MRS Communications

Early Career Materials Researcher Prospective

Check for updates

Molecular redox-active organic materials for electrochemical carbon capture

Hyowon Seo [ID], Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

Address all correspondence to Hyowon Seo at **hseo@mit.edu**

Abstract

This prospective is a forward-looking outlook for researchers investigating electrochemical carbon capture utilizing molecular redox-active organic materials, with the following objectives: (1) identifying the essential components of an electrochemical carbon capture system, (2) introducing design principles for the system utilizing redox-active organic materials, encompassing their physicochemical properties and other critical factors, (3) presenting representative examples, and (4) promoting further experimental and theoretical studies on the application of redox-active organic materials for electrochemical carbon capture.

Introduction

Climate change and its associated environmental challenges have emerged as critical issues that demand immediate attention. To tackle this problem, the Intergovernmental Panel on Climate Change (IPCC) has set an objective of limiting global warming to 1.5°C above preindustrial levels by curbing greenhouse gas emissions, particularly carbon dioxide (CO_2).[1] This goal necessitates a substantial reduction in CO_2 emissions and the implementation of various strategies, including carbon capture technologies.[2,3] Carbon capture technologies aim to reduce CO_2 levels in the atmosphere by capturing CO_2 from diverse sources such as flue gas, air, and oceans.[4] The captured CO_2 is subsequently stored in underground reservoirs, thereby mitigating climate change by decreasing its concentration in the atmosphere.

The most established carbon capture technology is based on the thermal stripping process of an amine absorbent, such as monoethanolamine.[4,5] Despite the maturity of the thermal stripping process, several challenges limit its widespread deployment, including high energy consumption,[4–6] degradation of amines under operating temperatures,[4,7] corrosiveness,[8] and volatility of amines.[9]

Electrochemical carbon capture has significant potential as an alternative technology to overcome these limitations. Inherently isothermal conditions,[10] flexible system sizes,[11] and locations utilizing renewable electricity are examples of advantages of electrochemical carbon capture over thermal systems. Furthermore, electrochemical carbon capture systems offer independent engineering of energy and scale, due to their unique cell configuration. Several electrochemical system designs have been developed, ranging from electrochemically mediated amine regeneration (EMAR),[10,12–14] solid redox-active electrodes,[11,15] bipolar membranes,[16] capacitive materials,[17] inorganic redox-active electrodes,[18–20] and organic redox-active materials in homogeneous electrolytes.[21–29] This prospective article focuses on molecular redox-active organic materials (ROMs) as crucial materials in developing efficient electrochemical carbon capture systems. Redox-active organometallic compounds are beyond the scope of this article.

Molecular ROMs hold promise for electrochemical carbon capture, as they offer several advantages over traditional systems. First, ROMs offer flexibility in chemical structures, which allows for the tuning of physicochemical properties such as redox potentials, electrochemical reversibility, and solubility. Second, scalability of molecular ROMs is noteworthy. The concentration of molecular ROMs in electrolytes can be increased, which directly enhances carbon capture capacity, further simplifying scale-up. Electrochemical systems based on molecular ROMs electrolyte solutions do not require efforts in the uniform fabrication of functionalized electrodes, making them more practical for the scaling-up process. Unlike inorganic materials based on precious metals, the synthesis of ROMs does not depend inherently on the abundance of materials on earth, which enables large-scale production. Third, the flexibility of system design is a general advantage of using molecular ROMs. Chemical design flexibility including polymerization and functionalization of electrodes often provides system design flexibility under various operation conditions. Homogeneous electrolyte solutions containing ROMs offer further flexibility, as they can be employed in various system configurations, which will be further discussed below.

General scheme for electrochemical carbon capture employing molecular ROMs is described in Fig. 1. Electron-rich activated absorbent (ROM^-) is generated via electrochemical reduction of ROM (step 1). This activated absorbent (ROM^-) captures CO_2 by functioning either as a nucleophile, forming a covalent bond with CO_2, or as a base, resulting in an increase in the pH of an aqueous solution, which enhances the solubility
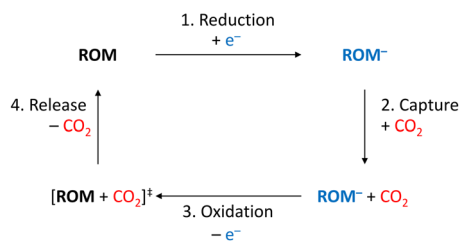
Figure 1. Square scheme for a typical electrochemical carbon capture and release cycle with molecular redox-active organic materials (ROMs).

Figure 2. Schematic illustration of an electrochemical carbon capture system in continuous flow.

of CO_2 (step 2). The regeneration of the ROM absorbent is achieved through the electrochemical oxidation step (step 3), which is often indistinguishable from the CO_2 release step (step 4).

In a pH swing process, given the rapid decomposition of carbonic acid into CO_2 and water, the concentration of CO_2, bicarbonate, and carbonate ions in water results in equilibrium that are determined by factors including CO_2 partial pressure, total dissolved inorganic carbon (DIC), and pH.[30] In a practical context, manipulating pH leads to alterations in the total DIC, making it an effective strategy for pH swing processes. In situations of higher pH, the elevated concentration of hydroxide ions enhances total DIC by CO_2 dissolution by favoring the formation of bicarbonate and carbonate ions. It is worth noting that during the CO_2 capture step during the pH swing in an aqueous solution at high pH conditions, CO_2 can interact with a hydroxide ion to form a bicarbonate ion or engage with two hydroxide ions to generate carbonate and water. The outcome of these reactions is contingent upon the specific pH environment, reflecting the dynamic nature of the CO_2 capture mechanism.

In this rapidly evolving area of research, although several classes of ROMs have been explored, a large number of molecular families remain underexplored. In this prospective article, overview of key components and the design principles of electrochemical carbon capture systems using ROMs are illustrated, as well as the current research status and advances using molecular ROMs. Furthermore, the challenges and future perspectives of utilizing ROMs in this promising field are discussed. The presented information highlights the importance of continued research in exploring the potential of various classes of ROMs for electrochemical carbon capture applications and provides a foundation for the development of more efficient and scalable electrochemical carbon capture technologies.

It is important to acknowledge the valuable contributions of prior review articles that have significantly shaped the understanding of electrochemical carbon capture. Notably, the review articles by Buttry and coworkers,[5] Hatton and coworkers,[31] and Yang and coworkers[32] have provided essential insights into various aspects of this field. These review articles have contributed greatly to the foundation of knowledge in electrochemical carbon capture systems and guided directions to the
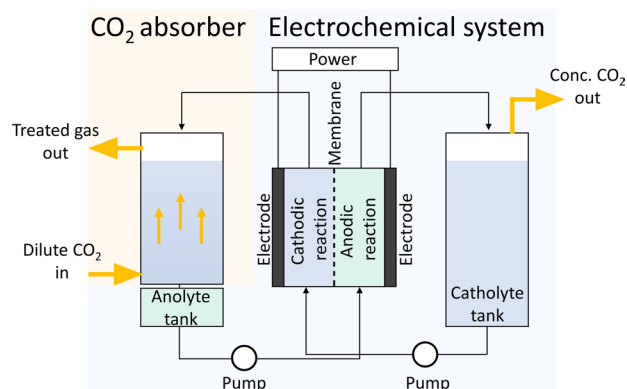
further development and wider applications. This prospective article aspires to complement these existing works by offering additional perspectives, design principles, challenges, and future directions in the realm of electrochemical carbon capture using molecular ROMs.

Electrochemical carbon capture systems

The electrochemical carbon capture systems that use ROMs electrolyte solutions consist of two main components: an electrochemical system and a CO_2 absorber, as illustrated in Fig. 2. The electrochemical system consists of an electrochemical cell framework equipped with two electrolyte tanks (anodic and cathodic reservoirs), a membrane, two electrodes, a power supply, and solutions containing ROMs and supporting electrolytes. The conversion of electrical energy to chemical energy occurs at the electrodes through the reduction of ROMs dissolved in the solution, which circulates between the tanks and corresponding compartments of the electrochemical cell and CO_2 absorber, driven by external pumps. The electrochemically reduced solution is transferred to the CO_2 absorber, where it comes into contact with the dilute CO_2 source. Subsequently, the saturated solution is transported to the anode side of the electrochemical cell, where anodic reaction takes place, resulting in the release of free CO_2 in a concentrated form, and the regeneration of the ROMs solution. To maintain charge balance, selective ions migrate across the membrane.

The utilization of ROMs in homogeneous solutions for electrochemical carbon capture offers a versatile approach to system configurations. These configurations can be categorized into two-stage, three-stage, and four-stage systems. Firstly, the two-stage system entails simultaneous absorbent reduction and CO_2 absorption at the cathode, while absorbent oxidation and CO_2 desorption occur at the anode. Secondly, the four-stage system decouples absorbent reduction and oxidation, which take place at the cathode and anode, respectively, from the processes of CO_2 absorption and desorption. Furthermore, there

are two possible three-stage systems that emerge by integrating either cathodic absorption or anodic desorption into an otherwise four-stage setup. Notably, recent examples featuring newly developed ROMs predominantly adopt the three-stage system involving cathodic reduction, CO_2 absorption, and coupled anodic oxidation and desorption. Within these three-stage systems, four distinct configurations can be considered: continuous flow, symmetric cycle, asymmetric cycle, and continuous two-cell flow systems, as depicted in Fig. 3. It is important to note that the choice between different system configurations depends on the specific requirements of the application, the characteristics of the ROMs and electrolytes, and the available resources. Each system has its own advantages and challenges, and the selection should be based on a comprehensive evaluation of the desired outcomes and operational conditions. The listed advantages and challenges pertain to a range of laboratory-scale systems used to evaluate new ROMs for electrochemical carbon capture. It is important to note that industrial-level scales might introduce additional advantages and challenges.

