

Redox-Mediated pH Swing Systems for Electrochemical Carbon Capture

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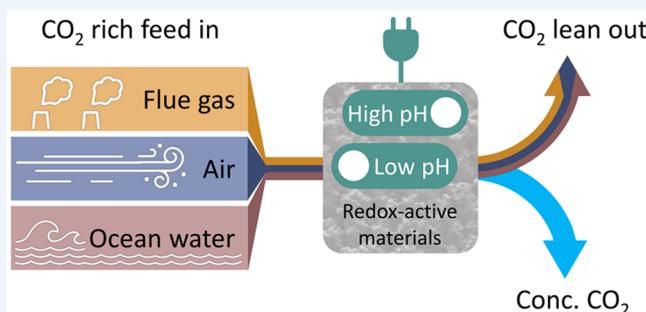
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CONSPICUS: The rising levels of atmospheric CO₂ and their resulting impacts on the climate have necessitated the urgent development of effective carbon capture technologies. Electrochemical carbon capture systems have emerged as a potential alternative to conventional thermal systems based on amine solutions due to their modularity, energy efficiency, and lower environmental impact. Among these, aqueous electrochemical pH swing systems that capitalize on the pH dependence of dissolved inorganic carbon (CO₂/HCO₃⁻/CO₃²⁻) speciation to capture and release CO₂ are of particular interest as they can be flexible in system design and in the range of electrochemical potentials used as well as being environmentally benign. In this Account, we present our recent findings in pH swing-based electrochemical carbon capture using redox-active materials, paving the way toward a sustainable solution for mitigating CO₂ emissions.

In the first section, we discuss the utilization of molecular redox-active organic materials in electrochemical carbon capture by the pH swing method. This electrochemical system configuration involves homogeneous aqueous electrolytes containing molecular redox-active compounds combined with inert carbon-based electrodes. We first present the development of redox-active amine and oxygen-insensitive neutral red (NR)-based systems. Notably, the discovery of 1-aminopyridinium (1-AP) as an electrochemically reversible compound enables efficient pH swing, leading to an impressive electron utilization of 1.25 mol of CO₂ per mole of electrons. Additionally, we explore an oxygen-insensitive neutral red/leuconeutral red (NR/NRH₂) redox system, which demonstrates potential applicability to direct air capture (DAC) systems with ambient air as a feed gas.

The second section focuses on the utilization of inorganic nanomaterials for redox-active electrodes for pH swing-based electrochemical carbon capture. In this system configuration, we employ redox-active electrodes for inducing reversible pH swings in aqueous electrolytes without interrupting other ionic species, except protons. Specifically, we explore the effectiveness of manganese oxide (MnO₂) electrodes for achieving selective CO₂ removal from simulated flue gas. We then demonstrate a bismuth/silver (Bi/BiOCl, Ag/AgCl) nanoparticle electrode system as a sodium-insensitive pH swing system for extracting dissolved inorganic carbon (DIC) from simulated seawater with high electrochemical energy efficiency.

Overall, these advances in pH swing-based electrochemical carbon capture offer promising preliminary solutions for combating climate change by capturing CO₂ from dilute sources such as flue gas and ambient air as well as enabling direct carbon removal from ocean water. While these systems have demonstrated impressive energy efficiency and environmental benefits using redox-active materials, they represent only the beginning of our research journey. Further development and optimization are currently underway as we strive to unlock their full potential for large-scale implementation, paving the way toward a sustainable and carbon-neutral future.



KEY REFERENCES

- Seo, H.; Rahimi, M.; Hatton, T. A. Electrochemical Carbon Dioxide Capture and Release with a Redox-Active Amine. *J. Am. Chem. Soc.* 2022, 144, 2164–2170.¹
This article explores pH swing for electrochemical

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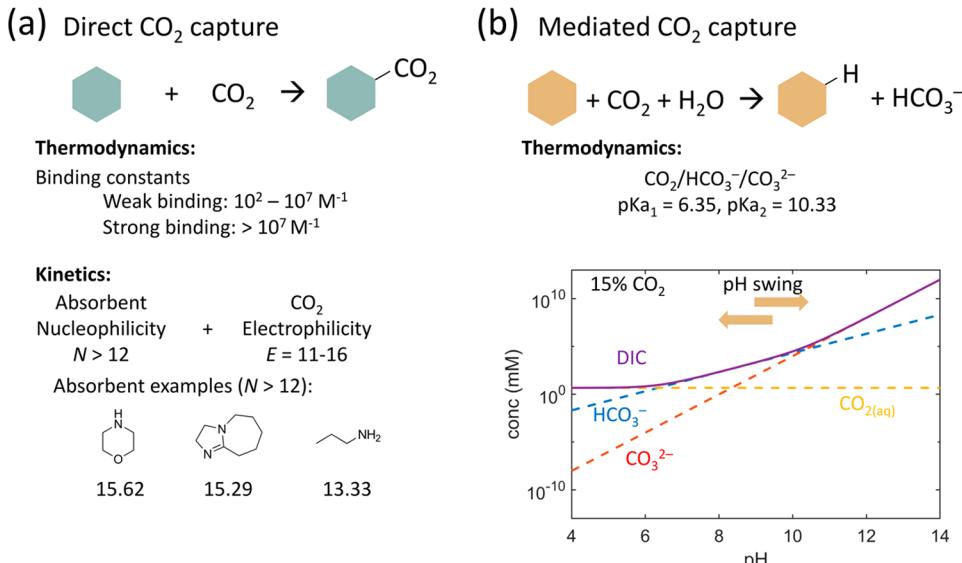


Figure 1. Direct and mediated CO_2 capture. (a) Direct CO_2 capture. E , electrophilicity parameters; N , nucleophilicity parameters. (b) Mediated CO_2 capture.

- carbon capture by exploitation of a redox-active amine in an aqueous solution.
- Seo, H.; Hatton, T. A. Electrochemical Direct Air Capture of CO_2 Using Neutral Red as Reversible Redox-Active Material. *Nat. Commun.* **2023**, *14*, 313.² This organic redox-active material shows an efficient electrochemical pH swing in a range of 7–12 with a great stability under ambient air. Electrochemical direct air capture was demonstrated.
 - Rahimi, M.; Catalini, G.; Puccini, M.; Hatton, T. A. Bench-Scale Demonstration of CO_2 Capture with an Electrochemically Driven Proton Concentration Process. *RSC Adv.* **2020**, *10*, 16832–16843.³ This inorganic redox-active material demonstrated an electrochemical pH swing in the presence of a bicarbonate buffer system as an absorbent for treating simulated flue gas.
 - Kim, S.; Nitzsche, M. P.; Rufer, S. B.; Lake, J. R.; Varanasi, K. K.; Hatton, T. A. Asymmetric Chloride-Mediated Electrochemical Process for CO_2 Removal from Oceanwater. *Energy Environ. Sci.* **2023**, *16*, 2030–2044.⁴ This membrane-free electrochemical two-cell system utilized bismuth and silver as inorganic redox-active materials. Proton concentration was efficiently modulated along with chlorine. Direct ocean capture was demonstrated.

1. INTRODUCTION

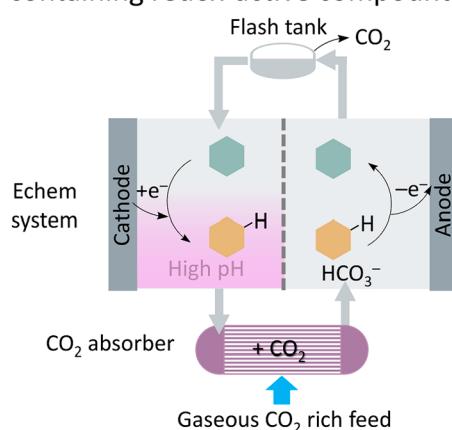
The IPCC report has unequivocally established the relationship between climate change and atmospheric CO_2 levels.⁵ By 2022, the concentration of CO_2 in the atmosphere had soared to 421 ppm, exceeding preindustrial levels by over 50%, with annual global CO_2 emissions totaling 36 billion tons. To counteract this alarming trajectory, carbon capture, utilization, and storage (CCUS) technologies have become essential in the overall drive for net-neutrality.⁶ CCUS technologies serve two important functions: point-of-emission carbon capture can be employed to leverage existing fossil fuel infrastructures while mitigating their associated greenhouse gas emissions, and ambient carbon capture systems can serve to lower CO_2

concentrations in the oceans and atmosphere. Both approaches capture CO_2 from dilute sources and release a concentrated CO_2 stream for sequestration, industrial utilization, or conversion to value-added products. To limit global warming to 2 °C, the 2022 IPCC scenarios call for a gigaton of installed capacity by 2050, emphasizing the urgency of developing and implementing these technologies.⁵

