduction step of bipyridine is possible (Ranjan et al., 2015). This leads to improved current efficiency of bipyridine over quinone systems. Monoalkylation of bipyridine reverts to a two-electron reduction to bind one CO<sub>2</sub> (Singh et al., 2020). DAC applications of these compounds are unlikely owing to their high susceptibility to reaction with oxygen gas.

Another example of redox-active molecules that binds with CO<sub>2</sub> at their reduced state is the vat dyes which are types of organic pigments (Apaydin et al., 2014). CO<sub>2</sub> capture and release capacity of quinacridone was demonstrated. In the study, quinacridone was coated as a thin film over the electrode. Although the neutral



**Figure 4. Electrochemically generated metal ions to regenerate amines in CO<sub>2</sub> capture**

(A) EMAR process schematics by Wang et al.<sup>64</sup>. The CO<sub>2</sub>-complexed amine solution is pumped from the absorber to the anode chamber of the regeneration unit where the electrochemically generated Cu<sup>2+</sup> from the Cu anode coordinates with the amine. The formation of this complex desorbs CO<sub>2</sub>. Once Cu<sup>2+</sup> is reduced at the cathode hence electroplates, amine is released and pumped back to the absorber column. Reprinted with permission from Ref.<sup>64</sup> Copyright 2020, American Chemical Society.

(B) Thermodynamic cycle of the EMAR system where blue and red lines correspond to the constant CO<sub>2</sub> partial pressure and constant amine loading, respectively. Reprinted with permission from Ref.<sup>64</sup> Copyright 2020, American Chemical Society.

(C) Schematics of the Cu-mediated CRAB process by Li et al.<sup>28</sup>. CO<sub>2</sub>-amine reaction enthalpy is converted to electrical power by the electro dissolution and stripping of Cu. Reprinted with permission from Ref.<sup>28</sup> Copyright 2020, Elsevier.

(D) Modeled thermodynamic pathway for the CRAB process with 2 M monoethanolamine at 25°C. Dashed lines indicate the endpoint of battery discharging in each cycle. For different Cu-loading, energy output per captured CO<sub>2</sub> is indicated for three cases (the outmost black, red, and blue cycles). Reprinted with permission from Ref.<sup>28</sup> Copyright 2020, Elsevier.

form of the dye was not soluble in water, its reduced form was soluble in the aqueous electrolyte and the loss of active material from the electrode limited its cycling. Furthermore, the redox potential of quinacridone was outside of the electrochemical window of water and this resulted in significant hydrogen evolution. Therefore, this particular technology is in need of stable redox carriers with reversible and robust redox reactions in the electrolyte media.

### Electrochemically generated metal ions

The concept of regenerating an amine absorber by breaking the CO<sub>2</sub>-amine complex through electrochemically generated metal ions has been demonstrated in a process referred to as electrochemically mediated amine regeneration (EMAR) (Figures 4A and 4B), which was developed by Hatton and colleagues in 2013 (Stern et al., 2013). The process uses ethylene diamine to capture CO<sub>2</sub>. Once the sorbent is saturated, it is pumped to a desorption chamber which is essentially an electrochemical cell that generates cupric ions from a Cu anode. Cu<sup>2+</sup> competitively interacts with the amine group in the diamine, thus releasing CO<sub>2</sub>. Once CO<sub>2</sub> is removed from the solution, the Cu<sup>2+</sup> is plated out onto the cathode and the solution is ready to be used again. Thermodynamic analysis of this process indicates that the energy