In the continuous flow system,[13,22] ROMs in the catholyte and anolyte are separated by a membrane [Fig. 3(a)]. ROMs in the solution are electrochemically reduced to be activated in the cathodic side of the electrochemical cell. The activated solution is then transferred to the CO_2 absorber, where it captures CO_2 from the diluted source. The saturated solution is subsequently transferred to the anode side of the cell, where electrochemical oxidation releases CO_2 and regenerates ROMs. The electrochemical reduction and oxidation occur in a single electrochemical cell, and the solution flows through each part
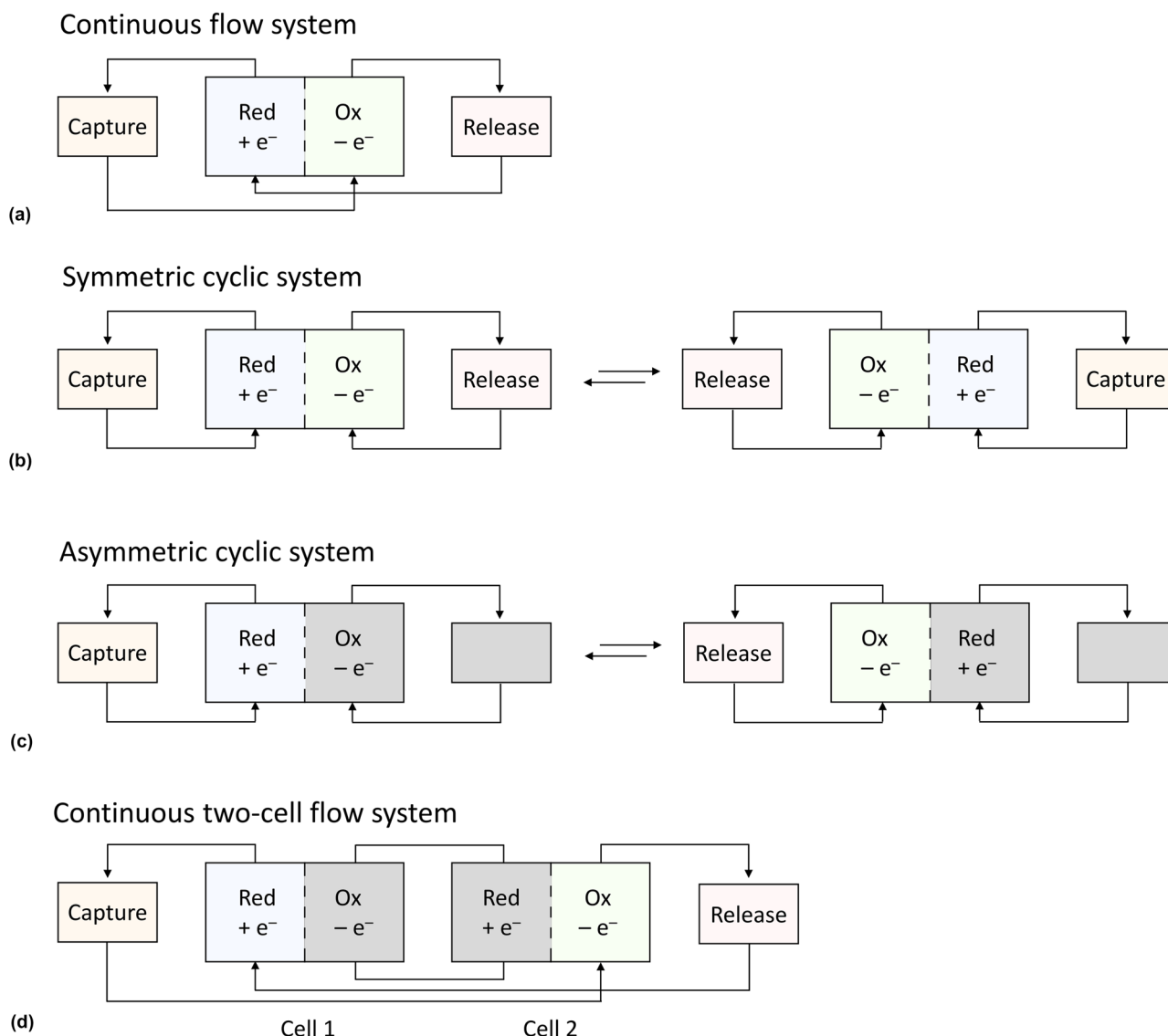

Figure 3. System configurations of electrochemical carbon capture using homogeneous ROMs electrolyte solutions.

in sequence. This setup, known as a single-pass configuration, offers advantages in the continuous capture and release of CO_2, providing simplicity to the system's design, fewer moving parts, and easier operation. However, it is worth noting that this configuration comes with certain challenges.

Due to the single-pass movement of electrolyte solutions through the electrochemical cell, limitations in solution flow rates and current densities can arise, posing challenges when attempting to scale up the system for larger applications. The performance of a single-pass setup is intricately linked to several interconnected factors that determine the residence time of the electrolyte solution within the electrochemical cell including the volume of the cathode/anode compartment, the concentration of the ROMs, the faradaic efficiency, and the current densities applied. It is important to recognize that current densities are not independent variables in this context. One notable aspect is that altering current densities often necessitates adjusting residence time to maintain optimal electrochemical performance, which can be achieved by lowering the flow rate of the solution. However, as the solution flow rate is reduced, a potential trade-off emerges, resulting in poorer transport of the ROMs. This, in turn, can lead to an increased overpotential within the electrochemical cell, as additional energy is required to overcome the diminished transport efficiency. This interdependency of cell volume, ROMs concentration, solution flow rate, and current densities adds a layer of complexity to system optimization. As such, optimizing one aspect may inadvertently affect others, potentially bringing about additional challenges.

In the symmetric cyclic system,[25] the cathode and anode parts of the cell are separated by a membrane, and solutions in each are not mixed [Fig. 3(b)]. At the cathode electrode of the cell, the cathodic solution of ROMs is generated by electrochemical reduction. The cathodic solution is then contacted by a CO_2 stream and captures CO_2. Once the solution is saturated with CO_2, the polarity of the cell is switched, and subsequent electrochemical oxidation of the saturated solution at the anode electrode releases CO_2 and regenerates ROMs. The cathodic and anodic solutions containing identical ROMs are coupled in a single electrochemical cell, where the alternate reduction and oxidation chemical process occurs on each side of the electrochemical cell. Cyclic system is advantageous in that independent scaling of the reaction rate (cell parameters) and the CO_2 capture capacity (electrolyte reservoir size) in the system. In contrast to the continuous flow setup as described above, rapid solution flow rates and low current densities can both be achieved due to multiple contacts of solution to electrode is possible.

Despite these advantages, challenges arise from the inherent dynamic nature of cyclic operations. The cyclic system involves transitioning between CO_2 capture and release stages, which can lead to transient fluctuations in the process. These transitions can introduce complexities in maintaining consistent current densities, faradaic efficiencies, and electrolyte conditions across various stages of the

cycle. Consequently, achieving optimal performance and stability within each stage while ensuring smooth transitions becomes a non-trivial task. Furthermore, the cyclic nature of the system necessitates intricate valving and control mechanisms to manage the sequence of operations. These additional components can contribute to increased mechanical complexity and maintenance requirements, potentially leading to operational inefficiencies and increased risk of mechanical failure.

The asymmetric cyclic system[24,29] is similar to the symmetric cyclic system regarding the electrochemical cell configuration, where the anodic and cathodic solutions are separated by a membrane, solutions are not mixed, and reduction and oxidation steps are sequential [Fig. 3(c)]. The difference from the symmetric cyclic system is that the anodic and cathodic solutions contain different ROMs, with one ROM having CO_2 capture activity, while the other ROM often does not. Due to the two different ROMs having different standard potential (E^0), the CO_2 release step by electrochemical oxidation often discharges electricity. This type of design most resembles redox-flow batteries, where electric energy stored as chemical energy can be discharged. However, a portion of the energy was consumed in concentrating CO_2, resulting in a significant drop in discharging voltage compared to the voltage utilized during charging.

The asymmetric cyclic system shares a comparable range of advantages and challenges with the symmetric cyclic system. An added advantage is that the assessment of new ROMs in the system can be simplified by pairing a well-studied ROM on one side. However, an extra challenge emerges due to the potential membrane crossover of two distinct chemicals, which could lead to capacity fading over time and require more frequent replenishment of electrolytes.

The continuous two-cell flow configuration[33] was designed for the continuous flow process using the asymmetric cyclic system [Fig. 3(d)]. The cathodic solution generated at the cathode electrode of cell 1 is pumped to the cathodic chamber to capture CO_2. Then the saturated solution is pumped to the anode side of cell 2, where electrochemical oxidation releases CO_2 and regenerates ROMs. The regenerated ROM solution is then pumped to the cathodic side of cell 1 to complete the cycle. Another ROM that has no CO_2 capture capacity is often combined with this system to couple in electrochemical cells 1 and 2.

The continuous two-cell flow configuration presents both the advantages and challenges of both the continuous flow system and the asymmetric cyclic system. It offers the simplicity of systems without cycling and energy charge and discharge capability accessed through asymmetric ROM coupling. However, it also shares the same set of disadvantages, including limited current density due to the single-pass nature, potential membrane crossover, and the relatively more complex system and operation than one-cell continuous flow system.

Design principles of organic redox-active molecules

The physicochemical properties of ROMs play a crucial role in determining the efficiency of electrochemical carbon capture systems. These properties include various factors including electrochemical properties, chemical and electrochemical stability, oxygen (O_2) and water stability, and solubility, which are discussed below. In addition to these factors, other important considerations in the design of such systems include the choice of electrolyte solution in aqueous and non-aqueous media, as well as the CO_2 source.

Electrochemical properties

Current electrochemical carbon capture systems prioritize minimizing operational costs, which primarily hinge on the electrochemical energy input.[32,34–36] This input can be divided into two: energy required by overpotential and thermodynamic minimum energy requirement, where the changes in CO_2 partial pressure and redox properties of ROMs are major contributors. Thus, in general, it is preferable to have a small potential gap between the reduction and oxidation steps to reduce energy consumption and subsequently lower the operational energy cost.

For a redox process with fast electron transfer kinetics, the concentration of the oxidized and reduced halves of the redox couple are related to the electrode potential, E, by the Nernst Eq. (1)

$$E = E^0 + \frac{RT}{nF} \ln \frac{[\text{Ox}]}{[\text{Red}]} \qquad (1)$$

where E^0 is the formal thermodynamic reduction potential, R is the gas constant, T is the temperature, n is the number of electrons transferred in the redox event, F is Faraday's constant, and [Ox] and [Red] are the interfacial concentrations of the oxidized and reduced species, respectively. In cyclic voltammetry (CV), the current response is observed as the concentrations of redox-active species at the electrode interface change over time, undergoing electron transfer to reach an equilibrium position as described by the Nernst equation.

