

Electrochemical approaches toward CO₂ capture and concentration

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Abstract

Carbon capture and concentration of low partial pressure CO₂ in air and flue gas is a key step in carbon abatement strategies. Traditional CO₂ capture methods employ temperature or pressure swings, however electrochemical swings, in which an applied potential modulates nucleophilicity, are also possible to mediate the capture and release of CO₂. In contrast to the breadth of electrochemical CO₂ reduction research, electrochemically-mediated CO₂ capture and concentration is an emerging field. Although some aspects are reminiscent to those in CO₂ reduction, like local pH gradients and (bi)carbonate equilibria, ultimately electrochemical CO₂ capture and concentration poses its own unique challenges that will benefit from insights from intercalative batteries, redox flow batteries, and bio-mimetic/-inspired design, among others. After an introduction to carbon capture and current chemical strategies, this review highlights promising emerging electrochemical methods to enable CO₂ capture and concentration; specifically discussed are transition metal redox and pH swings. It closes with an outlook and discussion of future research challenges.

Keywords: CO₂ capture, CCS, TM redox, organic redox, pH swings, nucleophiles

1. Introduction

Closing the anthropogenic carbon cycle will require affordable carbon capture technologies. In the near-term, carbon capture is envisioned as a combination of direct air capture (DAC) and point-source capture from existing CO₂ emitters like coal and gas power plants.¹ Despite global efforts, the economic feasibility of DAC remains debated²⁻⁴ and the progress of point-source capture is slower than what has been anticipated. For DAC the low CO₂ concentration in ambient air, ~ 410 ppm, inherently increases the costs of DAC² and for point-sources, despite having a much higher concentration of CO₂, additional difficulties include NO_x/SO_x contaminants and particulates present in flue gases.⁵

For nucleophilic sorbent-based CO₂ capture, CO₂ is selectively captured from a dilute stream by chemical ab-/adsorption. After achieving CO₂ saturation capacity the sorbent is regenerated, typically by a temperature or pressure swing that releases the CO₂ in a concentrated, high-purity stream in solution or gaseous form. The regenerated CO₂-lean sorbent is then re-used for further CO₂ capture. Broadly, the regeneration energy penalty, high costs, and loss of active sorbent are major barriers for wider implementation of carbon capture technologies.

Electrochemically-mediated CO₂ capture and concentration may offer solutions to overcome these barriers. Just as electrochemical CO₂ reduction is appealing for its promise of potential-dependent product distributions, electrochemical CO₂ capture is appealing for its potential-dependent control to alter the nucleophilicity of target species and to control reaction rates, possibly at ambient conditions.

This review highlights promising new electrochemical methods to enable the capture and release of electrophilic CO₂ for carbon capture technologies. This work is not meant to be exhaustive. For a comprehensive review of organic redox in aprotic media for CO₂ capture and release the reader is directed to a 2017 Perspective.⁶ Additionally, this review does not cover the full pathways of (photo)electrochemical CO₂ capture and reduction to solar fuels and other high value products. Although the capture methods described in the present work are applicable to and have been employed in artificial photosynthesis,⁷ the focus here is instead primarily on electrochemical CO₂ capture and concentration.

2. Principles of CO₂ capture and existing technologies

By the change in Gibbs free energy, the minimum energy required to split a dilute CO₂ stream into pure CO₂ and a CO₂-stripped stream at ambient pressure and temperature ranges from ~ 7 kJ (mol CO₂ captured)⁻¹ [0.2 GJ (metric ton CO₂)⁻¹] for flue gas (12 % CO₂) to ~ 22 kJ mol⁻¹ (0.5 GJ t-CO₂⁻¹) for DAC.^{2,8} Unless otherwise noted, all molar or gravimetric quantities in the rest of this review are referenced to the given quantity of CO₂ captured. Depending on the ultimate fate of the captured carbon, the CO₂ may remain concentrated in solution (e.g., for further electrochemical conversion) or released as high purity CO₂ and compressed to 100-150 bar for sequestration/transportation or gas-phase catalytic conversions. The minimum energy for compression from 1 to 150 bar is ~ 12 kJ mol⁻¹ [0.3 GJ t-CO₂⁻¹].⁸ While the compression step is

important for full consideration of the feasibility of near-term CO₂ capture, for this review, unless otherwise noted, the energetics of only the separation and/or regeneration step(s)—capture and concentration in solution or release of CO₂ near ambient pressure—will be considered.