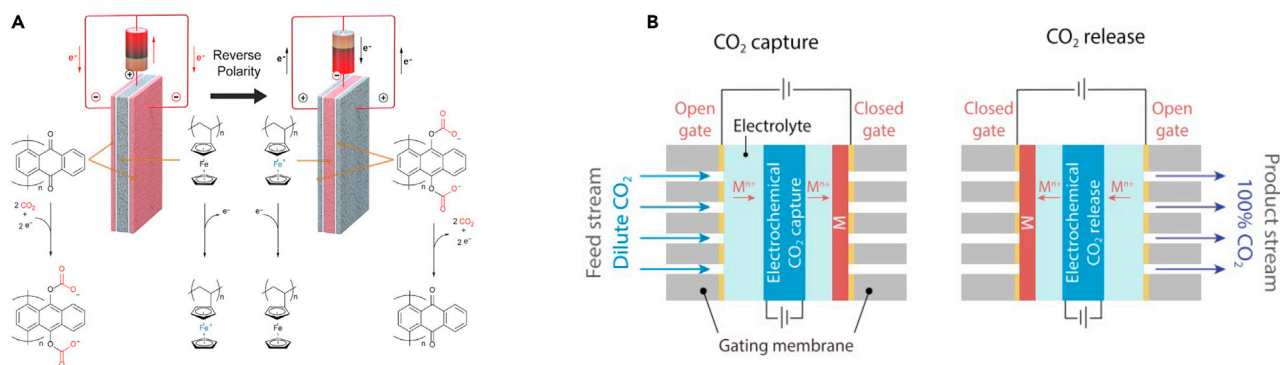
requirement for regeneration is approximately  $\sim 35\text{--}40$  kJ/mol  $\text{CO}_2$  (Wang et al., 2019, 2020), which is comparable to the energy requirement of thermal swing processes using monoethanolamine, MEA (40 kJ/mol  $\text{CO}_2$ ), and piperazine (38 kJ/mol  $\text{CO}_2$ ). The true advantage of the EMAR system is its “plug-and-play” nature. With only a need for electrical energy, the EMAR process can be installed without steam integration, significantly reducing installation costs and greatly expanding the range of applications for the device. The challenges in the EMAR system have been the volatility of the amine solvent and the gas accumulation on the electrode surface. These challenges have been addressed with some success by the electrolyte design and formulation. For example, an addition of a less volatile amine to the ethylenediamine (EDA) electrolyte could suppress the vapor pressure maintaining the  $\text{CO}_2$  capture efficiency, and an addition of an anionic surfactant, sodium dodecyl sulfate, could notably reduce the overall cell resistance (Rahimi et al., 2020c, 2020d). Very recently, a process similar to EMAR was demonstrated (Li et al., 2020), except the system produces electrical power from the energy of the absorption process that would be otherwise lost to heat dissipation. Although the majority of research has been on reducing the regeneration energy requirement, the heat that is produced as a result of the exothermic binding of  $\text{CO}_2$  to amine has not been utilized. In fact, to keep the absorber column temperature from rising, interstage cooling is applied. It is challenging to utilize such low-quality heat owing to the moderate temperatures of the absorber (i.e.,  $50^\circ\text{C}$ ). However, it was possible with a battery cell integration as shown in Figure 4C, referred to as the  $\text{CO}_2$ -regenerative amine-based battery (CRAB), to produce 8.2 kJ per mol of  $\text{CO}_2$  (Figure 4D). As Cu is stripped in the anode, it binds with the amine in the  $\text{CO}_2$ -lean solution. As this solution flows through the absorber next, it picks up  $\text{CO}_2$  then flows into the cathode where Cu electrodeposition takes place. Finally, the  $\text{CO}_2$ -rich and Cu-lean solution gets replenished in terms of the amine in the desorber. This process unlike the previous approaches still relies on some level of integration with a power plant. Furthermore, the estimated thermodynamics path does not take into account the overpotentials that are likely present in practice owing to electrolyte resistance and electrode kinetics. CRAB is a very early-stage technology with a lot of moving parts that need further optimization in terms of the active components like the amine and the metal to address the material imbalance in the electrochemical cell and the redox kinetics.

### Heterogeneous electrodes for $\text{CO}_2$ adsorption

The electrochemical separation of  $\text{CO}_2$  from post-combustion flue gas or air is also possible through the molecular engineering of selective electrodes. Compared to the approach of using a redox-active carrier in the electrolyte, electro-swing systems that involve redox electrodes have the advantage of not requiring a pumping system for the liquids (Voskian and Hatton, 2019). In an analogous fashion to liquid-phase redox reactions, quinone-based chemistries have been extensively applied to heterogeneous electrodes for  $\text{CO}_2$  capture and release ( $\text{Q} \leftrightarrow \text{Q}^{2-} \leftrightarrow \text{Q}(\text{CO}_2)^{2-}$ ).