CV is a versatile technique for the electrochemical characterization of ROMs, providing key electrochemical properties on their electrochemical stability, reversibility, redox potential differences, intermolecular interaction with CO_2, electron transfer kinetics, and sensitivity to air and water. It is important to consider that the results obtained from CV analysis are highly influenced by various experimental conditions such as solvent, ROMs concentration, CO_2 concentration, pH, supporting electrolyte, additives, scan rate and direction, working electrode, and reference electrode.

The minimum redox potential gap of the electrochemical carbon capture system is subsequently determined by the difference in peak potentials (ΔE_p) between the reduction and oxidation peaks of the ROMs under CO_2, as described in Fig. 4.
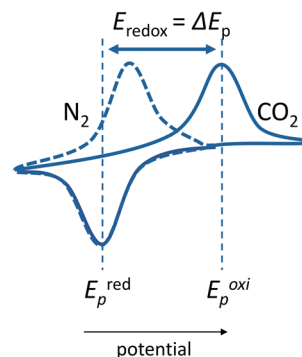
Figure 4. Schematic illustration of electrochemical redox potentials in CV under nitrogen and carbon dioxide.

To obtain this difference in peak potentials, the experimental conditions should be considered carefully. For example, in the case of using simulated flue gas (e.g., 5–20% CO_2 balanced by nitrogen) as a CO_2 feed gas during the capture and release of pure CO_2 without sweeping stream, the reduction peak potential measured under CO_2 saturated solution is appropriate to use in a flow system of multiple cycles. This is because, during the oxidation step, pure CO_2 is released and saturates the solution before making the gas output in a multiple-cycle system.

In most cases, when there is no intermolecular interaction between the ROMs and CO_2, no shift of the reduction potential peak is observed under nitrogen (N_2) and CO_2. A shift in the reduction peak potential may suggest intermolecular interaction between ROMs and CO_2 before or during the electrochemical reduction step.[38] Compared to the typical scenario where there is no change in reduction potentials under N_2 and CO_2, oxidation potentials obtained under the CO_2 atmosphere typically show a positive shift compared to those under N_2. This positive shift indicates the stabilization of the reduced ROM by CO_2 via covalent bond formation.[29,38,39] However, this may not always be the case for mediated processes, which do not form a direct covalent bond between ROM and CO_2.[22,24]

Rapid electron transfer kinetics for electrochemical steps is desired when designing efficient electrochemical carbon capture systems. This is because slower electron transfer kinetics can limit the current density and hinder scaling-up. To determine the electron transfer rate, a series of rotating disk electrode (RDE) analyses is often conducted. One common method to evaluate electron transfer kinetics (Levich analysis) is to plot the current against the square root of the rotation rate during sweeping rotation rates. This approach allows for the calculation of the kinetic rate constant (k^0), which are important indicators of rapid electron transfer kinetics.

Electrochemical properties of ROMs under air and water are a critical concern when designing electrochemical carbon capture systems. To study the sensitivity of ROMs toward air and water, CV analysis is often utilized.[36,38,39] The addition of O_2 or water can reduce the redox peak currents in CV, which raises concerns regarding the sensitivity of the ROMs toward

O$_2$ or water. This sensitivity can lead to issues such as re-oxidation and decomposition of the ROMs, ultimately reducing the operational lifetime of the system. Thus, it is crucial to perform thorough air and water sensitivity testing of ROMs through CV analysis, which can provide insights into the effects of O$_2$ and water on the electrochemical performance of ROMs. Detailed descriptions with examples are described in "Oxygen and water stability" section.

Electrochemical and chemical stability

The electrochemical and chemical stability of ROMs both play a crucial role in the cycling lifetime. Electrochemical stability relates to their stability during reduction/oxidation cycles, while chemical stability refers to the stability of the ROMs in their charged states irrespective of cycling behavior. Although these two stabilities are related, they do not necessarily correlate with each other.

Electrochemical stability is a critical factor in the performance and lifetime of ROMs for electrochemical carbon capture systems, and it involves two aspects: the electrochemical stability of ROMs and solvents. Specifically, the electrochemical stability of ROMs refers to their ability to maintain molecular integrity during electrochemical electron transfer reactions without decomposition. This requires perfect cycling with high faradaic efficiency and minimal side reactions. The electrochemical reversibility of a redox process can be established by measuring the ratio of peak currents of the reduction and oxidation processes in CV under N$_2$ and CO$_2$. A peak current ratio close to unity indicates that the redox process is electrochemically reversible. Although the absolute redox potential position is less critical than the relative positions of reduction and oxidation in designing electrochemical carbon capture systems, the absolute position is crucial for securing the electrochemical stability of solvents.[40] If the redox potentials are too close to the edge of the potential window of the solvent, multiple cycling may induce solvent decomposition, leading to system degradation.

The chemical reversibility of a redox process refers to the ability of the ROMs to revert to their original state after undergoing a redox reaction. This is typically evaluated by comparing the cyclic voltammograms obtained from the first and subsequent scans of the same ROMs. If the voltammograms are superimposable, then the redox process is considered chemically reversible. However, various decomposition pathways can compromise the chemical stability of ROMs, such as oxidation by O$_2$, protonation, hydrolysis, disproportionation, dimerization, polymerization, and CO$_2$ reduction.[41] To mitigate these degradation pathways, rational substituent design can be applied to develop chemically stable ROMs that prevent decomposition and capacity degradation, thereby leading to longer cycling time.

In addition to the inherent chemical stability of ROMs, their robustness in the presence of CO$_2$ and other gaseous constituents within operational frameworks warrants meticulous consideration. While the evaluation of chemical stability conventionally entails multiple CV measurements under inert conditions, it is imperative to extend this scrutiny to encompass the stability profile of ROMs under CO$_2$ exposure and potentially encompassing diverse gaseous impurities under the operational conditions. A demonstrative approach involves subjecting ROMs to repetitive CV cycles under simulated operational conditions, particularly during the nascent stages of novel ROM or system development. Moreover, the assessment of chemical stability can be fortified by comprehensive monitoring of capacity degradation and cell voltage for long-term operation, affording direct insights into the system's chemical robustness. Noteworthy strides in this domain are evident in recent investigations by Wang, Aziz, Ji, and coauthors, wherein an exemplary long-term stability assessment delineates a capacity fade rate of <0.01% per day sustained over a span exceeding 6 months.[42]

Oxygen and water stability

The stability of ROMs to O$_2$ and water is a common challenge that hinders their long-term cycling and broader applications, including direct air capture (DAC). To develop O$_2$- and water-stable ROMs that are selective for CO$_2$ binding, it is necessary to consider both their electrochemical and chemical stability toward common impurities including O$_2$ and water. CV serves as a rapid and accessible technique for investigating ROMs' sensitivity under various electrochemical potentials and their potential (electro)chemical interactions with common impurities like oxygen and water. However, recognizing the disparities in experimental conditions between CV and real-world operations, encompassing factors including concentration, electrode material, and time frame, stability ascertained via CV necessitates validation through extended operational periods. Complementing CV analysis, supplementary techniques like NMR, UV–vis, FTIR, and mass spectroscopies play a crucial role in assessing redox-active compounds.[39] These analytical methods prove invaluable in evaluating electrolyte integrity within operational settings, irrespective of the underlying degradation mechanism—whether it is electrochemical or chemical in nature.

The electrochemical sensitivity of ROMs to O$_2$ has been observed in quinones,[5,43–45] phenazines,[24,25] and unsaturated N-heterocycles[29] in aqueous and non-aqueous systems. Electrochemical O$_2$ stability of ROMs requires its reduction potentials more positive than those of O$_2$/O$_2^{\cdot-}$ couple. In cases where ROMs require lower potentials than that of O$_2$/O$_2^{\cdot-}$, reduced ROMs would be oxidized by O$_2$ to regenerate the resting-state ROMs and produce superoxide ion (O$_2^{\cdot-}$). In aprotic organic media, the formal potentials for O$_2$ reduction to superoxide ion couple are reported: − 1.16 V in DMSO, − 1.22 V in DMF, and − 1.25 V in ACN vs ferrocene/ferrocenium ion.[46] The sequence follows decreasing dielectric constants and the decreased dipolar solvation energies of superoxide ions in the respective solvents.

In aqueous conditions, oxygen can undergo several different pathways, which have been well documented in the Ref. 47. In

alkaline conditions, oxygen undergoes a four-electron pathway to form a hydroxide ion or a two-electron pathway to form a peroxide ion. The kinetics of oxygen reduction reactions (ORR) are complicated not only due to the multiple electronic transfer steps but also due to the profound influences of pH value, solvation, and polarity of electrolytes. Notably, the anthraquinone process has been effectively employed in the industrial-scale production of hydrogen peroxide, demonstrating the remarkable efficiency of peroxide formation through the reduced anthraquinone.[48–50] Any ROMs requiring similar or stronger reduction potentials than anthraquinone's may inadvertently undergo hydrogen peroxide formation as an undesired side reaction, ultimately diminishing the carbon capture capacity. Furthermore, particular care is required when a metal electrode is employed because metal and metal oxides are well studied to catalyze ORR in an aqueous media,[51–53] providing reactive oxygen species, which can reduce faradaic efficiency as well as degrade ROMs rapidly.

In addition to the inherent thermodynamic sensitivity of ROMs to oxygen, which is determined by their relative reduction potentials in relation to the oxygen reduction potential, factors such as the partial pressure of oxygen in the feed gas and oxygen solubility in the electrolytes can aid in mitigating oxygen sensitivity within the system. This is illustrated by the example of quinone's oxygen stability in a salt-concentrated environment, as demonstrated by Hatton,[38] where modulation of the electron transfer kinetics between the reduced ROM and oxygen effectively alleviated oxygen sensitivity concerns.