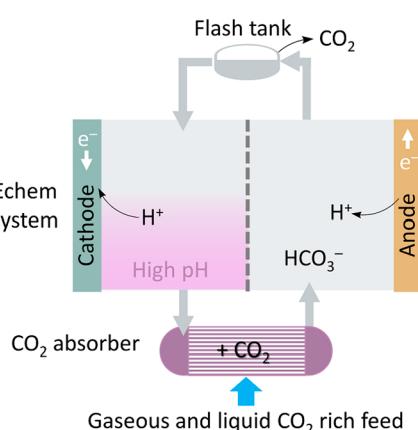
Conventional carbon capture systems, typically employing thermal swing processes utilizing aqueous amine solutions, face techno-economic challenges due to high energy requirements for thermal regeneration and absorbent replacement costs.^{8,9} Comprehensive comparisons in energetics are summarized in previous review articles.^{10–12} Furthermore, environmental impacts pose significant challenges, including the volatility of amines¹³ upon CO_2 contact and the disposal of waste generated in repeated use.^{14,15} In contrast, electrochemical carbon capture, featuring isothermal operation and nonvolatile redox-active materials, offers a promising alternative.^{10,16}

Early studies demonstrated the use of quinone derivatives in electrochemical systems in organic solvents.^{17–19} Later, aqueous systems, including the development of electrochemical-mediated amine regeneration (EMAR) developed by our laboratory in 2013, played a significant role in advancing this field.^{20–22} Recent investigations have centered on redox-active materials for pH swing,^{23,24} including our group's research endeavors.^{1–3,25} In this Account, we describe our scientific journey on pH swing-based electrochemical carbon capture systems using organic and inorganic redox-active materials in aqueous electrolytes. While this Account primarily highlights our recent work, we acknowledge and appreciate the remarkable contributions of other researchers in this field. For instance, Aziz, Kwabi, and co-workers have made significant strides in developing phenazine compounds for electrochemical pH swing carbon capture.^{23,26} Additionally, Atwater,²⁷ Eisaman,^{28,29} and Vermaas³⁰ have independently explored alternative approaches utilizing bipolar membrane electrodialysis (BPMED) systems. Their valuable research has contributed to the diverse landscape of pH swings for electrochemical carbon capture, distinct from our own

(a) Homogeneous aqueous electrolytes containing redox-active compound



(b) Water insoluble redox-active electrodes



(c)

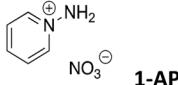
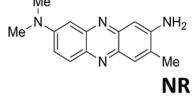
Echem cell type	Redox-active Materials	Energetics (kJ _e /mol)	Feed source	Geometric current density	Cycles demonstrated	Limitations observed
a	 1-AP	101 ^a	Simulated flue gas ^d	N/A in flow cell	5	• Large energy • Molecular stability
a	 NR	65 ^a	In house air	7.1 mA/cm ²	20	• Limited solubility • Limited current density • Electrolyte integrity
b	 MnO₂	33 ^b	Simulated flue gas ^d , 50 °C	c.a. 0.15 mA/cm ²	4	• Limited range of pH-swing • Electrode capacity
b	 Bi	122 ^c	Simulated ocean water ^e	0.125 mA/cm ²	10	• Cost of electrodes • Electrode capacity • Sluggish kinetics

Figure 2. Electrochemical systems and redox-active materials for pH swing in CO₂ capture studies. (a) Schematic illustration of an electrochemical setup utilizing homogeneous aqueous electrolytes containing molecular redox-active organic materials. (b) Schematic illustration of an electrochemical setup employing water-insoluble redox-active electrodes. (c) Summary of organic and inorganic redox-active materials employed for electrochemical pH swing. ^aEstimated energy consumption based on the redox potential gap obtained in cyclic voltammetry (CV) and electron utilization values. ^bEstimated energy consumption based on the simulated potential distribution. ^cCalculated based on the cell potential obtained during operation. ^d15% CO₂ balanced by nitrogen (N₂). ^e0.5 M sodium chloride (NaCl) and 2.5 mM sodium bicarbonate (NaHCO₃) in water. Reproduced with permission from ref 3. Copyright 2020 Rahimi et al., some rights reserved; exclusive licensee Royal Society of Chemistry. Distributed under a Creative Commons Attribution License 4.0 (CC BY) <https://creativecommons.org/licenses/by/4.0/>. Reproduced with permission from ref 4. Copyright 2023 Kim et al., some rights reserved; exclusive licensee Royal Society of Chemistry. Distributed under a Creative Commons Attribution License 4.0 (CC BY) <https://creativecommons.org/licenses/by/4.0/>.

investigations, enriching the possibilities for mitigating atmospheric CO₂ levels.

Despite CO₂'s thermodynamic stability and kinetic challenges, its electrophilicity and acidity allow for capture by suitable nucleophiles and bases. The direct CO₂ capture pathway involves the formation of a covalent bond between an absorber and CO₂ (Figure 1a). The reversibility of the CO₂-absorber reaction necessitates the consideration of binding constants as a measure of thermodynamic factors. Our recent studies on the structure–binding relationship of quinone derivatives and CO₂ revealed weak binding with constants

ranging from 10² to 10⁷ M⁻¹, while strong binding requires constants larger than 10⁷ M⁻¹.³¹ Kinetic rate constants, representing CO₂ absorption rates by aqueous monoethanolamine solutions, vary in a range of 5400–90400 dm³ mol⁻¹ s⁻¹, depending on experimental conditions.³² However, accurate measurement of kinetic rate constants demands specialized techniques such as the stopped flow method within the millisecond time frame of CO₂ binding. Alternatively, insight into kinetics can be obtained through general electrophilicity and nucleophilicity scales established by Mayr and co-workers.³³ Electrophilicity parameters for CO₂, as calculated

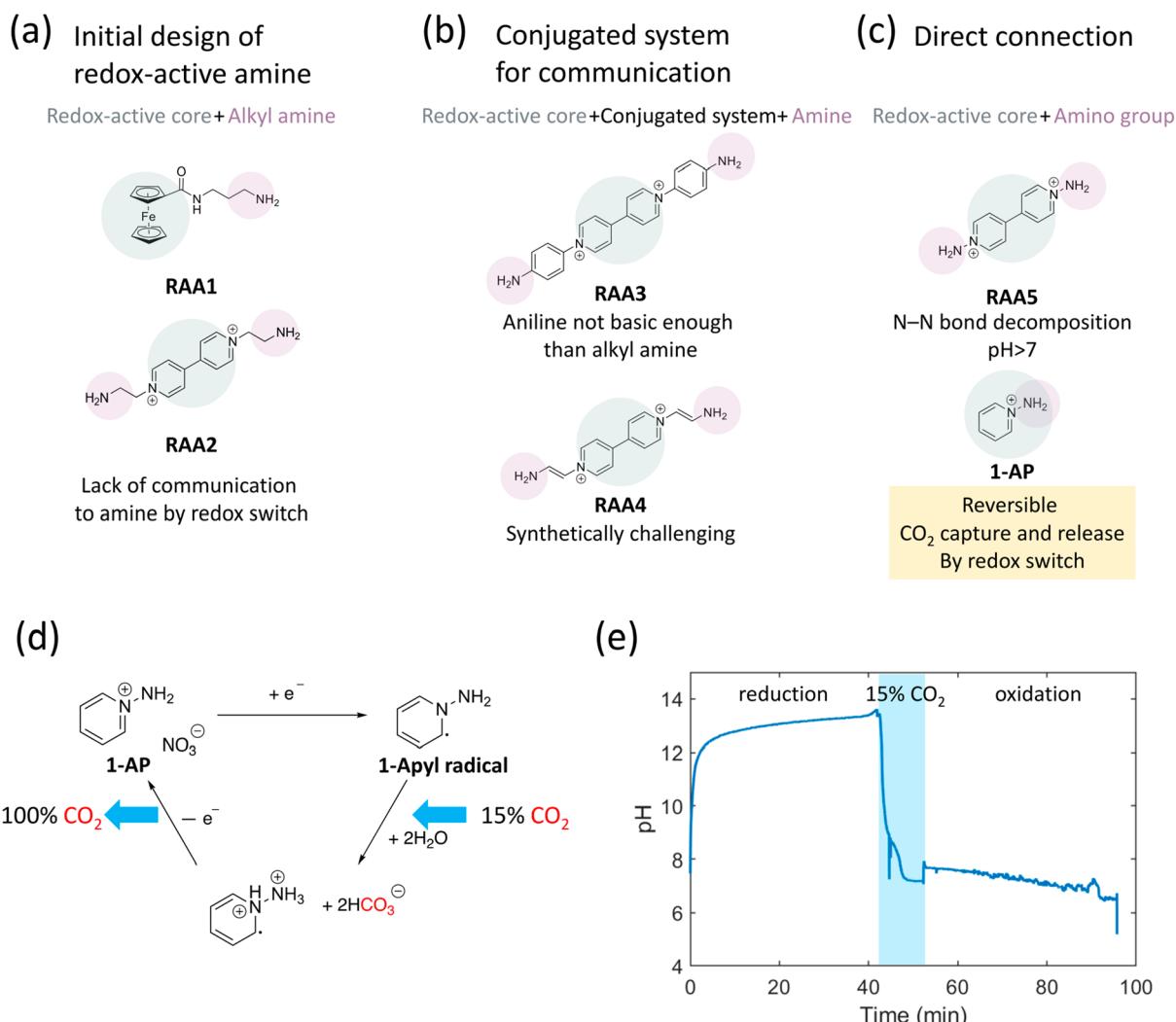


Figure 3. Development of a redox-active amine and its application for electrochemical CO₂ capture using pH swing in an aqueous electrolyte. (a) Design of redox-active amines with initial combination strategies. (b) Incorporation of a conjugated system for enhanced connection between the redox-active core and the amine moiety. (c) Direct attachment of the amino group onto the redox-active core. (d) Electrochemical working scheme illustrating the 1-AP/1-Apyl radical redox cycle. (e) pH profile depicting the changes during the electrochemical cycle of CO₂ capture and release.