Anthraquinone (AQ) was introduced for electrochemical  $\text{CO}_2$  capture in the form of thin-film electrodes (Wielend et al., 2018). The film electrodes, fabricated via an evaporation method, exhibited reversible capture and release of  $\text{CO}_2$  in aqueous solutions by forming an AQ-carbonate structure. Reversibility was confirmed by the observed stability in FTIR measurements upon fifty cycles of cyclic voltammetry experiments.  $\text{CO}_2$  capture from flue gas by the electro-swing system using AQ electrodes was also explored (Voskian and Hatton, 2019), using asymmetric redox systems. The system consisted of polyanthraquinone (PAQ)-carbon nanotube (CNT) composite cathodes, a polyvinylferrocene (PVF)-CNT composite anode, and an IL electrolyte. As shown in Figure 5A the reversible  $\text{CO}_2$  uptake and release take place at the PAQ-CNT electrode via carboxylation of quinone groups. This system achieved effective  $\text{CO}_2$  capture regardless of the  $\text{CO}_2$  feed concentration, and it exhibited exceptional recyclability in swing operation over 7000 cycles with high capacity and Faradaic efficiency retention. Moreover, this work demonstrated economic feasibility through a process model and energy analysis. However, the process still needs improvements in  $\text{CO}_2$  capacity and kinetics.

Recently, a  $\text{CO}_2$  capture system using PAQ electrodes has been further improved (Liu et al., 2020a). The  $\text{CO}_2$  separation efficiency of the PAQ-CNT electrodes was demonstrated to be enhanced by introducing gating membranes to control the gas transport. As shown in Figure 5B, the gas transport was controllable by the electrodeposition of zinc on the conductive layer of the gating membranes, through which the feed or product streams could pass. Through this strategy, it was possible to modulate the gas composition effectively in both capture and release without pressurizing  $\text{CO}_2$ . Another attempt to separate  $\text{CO}_2$  using quinone-based electrodes has recently been made by immobilizing quinone molecules to a support (Winter et al., 2021). A redox-responsive 2-aminoanthraquinone molecule was immobilized on core-shell



**Figure 5. Electro-swing-based CO<sub>2</sub> separation approaches with heterogeneous electrodes modified with quinones**

(A) PAQ-CNT composite cathode with PVF-CNT composite anode. Reprinted with permission from Ref (Voskian and Hatton, 2019). under CC BY-NC license. (B) Controllable gas transport to the PAQ-CNT electrodes achieved by electrodeposition of metal in the gating membranes (M-layer as shown in the graphics). Reprinted with permission from Ref (Liu et al., 2020a). under CC BY-NC license.

particles, and the composite electrodes reversibly captured and released CO<sub>2</sub>. Therefore, for the development of CO<sub>2</sub> separation using redox-active electrodes, new molecules based on the recent examples of 4,4'-bipyridine (Ranjan et al., 2015) and benzylthiolate (Singh et al., 2017a) could be investigated through polymerization or post-synthetic modification approaches.

## DRIVING MATERIALS SELECTION AND DISCOVERY – ROLE OF QUANTUM CHEMISTRY

High-throughput computational screening of several hundreds of materials to inform and aid experiments is now routine for applications ranging from energy storage to heterogeneous and electro-catalysis (Jain et al., 2016). When material performance is dictated primarily by the underlying electronic structure and/or nanoscale interactions with species of interest, quantum chemistry methods—which calculate the electronic structure by solving the approximate Schrodinger equation—are necessary to describe these characteristics. Density functional theory (DFT) is the most widely used quantum chemical modeling method for screening as it offers the most favorable cost-accuracy trade-off. This section highlights efforts toward using DFT calculations to calculate redox potentials of organic redox-active carriers, assess the feasibility of reversible CO<sub>2</sub> binding, and solvent sensitivities of CO<sub>2</sub> capture performance. There is vast untapped potential in the use of DFT-driven, high-throughput materials screening to accelerate the design and development of viable materials for electrochemical carbon capture and conversion.