Moreover, it is important to consider the general challenges posed by chemical stability in the presence of oxygen during the development of novel ROMs. As organic molecules are introduced at high concentrations within oxidative or reductive environments, the potential for (electro)chemical side reactions increases. While current concerns about the oxidative decomposition of ROMs are relatively minor, it is worth noting that the presence of superoxide radicals and hydrogen peroxide, generated through electron transfer from reduced ROMs to oxygen, could lead to various reactions with other transient radical species. This might give rise to oxidative decomposition pathways under an oxygen atmosphere, including reactions such as epoxidation and nucleophilic substitution.[54–57] This significance is particularly evident in alkaline solutions, where hydrogen peroxide and its anion act as more potent nucleophiles compared to the hydroxide ion. While comprehensive investigations have been conducted on decomposition pathways involving hydroxide ions,[57] there is still a valid broader concern surrounding hydrogen peroxide ions and superoxide radical species. Even though mechanistic studies on oxidative decomposition are limited to date, it is crucial to understand the potential degradation of ROMs due to oxygen exposure, which could result in capacity fade.

The electrochemical stability of ROMs with respect to water is associated with the stabilization of activated ROMs. It has been demonstrated that water[58,59] and other hydrogen bonding donors[21,60] exert an influence on the electrochemical properties of quinone derivatives. In particular, Barlow and Yang[61] presented a method for tuning the electrochemical potential of quinones by adding an alcohol as a hydrogen bonding donor to stabilize the reduced quinone dianion, thereby preventing oxygen sensitivity. Additionally, a system employing quinone in an ionic liquid environment reported the stabilization of reduced quinone through the inclusion of 5% water, although a reduced electrochemical window was observed.[21]

Chemical stability of ROMs in water should also be considered. Water can degrade the performance by decomposing ROMs such as Michael addition, and nucleophilic substitution.[41,62] Particularly, considering current electrochemical carbon capture systems in aqueous solutions that utilize a pH range of 6–14, the stability of ROMs under this pH range should be thoroughly investigated. A range of nucleophilic reactions to quinones, for example, are available in the Ref. 63. Nucleophiles such as water and hydroxide ions are predominant in operating conditions, especially in an alkaline solution. Therefore, the nucleophilic substitution of the ROMs should be addressed to improve stability.[64]

Concerns extend to water splitting during the design of electrochemical carbon capture systems using aqueous electrolytes. Proximity of the range of potentials of ROMs to the water splitting reduction potentials can trigger competing reactions like hydrogen evolution[65,66] or oxygen evolution reaction,[67] thereby diminishing carbon capture capacity and long-term stability. Despite carbon-based electrodes not being optimal catalysts for such reactions, cases requiring extreme potentials warrant assessment of hydrogen evolution and oxygen reduction as side reactions affecting both capacity and stability.

Solubility

The capacity of the electrochemical carbon capture system is directly proportional to the concentration of the ROMs in the solution. The solubility limit of ROMs, which varies with solvent, needs to be as high as possible to develop an electrochemical carbon capture system with high capacity with low energy consumption. The physical properties of the solvent, such as its pH value, viscosity, polarity, and dielectric constant, are critical factors that influence the solubility limit. The concentration of ROMs can be also adjusted by the additives and supporting electrolytes in the electrolytes. Under the same solvent and supporting electrolyte conditions, the concentration of ROMs can be increased by taking advantage of the flexible modification possible through the substitution of organic molecules.[68] In an aqueous system, hydrophilic ionic or polar substituents, such as sulfonates, carbonates, hydroxyl, amines, quaternary ammonium, and glymes, can be employed to increase the concentration of ROMs. In a non-aqueous system, lipophilic substituents such as alkyl chains can be utilized to enhance the solubility limit.

Aqueous vs non-aqueous electrolyte solution

The choice of electrolyte media for electrochemical carbon capture is a critical factor in designing an efficient electrochemical carbon capture system. Both aqueous and non-aqueous electrolyte media, including ionic liquids, using homogeneous ROMs electrolytes, have been utilized for electrochemical carbon capture. The choice of electrolyte media is significant because it can affect the CO_2 capture mechanism and therefore CO_2 capture kinetics. In protic aqueous media, protonation may take place on the nucleophilic site created by electrochemical reduction before making a covalent bond with CO_2.[69] The increase in pH resulting from ROMs protonation can promote the dissolution of CO_2 as a bicarbonate ion. Conversely, aprotic organic media and ionic liquids offer the possibility of capturing CO_2 being captured by direct covalent bond formation between the electrochemically generated nucleophile and CO_2.[11,36]

Every electrolyte media has its own set of advantages and disadvantages that need to be carefully evaluated. Aqueous electrolyte systems have numerous advantages such as non-flammability, high conductivity, high CO_2 solubility, high natural abundance, low cost, low viscosity, and minimal environmental impact. However, the use of aqueous electrolytes in electrochemical carbon capture systems is limited due to several challenges. Firstly, general ROMs have low solubilities in aqueous solutions. Secondly, electrochemically activated molecules in aqueous electrolytes can potentially be decomposed due to the presence of nucleophilic hydroxide ions and water molecules under neutral to basic pH conditions. Lastly, the potential window of aqueous electrolytes is relatively narrow, further limiting their use for electrochemical carbon capture applications.

Non-aqueous electrolyte systems are capable of dissolving a wide range of ROMs and have a broad potential window, making them promising candidates for electrochemical carbon capture. However, the use of non-aqueous solvents for electrochemical systems such as dimethylformamide (DMF), dimethylsulfoxide (DMSO), acetonitrile (ACN), and propylene carbonate (PC) has several disadvantages such as flammability, low conductivity, high environmental impact, and high cost.[70] Ionic liquids have emerged as a potential alternative to conventional electrolytes due to their unique properties, including high conductivity and lower environmental impact resulting from low volatility. Nevertheless, their high cost and high viscosity remain challenges that need to be addressed for their wider application in electrochemical carbon capture.

CO₂ source

Electrochemical carbon capture technologies are pursued for CO_2 capture from various CO_2 sources including flue gas and ambient air. However, the system design and approach to CO_2 capture can differ significantly depending on the specific source and CO_2 generating processes, leading to varying energy penalties.[71] Thus, the composition and properties of the feed gas should be carefully considered to develop an efficient electrochemical carbon capture system. Achieving this goal requires an understanding of the interactions between the gas mixture and the system's components, as well as the development of advanced materials and processes to optimize system performance.

Post-combustion capture is a process that involves the separation of CO_2 from flue gases produced after combustion.[72] The concentration of CO_2 in these flue gases typically ranges from 3 to 20 percent. Empirical data on the CO_2 concentration of flue gases generated by various processes such as boilers, turbines, hydrogen production, steel and aluminum production, and cement production have been reported in the Refs. 71 and 73. With the increasing need to reduce carbon emissions, post-combustion capture has become a viable solution for reducing the carbon footprint of existing coal-fired power plants. To this end, there is a growing interest in developing electrochemical systems that can be employed in post-combustion capture processes. Currently, most bench scale demonstration of electrochemical carbon capture utilized simulated flue gas (e.g., 15% CO_2 balanced by N_2). In practice, CO_2 sources contain other gaseous species such as O_2, nitrogen oxides (NOx), and sulfur oxides (SOx).[74] Those acidic gases such as NOx and SOx often show similar chemical reactivity toward to absorbent,[75] as most chemical absorbent uses its nucleophilicity and basicity to capture slightly acidic CO_2. In addition, it is essential to consider the temperature ranges of flue gases from 50 to 600°C depending on the source.

Direct air capture (DAC) is a process for capturing CO_2 directly from the ambient air as a means to mitigate climate change.[76] DAC is considered a viable option for CO_2 capture from decentralized and mobile emission sources such as vehicles, ships, or airplanes. However, there are several challenges associated with DAC, including the exceptionally low CO_2 concentration (approximately 421 ppm) in the presence of high concentrations of oxygen (21%) and water (0–3%).[77,78] Further considerations must be made for volatile organic compounds (VOCs) in the atmosphere.[79] The extremely low concentration of CO_2 in the air necessitates moving large volumes of air through the capture unit, making DAC a more energy-intensive and costly process than removing CO_2 from concentrated sources. In addition, the high volume of gas flow raises concerns about the volatility of the absorbent and electrolyte solution, which can shorten the lifetime of the system and increase environmental impact. Despite these challenges, current research directions in the field of electrochemical direct air capture using molecular redox-active materials are actively focusing on addressing these limitations. Notably, recent works from Hatton,[22] Liu,[29] and Yang[61] have been at the forefront of developing oxygen-stable systems to enhance the efficiency and feasibility of DAC with molecular ROMs. Although these works are in early stage compared to the more established post-combustion capture, these works represent significant strides in overcoming the hurdles posed by the presence of oxygen in the ambient air during CO_2 capture.

Quinone

Quinones are the most extensively studied ROMs for electrochemical carbon capture, presenting unique and robust reversible electrochemical properties.[36,37,80] The performance of electrochemical carbon capture is strongly dependent on the physicochemical and electrochemical properties of quinones, particularly molecular aromaticity and electronic structures.[37,80] The carbonyl functional groups of quinones act as a redox center and provide fast CO_2 capture kinetics by forming a covalent C–O bond between the carbonyl oxygen and CO_2 in non-aqueous media. The aromatic structure with various substituents affects the electrochemical redox potentials, stability, solubility, and CO_2 binding affinity. The facile synthetic access to various modified quinone structures makes them promising candidates for ROMs for electrochemical carbon capture.

In early studies of quinones for electrochemical carbon capture, non-aqueous media such as organic solvents and ionic liquids were used.[21,43] In aprotic media, quinones typically undergo two sequential electrochemical single-electron transfer events.[81] The quinone is reduced to generate a radical anion (semiquinone), and then the radical anion undergoes its second single-electron transfer to form a dianion at a more negative reduction potential.

The first demonstration of electrochemical carbon capture using a quinone compound was reported by Scovazzo in 2003.[43] In this study, 2,6-di-*tert*-butyl-1,4-benzoquinone was used to electrochemically concentrate CO_2 from 0.5 to 100% in a propylene carbonate solution. The electron utilization (i.e., mole of CO_2/mole of electron) was determined to be 0.43 in a batch setup.

