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Electrifying Carbon Capture by Developing Nanomaterials at the Interface of Molecular and Process Engineering

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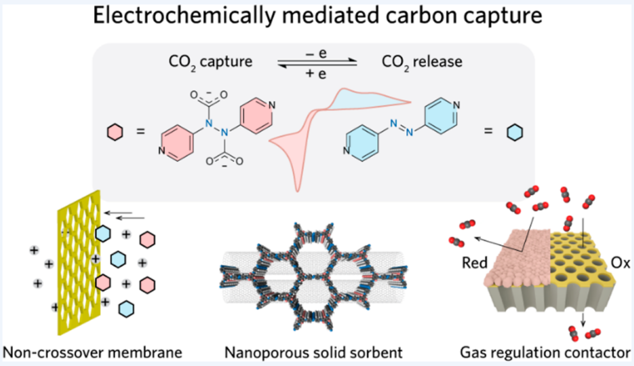

CONSPECTUS: Carbon capture is an indispensable step toward closing the anthropogenic carbon cycle. However, the large-scale implementation of conventional thermochemical carbon capture technologies is hindered by their low energy efficiency, limited sorbent stability, and complexity in infrastructure integration. A mechanistically different alternative, commonly known as electrochemically mediated carbon capture (EMCC), has garnered increasing research traction over the past few years and relies on electrochemical stimuli instead of thermal or pressure swings for the capture and release of carbon dioxide (CO_2). Compared to conventional methods, EMCC can be operated under mild conditions driven by intermittent renewable energy sources and has a flexible design to meet the multiscale demands of carbon capture, offering a potentially sustainable, energy-efficient, and cost-effective solution to CO_2 concentration from dilute mixtures or the ambient environment.

Nanomaterials have played a crucial role in carbon capture research. For instance, nanoporous materials can provide increased free volumes, surface areas, and active sites for carbon capture through physical or chemical adsorption from the gaseous phase. In contrast, EMCC relies on chemical absorption via acid−base interactions using solubilized CO_2 in electrolytes. Therefore, most EMCC sorbents and mediators explored so far have been developed as molecules rather than nanomaterials. In recent years, our team has been focusing on electrifying the carbon capture processes at the molecular, materials, and process levels. We seek to address the most pressing issues associated with EMCC, either in fixed-bed or flow systems, that prevent their practical use. These issues include parasitic reactions with molecular oxygen, insufficient electrode capacity utilization, sorbent crossover, etc. To address these problems, there is an urgent need to develop rationally designed nanomaterials at the interface of molecular electrochemistry and device engineering. This Account provides an overview of recent progress on developing new chemistries and engineering batch/continuous processes for EMCC. We discuss the limitations of current EMCC technology and emphasize why nanomaterials are critical for electrifying carbon capture. First, we introduce the design principles for EMCC sorbents based on redox-active organic CO_2 carriers and discuss metrics for their performance evaluation. Second, we showcase how molecular design can tackle problems of sorbent solubility, oxygen stability, and electrolyte compatibility in EMCC. Third, we discuss the early results of nanomaterials as solid sorbents in fixed-bed systems, nonswelling membranes for flow systems, and high-surface-area gas−liquid contactors. Finally, building on the foundation we established through our prior work, we offer perspectives on future directions for nanomaterials to help address the challenges in EMCC.

■ KEY REFERENCES

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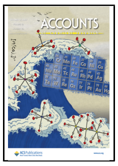

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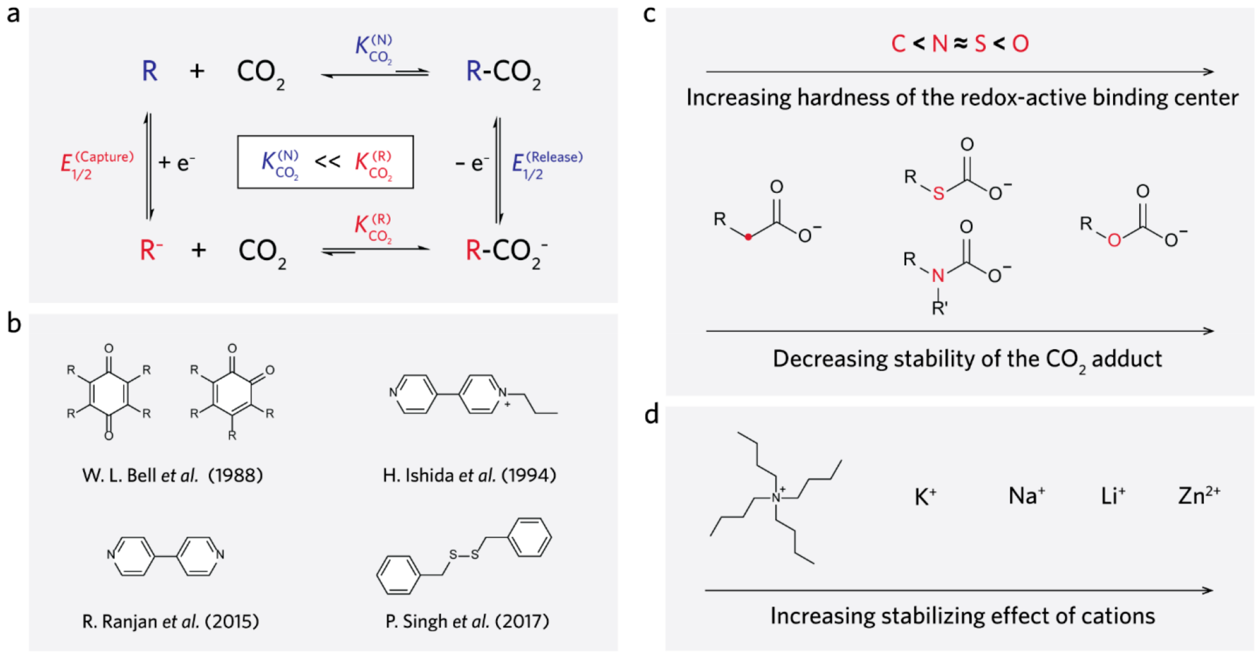

Figure 1. EMCC chemistry was based on redox-active CO_2 carriers. (a) Square scheme for the reductive CO_2 addition and oxidative CO_2 elimination reactions in redox-active CO_2 carriers. $K_{CO_2}^{(N)}$ and $K_{CO_2}^{(R)}$ stand for the CO_2 binding constants of the carrier in the neutral and reduced states, respectively. $E_{1/2}^{(Capture)}$ and $E_{1/2}^{(Release)}$ stand for the half-wave potentials for CO_2 capture and release, respectively. (b) Reported structural motifs as redox-active CO_2 carriers. (c) Effect of the chemical hardness of binding centers on the CO_2 adduct stability. (d) Effect of cations on the CO_2 adduct stability.

