Perspective and challenges in electrochemical approaches for reactive CO₂ separations

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SUMMARY
The desire toward decarbonization and renewable energy has sparked research interests in reactive CO₂ 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 CO₂ 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 CO₂ or facilitate its transport from a CO₂-rich side to a CO₂-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 CO₂ 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 likelihood 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 combating this temperature increase is by achieving net-zero emissions of the GHGs, especially from large emitters such as fossil fuel burning power plants. CO₂ 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).

CO₂ can be captured in a number of ways depending on its source. Many of these processes involve feeding CO₂-rich gas to an absorbent or adsorbent material that selectively captures CO₂, 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 CO₂ from post-combustion flue gas, capturing CO₂ from atmospheric air has recently gained more interest. Direct air capture (DAC) technology aims to separate CO₂ from the atmosphere, where the CO₂ 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 CO₂. 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 CO₂ should be geologically stored. Therefore, materials with high selectivity, significant CO₂ 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.
Removal of CO2 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 CO2 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 CO2 removal (6–9 GJ per ton of CO2). On a purely thermodynamic basis, the conversion of CO2 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 CO2 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 CO2 (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 CO2 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 CO2 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 CO2 specifically in comparison to the requirement of heat in thermal-swing and mechanical work in pressure-swing. Humidity-swing processes involve the absorption of CO2 with the hydroxide ion resin to form bicarbonate. As the resin uptakes CO2 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 CO2-saturated resin during desorption results in the hydration of the ions which provides the free energy for CO2 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). CO2 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 CO2 separations have been studied in a number of systems by Hatton and co-workers. One of the electrochemically mediated CO2 capture systems involves the use of redox-active carriers and another involves the use of amine absorbers that release CO2 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 CO2 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 CO2 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$_2$ separations with reported current densities ($i$) and faradaic efficiencies ($\eta$)

|                        | $E$ (kJ/mol CO$_2$) | $i$ (mA/cm$^2$) | $\eta$  | Advantages                                                                 | Disadvantages                                                                 | Ref                        |
|------------------------|---------------------|-----------------|---------|-----------------------------------------------------------------------------|-----------------------------------------------------------------------------|-----------------------------|
| **Amine-Based Systems**|                     |                 |         |                                                                             |                                                                             |                            |
| EMAR$^a$               | 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$^b$              | $-8.2^h$            | 3               | 0.45    | Harvests binding energy of CO$_2$-sorbent complex                          | Requires thermal amine regeneration with low-pressure steam                | (Li et al., 2020)           |
| **Redox-Active CO$_2$ Carriers** |           |                 |         |                                                                             |                                                                             |                            |
| 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 | (Gurkan et al., 2015;       | Scovazzo et al., 2003)    |
|                        |                     |                 |         |                                                                             | Slow diffusion in non-aqueous solvents                                    |                            |
| Disulfides             | 200                 | 3.03$^c$        | 0.934   | Less basic/susceptible to protonation than quinones                         | Sluggish oxidation kinetics                                                | (Singh et al., 2017a,      | 2017b)                     |
|                        |                     |                 |         |                                                                             | Large potential difference between reduction (CO$_2$ capture) and oxidation | (Singh et al., 2017a,      | (Singh et al., 2017b)     |
|                        |                     |                 |         |                                                                             | (CO$_2$ release) leading to inefficiencies                                 | (Singh et al., 2017a,      | (Singh et al., 2017b)     |
| **Biomimetic Proton Carriers for PCET$^d$** |           |                 |         |                                                                             |                                                                             |                            |
| Phenazine derivatives  | 21.6                | 10              | 0.958   | Moisture stable                                                             | Vulnerable to oxidizing gases                                             | (Xie et al., 2020b)        |                            |
|                        |                     |                 |         | High faradaic efficiency                                                   | (e.g., O$_2$ in DAC)                                                      |                            |
| Tiron                  | 105.6               | 18              | 0.55$^e$| High diffusion coefficient in aqueous media                                | Poor cycle performance owing to loss of alkalinity over multiple cycles    | (Huang et al., 2019)       |                            |
|                        |                     |                 |         |                                                                             |                                                                            |                            |
| FMN$^f$               | 9.8                 | 10              | 0.943   | Low cost redox-active species                                               | Slow and consistent capacity fade over multiple cycles                     | (Xie et al., 2020a)        |                            |
| **Membrane-Based Processes (pH swing)** |           |                 |         |                                                                             |                                                                             |                            |
| KOH Absorption/K$_2$CO$_3$ Electrolysis | 290–350          | 100             | 0.908   | CO$_2$ and H$_2$ 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$_2$ 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$^g$| Can be coupled with fuel cell technology                                    | Low CO$_2$ product purity                                                 | (Eisaman et al., 2009;      | (Landon and Kitchin, 2010; Matz et al., 2021) |
|                        |                     |                 |         | O$_2$ presence improves efficiency                                          |                                                                            |                            |

Energy consumptions ($E$) in kJ per mole of CO$_2$ 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$_2$ 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.