In 2015, Hatton and coworkers reported an electrochemical carbon capture system using 1,4-naphthoquinone as a ROM in ionic liquids [Fig. 5(a)].[21] Under the experimental conditions, 1,4-naphthoquinone undergoes a single two-electron reduction with simultaneous binding of CO_2. The high solubility of 1,4-naphthoquinone (0.56 and 1.9 M at 22 and 60°C,

respectively) in the high-polarity ionic liquid, 1-ethyl-3-methylimidazolium tricyanomethanide, [emim][tcm], enabled a high capture capacity of the system. The estimated minimum energy consumption was determined to be 17 kJ_e/mol.[21]

In 2021, to reveal the structure–property relationship of quinone derivatives, Hatton and coworkers studied 18 quinones with structural variations in two different classes, weakly and strongly CO_2 complexing quinones.[37] The experimental results indicated that CO_2 binds to quinone dianion of weakly complexing quinones, while CO_2 binds to quinone radical anion of strongly complexing quinones and the association of CO_2 to quinone radical anion leads second electron transfer facile.

In 2023, Hatton and coworkers developed a liquid quinone sorbent to achieve high concentrations for the electrochemical carbon capture system with high capacity [Fig. 5(c)].[33] The liquid quinone sorbent was synthetically prepared to attach diglymes for room temperature liquid. The liquid quinone was employed to develop a homogeneous electrochemical carbon capture process in continuous two-cell flow with a high concentration (0.7 M) of liquid quinone in and 2-(2-methoxyethoxy)ethanol (DEGME). Good electrochemical stability and robustness of the system were achieved by demonstration for 10 cycles in an asymmetric cyclic system. Promising experimental minimum energy requirement obtained to be between 35 and 220 kJ_e/mol.

Oxygen sensitivity of reduced quinones such as superoxide formation by O_2 is generally regarded as a source of inefficiency in electrochemical carbon capture systems employing ROMs, which hinder further development and wider applications.[37] Hatton and coworkers have shown that utilization of extremely salt-concentrated aqueous electrolytes, known as "water-in salt" electrolytes, can prevent parasitic superoxide formation, by the significant solubility difference between O_2 and CO_2, which is more than 200-fold.[38] In addition, the quinone-CO_2 adducts are more stable against oxidation compared to the corresponding quinone dianions due to their increased
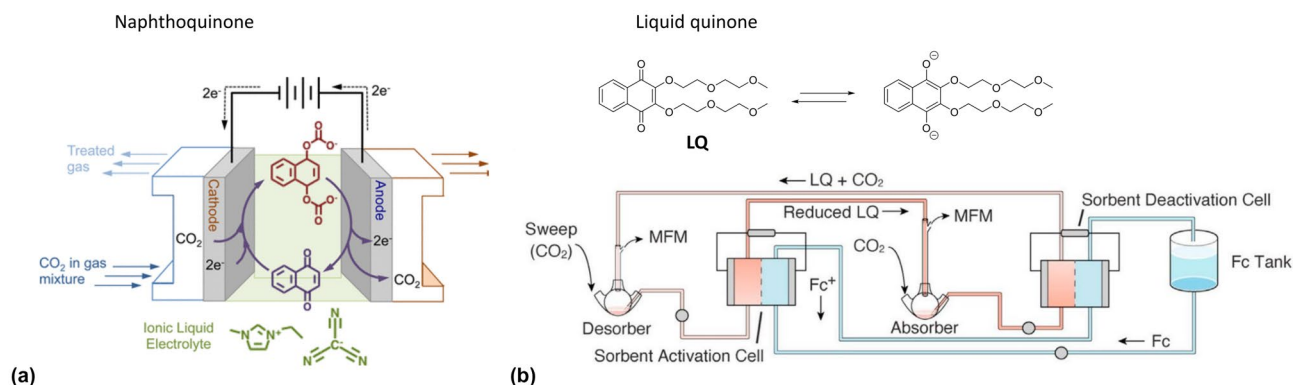
Figure 5. Quinones as ROMs in electrochemical carbon capture. (a) Schematic illustration of electrochemical CO_2 separation using 1,4-naphthoquinone. Reprinted with permission from Ref. 21. Copyright 2015, American Chemical Society. (b) Schematic illustration of electrochemical CO_2 separation using liquid quinone in continuous two-cell flow. Reprinted with permission from Ref. 33. Copyright 2022, Elsevier.

oxidation potential under the conditions with high supporting electrolyte (Lithium bis(trifluoromethanesulfonyl)imide, LiTFSI) concentration. The system's robustness was demonstrated by operating over 75 cycles with 95.5% coulombic efficiency. The minimum electrical energy requirement was obtained to be 56 kJ_e/mol using simulated flue gas (15% CO_2, 3% O_2, balanced by N_2).

In 2022, Yang and coworkers reported a strategy to suppress the oxygen sensitivity of reduced quinones by including an alcohol additive.[61] The addition of alcohol stabilized the dianion through intermolecular hydrogen bonding and shifted the redox potentials 350 mV positive. The electrochemical carbon capture in a batch H-cell was demonstrated using 2,3,5,6-tetrachloro-p-benzoquinone and ethanol, and a simulated flue gas (8% CO_2, 3% O_2, balanced by N_2). The minimum energy requirement was estimated to be 21 kJ_e/mol using 10% CO_2.
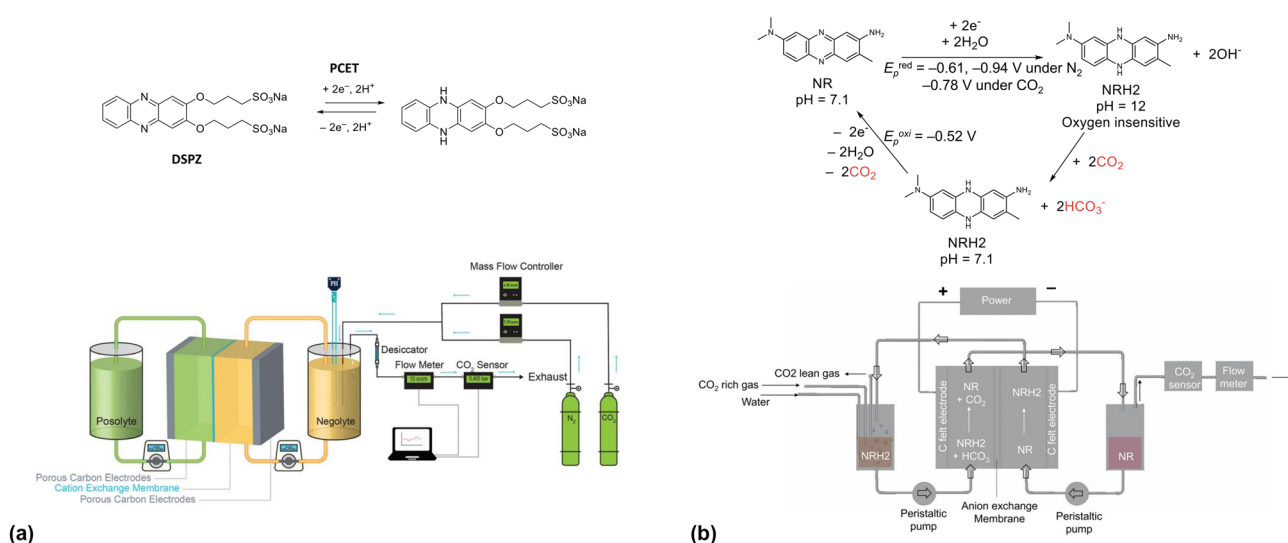
Phenazine

Phenazines have been identified as a promising class of compounds for electrochemical carbon capture due to their unique reversible electrochemical redox properties. These compounds possess a planar structure that allows for efficient electron transfer and a high degree of conjugation that makes them redox-active. Phenazine compounds have been investigated in aqueous media, where they exhibit reversible electrochemical reactions that involve the transfer of electrons and protons in protic media. Thus, pH swings have been utilized for CO_2 capture in aqueous electrolytes induced by electrochemical redox reactions of phenazine compounds.

In 2020, Aziz and colleagues reported the use of a phenazine derivative, sodium 3,30-(phenazine-2,3-diylbis(oxy)) bis(propane-1-sulfonate) (DSPZ), for electrochemical carbon capture through pH swing [Fig. 6(a)].[24] To improve aqueous solubility, sulfonate moieties were synthetically attached to the phenazine core, which is responsible for its redox activity. DSPZ undergoes proton-coupled electron transfer (PCET) involving two electrons and two protons, which can switch the electrolyte pH. The redox activity of DSPZ as a pH mediator allowed for the capture of CO_2 by forming an alkaline solution via the reduction of the redox molecule, and release of CO_2 through acidification by re-oxidation. The system's robustness was demonstrated over 20 cycles in an asymmetric cyclic setup, providing a minimum energy requirement of 48.9 kJ_e/mol using 46% CO_2. In recent studies, a structural modification was made to 2,2′-(phenazine-1,8-diyl)bis(ethane-1-sulfonate) (1,8-ESP) to improve its solubility and stability.[42] The modified compound was found to have a high solubility of 1.35 M and demonstrated long-term cycling over 220 cycles for 18 days, with a low capacity fade rate of 0.05% per day. The energy consumption required for this system was obtained to be 55.2 kJ_e/mol using 0.8 M of 1,8-ESP using 10% CO_2. Unfortunately, the lack of oxygen stability of these phenazine derivatives was not useful for DAC.