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- Liu, Y.; Chow, C.-M.; Phillips, K. R.; Wang, M.; Voskian, S.; Hatton, T. A. Electrochemically mediated gating membrane with dynamically controllable gas transport. *Sci. Adv.* **2020**, *6*, eabc1741−eabc1741.[4] *This paper reports a stimuli-responsive gating membrane to reversibly modulate gas permeation at the gas−electrolyte interface. Coupled with EMCC sorbents, the paper demonstrates the directional pumping of low-concentration CO_2 against the chemical potential gradient to near purity using electricity as the sole driving force.*

1. INTRODUCTION

Carbon capture plays a crucial role in mitigating climate change.[5] However, conventional thermochemical methods, such as amine scrubbing, require significant energy input and are susceptible to degradation due to the high operating temperatures needed for CO_2 release. Retrofitting thermochemical carbon capture technologies into industrial facilities can also be complex and costly. On the contrary, EMCC effectuates CO_2 capture and release by modulating the CO_2 affinity of sorption materials using electricity.[6] Electrochemical systems can operate under ambient conditions to limit degradation by heat and make swift transitions between operational and nonoperational states with minimum loss in efficiency, making them ideal for coupling with intermittent renewable energy sources. Moreover, the modularity of EMCC shows promise to fulfill the multiscale demands of carbon capture.

Various EMCC mechanisms have been reported, including direct capture using redox-active CO_2 carriers or indirect approaches such as electrolysis,[7] electrodialysis,[8] capacitive deionization,[9] proton-coupled electron transfer,[10] electrochemically mediated amine regeneration,[11] and others.[12] Most indirect EMCC processes induce CO_2 absorption and desorption by shifting the solution pH, and EMAR uses redox-active copper ions to regenerate amine-based solvents. Distinctively, redox-active CO_2 carriers are organic compounds that can reversibly complex and dissociate with CO_2 in their electro-reduced and oxidized forms, respectively.[6a] This Account focuses on redox-active CO_2 carriers due to their potential high efficiency, expansive chemical space to fine-tune sorbent properties, and compatibility with high-boiling-point solvents to mitigate evaporative loss.

Over the past decade, nanomaterials have provided abundant opportunities to advance carbon capture research. While progress on utilizing nanomaterials for CO_2 adsorption has been noteworthy,[13] advancements in leveraging their potential for EMCC are comparatively slow due to the distinct working principles involved. The former is based on host−guest chemistry, where free volume, surface area, and functionality are harnessed to enhance gaseous CO_2 adsorption. Materials such as zeolites,[14] metal−organic frameworks (MOFs),[13c] covalent organic frameworks (COFs),[13e] and solid-supported amines[13f] are promising adsorbents. On the other hand, EMCC via redox-active carriers hinges on tunable sorbent nucleophilicity at different electrochemical potentials, where CO_2 needs to be solubilized in electrolytes before complexing with the nucleophilic moieties. Therefore, research on EMCC has centered on the molecular level.[6c,15] As more systems are being developed, we envisage nanomaterials to have transformative potential in tackling critical issues in EMCC, for example, by serving as nanoporous electrodes, membranes, and gas−liquid contactors. Notably, research fields such as organic materials for electrochemical energy storage are close points of reference to EMCC, and material design principles in these fields can be borrowed to promote the development of EMCC. So far, reviews on EMCC have mainly focused on various process mechanisms, device engineering, and molecular sorbents.[6a,e,16] However, there is a lack of discussion on how nanomaterials can help overcome the reaction, transport, and stability challenges in EMCC. In addition, universal design principles of redox-active CO_2 carriers beyond quinones are generally missing. In this Account, we showcase our recent contributions to developing redox-active CO_2 carriers and processes that build a strong foundation for constructing functional EMCC nanomaterials. We also give our perspective on the rational design of nanomaterials to address EMCC challenges.

2. BRIDGING MOLECULAR REDOX-ACTIVE CO_2 CARRIERS AND EMCC PROCESSES

2.1. Chemistry and Design Principles of Redox-Active CO_2 Carriers

The concept of EMCC using redox-active carriers was first demonstrated in the late 1980s when quinones were explored for life-support systems in spacecraft.[15a] The quinoid species, supported by a nonaqueous electrolyte, exhibit no CO_2 affinity in the neutral state but become much stronger Lewis bases to capture acidic CO_2 upon electro-reduction (Figure 1a). The resulting acid−base adduct can be subsequently electro-oxidized to release pure CO_2 and regenerate the sorbent. Depending on the structural feature and CO_2 affinity, a two-electron-reduced quinone molecule can capture one or two molecules of CO_2 following different reaction pathways.[15b,17] Research on EMCC using redox-active carriers has been heavily centered on quinones. Before the advent of our redox-tunable sp^2-N Lewis bases,[1] 4-pyridinyl-1-propylpyridinium,[15c] 4,4′-bipyridine,[15e] and dibenzyldisulfide[15f] were the only examples showing electrochemically reversible CO_2 complexation other than quinones with performance yet to be evaluated in actual EMCC devices (Figure 1b). Nevertheless, there is an increasing awareness that new chemistries are required to overcome the intrinsic limitations of existing sorbents, such as parasitic reactions with molecular oxygen (O_2) and inadequate CO_2 affinity, with some design guidelines proposed.[6c,15g]

For practical EMCC systems, the CO_2 affinity of redox-active carriers should be judiciously adjusted to avoid high-energy sorbent regeneration or an unstable CO_2 adduct. We propose that the hard−soft acid−base (HSAB) theory[18] can guide the design of CO_2 carriers by providing predictive insights into sorbent redox properties, adduct stability, and CO_2 complexation pathways. In HSAB theory, "hard" refers to weakly polarizable species with small sizes and high charge states, while "soft" denotes strongly polarizable species with large sizes and low charge states. Stable adducts are more likely to be formed between hard acids and bases via ionic bonding or soft acids and bases via covalent interaction.[19] This theory helps explain the high energy requirement of amine scrubbing: amines are hard Lewis bases (chemical hardness of ∼6.9) while CO_2 is a relatively hard Lewis acid (chemical hardness of 6.9),[18] giving rise to strong adduct formation.

Since electron transfer is hindered in weakly polarizable species,[20] CO_2 carriers shall be designed using soft Lewis bases to trigger redox properties. Soft sorbents (e.g., phenolate) result in relatively weak CO_2 adducts, which can decrease the energy consumption for the CO_2 separation at the fundamental chemistry level. Notably, the local hardness[21] of CO_2 binding sites can be utilized to predict CO_2 adduct stability and prevent irreversible pathways (Figure 1c). Although the CO_2 molecule is a hard acid, the C center is relatively soft and can form stronger bonds with soft atoms. Therefore, the CO_2 adduct stability increases in the order of carbonate (C−O) < carbamate (C−N) ≈ thiocarbonate (C−S) < carboxylate (C−C) as the local hardness of redox-active binding sites decreases in the order of O > N ≈ S > C. For instance, the comparatively weak carbonate-type adducts in EMCC often result in difficulties in their unambiguous characterizations (NMR or X-ray techniques),[15a,b] while adducts with N or S bases can be confirmed by FTIR and NMR, suggesting their greater stability.[1,15f] When designing redox-active carriers, the generation of free carbonanions should be avoided, as regioselectivity may lead to irreversible C−C formation via the Kolbe−Schmitt pathway, which has been observed in the decomposition of 1,4-benzoquinone during electro-reduction under a CO_2 atmosphere.[22]

The choice of the supporting electrolyte is also crucial (Figure 1d). Commonly used cations (Li^+, Na^+, K^+, etc.) are Lewis acids and may kinetically hinder CO_2 adduct formation by forming complexes with reduced sorbents.[23] Nevertheless, harder cations such as Na^+ can facilitate the second electron transfer of quinone[2] and sp^2-nitrogen bases compared to tetrabutylammonium via electrostatic stabilization.[1] Furthermore, hard cations can be harnessed to thermodynamically stabilize weak CO_2 adducts. For instance, CO_2 adducts with hydrazinides (reduced azo compounds) precipitate with high stability in the presence of Zn^{2+}.[1] This occurs because CO_2 complexation typically gives rise to carbonate,[15a] thiocarbonate,[15f] or carbamate[15c] anions, where the locally hard oxygen atoms can afford stronger interactions with hard cations. Therefore, the aforementioned trade-off must be carefully considered when designing an EMCC system.