### Computational methods and frameworks

To select the appropriate level of theory for electrochemical systems of interest, one must rely on benchmarking studies (Neugebauer et al., 2020) because density functional approximations differ in their prediction accuracies for various material properties. A key shortcoming of DFT is spurious charge delocalization. While modeling interactions between radical/ionic redox species and CO<sub>2</sub>, for instance, this error can manifest in incorrect charge assignments to each of these interacting fragments. Constrained density functional theory (CDFT) overcomes this limitation as it enables the specification of excess charge and spin on each fragment and converges electronic structure calculations in a way that satisfies these constraints (Wu and Van Voorhis, 2006). Computational characterization methods such as energy decomposition analysis (EDA) break down interfragment interactions from electronic structure calculations into physically meaningful terms including dispersion, Pauli repulsions, electrostatics, polarization, and charge transfer (Hopffgarten and Frenking, 2012). Although rarely employed in probing characteristics of CO<sub>2</sub> capture materials (Park et al., 2014), EDA is a powerful tool for characterizing redox-sorbent interactions, identifying dominant contributors to binding, and enabling systematic tuning of redox substituents. Solvent screening effects in CO<sub>2</sub> electroreduction are also captured with the most recently developed version of EDA (Mao et al., 2021), to be used alongside implicit solvent models, such as polarizable continuum models (PCMs) and conductor-like screening models (COSMO), all of which treat the solvent as a dielectric continuum (Tomasi et al., 2005).

These DFT calculations based on implicit solvation models are combined with the harmonic oscillator approximation and thermochemical cycles to determine reduction potentials and their solvent sensitivity for redox-active species such as quinones (Bachman et al., 2014). Most computational studies focus on

determining the favorability of CO<sub>2</sub> binding to bipyridinium/pyrrolidinium compounds (Singh et al., 2020), benzyl thiolate (Singh et al., 2017a), and pyridinic nitrogen-doped CNT electrodes (Jiao et al., 2014). A notable exception is a work by Harris and Bushnell, who calculate reduction potentials as well as free energy changes associated with the complete cycle of capture and release for benzyl-disulfide, diselenide, and ditelluride compounds (Harris and Bushnell, 2019). This study finds that the most thermoneutral pathway, which is considered favorable for carbon capture, is offered by benzyl-ditelluride. Beyond these studies that probe CO<sub>2</sub> binding to redox-active species, computational modeling can be employed to explore more complex aspects of reactive CO<sub>2</sub> separations. For instance, CO<sub>2</sub> affinities can be compared directly with those for potentially competing species present in air such as O<sub>2</sub>, H<sub>2</sub>O vapor, and acidic gases. DFT studies can also be extended to identifying possible electrode degradation pathways that are initiated by the binding of these competing species.

It is important to note that while implicit solvation models can be employed to generate reliable estimates of redox potentials, they are inadequate when solvent molecules interact chemically (and not just electrostatically) with the solute, typically in the form of hydrogen bonds (Kim et al., 2016). This can occur both in protic solvents as well as ILs, with the latter known to form hydrogen bonds with quinones in electrochemical CO<sub>2</sub> capture (Gurkan et al., 2015). To capture the impact of these interactions on redox potentials and CO<sub>2</sub> binding affinities, the explicit inclusion of solvent molecules becomes necessary. To the best of our knowledge, explicit models have yet to be applied to IL systems for CO<sub>2</sub> separation, although studies are available that illustrate their use for the solvation of organic molecules by ILs (Payal et al., 2012).

### High-throughput screening and discovery

DFT or CDFT-based descriptor-driven screening of properties of amines (such as pK<sub>a</sub>'s) and amino-functionalized ILs is a promising means to guide the selection of viable starting candidates for developing CO<sub>2</sub> capture methods from flue gas (Jing et al., 2018; Yang et al., 2017). The experimental studies described in this perspective motivate the future development of similar screening methods for redox-active quinones and benzyl chalcogenide derivatives for electrochemical DAC. Rapid screening and identification of viable CO<sub>2</sub> carrier nucleophiles are possible by using DFT-based redox potentials and CO<sub>2</sub> binding affinities (or for instance relative binding affinities of CO<sub>2</sub> vis-à-vis O<sub>2</sub>) as descriptors. For heterogeneous electrodes, quinone carboxylation energies calculated from DFT can serve as descriptors that inform the choice of electrode material. High-throughput DFT calculations to facilitate such screening studies can now be streamlined using scientific workflows such as FireWorks and AiiDA (Jain et al., 2015; Huber et al., 2020).