In 2023, Hatton and coworkers demonstrated electrochemical DAC using neutral red (NR), a commercial phenazine dye compound, in an aqueous electrolyte with ambient air as the feed gas [Fig. 6(b)].[22] The solubility of NR in 1 M potassium chloride aqueous electrolyte was improved to 306 mM by the addition of 1 M nicotinamide, a hydrotropic solubilizing agent. While this improvement in solubility was claimed to be sixfold, it is noteworthy that the improved solubilities are still relatively low with lack of information of the solubility of the reduced species. Practical application of this system warrants higher solubilities in both oxidized and reduced forms of ROMs. To show the oxygen stability of the system, UV–vis studies were

Figure 6. Phenazines as ROMs in electrochemical carbon capture. (a) Schematic illustration of electrochemical CO_2 separation using DSPZ. Reprinted with permission from Ref. 24. Copyright 2022, Royal Society of Chemistry. (b) Schematic illustration of electrochemical direct air capture using neutral red. Reprinted with permission from Ref. 22, under CC BY 4.0 license.
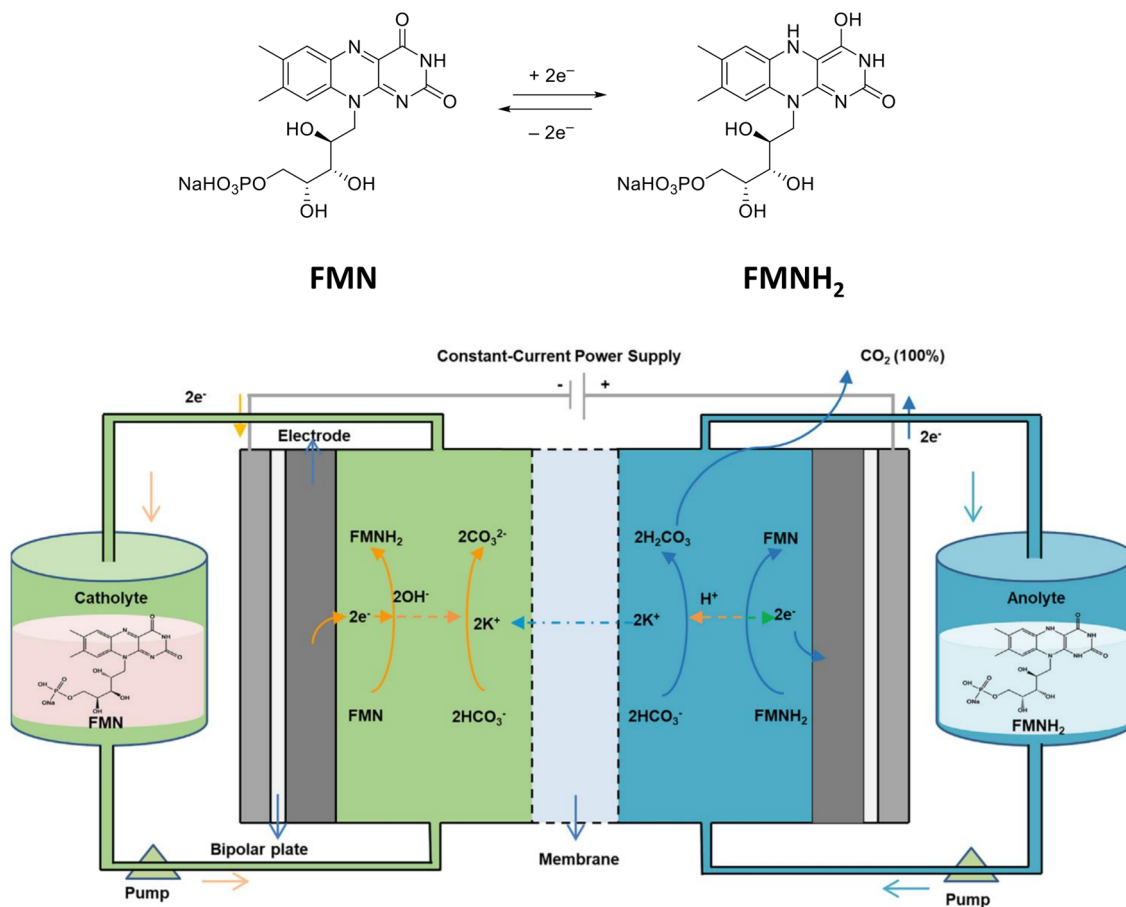
Figure 7. Alloxazine as an ROM in electrochemical carbon capture. Schematic illustration of electrochemical CO_2 separation using FMN. Reprinted with permission from Ref. 26. Copyright 2020, Elsevier.

conducted under pure O_2 and ambient air. The electrochemical reversibility of NR was established by a series of cyclic voltammetry (CV) experiments under N_2 and CO_2, and it was found that the mechanism involved a stepwise H e e H process in a pH range of 6–12 in protic media.[82] A continuous flow system was built to demonstrate 96 h of operation, which corresponds to 20 circulations of electrolytes using 50 mM NR. The minimum energy requirement was estimated to be 65 kJ$_e$/mol using ambient air and 35 kJ$_e$/mol using 15% CO_2.

Alloxazine

Alloxazine is a heterocyclic compound that contains a fused ring system consisting of pyrimidine and pyrazine rings. This compound is found as the core structure of riboflavin, also known as vitamin B2, and its redox activity plays a crucial role in electron transfer reactions in biological systems. Due to its redox properties, alloxazine has attracted attention as a promising candidate for electrochemical carbon capture applications.

In 2020, Xie and coworkers employed a biological proton carrier g riboflavin-5′-monophosphate (FMN) to demonstrate the electrochemical carbon capture by pH swing of aqueous

electrolytes via PCET, which involves the transfer of two electrons and two protons (Fig. 7).[26] Symmetric cyclic system was constructed and run for 21 cycles to demonstrate the system's robustness using 25 mM of FMN. The energy consumption was estimated to be 9.8 kJ$_e$/mol CO_2 using 15% CO_2 at 60°C.

Aromatic azo

Aromatic azo compounds are molecules consisting of two aromatic rings connected by an N=N double bond. Due to the unique conjugated system by this double bond, aromatic azo compounds show reversible electrochemical redox activity.

Azopyridine (Azpy) was selected to demonstrate the electrochemical carbon capture owing to its high reduction potential among a chemical library of redox-tunable Lewis bases featuring sp^2 nitrogen centers including 4,4′-bipyridine, quinoxaline, phenazine, 2,1,3-benzothiadiazole, azobenzene, and azopyridine (Fig. 8).[29] The electrochemical carbon capture system utilizing Azpy in an asymmetric cyclic system was tested under simulated flue gas (20% CO_2) for 20 cycles. The stability of Azpy toward O_2 was demonstrated under mixed gas conditions containing 18.5% CO_2 and 3% O_2 over 14 cycles, with Coulombic
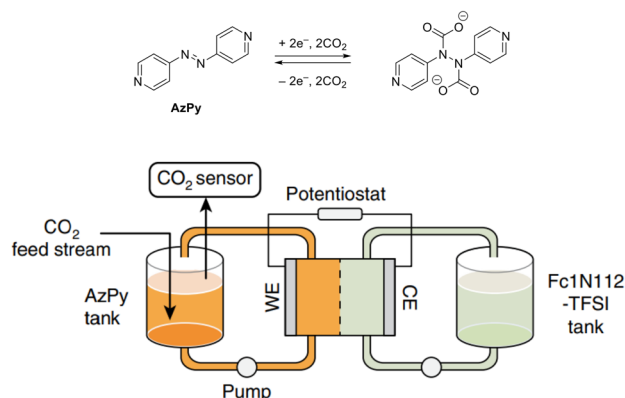
Figure 8. Azopyridine as a ROM in electrochemical carbon capture. Schematic illustration of electrochemical CO_2 separation using AzPy. Reprinted with permission from Ref. 29. Copyright 2023, Springer Nature.

Figure 9. Pyridinyl radical as a ROM in electrochemical carbon capture. Reprinted with permission from Ref. 23. Copyright 2022, American Chemical Society.

efficiencies ranging from 87 to 97%. However, degradation of performance was observed at higher O_2 concentration conditions (5%). The electrochemical analysis showed a 1.3 V of peak potential gap between the potentials for CO_2 capture (− 1.2 V vs Ferrocene/Ferrocinium ion) and release (0.1 V) with NaTFSI as a supporting electrolyte in diethylene glycol dimethyl ether. The electrical energy consumption required for the capture and release cycle utilizing Azpy redox cycle was calculated to be 120 kJ$_e$/mol, based on the voltage gap between the onset potentials of reduction and oxidation under a CO_2 atmosphere.

Pyridinyl radical

The electrochemical reduction of 1-aminopyridinium (1-AP) salts to stable pyridinyl radicals has been studied as a potential electrochemical CO_2 absorbent (Fig. 9)[23] 1-AP nitrate has been utilized as a redox-active amine absorbent in an aqueous solution for electrochemical CO_2 capture through pH modulation. The results of the study showed reversible electrochemical redox-active amine cycles, which allowed for CO_2 capture and release with electron utilization of up to 1.25, from a wide range of CO_2 concentrations. The redox-active amine demonstrated the moderate stabilities under O_2, and its minimum energy requirement was estimated to be 162 kJ$_e$/mol for DAC based on the peak potential gap obtained by CV analysis. This pyridinyl radical redox chemistry presents a promising approach for electrochemical carbon capture, although it is currently in the early stages of development.

Bipyridine

Bipyridine is a heterocyclic compound with two pyridine rings linked by a central carbon–carbon bond. Bipyridine-based materials are characterized by their reversible redox activity and their ability to generate stable radical species through redox
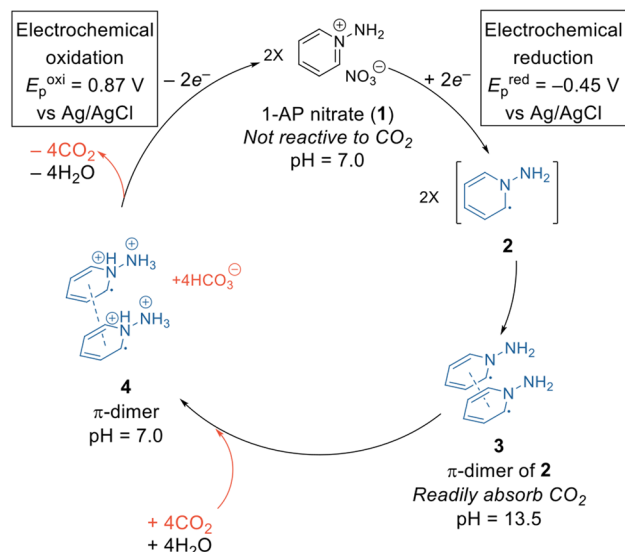
reactions, which makes them unique and versatile materials.[83] Due to these properties, bipyridine-based materials have found widespread applications in a variety of fields, such as optics,[84] molecular machines,[85] and batteries.[86] Furthermore, bipyridine shows great promise as a tool for electrochemical carbon capture.

In two separate studies, the bipyridine scaffold was employed as a reactive organic mediator for electrochemical carbon capture. The first study in 1994 demonstrated the use of N-propyl-4,4′-bipyridinium cation as a CO_2 absorbent through electrochemical reduction to its radical, which forms a C–N bond with CO_2.[87] In 2015, 4,4′-bipyridine (Bipy) was studied in the presence of CO_2, where electrochemical single-electron reduction forms the radical anion that captures CO_2 (Fig. 10).[27] The resulting Bipy–CO_2 adduct was electrochemically oxidized to regenerate the resting-state Bipy and release CO_2. The positive shift in the oxidation potential of the Bipy radical anion under CO_2 was attributed to the stabilization of the adduct by CO_2. While no cyclic experiment was demonstrated, the overall energy cost for the capture and release cycle is governed by the peak potential gap (0.7 V), at which capture and release occur, − 2.0 and − 1.3 V, respectively.