2.2. Metrics for EMCC Performance Evaluation

EMCC is an emerging field requiring collective efforts from chemists, materials scientists, and engineers. Therefore, we define the following key metrics to standardize the evaluation of the EMCC performance among researchers of different backgrounds.

At the molecular level, cyclic voltammetry (CV) is the most convenient tool to examine redox-active CO_2 carriers. Redox-active carriers must exhibit good electrochemical reversibility and a sufficient CO_2 binding constant (K_{CO_2}, details in *vide post*) (Figure 1a). Importantly, their redox potentials should be more positive than the oxygen reduction potential to suppress parasitic reactions. The voltage difference between CO_2 association and dissociation can be employed to calculate the theoretical minimum-energy requirement for separation.[1]

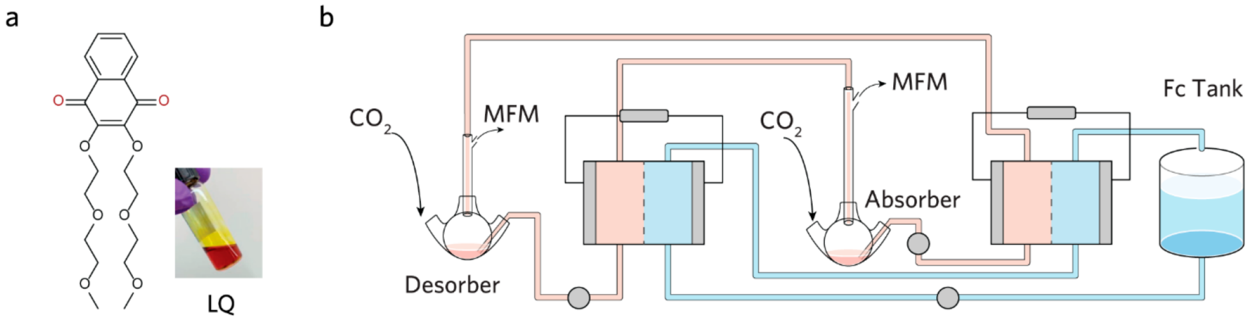

Figure 2. Quinone-based redox-active CO_2 carrier for continuous-flow EMCC. (a) Molecular structure of LQ, which is a liquid in its pure form at room temperature, as shown in the photograph. (b) Schematic of the continuous-flow system. Fc stands for ferrocene or its derivative, which was used as a counter-electrolyte for charge balancing. Adapted with permission from ref 2. Copyright 2021 Cell.

For practical implementations, a minimum log K_{CO_2} of ∼3.0 is required for point source capture and ∼5.5 is required for direct air capture.[15a,17c] In a stepwise two-electron reduction process,[15a,17b] K_{CO_2} can be calculated with

$$K_{CO_2} = \frac{\exp\left(\frac{F}{RT}\Delta E_2\right) - 1}{[CO_2]} \qquad (1)$$

F is the Faraday constant, R is the ideal gas constant, T is temperature, ΔE_2 is the difference between the second reduction potentials under CO_2 and N_2, and $[CO_2]$ is the dissolved CO_2 concentration. Besides, spectrophotometric experiments, such as the Benesi−Hildebrand titration method, can also estimate K_{CO_2}.[17c,24]

At the process level, most EMCC systems are categorized as either fixed-bed or flow systems. Solid sorbents are immobilized on conductive electrodes in fixed-bed systems, while liquid solvents are circulated through electrochemical cells in flow systems. Therefore, the solubility of the redox-active carriers is another important consideration. Low solubility is preferred in fixed-bed systems to prevent active material loss, while high solubility is necessary for flow systems to ensure high CO_2 capture capacity.[6b,10c]

Several general parameters can be utilized to evaluate the EMCC performance across different systems. First, the theoretical amount of CO_2 captured (or released) per electron transferred, namely, the theoretical CO_2 capacity, should be derived based on the working mechanism of the redox-active carrier. For example, anthraquinone has a theoretical capacity of one CO_2 molecule per electron, while 1,4-ditertbutylbenzoquinone requires two electrons to bind one CO_2 molecule.[3,17a] Second, the actual CO_2 capacity can be calculated by normalizing the total amount of CO_2 captured (or released) by the number of electrons consumed. We define the CO_2 capacity utilization efficiency as the ratio between the actual and theoretical CO_2 capacities, with the ideal target equal to unity.[1,2] Moreover, the release/capture efficiency (the ratio of CO_2 released over captured) and Coulombic efficiency shall be measured to evaluate the chemical and electrochemical reversibility of EMCC, respectively.[1,2] Finally, the energy consumption (mol kJ^{-1}) is essential for comparison with existing carbon capture methods, although the scale of current EMCC processes remains relatively small.

2.3. Addressing the Intrinsic Limitations of Redox-Active CO_2 Carriers at the Molecular Level

Several longstanding issues hinder the practical uses of the most well-studied quinones as CO_2 carriers, including nonideal sorbent solubility, low O_2 stability, and the necessity of aprotic electrolytes to enable desired electrochemical reactions.

First, quinones have poor solubility in organic electrolytes, which limits the capacity of flow EMCC systems. To address this issue, we demonstrated a polyether-modified liquid quinone (LQ) that is highly miscible with ether-based solvents (Figure 2).[2,25] LQ significantly increased the sorbent concentration to 3.19 M under neat conditions and to at least 1.1 M under sodium salt-glyme diluted conditions, comparable to the working capacities of conventional amine solvents.[26] EMCC performance was evaluated in a cyclic CO_2 capture and release process using a flow cell. Under a 15% CO_2 feed, the LQ exhibited a CO_2 capacity utilization efficiency of close to 70%, an average release/capture efficiency of nearly 100%, and an average Coulombic efficiency of ∼90% over 10 cycles. Furthermore, LQ enabled a continuous-flow EMCC demonstration in which the molecule was reduced in one flow cell, contacted with CO_2 in an absorber, oxidized in another flow cell, pumped to release CO_2 in a desorber, and cycled back to the first cell. The continuous system displayed a work of capture between 35 and 220 kJ mol^{-1} depending on the operating conditions (lower work is required at a lower current). The number remains high compared to the state-of-the-art amine scrubbing (∼40 kJ mol^{-1} of electrical equivalent work)[11] due to the relatively large ohmic (especially membrane resistance) and mass transfer losses, highlighting the need for novel materials to improve the transport properties of EMCC systems.