by Mayr and colleagues, range from 11 to 16 (DFT calculation = 11; experimental = 16),³⁴ and it is widely acknowledged that CO₂ can react with a nucleophile possessing a nucleophilicity parameter of 12 or higher. Noteworthy established CO₂ absorbents, such as propylamine,³⁵ morpholine,³⁶ and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU),³⁷ possess nucleophilicity parameters exceeding 13. Conversely, weak nucleophiles like pyridine³⁸ exhibit nucleophilicity parameters lower than 11.

Mediated CO₂ capture, specifically the pH swing method utilizing water, relies on the manipulation of dissolved inorganic carbon (DIC) concentrations in water through pH swings based on the thermodynamic equilibrium of CO₂/HCO₃⁻/CO₃²⁻ (Figure 1b). This equilibrium is governed by the pK_a values of CO₂/HCO₃⁻ (pK_a = 6.35) and HCO₃⁻/CO₃²⁻ (pK_a = 10.33). Figure 1b illustrates the concentrations of DIC, CO₂(aq), HCO₃⁻, and CO₃²⁻ under simulated flue gas conditions in equilibrium with 15% CO₂. The DIC remains relatively constant at pH values below 6, limited to that of CO₂(aq) in equilibrium by Henry's law. Beyond pH 6, HCO₃⁻ and CO₃²⁻ become abundant, leading to an exponential

increase in total DIC. The change in DIC indicates that alkaline solutions can be used to capture CO₂, and lowering the pH triggers CO₂ release. By cycling through the pH swing process, concentrated CO₂ can be effectively separated from the dilute source.

We explored two distinct electrochemical pH swing systems. First, we developed an electrochemical setup using homogeneous aqueous electrolytes containing molecular redox-active materials (Figure 2a). In this configuration, inert carbon-based electrodes were employed, and the redox-active compounds dissolved in the electrolyte underwent electrochemical modulation. Within the cathodic compartment of the cell, the redox-active compound was subjected to electrochemical reduction and protonation, leading to an increase in solution pH. The resulting alkaline electrolytes were exposed to dilute gaseous CO₂, capturing CO₂ as bicarbonate/carbonate ions. Subsequently, the solution underwent electrochemical oxidation to release concentrated CO₂ and regenerate the redox-active compound, completing the cycle. This type of electrochemical setup employed molecular organic materials,

such as 1-aminopyridinium (1-AP)¹ and neutral red (NR),² in our investigations.

Second, in **Figure 2b**, we constructed an electrochemical setup utilizing water-insoluble redox-active electrodes and investigated the pH swings of aqueous electrolytes. In the cathodic compartment of the cell, the electrode was electrochemically reduced, leading to an increase in solution pH, which facilitated the capture of CO₂ from diluted sources. Subsequently, the CO₂-saturated solution was acidified through electrochemical oxidation of the electrode, releasing concentrated CO₂ and regenerating the solution pH. Notably, this setup allowed for the utilization of both gaseous and liquid CO₂ sources as cyclic operation of the redox-active materials did not contaminate the electrolytes. Inorganic solid materials, such as manganese oxide (MnO₂)^{3,25} and bismuth (Bi),⁴ were employed to construct this electrochemical system architecture in our investigations.

In **Figure 2c**, a table summarizes the four different systems discussed in this Account. This table provides a concise overview of key details for each system, including energetics, feed source, current density, demonstrated cycles, and observed limitations. These details are discussed in greater depth in sections 2 and 3.

2. MOLECULAR REDOX-ACTIVE ORGANIC MATERIALS

2.1. Redox-Active Amine

Our group has developed various electrochemical CO₂ capture and release technologies such as the EMAR system involving Cu(0)/Cu(II) redox cycles.^{20–22} This cyclic process requires periodic voltage polarity reversals and switching of the flows to the two chambers in the electrochemical cell. We recognized that the development of a redox-active amine cycle is desirable to enable a homogeneous continuous flow system for scalability. In this regard, we designed a novel redox-active amine and demonstrated a reversible CO₂ capture and release in an aqueous electrolyte.¹

To develop a redox-active amine, we initially explored the attachment of alkyl amines to well-established redox-active cores such as ferrocene (RAA1) and bipyridine (RAA2) (**Figure 3a**). However, we observed that the amine's interaction with CO₂ was not effectively controlled by the redox switch. This led us to conclude that the lack of effective communication between the amine and the redox-active core, bridged solely by saturated C–C bonds, hindered the desired effect. Subsequently, we designed redox-active amines with unsaturated systems connecting the amine and redox core, including aniline (RAA3) and vinyl amine (RAA4) (**Figure 3b**). However, aniline was found to be insufficiently basic/nucleophilic to capture CO₂, and obtaining enough vinyl amine for electrochemical analysis posed significant synthetic challenges. In the final set of redox-active amines, we explored the direct attachment of the amino group to the redox-active core (**Figure 3c**). The attachment of the amino group to the N atoms on bipyridine (RAA5) proved to be stable only under acidic pH conditions, as N–N bond decomposition was observed at pH values higher than 7. Later, we discovered the stability and redox activity of 1-aminopyridinium (1-AP) in water. The 1-AP/1-aminopyridinyl (1-APyl) radical redox cycle exhibited solution pH swing through electrochemical potential, allowing for CO₂ capture and release.

The electrochemical working scheme is depicted in **Figure 3d**. 1-AP undergoes single-electron reduction, providing the 1-APyl radical, which exhibits increased electron density in the pyridine ring and enhanced basicity. The amino group can be protonated and the solution pH increases, enabling CO₂ capture as bicarbonate/carbonate ions. Subsequently, the solution containing the 1-APyl radical is subjected to electrochemical oxidation, leading to CO₂ release and 1-AP regeneration, completing the cycle.

In situ pH measurements were conducted to monitor the solution during this process (**Figure 3e**). The pH of the solution containing 200 mM 1-AP increased to 13 upon electrochemical reduction, indicating the strong basic character of the reduced 1-APyl radical. The estimated pK_{a2} value is 25.8, assuming that pK_{a1} is significantly lower than pK_{a2}. Notably, this pK_{a2} value significantly exceeds those of typical primary amines (ethylenediamine pK_a = 10.7; monoethanolamine pK_a = 9.5). Saturation with 15% CO₂ (balanced by N₂) led to a pH drop to 7, and after electrochemical oxidation, the pH remained around 7, thereby completing this electrochemical pH swing cycle.

The batch H-cell cyclic experiment encompassing five cycles using 200 mM 1-AP solution demonstrated a high electron utilization, reaching up to 1.25 mol of CO₂ per mole of electrons, enabled by the capture of two CO₂ molecules per amine in an aqueous solution. The energy input required was estimated to be 101 kJ_e/mol of CO₂, based on the redox peak potential gap (1.32 V) obtained in CV and an electron utilization value of up to 1.25. The electron utilization value was calculated based on the amount of CO₂ released in a H-cell, monitored by an FTIR CO₂ sensor and a mass-flow meter (MFM). Detailed information on the estimation of energy consumption can be found in the Supporting Information of ref 1. The 1-APyl radical compound exhibited notable stability at room temperature, and its resilience toward oxygen was also suggested. When directly capturing CO₂ from ambient air as the feed gas, an electron utilization of 0.78 was achieved, requiring 162 kJ_e/mol of CO₂ for DAC, approaching the target energy consumption (400 kJ/mol, equivalent to 120 kJ/mol with a Carnot efficiency of 0.3) for DAC technologies.³⁹

While our research has shown promising results, it has also uncovered certain limitations. We have encountered challenges related to the substantial potential gap required for the redox process and the stability of the molecular compounds used. Specifically, we observed N–N bond cleavage and subsequent dimerization occurring at the gas–liquid interface of the electrolytes. Our hypothesis suggests that adequate water solvation is pivotal in stabilizing these radical species. Conversely, insufficient solvation, particularly in scenarios involving constant surface water evaporation during gas bubbling, compromises the molecular integrity, causing decomposition. Our ongoing research is directed toward addressing these limitations through molecular engineering, investigating the molecular stability under various conditions, thereby improving the energetics and lifetime of the system.