$^a$Electrochemically mediated amine regeneration.
$^b$CO$_2$-regenerative amine-based battery.
$^c$obtained from the computer model.
$^d$PCET = proton-coupled electron transfer.
$^e$in mol CO$_2$ per mole e$^-$. 
$^f$riboflavin 5’-monophosphate sodium salt hydrate.
$^g$CO$_2$ removal efficiency from 1000 sccm air containing 400 ppm CO$_2$.
$^h$Theoretical energy created by the battery; the calculation did not account for the energy use associated with the low-pressure steam and the overpotentials.
side to the anolyte side in an electrochemical cell with gas diffusion electrodes. In an alkaline solution, CO₂, 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 (CO₂ + OH⁻ → HCO₃⁻). Bicarbonate can then further react with another hydroxide to form a carbonate ion and water in pH's higher than 8 (HCO₃⁻ + OH⁻ → CO₃²⁻ + H₂O). In an electric field, the anions move toward the anode where the pH is lowered owing to the oxygen evolution reaction (4OH⁻ → O₂ + 2H₂O + 4e⁻), thus reversing the catholyte reactions and releasing CO₂. The large dependence of the solubility of CO₂ on pH enables the reversible capture and release of CO₂ 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 CO₂ 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 CO₂ separation by an electrochemical membrane module with polyamide soaked with aqueous potassium carbonate for air revitalization in confined spaces. Increased CO₂ 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 CO₂ 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 CO₂ in the form of bicarbonate. Bicarbonate forms as a result of CO₂ 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 CO₂ and O₂ (Equations 3 and 4).

Cathode:

\[ \text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 4 \text{OH}^- \]  
\[ \text{(Equation 1)} \]

\[ 4 \text{CO}_2 + 4 \text{OH}^- \rightarrow 4\text{HCO}_3^- \]  
\[ \text{(Equation 2)} \]

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 CO₂, as the separated CO₂ always contains a side gas such as O₂. The US Department of Energy’s target of a 90% CO₂ 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 CO₂:O₂. Therefore, these systems need a valorization process to follow where O₂ or other impurities are tolerable. Most recently, it was demonstrated (Matz et al., 2021) the removal of CO₂ from the air upstream of a hydroxide exchange membrane fuel cell. In this electrochemically driven CO₂ capture process associated with the fuel cell, high purity of CO₂ could be produced by suppressing the generation of O₂ at the anode by the flow of hydrogen gas (2 OH⁻ + H₂ → 2 H₂O + 2 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 CO₂ 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 CO₂ by forming an alkaline solution via the reduction of the redox molecule and to release CO₂ 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 CO₂ 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 CO₂ 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 CO₂ (Xie et al., 2020a).

It was also attempted to modulate pH using electrodes by applying proton intercalating MnO₂ for CO₂ capture (Rahimi et al., 2020a). MnO₂ stored and released protons by the redox reaction of Mn(IV)/Mn(III) and the corresponding intercalation/deintercalation of H⁺. This work showed not only the effective CO₂ separation via pH modulation with reversible MnO₂ protonation, but also the practical feasibility of this system by the development of a thermodynamic model integrating a K₂CO₃-based CO₂ 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 CO₂ from a K₂CO₃ 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 CO₂ separation system.

**ELECTROCHEMICALLY MEDIATED CO₂ SEPARATION**

Slightly different than the electrochemical gas separations discussed above, electrochemically mediated CO₂ separations involve electrochemically generated nucleophiles that act as CO₂ carriers or electrochemically generated metal ions which disrupt the CO₂ binding of the amine absorbers. The carrier molecules have no affinity to CO₂ at their neutral state but bind with CO₂ at their reduced state. The redox mechanism facilitates the pumping of CO₂ 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 electro-active species in quest of regenerable CO₂ removal systems for the National Aeronautics and Space Administration’s long space missions. Simpson et al. (Comeau Simpson and Durand, 1990) electrochemically
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-CO₂ bond is replaced with the interaction with the amine and the metal ions (i.e., cupric ions) thereby regenerating the amine and releasing CO₂. We discuss CO₂ separation by redox carriers studied to date and the metal electroplating/stripping to facilitate absorber regeneration later in discussion.

**Electrochemically generated nucleophiles as CO₂ carriers**

One common example of a CO₂ carrier is quinones that contain carbonyl groups. Upon reduction, they yield nucleophiles that bind with CO₂. The concept of electrochemically mediated CO₂ 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 CO₂ separation capacity can be improved while also improving the efficiency (Figure 3A). The reduction and the consecutive CO₂-binding potential of 1,4-naphthaquinone (1,4-NQ) in an imidazolium tricyanomethanide ([emim][tcmm]) IL translated to favorable energetics over the amine solvent regeneration by thermal-swing.