Second, O_2 is a common impurity in gas streams for carbon capture. However, most redox-active carriers, such as quinones and disulfides, have more negative reduction potentials than O_2. This results in parasitic oxygen reduction to superoxide (O_2^-), undermining the energy efficiency. Moreover, highly reactive O_2^- can deteriorate electrochemical cell components, posing severe stability issues. Only a small number of quinones exhibit redox potentials anodic to that of oxygen reduction, yet they remain sensitive to O_2 as reported in the seminal work by Scovazzo et al.[17a] So far, research has mainly focused on tuning the chemical functionalities of quinones to positively shift their potentials, despite the trade-off of decreased K_{CO_2}.[17b,27] Recently, an alternative strategy to tune the reduction potential of a tetrachlorobenzoquinone (TCQ) molecule was proposed by adding alcohol additives to the electrolyte.[17c] Leveraging

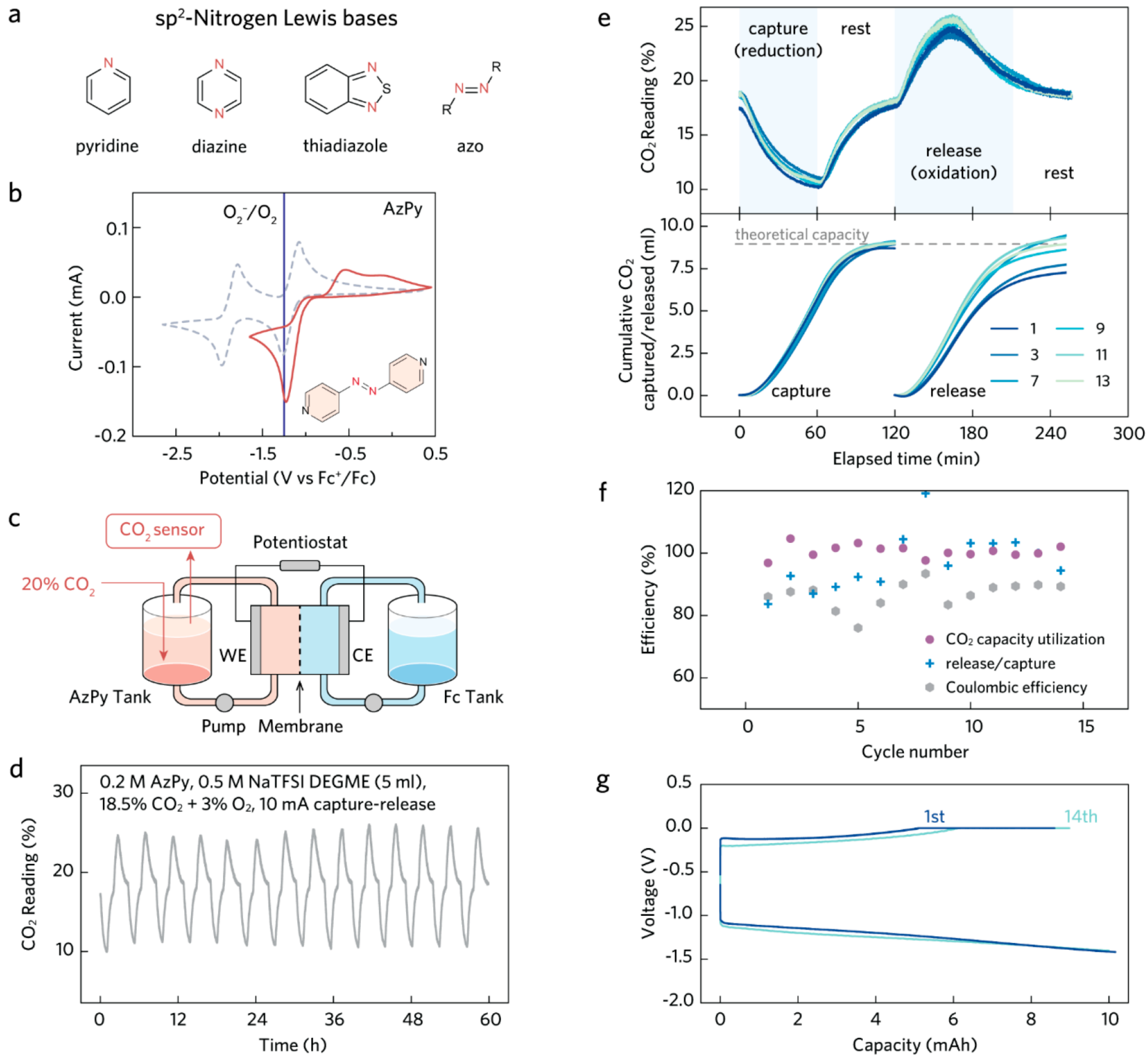

Figure 3. Redox-active CO_2 carriers based on Lewis sp^2-N Lewis bases. (a) Chemical structures of key functionalities. (b) CV of AzPy under N_2 and CO_2. (c) Schematic of the flow system for EMCC performance evaluation. (d) CO_2 capture−release cycling with a feed of 18.5% CO_2 and 3% O_2 at a current of 2 mA cm^{-2}. (e) CO_2 readings for selected capture−release cycles (top) and the cumulative amount of CO_2 captured/released in each cycle (bottom). (f) CO_2 capacity utilization efficiency (purple), release/capture efficiency (blue), and Coulombic efficiency (gray). (g) Corresponding voltage−capacity curves for the 1st and 14th cycles. Adapted with permission from ref 1. Copyright 2022 Nature Publishing Group.

the intermolecular hydrogen bonding interaction between the quinone carbonyl oxygen and the alcohol hydroxyl proton, the reduction potential of TCQ was anodically shifted by ∼200 mV with log K_{CO_2} maintained at ∼4.

Besides quinones, a vast chemical space exists to search for EMCC sorbents with high O_2 stability. In history, the renowned anthraquinone process initially employed azo compounds to catalyze the industrial production of hydrogen peroxide via oxygen reduction, but they were eventually replaced by anthraquinone, likely due to inefficiencies.[28] This led us to hypothesize that organic compounds with redox-active nitrogen centers may exhibit lower reactivity toward O_2 than quinones. Furthermore, nitrogen-based sorbents may display higher carbon capture efficiency due to the aforementioned thermodynamic stability of carbamates over carbonates. To verify this hypothesis, we recently built a library of redox-active CO_2 carriers with sp^2-N centers (pyridine, diazine, thiadiazole, and azo functionalities), all of which can bind two CO_2 molecules in their two-electron-reduced forms (Figure 3). We showed that 4,4′-azopyridine (AzPy) and 2,7-ditrifluoromethyphenazine are stable against the oxygen reduction reaction (Figure 3b). In a bench-scale flow system (Figure 3c), AzPy can concentrate CO_2 from a mixture of 18.5% CO_2 and 3% O_2 with a near unity capacity utilization efficiency, an average release/capture efficiency of 97%, and an average Coulombic efficiency of 87% over 14 cycles (Figure 3d−f). The electrical energy consumption under this simulated flue gas was 120 kJ mol^{-1} (Figure 3g).[10c,29]