2.2. DAC Using an Oxygen-Stable Redox-Active Neutral Red

In our pursuit of novel redox-active materials for electrochemical CO₂ capture, we recently developed an oxygen-stable neutral red/leuco-neutral red (NR/NR_{H2}) redox system specifically designed for DAC using pH swing in an aqueous electrolyte.² Oxygen sensitivity has been a persistent challenge

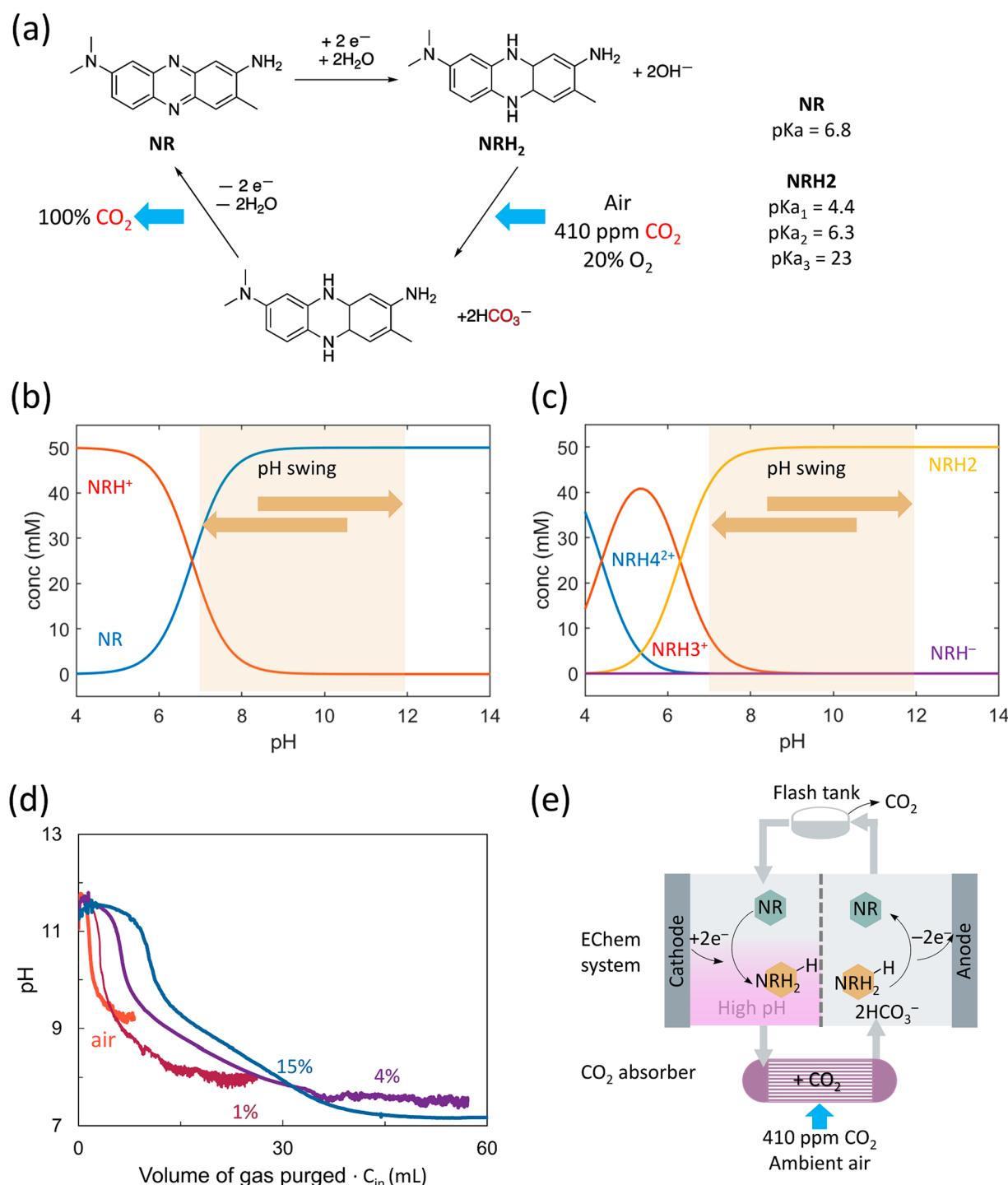


Figure 4. DAC via pH swing using the NR/NRH₂ redox cycle as an oxygen-insensitive redox-active material. (a) Electrochemical working scheme of NR in water. pK_a values of the oxidized form and reduced form are presented. (b) NR and the protonated form NRH equilibrium by pH. (c) NRH₂ and the protonated forms equilibrium by pH. (d) pH profile during contact with the CO₂ feed. Reproduced with permission from ref 2. Copyright 2023 Seo et al., some rights reserved; exclusive licensee Springer Nature. Distributed under a Creative Commons Attribution License 4.0 (CC BY) <https://creativecommons.org/licenses/by/4.0/>. (e) Schematic illustration of electrochemical setup using the NR/NRH₂ redox system for DAC.

in numerous electrochemical systems, including electrochemical carbon capture,^{31,40,41} as it leads to the oxidation of the activated absorber, resulting in reduced system efficiency. This issue arises due to the inherently negative potential required to activate an absorber for binding CO₂.³¹ The single-electron reduction of an oxygen molecule necessitates

−1.16 V⁴² vs Fc/Fc⁺ in DMSO and −0.385 V vs Ag/AgCl in water at pH 7.⁴³ In this regard, any redox-active material that requires more negative potentials than those is thermodynamically susceptible to oxidation by oxygen.

To overcome this obstacle, we focused on developing a pH swing process for DAC, which typically requires less negative