Figure 2. Proton-coupled electron transfer reactions for CO₂ capture processes

(A–C) (A) Schematics of the system studied by Xie et al. that utilizes phenazine derivatives to drive the CO₂ absorption by pH modulation in aqueous HCO₃⁻/CO₃²⁻. Reprinted with permission from Ref (Xie et al., 2020b). Copyright 2020, Elsevier; (B) CO₂ capture with K₂CO₃ as the absorbent (cation not shown for simplicity) and (C) a schematic diagram of the process. The proton deintercalation from the electrode shifts the CO₂(H₂O)/HCO₃⁻↔CO₃²⁻↔CO₂(aq) equilibrium toward CO₂ 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.
In addition to quinones, sulfur-containing redox carriers have been developed by Buttry and colleagues (Singh et al., 2017a). Benzyldisulfide (BDS), upon reduction forms two benzothiolate anions, which can react with CO2 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 CO2 scavenging, the oxidation potential of the thiocarbonate to disulfide and simultaneous CO2 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 CO2 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 (Q2-) via the radical anion formation (Q•-) under argon occurs by a 2-step single electron transfer reaction (Q / Q•-) whereas, under CO2 there is a single wave that corresponds to the two-electron reduction and complexation with CO2. 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 CO2 redox carrier BDS in 1-butyl-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([Pyr14][Tf2N]) 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 CO2 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 CO2 (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 CO2 at their reduced state is the vat dyes which are types of organic pigments (Apaydin et al., 2014). CO2 capture and release capacity of quinacridone was demonstrated. In the study, quinacridone was coated as a thin film over the electrode. Although the neutral
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 CO2-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 CO2. 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. Cu2+ competitively interacts with the amine group in the diamine, thus releasing CO2. Once CO2 is removed from the solution, the Cu2+ 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 ~35–40 kJ/mol CO₂ (Wang et al., 2019, 2020), which is comparable to the energy requirement of thermal swing processes using monoethanolamine, MEA (40 kJ/mol CO₂), and piperazine (38 kJ/mol CO₂). 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 CO₂ 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 CO₂ 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°C). However, it was possible with a battery cell integration as shown in Figure 4C, referred to as the CO₂-regenerative amine-based battery (CRAB), to produce 8.2 kJ per mol of CO₂ (Figure 4D). As Cu is stripped in the anode, it binds with the amine in the CO₂-lean solution. As this solution flows through the absorber next, it picks up CO₂ then flows into the cathode where Cu electrodeposition takes place. Finally, the CO₂-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 CO₂ adsorption**

The electrochemical separation of CO₂ 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 CO₂ capture and release (Q ↔ Q²⁻ ↔ Q(CO₂)₂⁻).

Anthraquinone (AQ) was introduced for electrochemical CO₂ capture in the form of thin-film electrodes (Wieland et al., 2018). The film electrodes, fabricated via an evaporation method, exhibited reversible capture and release of CO₂ 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. CO₂ 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 CO₂ uptake and release take place at the PAQ-CNT electrode via carboxylation of quinone groups. This system achieved effective CO₂ capture regardless of the CO₂ 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 CO₂ capacity and kinetics.

Recently, a CO₂ capture system using PAQ electrodes has been further improved (Liu et al., 2020a). The CO₂ 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 CO₂. Another attempt to separate CO₂ 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
particles, and the composite electrodes reversibly captured and released CO₂. Therefore, for the development of CO₂ 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 Schrödinger 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 CO₂ binding, and solvent sensitivities of CO₂ 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 CO₂, for instance, this error can manifest in incorrect charge assignments to each of these interacting fragments. Constrained density functional theory (C-DFT) 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ binding to redox-active species, computational modeling can be employed to explore more complex aspects of reactive CO₂ separations. For instance, CO₂ affinities can be compared directly with those for potentially competing species present in air such as O₂, H₂O 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 CO₂ capture (Gurkan et al., 2015). To capture the impact of these interactions on redox potentials and CO₂ 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 CO₂ 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 pKₐ’s) and amino-functionalized ILs is a promising means to guide the selection of viable starting candidates for developing CO₂ 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 CO₂ carrier nucleophiles are possible by using DFT-based redox potentials and CO₂ binding affinities (or for instance relative binding affinities of CO₂ vis-à-vis O₂) 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ capture to be economically feasible, as summarized later in discussion.

**ELECTRODE DESIGN**

- The continued development of redox-active molecules and redox-active materials for CO₂ 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 CO₂ capture systems, a major challenge is to generate materials with high binding affinities, especially for dilute streams such as CO₂ 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 CO₂ 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 CO₂.

**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 CO₂ (Eisaman et al., 2011b).

- The electrochemical engineering of the CO₂ 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 CO₂ 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 CO₂ conversion to high-value products has been extensively studied, low selectivity remains a significant issue. Furthermore, concentrated CO₂ is required in many cases. The low concentration of CO₂ 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 CO2 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 CO2 solubilities compared to aqueous systems (Wang et al., 2010). Therefore, they can better separate CO2 from dilute mixtures and maintain CO2 at the electrode interface. However, for electrochemically mediated separations with redox carriers, very high CO2 solubilities are not desired, as this can result in CO2 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 CO2 should be optimized for a net CO2 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 electrolyte 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 CO2 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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