Third, aprotic electrolytes or ionic liquids are typically required by redox-active CO_2 carriers due to their low volatility and compatibility with the CO_2 complexation mechanism. Nevertheless, aqueous electrolytes represent a potentially cost-efficient, low-toxicity, and safe alternative. However, molecules such as quinones may also behave as redox-active proton carriers in protic solvents (1,4-benzohydroquinone has a pK_a of 10.8),[30] leading to competition between CO_2 complexation

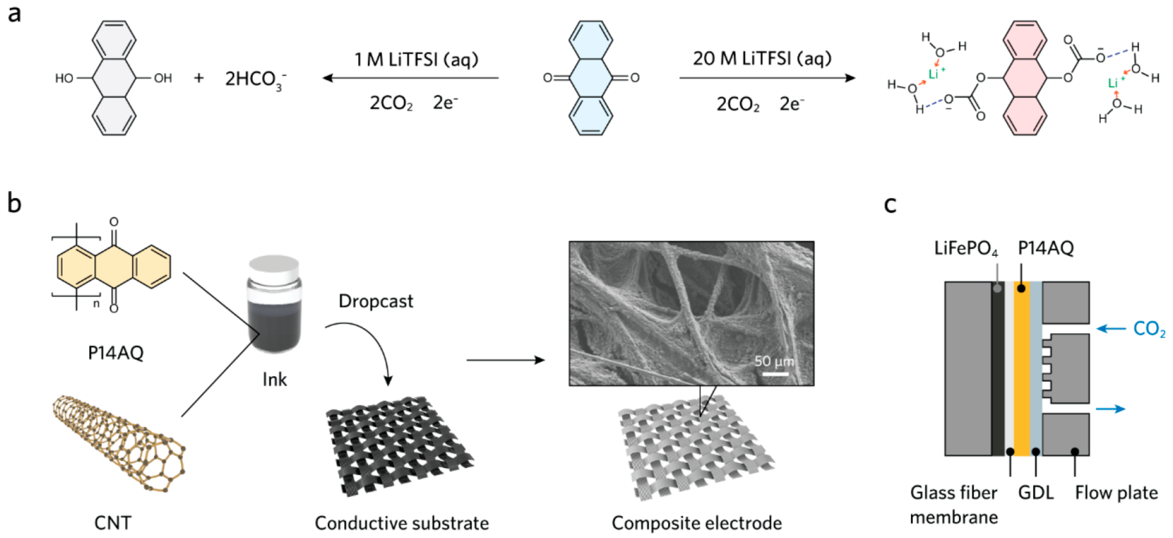

Figure 4. Improving the compatibility of redox-active CO_2 carriers with water via a salt-concentrated aqueous electrolyte. (a) CO_2 capture pathways in conventional and salt-concentrated aqueous electrolytes. (b) Schematic of preparing composite sorbent electrodes. (c) EMCC in a fixed-bed configuration using P14AQ as the solid sorbent. Adapted with permission from ref 3. Copyright 2020 Nature Publishing Group.

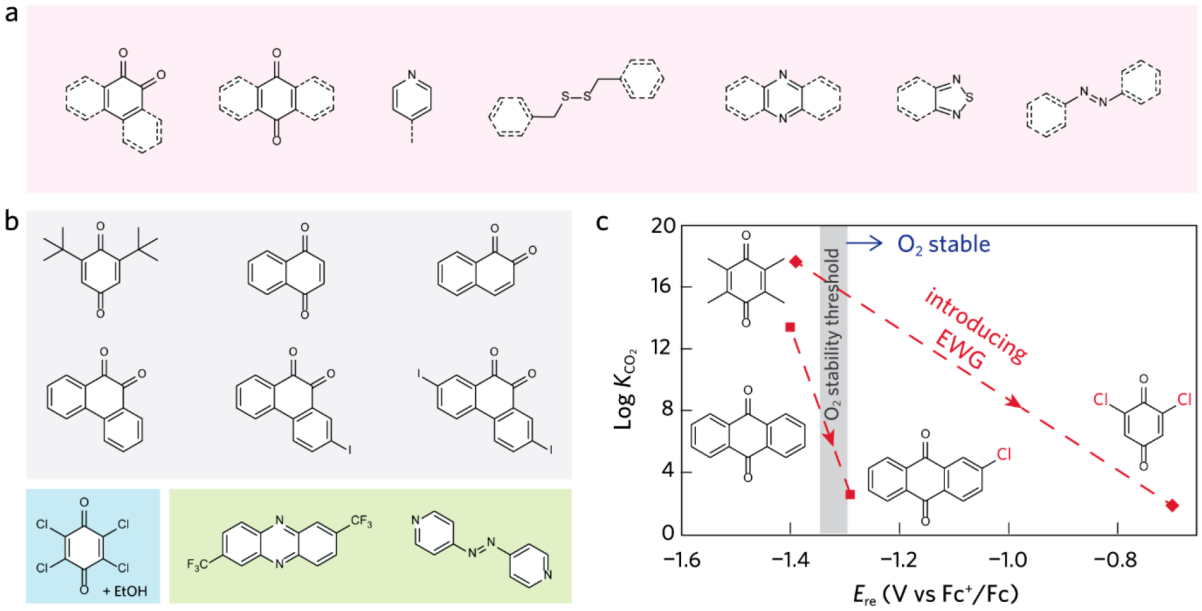

Figure 5. Summary of redox-active CO_2 carriers. (a) Structural motifs for constructing nanomaterials as redox-active CO_2 carriers. (b) Existing molecular sorbents with redox potentials anodic to O_2 reduction. (c) A scaling relationship exists between the redox potential and CO_2 binding constant, rendering quinones susceptible to chemical modification.

and protonation to undermine the efficiency of direct CO_2 capture. We demonstrated a method to overcome the water incompatibility issue using salt-concentrated aqueous electrolytes (Figure 4a). Capitalizing on the "water-in-salt" concept for battery applications,[31] we formulated a salt-concentrated electrolyte consisting of 20 M lithium bis(trifluoromethanesulfonyl)imide (LITFSI) in water, which is fully compatible with quinone-based CO_2 carriers. Due to the cation solvation effect, no free-state water molecules exist in the salt-concentrated electrolytes, giving rise to the following benefits: (1) The competing protonation reaction is minimized. (2) The electrochemical working window of the electrolyte is greatly enlarged, inhibiting undesirable water-splitting reactions. (3) Sorbent dissolution from the electrode is hindered, ensuring capacity retention and long-term cycling stability. (4) The oxygen reduction potential is cathodically shifted, suppressing parasitic reactions. By employing poly(1,4-anthraquinone) (P14AQ, Figure 4b)[29e] as a solid sorbent, we constructed a gas device (Figure 4c) and achieved a CO_2 capacity utilization efficiency of >86% at a high current of 0.5 A g^{-1} under a pure CO_2 gas feed.

2.4. Opportunities for New Redox-Active CO_2 Carriers

Figure 5a summarizes the redox-active CO_2 binding sites explored to date. Example molecules with redox potentials anodic to oxygen reduction are given in Figure 5b. These structural motifs serve as the basis for chemical modification and nanomaterial design to enable efficient EMCC processes.