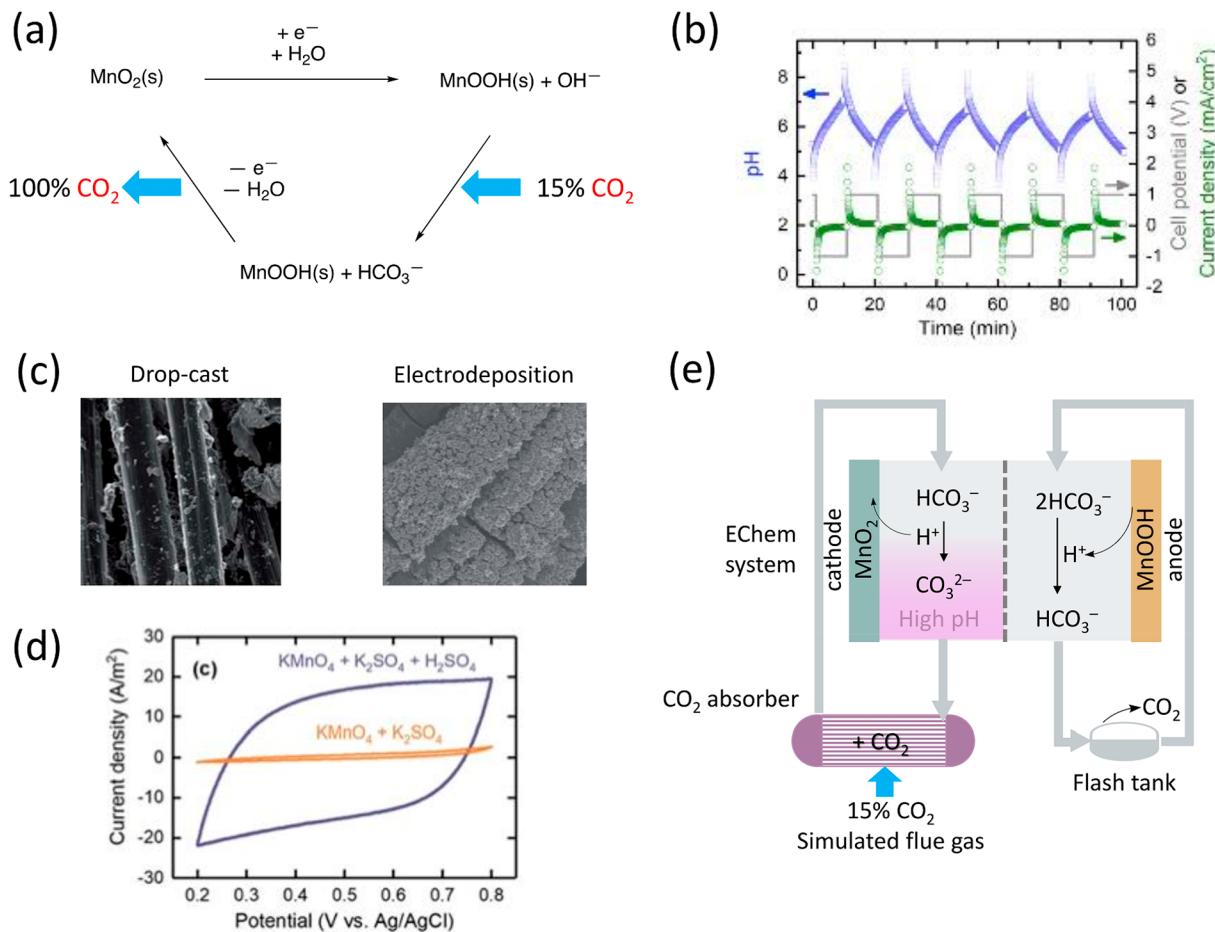


Figure 5. Electrochemical CO_2 capture using the $\text{MnO}_2/\text{MnOOH}$ redox cycle. (a) Electrochemical working scheme of the $\text{MnO}_2/\text{MnOOH}$ redox cycle. (b) Solution pH (blue) and current density (green) of a symmetrical cell with MnO_2 electrodes cast on to carbon felt. Reproduced with permission from ref 25. Copyright 2020 Elsevier. (c) SEM images of electrodes prepared by coprecipitation followed by casting (left) and cathodic electrodeposition (right). Reproduced with permission from ref 3. Copyright 2020 Rahimi et al., some rights reserved; exclusive licensee Royal Society of Chemistry. Distributed under a Creative Commons Attribution License 4.0 (CC BY) <https://creativecommons.org/licenses/by/4.0/>. (d) CV of the electrodeposited electrodes prepared by cathodic electrodeposition. Reproduced with permission from ref 3. Copyright Rahimi et al., some rights reserved; exclusive licensee Royal Society of Chemistry. Distributed under a Creative Commons Attribution License 4.0 (CC BY) <https://creativecommons.org/licenses/by/4.0/>. (e) Schematic illustration of electrochemical CO_2 capture setup using the $\text{MnO}_2/\text{MnOOH}$ redox system.

potentials than direct CO_2 binding and thus has a higher likelihood of remaining stable under air conditions. By employing mild negative potentials and strategically switching the pH, we find that CO_2 capture becomes viable despite potentially diminished electron utilization. Initially, our project aimed to identify an oxygen-stable redox-active compound through an extensive survey of commercial redox-active compounds featuring phenazine, phenothiazine, and phenoxazine moieties, which led to the identification of a suitable candidate, neutral red (NR).

As depicted in the electrochemical working scheme in Figure 4a, NR undergoes a two-electron, two-proton reduction in an aqueous electrolyte. The transfer of electrons and protons occurs in a stepwise manner.⁴⁴ CV results obtained under varying pH conditions align well with the previously reported H-e-e-H mechanism for electron and proton transfer. Once NRH_2 is formed, the increased pH facilitates the capture of CO_2 from the diluted source. The electrochemical system was tested using simulated flue gas (15% CO_2 , balanced by N_2) and ambient air. Subsequent electrochemical oxidation resulted in

the release of concentrated CO_2 , accompanied by NR regeneration, thereby completing the cycle.

Due to the presence of four basic nitrogen atoms in the molecule, NR and NRH_2 exhibit multiple protonation states, with known pK_a values except for pK_{a3} of NRH_2 .⁴⁵ The estimation of the pK_{a3} value was accomplished by analyzing the pH values during the electrochemical reduction of NR. Protonated NR (NRH^+) and NR exist in equilibrium, with a pK_a value of 6.8 (Figure 4b). This implies that, at the beginning pH of the cycle (pH 7), NR and NRH^+ are present in approximately equal amounts. However, as the solution pH increases to 12 during electrochemical reduction, a majority of NR exists in its deprotonated form for the remainder of the reduction period. This pH-dependent equilibrium switch during reduction significantly impacts the kinetics of the electrochemical reduction step, particularly involving protonation as the initial step.⁴⁴ Consequently, this can result in slower electrochemical kinetics during the reduction step, limiting achievable current densities within the water stability window.

Once the electrochemical reduction step is complete, NRH_2 becomes the predominant species within a pH range higher than 8. On saturation with CO_2 , the pH drops below 8, and NRH_2 can undergo further protonation to form NRH_3^+ . This additional protonation generates extra hydroxide ions, enhancing the capacity for the CO_2 capture. Experimental pH values obtained for a 50 mM NRH_2 solution saturated under varying CO_2 percentages (balanced by N_2) are presented in Figure 4d. At 15% CO_2 , the pH was measured to be 7.1; at 4% CO_2 , it was 7.4; at 1% CO_2 , it was 8.0; and in air, it reached 9.2. The high capture capacity (moles of CO_2 per moles of NR) of 1.56 observed under 15% CO_2 conditions is partly attributed to the equilibrium pH values at 7.1, which influences the NRH_2 protonation to NRH_3^+ .

A continuous flow system was implemented to achieve continuous treatment of a CO_2 -rich feed stream (Figure 4e). The system consists of an electrochemical cell and a CO_2 absorber. The estimated minimum electrochemical energy requirements range from 35 kJ/mol when utilizing a 15% CO_2 (balanced by N_2) feed to 65 kJ/mol when using air. The output gas was monitored by a FTIR CO_2 sensor for the quality and MFM for the quantity. Experimental results were obtained by bubbling CO_2 into a 30 mL catholyte solution at a flow rate of about 1000 mL/min during the DAC demonstration. While we have achieved 96 h of stable operation with ambient air as the feed, we plan to enhance the CO_2 absorber to combat issues like catholyte splashing and water evaporation due to the rapid air feed rate. Our ongoing efforts involve implementing a hollow fiber contactor within the CO_2 absorber,⁴⁶ aiming to boost absorption kinetics and reduce potential degradation from the bubbling process, ultimately improving system performance and longevity.

3. INORGANIC REDOX-ACTIVE ELECTRODES

3.1. MnO_2 Nanoparticles

In addition to investigating molecular redox-active organic compounds for homogeneous aqueous electrolytes, we studied water-insoluble inorganic redox-active electrodes for the pH swing process in electrochemical carbon capture. This strategy enabled us to control and reverse solution pH by electrochemical modulation of the electrodes themselves and not of the solution components, allowing for the cyclic CO_2 capture and release in a noninvasive way. Our initial progress in this area was achieved through the utilization of MnO_2 and its reduced form, manganese oxyhydroxide (MnOOH), as electrodes.^{3,25}

The electrochemical working scheme is illustrated in Figure 5a. MnO_2 undergoes electrochemical reduction accompanied by proton intercalation to form MnOOH , exhibiting a proton intercalation efficiency of 0.7 (moles of proton intercalated per mole of electron). The remaining 0.3 mol of electrons are likely reducing interior MnO_2 that is inaccessible due to the slow diffusion of protons in MnO_2 —higher electron utilizations have been achieved in the literature, but at the expense of dramatically decreased MnO_2 loading and capacity.⁴⁷ As a result of the reduced proton concentration in the solution, the pH increases, facilitating the CO_2 capture. Subsequently, the solution undergoes electrochemical oxidation to release CO_2 while regenerating MnO_2 .

We successfully achieved reversible pH swings of between 5 and 7 through electrochemical means using an MnO_2 -based electrode prepared via coprecipitation and casting, despite the

initially low current density and limited electrode capacity (Figure 5b). To enhance electrode fabrication, we employed an electrodeposition technique, resulting in a uniform and thick layer of MnO_2 on a carbon felt electrode, as revealed in the SEM images (Figure 5c). The addition of 0.01 M sulfuric acid facilitated cathodic electrodeposition as the acidic environment promoted the reduction of MnO_4^- to MnO_2 . The pseudocapacitive behavior of the electrodes was evaluated through CV, confirming that the electrode fabricated with an acidified KMnO_4 solution exhibited a rectangular shape, indicative of favorable pseudocapacitive behavior and its suitability for proton intercalation/deintercalation reactions. Conversely, the electrode fabricated without acid showed significantly lower current densities, highlighting the significance of acidification to enhance the pseudocapacitive behavior of the electrodeposited electrodes. The system features MnO_2 as the cathode and MnOOH as the anode, with a circulating aqueous solution of potassium chloride, potassium carbonate buffer, and 3% glycine, which was introduced as an absorption promoter (Figure 5e). In the cathode compartment, MnO_2 undergoes electrochemical reduction to MnOOH , accompanied by proton intercalation, which alkalinizes the electrolyte, enabling the capture of CO_2 from the CO_2 absorber. Once the reduction step is complete, the cyclic system switches polarity to oxidize MnOOH back to MnO_2 , releasing protons in the electrolyte. This pH reduction step results in lower DIC levels in the electrolytes, facilitating the separation of gaseous CO_2 from the flash tank. This system demonstrated the separation of CO_2 with a simulated 33 kJ/mol of CO_2 of electrochemical work from a simulated flue gas stream containing 15% CO_2 (balanced by N_2), with the estimation of the amount of CO_2 released based on the pH change of the catholyte.