With such descriptors as starting points for emerging genetic algorithms (Henault et al., 2020; Jensen, 2019) or reinforcement learning methods (Gómez-Bombarelli et al., 2018), the discovery of novel redox-active organic compounds with desired performance characteristics can be automated. Examples of the use of DFT-driven screening and discovery based on machine learning include the identification of organic chromophores for photovoltaic applications (Hachmann et al., 2011). Even though these studies can be limited in their focus on a few key parameters and uncertainties in calculated quantities, they provide means to rapidly identify the most promising candidates for desired applications and therefore accelerate experiments and further theoretical investigations. By combining DFT screening studies with recent advancements in machine learning, researchers can quickly gain insight into the chemical features that will promote efficient electrochemical DAC.

### OUTLOOK

The most widely studied electrochemical approach in reactive CO<sub>2</sub> separations is electrolysis and bipolar membrane electrodialysis. In these systems, the persistent issue that has not been resolved is the overpotentials and specifically the ohmic losses which lead to electrical energy consumption that add to the energy penalty. More recent concepts that utilize redox-active carriers tend to require less energy than these approaches and the CO<sub>2</sub> separation efficiency can be further improved by incorporating pH-swing mediators as in PCET systems. However, the stability issues in these systems have not been tackled for practical conditions (i.e., when oxygen and other volatiles are present). Technologies such as EMAR and CRAB present innovative ways to replace the thermal regeneration step of conventional systems while offering modularity and smaller footprint. Direct reporting of CO<sub>2</sub> capture rates in addition to energy consumption can serve as another benchmark for future literature, as the rate of capture will significantly impact the implementation of these technologies. However, the improved design of electrolytes, electrodes, and the

process is still necessary across all of the electrochemical approaches for CO<sub>2</sub> capture to be economically feasible, as summarized later in discussion.

## ELECTRODE DESIGN

- The continued development of redox-active molecules and redox-active materials for CO<sub>2</sub> capture and release is needed to improve electrochemical capture systems. By utilizing the potential-responsive properties of redox materials in different configurations, it is feasible to switch the surface polarity with small energy input, and the selective interaction with specific molecules can be varied depending on their structural differences. For CO<sub>2</sub> capture systems, a major challenge is to generate materials with high binding affinities, especially for dilute streams such as CO<sub>2</sub> in DAC. At the same time, optimizing the regeneration efficiency and redox potentials to minimize the energetics of the potential swing step are also important considerations. Fundamentally, tailoring the electronic structure for optimal binding, thermodynamics, and even predictive control are future challenges envisioned in this field.
- A second challenge is the presence of side reactions, which can lower current efficiency and cause degradation of the electrode. These can stem from factors such as competing acid gases, water, or oxygen content. Therefore, continued chemical design of both homogeneous and heterogeneous redox-responsive materials is expected to increase their chemical and electrochemical stability in the presence of various competing species, while still enhancing binding affinity toward CO<sub>2</sub> across a range of concentrations. This will be a key goal in future materials design.
- The creation of new hierarchical materials with electrochemically-responsive properties and high porosity can be envisioned. A major challenge with polymeric systems is their low surface area compared to ordered porous materials. Morphology and structural design, either through organic synthesis or composite material processing can be key to improving the performance of electrodes for electrochemical adsorption or permeation of CO<sub>2</sub>.