Chemical modification is necessary to improve key sorbent properties, such as CO_2 affinity, solubility, processability, and stability against impurities. According to the Hammett

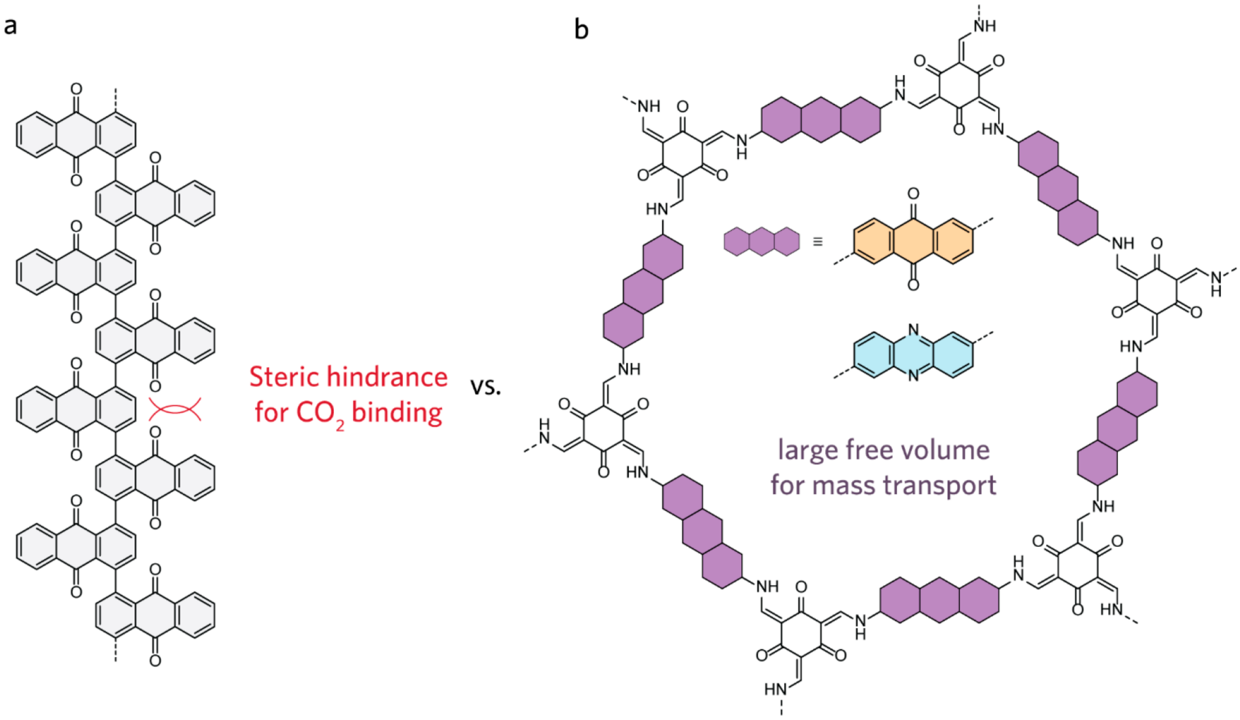

Figure 6. Solid EMCC sorbents were based on linear polymers and porous crystalline COFs.

equation, a linear free-energy relationship exists between substituent groups and reactivities of a molecule,[17b,27,32] which causes the CO_2 affinity of redox-active carriers to be highly susceptible to chemical modifications. For example, introducing electron-withdrawing groups (EWGs) to anodically shift the reduction potential usually results in a substantial decrease in K_{CO_2} (Figure 5c). Therefore, it is crucial in future research to develop new classes of redox-active motifs and molecular design concepts to break the scaling relationship for more versatile sorbent property tuning.

3. PROSPECTIVE NANOMATERIALS FOR EMCC

The maturation of EMCC technologies hinges on a fundamental understanding and engineering optimization not only at the molecular level but also at the nanoscale. Here, we highlight three pressing research directions in nanomaterials development for EMCC. First, polymeric CO_2 carriers are desirable in fixed-bed systems to mitigate sorbent dissolution and ensure fast kinetics and high capacity utilization. Second, nonswelling size-selective membranes are desired in flow systems to prevent sorbent crossover. Finally, gas−liquid membrane contactors are needed for scalability by facilitating gas solubilization.

3.1. Nanomaterials as Redox-Active Solid Sorbents

In designing redox-active solid sorbents for fixed-bed EMCC, the following principles shall be considered: (1) they should exhibit limited dissolution into an electrolyte for capacity retention; (2) they should have good electrical conductivity and intimate contact with the conductive substrate for high capacity utilization; and (3) they should possess enriched diffusion channels for rapid ion and gas transport.

In line with the development of organic electrode materials for battery applications, an effective strategy to minimize dissolution involves polymerizing redox-active moieties. A multistack fixed-bed EMCC model has been reported using P14AQ as the redox-active CO_2 carrier and polyvinylferrocene as the counter electrode.[29e] P14AQ was mixed with multiwalled carbon nanotubes (CNT) and dip-coated onto conductive substrates such as nonwoven carbon fiber mats (Figure 4b). This composite structure promoted the utilization of redox-active moieties in P14AQ, as CNT not only enhanced the electrical conductivity but also provided a porous matrix for better electrolyte penetration. When supplied with pure CO_2, the fixed-bed device exhibited ∼65% utilization of quinone units for CO_2 capture. The author attributed the lost capacity to the incomplete charging of quinones not exposed to the electrolyte. From a molecular design standpoint, the proximity of the carbonyl groups in P14AQ may create significant steric hindrance for CO_2 binding, which also prevents the full utilization of the CO_2 capacity (Figure 6a).

A drawback of using small molecules or linear polymers as solid EMCC sorbents is their tendency to form tightly packed structures. As a result, most redox-active species will be embedded within aggregates, and only the surface is accessible to electrolytes and CO_2, causing low capacity utilization. Crystal engineering is an effective strategy to maximize electrode−electrolyte interfaces and improve capacity utilization.[33] By breaking down closely packed bulk structures into smaller nanoparticles, the surface area of organic redox-active species can be enhanced, thereby promoting better mass and charge transport.