3.2. Direct Ocean Capture Using Bismuth Nanoparticles

pH swings mediated by inorganic redox-active electrodes require cyclic uptake and release of ions, so the separations they drive are inherently nonintrusive: they can be used for selective removal of DIC without permanently altering the makeup of the other electrolyte species. For this reason, pH swing processes are strong candidates for applications in direct ocean capture (DOC), where selective removal of only DIC species is desired. Approximately 25% of anthropogenic CO_2 emissions are ultimately absorbed by the world's oceans, acidifying the water and harming marine life.⁴⁸ Processes selectively removing DIC from ocean water aim to reverse this process, with subsequent reuptake of atmospheric CO_2 resulting in a net reduction in environmental CO_2 concentrations. Processes for removing CO_2 from seawater via pH swing have been demonstrated in using electrodeionization⁴⁹ and electrodialysis,^{27–29,50} but prior to our work, it had not been achieved with capacitive electrodes. By developing electrodes suitable for an oceanic pH swing, we aimed to enable a system leveraging the high volumetric concentrations of DIC in seawater (100 mg/L) for ambient CO_2 removal without addition of chemicals.^{51,52}

The pH swing system utilizing MnO_2 nanoparticle electrodes described in the above section requires potassium-based supporting salts for the proton intercalation step.^{3,25} The cation intercalation sites generated during MnO_2 reduction exclude potassium ions but are insufficiently selective for protons over the sodium ions found in abundance in seawater (~0.5 M); therefore, MnO_2 electrodes as developed cannot be

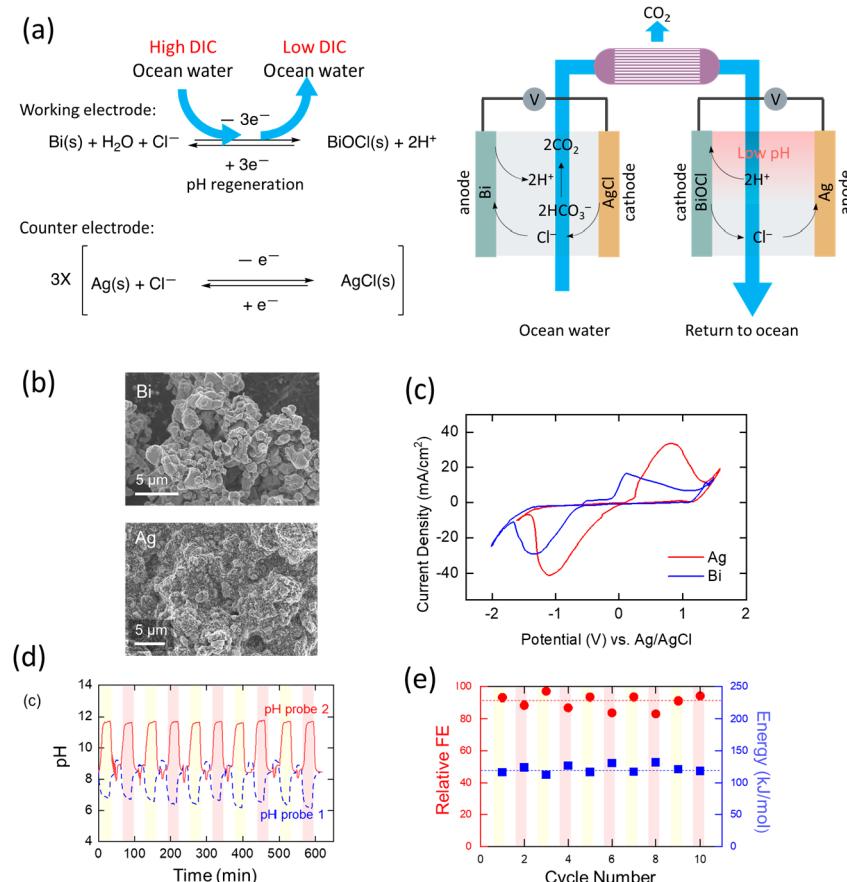
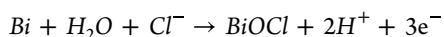


Figure 6. Electrochemical CO₂ removal from seawater using an asymmetric bismuth/silver cell. (a) Schematic of the DOC system and working mechanism. (b) SEM images of the bismuth and silver nanoparticle electrodes. (c) CV of silver and bismuth electrodes. (d) System performance over repeated cycles. (e) Corresponding energetics and faradaic efficiency. Reproduced with permission from ref 4. Copyright Kim et al., some rights reserved; exclusive licensee Royal Society of Chemistry. Distributed under a Creative Commons Attribution License 4.0 (CC BY) <https://creativecommons.org/licenses/by/4.0/>.

directly employed for seawater pH swings. Rather than relying on selective intercalation or ion exchange of protons, we instead employed bismuth nanoparticles to split water through the electrochemical formation of bismuth oxychloride (BiOCl):⁵³



We paired this electrode with a silver/silver chloride counter electrode in a two-cell system, sequentially acidifying and alkalinizing through discharge/charge with periodic alternations of the flow direction. The high selectivity of the Ag electrode for Cl⁻ ions precludes potential parasitic proton intercalation, which can potentially afflict cation storage electrodes intended to capture sodium ions. The working principle of the chloride-mediated pH swing system is illustrated in Figure 6a. In the initial stage, the Bi/AgCl battery is discharged, introducing HCl to lower the pH. Once sufficient protons have been added to lower the total DIC at pH ≈ 6, the dissolved-gas-phase CO₂ can then be removed via vacuum degassing in a membrane contactor. The DIC-lean seawater is then realkalized with an equal removal of HCl to recharge the second BiOCl/Ag battery—the reduced buffering capacity due to DIC removal from the simulated seawater yields a more strongly alkaline effluent that can now draw down atmospheric CO₂.

For a bench-scale demonstration, electrodes were fabricated by ball-milling Bi or Ag with conductive carbon and blade

coating a suspended slurry, resulting in the high-surface area morphology shown in the SEM images displayed in Figure 6b. The CV in Figure 6c indicates good cyclability, but significant overpotentials for bismuth oxychloride reduction are evidenced by the 450 mV gap between the two characteristic arcs (peaking at 0.125 and -1.34 V vs Ag/AgCl, with respective apparent onset potentials at -0.15 and -0.55 V). This kinetic sluggishness is attributed to the low activity of protons at near-neutral pH values.⁵³ The assembled electrochemical system showed excellent performance with simulated seawater (NaCl and NaHCO₃ only). By swinging between pH values of 6–11 (Figure 6d), CO₂ could be recovered from the acidified seawater using a 5 mL/min N₂ sweep stream to simulate vacuum conditions on the tube side of the membrane contactor. Downstream FTIR measurements of 8000–10000 ppm by FTIR correspond to 87% of DIC removal, corresponding to a 90% faradaic efficiency and an electrochemical energy of 122 kJ_e/mol (Figure 6e, energetics for the pH swing only).

Ongoing research in our group is focusing on increasing the capacities and achievable current densities with the bismuth/silver electrodes, and alternate electrode chemistries are being explored to reduce the capital expenses associated with industrial embodiments of DOC processes. The effects of divalent cations on system performance were not explored in depth in the initial study, but the prevention of inorganic

electrode fouling requires further research. In the pH range of 9.6–10, calcium carbonate (CaCO_3) formation can become significant if a substantial amount of CO_2 has not been removed; beyond pH 10, magnesium hydroxide ($\text{Mg}(\text{OH})_2$) formation also begins to occur.^{28,30} The extent of degradation in performance is highly dependent on precipitation kinetics, and it is important to minimize the impacts of these effects without significant sacrifices in energy efficiency.

4. CONCLUSION AND OUTLOOK

In this Account, we summarize recent work on pH swing-based electrochemical carbon capture, developing homogeneous and heterogeneous redox-active materials for diverse system architectures and applications. The first approach utilizes molecular redox-active organic materials like 1-AP and NR, enabling CO_2 capture and release from gaseous CO_2 inputs. A DAC system employing oxygen-insensitive NR/NRH₂ with ambient air as the feed gas was demonstrated. Heterogeneous approaches explored inorganic redox-active electrodes, such as MnO₂ and bismuth nanomaterials, for treatment of gaseous and liquid CO_2 feeds. Selective extraction of DIC from seawater was achieved using bismuth/silver-based systems, offering promising solutions for ocean acidification mitigation.