## ELECTROCHEMICAL SYSTEM DESIGN

- It is desirable to reduce the overall cell resistance in the electrochemical process in order to lower the energy requirement. The most sensitive and costly component in this regard is the ion-exchange membrane which controls the mass transfer. Therefore, to improve the overall efficiency, it would be essential to develop thin, yet robust membranes that prevent co-ion crossover. Moreover, it will be important to control the gas bubbles inside the cell. The presence of gas bubbles can lead to blocking of electroactive surface area and an increase in resistance. In addition to interfacial engineering at the electrode/electrolyte to prevent bubble buildup, future studies should consider optimization of operational parameters such as the pressure of CO<sub>2</sub> (Eisaman et al., 2011b).
- The electrochemical engineering of the CO<sub>2</sub> capture device is essential for efficient electrochemical gas capture systems. In order to enable continuous gas reaction in a flow cell configuration, gas-diffusion electrodes (GDEs) are used to facilitate the rapid access of the gas to the electrode (Pan and Yang, 2020; Higgins et al., 2019). Therefore, the development of more efficient GDEs capable of enlarging the gas-electrode contact area, along with the introduction of the hydrophobic gas diffusion layer and the formation of a composite with the redox material, will be the key for improving the performance of electrochemical CO<sub>2</sub> separation, as well as for scale-up of the system.
- In the as-described processes coupled with the amine sorbents or wet scrubbers, liquid formulation, and handling play a significant role in terms of both operational cost and sorption efficiency. Optimization of parameters such as volatility, viscosity, and composition will be crucial for the efficiency of the combined system.
- Direct flue gas conversion could be a long-term carbon dioxide utilization strategy. Although the fabrication of electrodes for electrocatalytic CO<sub>2</sub> conversion to high-value products has been extensively studied, low selectivity remains a significant issue. Furthermore, concentrated CO<sub>2</sub> is required in many cases. The low concentration of CO<sub>2</sub> and presence of impurities (Ko et al., 2020; Luc et al., 2019) in dilute feed gas streams present a barrier for direct conversion at this time. In order to solve these challenges, through improvements of catalytic electrode materials or gas introduction systems, notable results have been recently reported (Xu et al., 2020; Maina et al., 2021; Zhao et al., 2020). Through this process intensification that enables direct conversion from flue gas, in

combination with the electrochemical CO<sub>2</sub> capture strategy, significant cost reduction, and efficiency improvement can be envisioned.

## ELECTROLYTE DESIGN

- Functional electrolytes with high loading of alcohol and amine moieties have superior CO<sub>2</sub> solubilities compared to aqueous systems (Wang et al., 2010). Therefore, they can better separate CO<sub>2</sub> from dilute mixtures and maintain CO<sub>2</sub> at the electrode interface. However, for electrochemically mediated separations with redox carriers, very high CO<sub>2</sub> solubilities are not desired, as this can result in CO<sub>2</sub> transport in the opposite direction of the redox carrier transport; their concentration gradient profiles would work against each other. The solubilities of the redox carrier and CO<sub>2</sub> should be optimized for a net CO<sub>2</sub> separation.
- It is important to examine the redox potentials and redox reversibility of the redox carriers in the electrolyte of interest as these potentials are highly influenced by the solvation media. Ideally, the reduction of the carrier and the oxidation of the generated nucleophile should be closer than 60 mV for the process to be reversible and robust.
- It is desirable for the electrolytes to have low volatility to maintain adequate wetting of the electrodes and suppress solvent loss. Electrolytes such as ILs and deep eutectic solvents (DESs) (Garcia et al., 2015) have high salt concentrations and low volatility as well as tunable physical properties. Therefore they are potential multifunctional electrolytes for integrated capture and conversion processes. However, these electrolytes generally suffer from high viscosities and low conductivities which lead to transport rates that are much slower than desired for practical purposes. Formulations of these electrolytes with aqueous systems could be interesting.
- The double-layer structure of the electrolyte, especially for more complex electrolytes must be investigated further, as the effects of the electrode-electrolyte interfacial structure and surface adsorbed species may be significant for the electron transfer kinetics which would ultimately control the CO<sub>2</sub> separation or conversion rate.

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## AUTHOR CONTRIBUTIONS

All authors jointly conceptualized the paper and contributed to the writing of the manuscript. B.G. led the discussions on the electrochemical and electrochemically mediated separations with a focus on the electrolyte. X.S. led the discussions with a focus on the electrodes and process design. A.K. constructed the review table and discussed the very early stage technologies. S.M.S. led the discussions on the role of quantum chemistry. A.R.K. and K.J.K. contributed to the discussions of the calculations with the density functional theory.

## DECLARATION OF INTERESTS

The authors declare no competing interests.

## INCLUSION AND DIVERSITY

One or more of the authors of this paper self-identifies as an underrepresented ethnic minority in science.

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