Here, we postulate that nanoporous materials[34] are good candidates for solid EMCC sorbents due to the following benefits: (1) redox-active functionalities can be uniformly distributed in permanently porous networks, reducing steric hindrance for CO_2 complexation; (2) solubility is further decreased to prevent dissolution due to cross-linked structures; (3) large surface areas ensure sufficient contact among the binding sites, electrolyte, and CO_2; (4) enriched diffusion channels for CO_2 transport and ion conduction; (5) conjugated linkage to enhance electrical conductivity; and

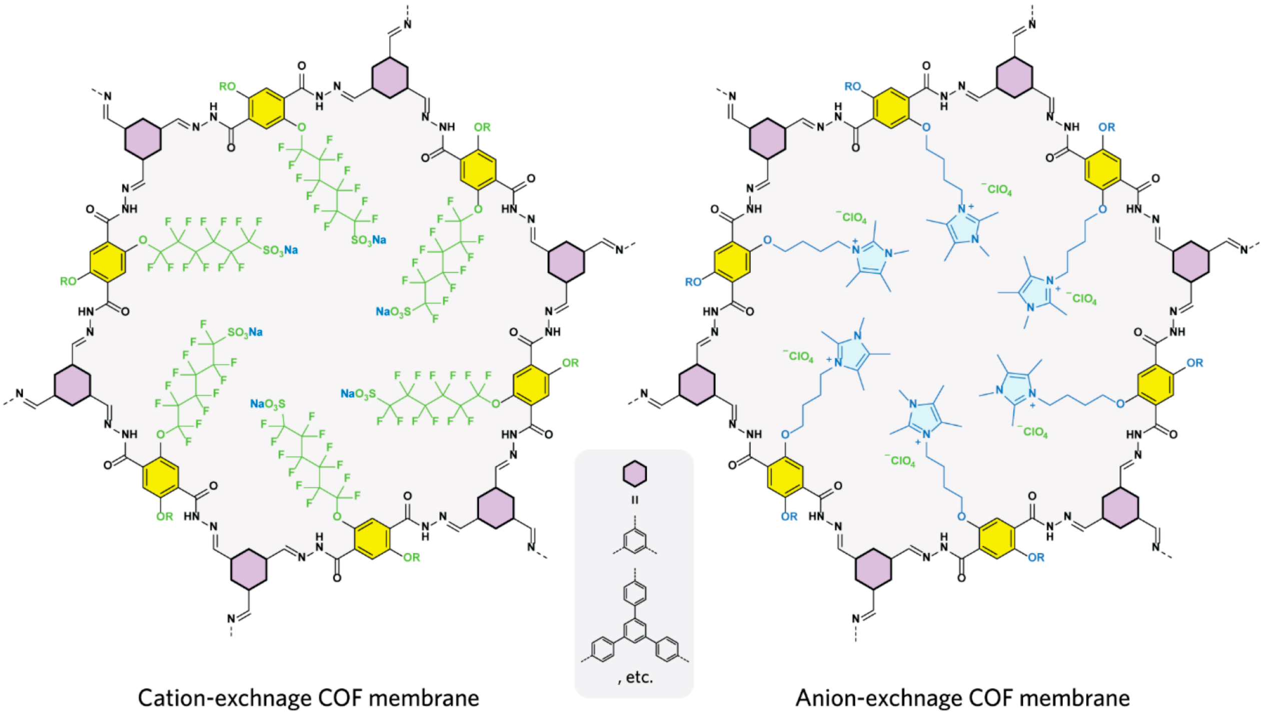

Figure 7. Proposed materials for nonswelling size-selective membranes with ion-exchange properties in nanoporous channels.

(6) gas selectivity through pore size exclusion and pore wall functionalization.[13d,35] Taking advantage of the high topological predictability and chemical robustness of COFs, we showcase nanoporous EMCC sorbents by incorporating redox-active CO_2 binding motifs into the COF backbones (Figure 6b). Other microporous materials such as MOFs may also be utilized if their metal nodes are electrochemically stable. Additional functionalities, such as hydrogen bond donors, can be integrated into the frameworks to fine-tune the CO_2 binding behaviors via secondary interactions. Once suitable nanomaterials are identified, they must be produced economically on a large scale to be implemented practically,[36] and the durability of these materials is pivotal.

3.2. Nonswelling Size-Selective Membranes to Mitigate Crossover Issues

A typical flow EMCC system contains a sorbent tank and a counter-electrolyte tank, where two liquids of different compositions flow through the two compartments of an electrochemical cell separated by a membrane (Figure 3c).[1,2] However, such systems still suffer from low Coulombic efficiency due to the lack of suitable membranes to prevent the crossover of CO_2 carriers or counter-electrolyte molecules in organic electrolytes. The commonly used ion-exchange membranes (e.g., Nafion) consisting of linear ionomers tend to swell in organic solvents, leading to the fast permeation of redox-active species. In contrast, membranes constructed from rigid framework polymers may restrict pore swelling, thereby mitigating the crossover issue. Besides, nonswelling membranes can also be made from cross-linked organic polymers,[37] inorganic materials,[38] and crystalline porous materials.[39] To fulfill the requirements for flow systems, the permeance of these nonswelling materials used previously in static electrochemical systems must be examined under stirring/flowing conditions with more electrolyte solvents.

In redox-flow battery research,[40] Doris et al. fabricated a membrane based on cross-linked polymers of intrinsic microporosity, which possesses a pore size of 0.9 nm (in the dry state) to exclude molecular shuttling in organic electrolytes.[41] This work provides a potential solution to sorbent crossover in EMCC. So far, research progress on size-selective membranes for nonaqueous electrolytes is slow due to the lack of suitable materials and challenges in synthesis. We envisage that reticular materials[39,42] such as COFs and MOFs, are potential candidates for nonswelling membranes due to their rigid polymeric network, easy functionalization, predictable pore size (<0.5 to 10 nm), good ionic conductivity, and chemical stability against organic solvents. Using two-dimensional COFs as examples, we briefly discuss the design principles of such nanoporous membranes. First, the membrane should be constructed using rigid structural motifs (e.g., sp^2 carbons in conjugated networks) to prevent pore swelling. Second, the pore size can be tailored by the judicious choice of molecular building units and further tuned by pore-wall functionalization. Third, anionic or cationic side chains can be anchored onto the pore walls, allowing single-ion conduction in the channels. Finally, minimizing grain boundaries and large pores in the membrane is also crucial. As shown in Figure 7, such designs can potentially preclude the permeation of redox-active species across the membrane while allowing ion exchange between the two electrolyte compartments.

3.3. Nanomaterials to Facilitate Gas Transport

As described by thermodynamic modeling, rapid CO_2 transport is desirable in EMCC.[43] Facile gas transport to CO_2-binding sites translates to better capture kinetics, and well-facilitated release of CO_2 to the gas phase during desorption reduces the degree of CO_2 supersaturation in electrolytes, avoiding bubble nucleation and current heterogeneities. Some nanomaterial engineering strategies to build