Challenges exist for both organic and inorganic materials. Molecular organic materials could be decomposed through side reactions, impacting system lifetime and capacity, requiring rational molecular design to develop stable molecules, and enhancing system durability. While inorganic material-based electrodes generally exhibit better stability over time, scaling up the system is complex due to the limited surface area-to-volume ratio, necessitating careful electrode design.

Additionally, in the context of electrochemical systems designed for flue gas treatment, considering the impact of temperature alongside gas composition is essential. Existing literature provides empirical data on flue gas composition, which typically contains 1–33% CO_2 ,^{54,55} along with varying levels of oxygen, NO_x, and SO_x.^{55,56} Flue gases are often extremely hot, exiting at around 150 °C before being released into the stack.⁵⁷ A necessary pretreatment step involves lowering the flue gas temperature to a range of 30–50 °C, aligning with the optimal operating temperature for most carbon capture technologies, including electrochemical methods. While higher temperatures have the potential to enhance reaction kinetics, thereby reducing energy consumption, maintaining the electrochemical system's integrity is crucial, particularly for membrane components, which may have specific temperature requirements for optimal operation.

Looking forward, pH swing electrochemical carbon capture offers promise in combating climate change. Advantages such as isothermal operation, modularity, and water-based pH swing processes make them attractive for large-scale deployment while mitigating environmental concerns associated with conventional volatile amine solutions.

Future development of pH swing for electrochemical carbon capture requires further optimization of redox-active materials, electrode designs, and system configurations to enhance the overall performance, scalability, stability, and cost-effectiveness. Extensive research on electrochemical behavior and potential side reactions under real-world operational conditions, including in the presence of CO_2 and other impurities, is crucial for better understanding and predicting material and system performance. Moreover, the exploration of new redox-

active materials offers exciting opportunities, as the current investigation represents only a fraction of the vast chemistry world that can be tapped. Continued efforts in these directions will drive advances in sustainable carbon capture and contribute to a greener future.

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Notes

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■ REFERENCES

- (1) Seo, H.; Rahimi, M.; Hatton, T. A. Electrochemical Carbon Dioxide Capture and Release with a Redox-Active Amine. *J. Am. Chem. Soc.* **2022**, *144*, 2164–2170.
- (2) Seo, H.; Hatton, T. A. Electrochemical Direct Air Capture of CO₂ Using Neutral Red as Reversible Redox-Active Material. *Nat. Commun.* **2023**, *14*, 313.
- (3) Rahimi, M.; Catalini, G.; Puccini, M.; Hatton, T. A. Bench-Scale Demonstration of CO₂ Capture with an Electrochemically Driven Proton Concentration Process. *RSC Adv.* **2020**, *10*, 16832–16843.
- (4) Kim, S.; Nitzsche, M. P.; Rufer, S. B.; Lake, J. R.; Varanasi, K. K.; Hatton, T. A. Asymmetric Chloride-Mediated Electrochemical Process for CO₂ Removal from Oceanwater. *Energy Environ. Sci.* **2023**, *16*, 2030–2044.
- (5) 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 ed.; Cambridge University Press: 2023; DOI: [10.1017/9781009325844](https://doi.org/10.1017/9781009325844).
- (6) Bui, M.; Adjiman, C. S.; Bardow, A.; Anthony, E. J.; Boston, A.; Brown, S.; Fennell, P. S.; Fuss, S.; Galindo, A.; Hackett, L. A.; Hallett, J. P.; Herzog, H. J.; Jackson, G.; Kemper, J.; Krevor, S.; Maitland, G. C.; Matuszewski, M.; Metcalfe, I. S.; Petit, C.; Puxty, G.; Reimer, J.; Reiner, D. M.; Rubin, E. S.; Scott, S. A.; Shah, N.; Smit, B.; Trusler, J. P. M.; Webley, P.; Wilcox, J.; Mac Dowell, N. Carbon Capture and Storage (CCS): The Way Forward. *Energy Environ. Sci.* **2018**, *11*, 1062–1176.
- (7) Meng, F.; Meng, Y.; Ju, T.; Han, S.; Lin, L.; Jiang, J. Research Progress of Aqueous Amine Solution for CO₂ Capture: A Review. *Renew. Sustain. Energy Rev.* **2022**, *168*, 112902.
- (8) Panja, P.; McPherson, B.; Deo, M. Techno-Economic Analysis of Amine-Based CO₂ Capture Technology: Hunter Plant Case Study. *Carbon Capture Sci. Technol.* **2022**, *3*, 100041.
- (9) Fasih, M.; Efimova, O.; Breyer, C. Techno-Economic Assessment of CO₂ Direct Air Capture Plants. *J. Clean. Prod.* **2019**, *224*, 957–980.
- (10) Rahimi, M.; Khurram, A.; Hatton, T. A.; Gallant, B. Electrochemical Carbon Capture Processes for Mitigation of CO₂ Emissions. *Chem. Soc. Rev.* **2022**, *51*, 8676–8695.
- (11) Roy, P.; Mohanty, A. K.; Misra, M. Prospects of Carbon Capture, Utilization and Storage for Mitigating Climate Change. *Environ. Sci. Adv.* **2023**, *2*, 409–423.
- (12) Chai, S. Y. W.; Ngu, L. H.; How, B. S. Review of Carbon Capture Absorbents for CO₂ Utilization. *Greenh. Gases Sci. Technol.* **2022**, *12*, 394–427.
- (13) Nguyen, T.; Hilliard, M.; Rochelle, G. T. Amine Volatility in CO₂ Capture. *Int. J. Greenh. Gas Control* **2010**, *4*, 707–715.
- (14) Gouédard, C.; Picq, D.; Launay, F.; Carrette, P.-L. Amine Degradation in CO₂ Capture. I. A Review. *Int. J. Greenh. Gas Control* **2012**, *10*, 244–270.
- (15) Mazari, S. A.; Si Ali, B.; Jan, B. M.; Saeed, I. M.; Nizamuddin, S. An Overview of Solvent Management and Emissions of Amine-Based CO₂ Capture Technology. *Int. J. Greenh. Gas Control* **2015**, *34*, 129–140.
- (16) Zito, A. M.; Clarke, L. E.; Barlow, J. M.; Bím, D.; Zhang, Z.; Ripley, K. M.; Li, C. J.; Kummeth, A.; Leonard, M. E.; Alexandrova, A. N.; Brushett, F. R.; Yang, J. Y. Electrochemical Carbon Dioxide Capture and Concentration. *Chem. Rev.* **2023**, *123*, 8069–8098.
- (17) Scovazzo, P.; Poschusta, J.; DuBois, D.; Koval, C.; Noble, R. Electrochemical Separation and Concentration of < 1% Carbon Dioxide from Nitrogen. *J. Electrochem. Soc.* **2003**, *150*, D91.
- (18) Mizen, M. B.; Wrighton, M. S. Reductive Addition of CO₂ to 9,10-Phenanthrenequinone. *J. Electrochem. Soc.* **1989**, *136*, 941–946.
- (19) DuBois, D. L.; Miedaner, A.; Bell, W.; Smart, J. C. Electrochemical Concentration of Carbon Dioxide. In *Electrochemical and Electrocatalytic Reactions of Carbon Dioxide*; Elsevier: 1993; pp 94–117; DOI: [10.1016/B978-0-444-88316-2.50008-5](https://doi.org/10.1016/B978-0-444-88316-2.50008-5).
- (20) Stern, M. C.; Simeon, F.; Herzog, H.; Hatton, T. A. Post-Combustion Carbon Dioxide Capture Using Electrochemically Mediated Amine Regeneration. *Energy Environ. Sci.* **2013**, *6*, 2505.
- (21) Rahimi, M.; Diederichsen, K. M.; Ozbek, N.; Wang, M.; Choi, W.; Hatton, T. A. An Electrochemically Mediated Amine Regeneration Process with a Mixed Absorbent for Postcombustion CO₂ Capture. *Environ. Sci. Technol.* **2020**, *54*, 8999–9007.
- (22) Wang, M.; Hariharan, S.; Shaw, R. A.; Hatton, T. A. Energetics of Electrochemically Mediated Amine Regeneration Process for Flue Gas CO₂ Capture. *Int. J. Greenh. Gas Control* **2019**, *82*, 48–58.
- (23) Jin, S.; Wu, M.; Gordon, R. G.; Aziz, M. J.; Kwabi, D. G. pH Swing Cycle for CO₂ Capture Electrochemically Driven through Proton-Coupled Electron Transfer. *Energy Environ. Sci.* **2020**, *13*, 3706–3722.
- (24) Xie, H.; Wu, Y.; Liu, T.; Wang, F.; Chen, B.; Liang, B. Low-Energy-Consumption Electrochemical CO₂ Capture Driven by Biomimetic Phenazine Derivatives Redox Medium. *Appl. Energy* **2020**, *259*, 114119.
- (25) Rahimi, M.; Catalini, G.; Hariharan, S.; Wang, M.; Puccini, M.; Hatton, T. A. Carbon Dioxide Capture Using an Electrochemically Driven Proton Concentration Process. *Cell Rep. Phys. Sci.* **2020**, *1*, 100033.
- (26) Pang, S.; Jin, S.; Yang, F.; Alberts, M.; Li, L.; Xi, D.; Gordon, R. G.; Wang, P.; Aziz, M. J.; Ji, Y. A Phenazine-Based High-Capacity and High-Stability Electrochemical CO₂ Capture Cell with Coupled Electricity Storage. *Nat. Energy* **2023**, *8*, 1126.
- (27) Digdaya, I. A.; Sullivan, I.; Lin, M.; Han, L.; Cheng, W.-H.; Atwater, H. A.; Xiang, C. A Direct Coupled Electrochemical System for Capture and Conversion of CO₂ from Oceanwater. *Nat. Commun.* **2020**, *11*, 4412.
- (28) de Lannoy, C.-F.; Eisaman, M. D.; Jose, A.; Karnitz, S. D.; DeVaul, R. W.; Hannun, K.; Rivest, J. L. B. Indirect Ocean Capture of Atmospheric CO₂: Part I. Prototype of a Negative Emissions Technology. *Int. J. Greenh. Gas Control* **2018**, *70*, 243–253.
- (29) Eisaman, M. D.; Rivest, J. L. B.; Karnitz, S. D.; de Lannoy, C.-F.; Jose, A.; DeVaul, R. W.; Hannun, K. Indirect Ocean Capture of Atmospheric CO₂: Part II. Understanding the Cost of Negative Emissions. *Int. J. Greenh. Gas Control* **2018**, *70*, 254–261.
- (30) Sharifian, R.; Boer, L.; Wagterveld, R. M.; Vermaas, D. A. Oceanic Carbon Capture through Electrochemically Induced In Situ Carbonate Mineralization Using Bipolar Membrane. *Chem. Eng. J.* **2022**, *438*, 135326.
- (31) Simeon, F.; Stern, M. C.; Diederichsen, K. M.; Liu, Y.; Herzog, H. J.; Hatton, T. A. Electrochemical and Molecular Assessment of Quinones as CO₂-Binding Redox Molecules for Carbon Capture. *J. Phys. Chem. C* **2022**, *126*, 1389–1399.
- (32) Aboudheir, A.; Tontiwachwuthikul, P.; Chakma, A.; Idem, R. Kinetics of the Reactive Absorption of Carbon Dioxide in High CO₂-Loaded, Concentrated Aqueous Monoethanolamine Solutions. *Chem. Eng. Sci.* **2003**, *58*, 5195–5210.
- (33) Mayr's Database Of Reactivity Parameters: Searches. <https://www.cup.lmu.de/oc/mayr/reaktionsdatenbank2/> (accessed 2023-07-22).
- (34) Li, Z.; Mayer, R. J.; Ofial, A. R.; Mayr, H. From Carbodiimides to Carbon Dioxide: Quantification of the Electrophilic Reactivities of Heteroallenes. *J. Am. Chem. Soc.* **2020**, *142*, 8383–8402.
- (35) Minegishi, S.; Mayr, H. How Constant Are Ritchie's "Constant Selectivity Relationships"? A General Reactivity Scale for n-, π -, and σ -Nucleophiles. *J. Am. Chem. Soc.* **2003**, *125*, 286–295.
- (36) Brotzel, F.; Chu, Y. C.; Mayr, H. Nucleophilicities of Primary and Secondary Amines in Water. *J. Org. Chem.* **2007**, *72*, 3679–3688.
- (37) Baidya, M.; Mayr, H. Nucleophilicities and Carbon Basicities of DBU and DBN. *Chem. Commun.* **2008**, No. 15, 1792.
- (38) Brotzel, F.; Kempf, B.; Singer, T.; Zippe, H.; Mayr, H. Nucleophilicities and Carbon Basicities of Pyridines. *Chem. - Eur. J.* **2007**, *13*, 336–345.