Thiolate

The electrochemical generation of thiolate by cleavage of the S–S bond of disulfide has been investigated as a CO_2 capture absorbent (Fig. 11).[28] Upon two-electron reduction, disulfide is cleaved to produce two thiolate species, which act as nucleophiles to CO_2 to form thiocarbonate. The thiocarbonate can be electrochemically oxidized to release CO_2 and regenerate the disulfide. The peak potential gap is reported to be 1.9 V between the reduction (− 2.2 V) and oxidation (− 0.3 V) under
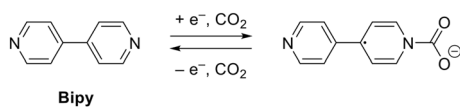
Figure 10. Bipyridine as a ROM in electrochemical carbon capture.
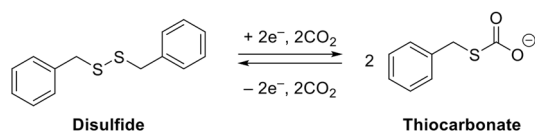
Figure 11. Disulfide–thiolate redox couple as a ROM in electrochemical carbon capture.

CO_2 in ionic liquids. Although cyclic experiments have not been demonstrated, the overall energy cost of the capture and release cycle is controlled by the peak potential gap (1.9 V).

Conclusion and outlook

Electrochemical carbon capture systems are a promising technology with the potential to play a significant role in sustainability, energy transition, and climate change mitigation. Over the last decade, the introduction of electrochemical carbon capture using molecular ROMs has extended the range of chemistries in both aqueous and non-aqueous electrolytes. Molecular ROMs offer several advantages for electrochemical carbon capture, including a vast molecular diversity, highly customizable physicochemical properties, scalability, and system design flexibility.

Although significant efforts have been made in electrochemical carbon capture systems utilizing molecular ROMs, there remains a great deal of room for improvement in material and system design to enhance their performance, including capacity, stability, energy consumption, and efficiency. Developing effective ROMs with accompanying membranes, electrodes, and systems will be critical for scaling-up and expanding the applications. Given the infant stage of this area of research, there is a tremendous opportunity for experts in organic materials, synthesis, catalysis, electrochemistry, and process engineering to contribute to this field.

An important challenge in electrochemical carbon capture research is to minimize energy consumption, while simultaneously maximizing capacity and long-term stability, for large-scale and widespread applications. Low energy consumption can be accomplished by utilizing redox couple under CO_2 with a narrow redox potential gap, which can be achieved by the intelligent design of the molecules. Of particular interest are ROMs capable of capturing more than one CO_2 per electron transferred, as well as mediated systems to avoid the formation of direct covalent bonds, which typically require high energy input to break. Although some molecular engineering work has been conducted to investigate the structure–property relationships of quinone derivatives, a large number of

derivatives remain unexplored. In addition to quinones, other redox-active molecular species, as described in this article, need to be investigated to understand their structure–property relationships through molecular engineering experimentally and computationally.

To achieve the widespread application of electrochemical carbon capture systems, it is necessary to conduct studies under a variety of CO_2 feed gas conditions, including differences in concentration, composition, temperature, and pressure. While current research often focuses on simulated flue gas, for example, containing 15% CO_2 balanced with N_2, practical flue gas capture requires stability toward oxygen, nitrous oxides, and varying temperatures and pressures. Of particular challenge is the sensitivity of most electrochemically reduced ROMs to oxygen, which prevents their operation under various oxygen-containing conditions. Thus, chemical and electrochemical stability of the system under the conditions with impurities is advised to consider at an early stage in the development of molecular ROMs for electrochemical carbon capture, to ensure their suitability for widespread adoption and address the urgent need for carbon capture.

To advance the development of electrochemical carbon capture systems using molecular ROMs, research efforts should focus on a wide variety of molecular redox-active species, from those with known structures and derivatives to new classes of structures. Essential physicochemical properties should be investigated including electrochemical properties, electrochemical and chemical stability, solubility, and oxygen and water stability to establish robust systems. In addition, special attention should be given to the selection of appropriate electrolyte solutions and CO_2 sources, to improve the practical applicability. All these efforts will contribute to the development of more efficient, stable, and effective electrochemical carbon capture systems, and help address the pressing need for carbon capture.

Data availability
All data presented here have been previously published and cited.

Declarations

Conflict of interest

The author has no relevant financial or non-financial interests to disclose.

Open Access

This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

References

1. Intergovernmental Panel On Climate Change (Ipcc), *Climate Change 2022 – Impacts, Adaptation and Vulnerability: Working Group II Contribution to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*, 1st edn. (Cambridge University Press, Cambridge, 2023)
2. G. Luderer, Z. Vrontisi, C. Bertram, O.Y. Edelenbosch, R.C. Pietzcker, J. Rogelj, H.S. De Boer, L. Drouet, J. Emmerling, O. Fricko, S. Fujimori, P. Havlík, G. Iyer, K. Keramidas, A. Kitous, M. Pehl, V. Krey, K. Riahi, B. Saveyn, M. Tavoni, D.P. Van Vuuren, E. Kriegler, Nat. Clim. Change **8**, 626–633 (2018)
3. G. Iyer, L. Clarke, J. Edmonds, A. Fawcett, J. Fuhrman, H. McJeon, S. Waldhoff, Energy Clim. Change **2**, 100043 (2021)
4. M. Bui, C.S. Adjiman, A. Bardow, E.J. Anthony, A. Boston, S. Brown, P.S. Fennell, S. Fuss, A. Galindo, L.A. Hackett, J.P. Hallett, H.J. Herzog, G. Jackson, J. Kemper, S. Krevor, G.C. Maitland, M. Matuszewski, I.S. Metcalfe, C. Petit, G. Puxty, J. Reimer, D.M. Reiner, E.S. Rubin, S.A. Scott, N. Shah, B. Smit, J.P.M. Trusler, P. Webley, J. Wilcox, N. Mac Dowell, Energy Environ. Sci. **11**, 1062–1176 (2018)
5. J.H. Rheinhardt, P. Singh, P. Tarakeshwar, D.A. Buttry, ACS Energy Lett. **2**, 454–461 (2017)
6. T.N.G. Borhani, A. Azarpour, V. Akbari, S.R. Wan Alwi, Z.A. Manan, Int. J. Greenhouse Gas Control **41**, 142–162 (2015)
7. G.T. Rochelle, Curr. Opin. Chem. Eng. **1**, 183–190 (2012)
8. A. Krzemień, A. Więckol-Ryk, A. Smoliński, A. Koteras, L. Więcław-Solny, J. Loss Prev. Process Ind. **43**, 189–197 (2016)
9. T. Nguyen, M. Hilliard, G.T. Rochelle, Int. J. Greenhouse Gas Control **4**, 707–715 (2010)
10. M.C. Stern, F. Simeon, H. Herzog, T.A. Hatton, Energy Environ. Sci. **6**, 2505 (2013)
11. S. Voskian, T.A. Hatton, Energy Environ. Sci. **12**, 3530–3547 (2019)
12. M. Rahimi, K.M. Diederichsen, N. Ozbek, M. Wang, W. Choi, T.A. Hatton, Environ. Sci. Technol. **54**, 8999–9007 (2020)
13. M. Wang, T.A. Hatton, Ind. Eng. Chem. Res. **59**, 10120–10129 (2020)
14. M. Wang, S. Hariharan, R.A. Shaw, T.A. Hatton, Int. J. Greenhouse Gas Control **82**, 48–58 (2019)
15. A. Hemmatifar, J.S. Kang, N. Ozbek, K. Tan, T.A. Hatton, Chemsuschem **15**, e2021025 (2022). https://doi.org/10.1002/cssc.202102533
16. R. Sharifian, L. Boer, R.M. Wagterveld, D.A. Vermaas, Chem. Eng. J. **438**, 135326 (2022)
17. K.J. Lamb, M.R. Dowsett, K. Chatzipanagis, Z.W. Scullion, R. Kröger, J.D. Lee, P.M. Aguiar, M. North, A. Parkin, Chemsuschem **11**, 137–148 (2018)
18. M. Rahimi, G. Catalini, S. Hariharan, M. Wang, M. Puccini, T.A. Hatton, Cell Rep. Phys. Sci. **1**, 100033 (2020)
19. M. Rahimi, G. Catalini, M. Puccini, T.A. Hatton, RSC Adv. **10**, 16832–16843 (2020)
20. S. Kim, M.P. Nitzsche, S.B. Rufer, J.R. Lake, K.K. Varanasi, T.A. Hatton, Energy Environ. Sci. **16**, 2030–2044 (2023). https://doi.org/10.1039/D2EE03804H
21. B. Gurkan, F. Simeon, T.A. Hatton, ACS Sustain. Chem. Eng. **3**, 1394–1405 (2015)
22. H. Seo, T.A. Hatton, Nat. Commun. **14**, 313 (2023)
23. H. Seo, M. Rahimi, T.A. Hatton, J. Am. Chem. Soc. **144**, 2164–2170 (2022)
24. S. Jin, M. Wu, R.G. Gordon, M.J. Aziz, D.G. Kwabi, Energy Environ. Sci. **13**, 3706–3722 (2020)
25. H. Xie, Y. Wu, T. Liu, F. Wang, B. Chen, B. Liang, Appl. Energy **259**, 114119 (2020)
26. H. Xie, W. Jiang, T. Liu, Y. Wu, Y. Wang, B. Chen, D. Niu, B. Liang, Cell Rep. Phys. Sci. **1**, 100046 (2020)
27. R. Ranjan, J. Olson, P. Singh, E.D. Lorance, D.A. Buttry, I.R. Gould, J. Phys. Chem. Lett. **6**, 4943–4946 (2015)
28. P. Singh, J.H. Rheinhardt, J.Z. Olson, P. Tarakeshwar, V. Mujica, D.A. Buttry, J. Am. Chem. Soc. **139**, 1033–1036 (2017)
29. X. Li, X. Zhao, Y. Liu, T.A. Hatton, Nat Energy **7**, 1065–1075 (2022)
30. R.E. Zeebe, D.A. Wolf-Gladrow, *CO2 in Seawater: Equilibrium, Kinetics, Isotopes, Elsevier Oceanography Series* (Elsevier, Amsterdam, 2001)
31. J.S. Kang, S. Kim, T.A. Hatton, Curr. Opin. Green Sustain. Chem. **31**, 100504 (2021)
32. J.M. Barlow, L.E. Clarke, Z. Zhang, D. Bím, K.M. Ripley, A. Zito, F.R. Brushett, A.N. Alexandrova, J.Y. Yang, Chem. Soc. Rev. **51**, 8415–8433 (2022)
33. K.M. Diederichsen, Y. Liu, N. Ozbek, H. Seo, T.A. Hatton, Joule. **6**, 221–239 (2022)
34. M. Rahimi, A. Khurram, T.A. Hatton, B. Gallant, Chem. Soc. Rev. **51**, 8676–8695 (2022)
35. Y. Liu, É. Lucas, I. Sullivan, X. Li, C. Xiang, iScience **25**, 105153 (2022)
36. B. Gurkan, X. Su, A. Klemm, Y. Kim, S. Mallikarjun Sharada, A. Rodriguez-Katakura, K.J. Kron, iScience **24**, 103422 (2021)
37. F. Simeon, M.C. Stern, K.M. Diederichsen, Y. Liu, H.J. Herzog, T.A. Hatton, J. Phys. Chem. C. **126**, 1389–1399 (2022)
38. Y. Liu, H.-Z. Ye, K.M. Diederichsen, T. Van Voorhis, T.A. Hatton, Nat Commun. **11**, 2278 (2020)
39. S. Khwa Museveni, G. Nakitare Nambafu, N. Kollongei, Mater. Sci. Energy Technol. **6**, 561–566 (2023)
40. C. Schotten, T.P. Nicholls, R.A. Bourne, N. Kapur, B.N. Nguyen, C.E. Willans, Green Chem. **22**, 3358–3375 (2020)
41. Y. Liu, Q. Chen, X. Zhang, J. Ran, X. Han, Z. Yang, T. Xu, Curr. Opin. Electrochem. **32**, 100895 (2022)
42. S. Pang, S. Jin, F. Yang, M. Alberts, L. Li, D. Xi, R. Gordon, P. Wang, M. Aziz, Y. Ji, A phenazine-based high-capacity and high-stability electrochemical CO2 capture cell with coupled electricity storage. Nat Energy (2023). https://doi.org/10.1038/s41560-023-01347-z
43. P. Scovazzo, J. Poshusta, D. DuBois, C. Koval, R. Noble, J. Electrochem. Soc. **150**, D91 (2003)
44. P.S. Guin, S. Das, P.C. Mandal, Int. J. Electrochem. **2011**, 1–22 (2011)
45. A.T. Murray, S. Voskian, M. Schreier, T.A. Hatton, Y. Surendranath, Joule. **3**, 2942–2954 (2019)
46. D. Vasudevan, H. Wendt, J. Electroanal. Chem. **392**, 69–74 (1995)
47. X. Ge, A. Sumboja, D. Wuu, T. An, B. Li, F.W.T. Goh, T.S.A. Hor, Y. Zong, Z. Liu, ACS Catal. **5**, 4643–4667 (2015)
48. J.M. Campos-Martin, G. Blanco-Brieva, J.L.G. Fierro, Angew. Chem. Int. Ed. **45**, 6962–6984 (2006)
49. T. Nishimi, T. Kamachi, K. Kato, T. Kato, K. Yoshizawa, Eur. J. Org. Chem. **2011**, 4113–4120 (2011)
50. Y. Lu, A. Sehrish, R. Manzoor, K. Dong, Y. Jiang, Chem Rep. **1**, 81–101 (2019)
51. X. Wang, Z. Li, Y. Qu, T. Yuan, W. Wang, Y. Wu, Y. Li, Chem. **5**, 1486–1511 (2019)