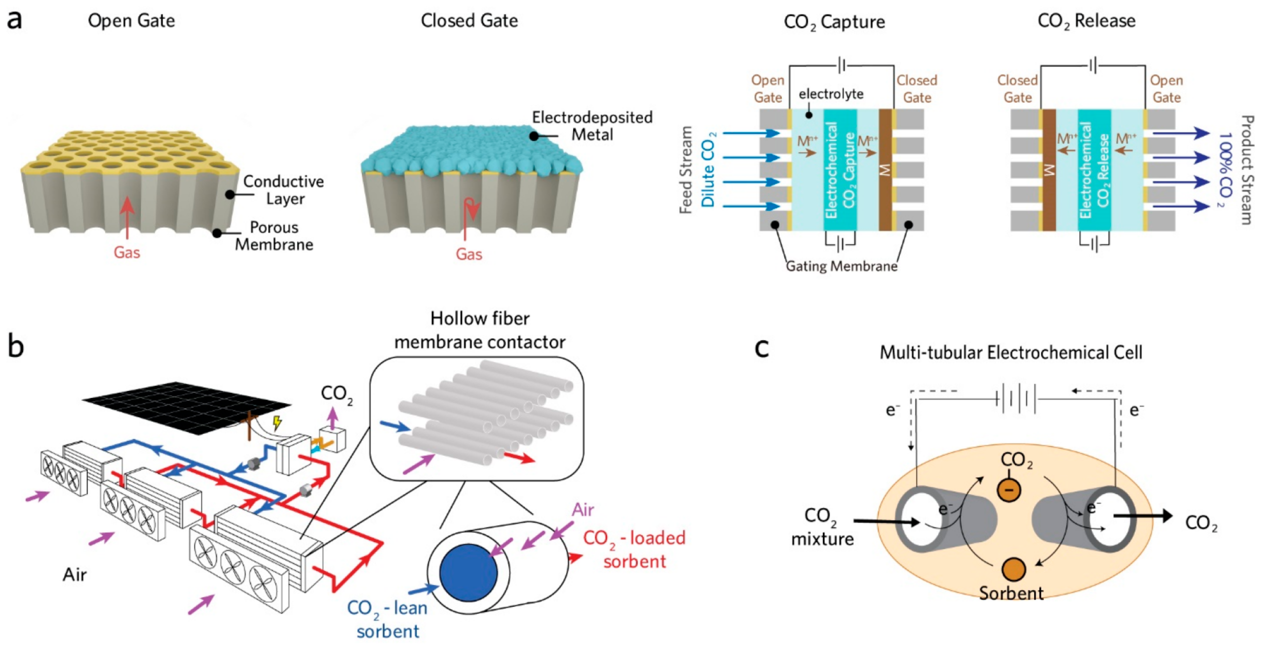

Figure 8. Regulating transport at the gas−liquid interface via nanomaterials. (a) Electrochemically responsive gating membrane for EMCC. (b) Hollow fiber membrane contactor for direct air capture. (c) Porous, tubular gas diffusion EMCC electrodes. Adapted with permission from ref 46, copyright 2022, American Chemical Society and ref 47, copyright 2023, American Chemical Society.

favorable solid−liquid−gas interfaces for expedited CO_2 transport in EMCC are discussed below.[44]

To regulate gas transport at the gas−liquid interface, we developed a gas gating mechanism based on the reversible deposition of nanocrystalline zinc on a porous membrane (Figure 8a). Without an applied current, gas is transported to the electrolyte through the porous membrane. Upon applying a current, a homogeneous layer of zinc nanoparticles is deposited on the membrane to impede gas flow. Employing this new mechanism, we built an EMCC device by sandwiching a P14AQ-CNT sorbent electrode between two gating membranes. During capture, only the feed-side membrane gate is open, allowing CO_2 to enter the system and be absorbed by P14AQ. Once the sorbent reaches capacity, a current is applied on the gating membranes to close the feed-side gate while simultaneously opening the product-side gate. Subsequently, the applied current on the sorbent electrode is switched for CO_2 release. This gating configuration avoids the concentration-gradient-driven crossover of CO_2 from the product stream back into the dilute feed stream. Furthermore, the system performance is improved due to the enhanced transport properties and absorption/desorption kinetics of thin electrodes and compact devices. This work paves the way for nanoengineering electrode and membrane materials to improve the EMCC performance.

Tubular structures can result in surface areas much higher than those of their planar counterparts. Thus, hollow fiber membranes (HFMs) have attracted substantial interest as gas−liquid contactors for CO_2 capture from air (Figure 8b).[45] HFMs are a class of tubular membranes with a hollow lumen and a nanoporous shell usually fabricated from polymers such as cellulose acetate, polysulfone, poly(ether sulfone), and polyvinylidene fluoride.[46] In EMCC, redox-active CO_2 carriers and the gas feed can flow separately through the lumen or the exterior of HFMs to maximize the gas−liquid contact. Recently, a multitubular electrochemical cell was demonstrated using CNT-coated hollow fiber membranes as electrodes, enabling continuous CO_2 separation from 15% CO_2 feed (Figure 8c).[47] The authors chose commercially available polypropylene membranes with a small thickness (200 μm) and a small pore size (0.2 μm) to minimize the mass transfer resistance and membrane flooding. The exterior of the HFM electrodes contacts the electrolyte with solubilized quinone while gas flows inside the lumen. Consequently, CO_2 is captured from the feed upon reduction of the HFM electrodes, and pure CO_2 can be released into the lumen upon oxidizing the CO_2 adduct, where it joins a sweep stream. This approach circumvents the sorbent crossover issue by avoiding the need for a membrane between the cathode and anode. Apart from the innovative electrochemical cell geometry, this work also emphasizes the need for redox-active CO_2 carriers with narrow potential gaps between capture and release to achieve a more energy-efficient system. This is because most existing carriers in their reduced form are much easier to oxidize than their CO_2 adduct counterpart. Therefore, in this HFM configuration, the oxidation of the reduced sorbent may occur more rapidly than that of the CO_2 adduct, resulting in sorbent deactivation rather than CO_2 release to undermine the CO_2 capacity utilization.

4. SUMMARY AND PERSPECTIVE

EMCC has shown early promise toward efficient and reliable carbon capture technologies. As part of the community, we have been working on creating new libraries of sorbents, addressing electrolyte incompatibility, developing nanomaterials for regulating gas transport, and engineering new processes to improve EMCC efficiency and facilitate practical applications. Although we focus on redox-active CO_2 carriers in this Account, the chemistry discussed can also provide insight into designing proton carriers for EMCC involving pH-swing mechanisms.

To further push the limit of EMCC, new chemistries must be discovered to address the intrinsic limitations of existing systems. These include the susceptibility of CO_2 affinity to chemical modifications, the large electrochemical polarization between reductive CO_2 addition and oxidative CO_2 elimination, the parasitic reactions involving O_2, and sorbent and electrolyte degradation.

Incorporating new chemistry into various EMCC configurations requires materials innovation at the nanoscale. In fixed-bed EMCC, new classes of nanoporous solid sorbents must be designed to enhance capacity utilization and CO_2 capture kinetics. In flow EMCC, the need arises for nonswelling size-selective membranes to tackle active species crossover. Reticular materials, such as MOFs and COFs, present promising potential as both solid sorbents and membranes due to their rigid, well-defined structures, tailor-made pore sizes, and ease of incorporating redox-active building units.

Finally, we advocate for more extensive theoretical calculations to understand the redox responsiveness of the CO_2 affinity of EMCC sorbents and their electrochemical reaction pathways. The need for scalers and descriptors is paramount in predicting the redox potential, CO_2 affinity, and solubility of CO_2 carriers for more efficient system design. With the above problems addressed, we believe the energetics of EMCC can be made competitive against amine scrubbing while operating at practically relevant current densities, together with more economical and durable process components to lower the capital and operating costs. Given the modularity of EMCC processes, they offer a unique opportunity for the removal of CO_2 from industrial facilities with limited land availability and more distributed streams. With the rapid development of renewable energy and the advancements in nanomaterials, the outlook of EMCC is strong, and the era of carbon capture driven by nonthermal stimuli can be just around the corner.

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