- (39) House, K. Z.; Baclig, A. C.; Ranjan, M.; van Nierop, E. A.; Wilcox, J.; Herzog, H. J. Economic and Energetic Analysis of Capturing CO₂ from Ambient Air. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108*, 20428–20433.
- (40) Jeziorek, D.; Ossowski, T.; Liwo, A.; Dyl, D.; Nowacka, M.; Woźnicki, W. Theoretical and Electrochemical Study of the Mechanism of Anthraquinone-Mediated One-Electron Reduction of Oxygen: The Involvement of Adducts of Dioxygen Species to Anthraquinones. *J. Chem. Soc. Perkin Trans. 2* **1997**, No. 2, 229–236.
- (41) Liu, Y.; Ye, H.-Z.; Diederichsen, K. M.; Van Voorhis, T.; Hatton, T. A. Electrochemically Mediated Carbon Dioxide Separation with Quinone Chemistry in Salt-Concentrated Aqueous Media. *Nat. Commun.* **2020**, *11*, 2278.
- (42) Vasudevan, D.; Wendt, H. Electroreduction of Oxygen in Aprotic Media. *J. Electroanal. Chem.* **1995**, *392*, 69–74.
- (43) Koppenol, W. H.; Stanbury, D. M.; Bounds, P. L. Electrode Potentials of Partially Reduced Oxygen Species, from Dioxygen to Water. *Free Radic. Biol. Med.* **2010**, *49*, 317–322.
- (44) Halliday, C.; Matthews, D. C. Some Electrochemical and Photoelectrochemical Properties of 3-Amino-7-Dimethylamino-2-Methylphenazine (Neutral Red) in Aqueous Solution. *Aust. J. Chem.* **1983**, *36*, 507.
- (45) Pauliuikaite, R.; Brett, C. M. A. Poly(Neutral Red): Electrosynthesis, Characterization, and Application as a Redox Mediator. *Electroanalysis* **2008**, *20*, 1275–1285.
- (46) Diederichsen, K. M.; Hatton, T. A. Nondimensional Analysis of a Hollow Fiber Membrane Contactor for Direct Air Capture. *Ind. Eng. Chem. Res.* **2022**, *61*, 11964–11976.
- (47) Toupin, M.; Brousse, T.; Bélanger, D. Charge Storage Mechanism of MnO₂ Electrode Used in Aqueous Electrochemical Capacitor. *Chem. Mater.* **2004**, *16*, 3184–3190.
- (48) Gruber, N.; Bakker, D. C. E.; DeVries, T.; Gregor, L.; Hauck, J.; Landschützer, P.; McKinley, G. A.; Müller, J. D. Trends and Variability in the Ocean Carbon Sink. *Nat. Rev. Earth Environ.* **2023**, *4*, 119–134.
- (49) Willauer, H. D.; DiMascio, F.; Hardy, D. R.; Williams, F. W. Development of an Electrolytic Cation Exchange Module for the Simultaneous Extraction of Carbon Dioxide and Hydrogen Gas from Natural Seawater. *Energy Fuels* **2017**, *31*, 1723–1730.
- (50) Patterson, B. D.; Mo, F.; Borgschulte, A.; Hillestad, M.; Joos, F.; Kristiansen, T.; Sunde, S.; van Bokhoven, J. A. Renewable CO₂ Recycling and Synthetic Fuel Production in a Marine Environment. *Proc. Natl. Acad. Sci. U. S. A.* **2019**, *116*, 12212–12219.
- (51) Millero, F. J. The Marine Inorganic Carbon Cycle. *Chem. Rev.* **2007**, *107*, 308–341.
- (52) Sharifian, R.; Wagterveld, R. M.; Digdaya, I. A.; Xiang, C.; Vermaas, D. A. Electrochemical Carbon Dioxide Capture to Close the Carbon Cycle. *Energy Environ. Sci.* **2021**, *14*, 781–814.
- (53) Nam, D.-H.; Choi, K.-S. Bismuth as a New Chloride-Storage Electrode Enabling the Construction of a Practical High Capacity Desalination Battery. *J. Am. Chem. Soc.* **2017**, *139*, 11055–11063.
- (54) Wang, X.; Song, C. Carbon Capture From Flue Gas and the Atmosphere: A Perspective. *Front. Energy Res.* **2020**, *8*, 560849.
- (55) Halliday, C.; Hatton, T. A. Sorbents for the Capture of CO₂ and Other Acid Gases: A Review. *Ind. Eng. Chem. Res.* **2021**, *60*, 9313–9346.
- (56) D'Alessandro, D. M.; Smit, B.; Long, J. R. Carbon Dioxide Capture: Prospects for New Materials. *Angew. Chem., Int. Ed.* **2010**, *49*, 6058–6082.
- (57) Shatskikh, Y. V.; Sharapov, A. I.; Byankin, I. G. Analysis of Deep Heat Recovery From Flue Gases. *J. Phys. Conf. Ser.* **2017**, *891*, 012188.