52. Q. Jia, S. Ghoshal, J. Li, W. Liang, G. Meng, H. Che, S. Zhang, Z.-F. Ma, S. Mukerjee, J. Am. Chem. Soc. **139**, 7893–7903 (2017)
53. Y. Wang, J. Li, Z. Wei, J. Mater. Chem. A **6**, 8194–8209 (2018)
54. K. Wedege, E. Dražević, D. Konya, A. Bentien, Sci Rep. **6**, 39101 (2016)
55. J.M. Saa, J. Morey, C. Rubido, J. Org. Chem. **51**, 4471–4473 (1986)
56. T.M. Penning, Toxicol. Res. **6**, 740–754 (2017)
57. D. Jeziorek, T. Ossowski, A. Liwo, D. Dyl, M. Nowacka, W. Woźnicki, J. Chem. Soc. Perkin Trans. **2**, 229–236 (1997)
58. Y. Hui, E.L.K. Chng, C.Y.L. Chng, H.L. Poh, R.D. Webster, J. Am. Chem. Soc. **131**, 1523–1534 (2009)
59. R.P.-A. Staley, E.M. Lopez, L.A. Clare, D.K. Smith, J. Phys. Chem. C **119**, 20319–20327 (2015)
60. N. Gupta, H. Linschitz, J. Am. Chem. Soc. **119**, 6384–6391 (1997)
61. J.M. Barlow, J.Y. Yang, J. Am. Chem. Soc. **144**, 14161–14169 (2022)
62. D.P. Tabor, R. Gómez-Bombarelli, L. Tong, R.G. Gordon, M.J. Aziz, A. Aspuru-Guzik, J. Mater. Chem. A **7**, 12833–12841 (2019)
63. A.A. Kutyrev, Tetrahedron **47**, 8043–8065 (1991)
64. V.K. Tandon, H.K. Maurya, Tetrahedron Lett. **50**, 5896–5902 (2009)
65. X. Wang, C. Xu, M. Jaroniec, Y. Zheng, S.-Z. Qiao, Nat Commun. **10**, 4876 (2019)
66. Z. Zhou, Z. Pei, L. Wei, S. Zhao, X. Jian, Y. Chen, Energy Environ. Sci. **13**, 3185–3206 (2020)
67. J.C. Fornaciari, L.-C. Weng, S.M. Alia, C. Zhan, T.A. Pham, A.T. Bell, T. Ogitsu, N. Danilovic, A.Z. Weber, Electrochim. Acta **405**, 139810 (2022)
68. J.A. Cisneros, M.J. Robertson, B.Q. Mercado, W.L. Jorgensen, A.C.S. Med. Chem. Lett. **8**, 124–127 (2017)
69. J.D. Watkins, N.S. Siefert, X. Zhou, C.R. Myers, J.R. Kitchin, D.P. Hopkinson, H.B. Nulwala, Energy Fuels **29**, 7508–7515 (2015)
70. C.J. Clarke, W.-C. Tu, O. Levers, A. Bröhl, J.P. Hallett, Chem. Rev. **118**, 747–800 (2018)
71. X. Wang, C. Song, Front. Energy Res. **8**, 560849 (2020)
72. S.E. Zanco, J.-F. Pérez-Calvo, A. Gasós, B. Cordiano, V. Becattini, M. Mazzotti, ACS Eng. Au. **1**, 50–72 (2021)
73. J. Husebye, A.L. Brunsvold, S. Roussanaly, X. Zhang, Energy Procedia. **23**, 381–390 (2012)
74. G.V. Last, M.T. Schmick, *Identification and Selection of Major Carbon Dioxide Stream Compositions* (PNNL-20493, 1019211, 2011). https://doi.org/10.2172/1019211
75. C. Halliday, T.A. Hatton, Ind. Eng. Chem. Res. **60**, 9313–9346 (2021)
76. E.S. Sanz-Pérez, C.R. Murdock, S.A. Didas, C.W. Jones, Chem. Rev. **116**, 11840–11876 (2016)
77. M. Erans, E.S. Sanz-Pérez, D.P. Hanak, Z. Clulow, D.M. Reiner, G.A. Mutch, Energy Environ. Sci. **15**, 1360–1405 (2022)
78. L. Küng, S. Aeschlimann, C. Charalambous, F. McIlwaine, J. Young, N. Shannon, K. Strassel, C. Maesano, R. Kahsar, D. Pike, M. Van Der Spek, S. Garcia, A roadmap for achieving scalable, safe, and low-cost direct air carbon capture and storage. Chemistry (2023). https://doi.org/10.26434/chemrxiv-2023-5f00r-v3
79. R. Atkinson, J. Arey, Chem. Rev. **103**, 4605–4638 (2003)
80. A.T. Bui, N.A. Hartley, A.J.W. Thom, A.C. Forse, J. Phys. Chem. C. **126**, 14163–14172 (2022)
81. A.W. Alherz, H.A. Petersen, N.R. Singstock, S.N. Sur, C.B. Musgrave, O.R. Luca, Energy Adv. **1**, 900–907 (2022)
82. C. Halliday, D. Matthews, Aust. J. Chem. **36**, 507 (1983)
83. J. Ding, C. Zheng, L. Wang, C. Lu, B. Zhang, Y. Chen, M. Li, G. Zhai, X. Zhuang, J. Mater. Chem. A **7**, 23337–23360 (2019)
84. E. Hwang, S. Seo, S. Bak, H. Lee, M. Min, H. Lee, Adv. Mater. **26**, 5129–5136 (2014)
85. A. Trabolsi, N. Khashab, A.C. Fahrenbach, D.C. Friedman, M.T. Colvin, K.K. Cotí, D. Benítez, E. Tkatchouk, J.-C. Olsen, M.E. Belowich, R. Carmielli, H.A. Khatib, W.A. Goddard, M.R. Wasielewski, J.F. Stoddart, Nat. Chem. **2**, 42–49 (2010)
86. T. Janoschka, N. Martin, U. Martin, C. Friebe, S. Morgenstern, H. Hiller, M.D. Hager, U.S. Schubert, Nature **527**, 78–81 (2015)
87. H. Ishida, T. Ohba, T. Yamaguchi, K. Ohkubo, Chem. Lett. **23**, 905–908 (1994)

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.