An ideal sorbent is reversible: it is able to selectively and quickly uptake CO₂ from a dilute stream and subsequently able to release all of the retained CO₂ when desired, all at high capacity. Both the basicity of the sorbent, measured by the pK_a, and its affinity for CO₂, measured by enthalpy of CO₂ ad-/absorption, are key sorbent parameters. The pK_a can affect the rate of capture and the chemical form of the captured CO₂ in solution. The heat of reaction is an indicator of the strength of the interactions between CO₂ and the sorbent. The ideal ratio $\Delta H_{\text{abs}}/\Delta H_{\text{ads}}$ is often a balance between low throughput at low enthalpies and unsustainably large pressure or temperature swings required for sorbent regeneration at high enthalpies, which lead to sorbent degradation and limited lifetime. The most common swings to drive off the CO₂ are a decrease in pressure, increase in temperature, and introduction of moisture, but magnetic fields have also been used.⁹

Point-sources are found in the energy sector, where CO₂ can be captured from power plants in both pre- and post-combustion processes, as well as in oxy-combustion;¹⁰ and in the industrial sector, with some particularly large exhaust CO₂ mole fractions found in natural gas processing, cement, steel, refineries, and paper plants.¹¹ Many, though not all, of these point-sources have a steam cycle, which makes CO₂ capture using thermal regeneration methods particularly appealing. In principle, DAC can be carried-out anywhere, so capture and sorbent regeneration using renewable-based electricity or fuels for DAC is desirable. Since carbon capture must be powered by existing energy sources, full-cycle carbon analyses are needed to assess the feasibility of any capture system.

Any alternative electrochemical capture technology must be favorable to or competitive with existing methods in terms of regeneration energy/cost, useful lifetime, safety/environmental impact, carbon balance, and ease of implementation/retrofitting. Thus, before going into electrochemical methods for CO₂ capture we briefly benchmark a selection of capture methods for comparison based on carbonate and carbamate adducts.

2.1. Aqueous and supported amines. CO₂ capture by aqueous amine absorption or supported amine adsorption can proceed by carbamate/protonated amine pairs, and/or bicarbonate formation, depending on the identity of the amine, the CO₂ loading, and for supported amines, whether there is moisture or not. The general possible reactions are carbamate formation: $2R_1R_2NH + CO_2 \leftrightarrow R_1R_2NH_2^+ R_1R_2NCO_2^-$, with one CO₂ for every two amine groups for primary and secondary amines; and bicarbonate formation, $R_1R_2R_3N + H_2O + CO_2 \leftrightarrow R_1R_2R_3NH^+ HCO_3^-$, for all amine types. Amines generally have high heats of ad-/absorption, ~ 60–90 kJ mol⁻¹.

Carbon capture with aqueous alkanolamines and alkanamines, considered by many to be the near-term carbon capture technology of choice, is a mature technology first patented in the 1930s,¹² and has since been applied to remove CO₂ from coal power plants, natural gas, and

other gaseous products.¹³ Several pilot- and demonstration-scale coal-fired power plants with amine-based post-combustion capture are currently in operation, the largest being Boundary Dam (Canada, 115 MW, 2014)¹⁴ and Petra Nova (USA, 240 MW, 2016)¹⁵, each capturing and sequestering roughly 3000-5000 metric tons CO₂ (t-CO₂) per day. The larger endeavor Project Tundra is currently in the planning stages (USA, 455 MW, est. 2022).¹⁶ Amine-based CO₂ capture lowers the overall efficiency of electricity generation by use of stripping steam (~ 100–150 °C) to regenerate the amine solution, as well as through pump and compression work. This decreased efficiency is passed on to the consumer as increased electricity costs.^{13,17}

High stripper temperatures exacerbate amine decomposition. O₂, SO_x, and NO_x as contaminants in flue gas streams can oxidize amines, leading to instability at both absorber (~ 40 °C) and stripper conditions and eventual formation of carcinogenic nitrosamine and nitramine compounds.¹⁸ Alkanolamines and alkanamines studied for CO₂ scrubbing can be corrosive, toxic, and difficult to handle, thus the suitability of amino acids has also been explored as replacements.¹⁹ Some corrosion inhibitors, like Cu²⁺, also catalyze amine decomposition at stripper temperatures.²⁰ Beyond health and safety concerns, undesired reactivity also reduces the CO₂ capacity of amine solutions. Tailoring amine and additive chemistry and plant optimization remain active areas of research.^{5,10,21–23}

These optimizations have reduced the regeneration duty for flue gas conditions (~ 12 % CO₂) from > 4 GJ t-CO₂⁻¹ (180 kJ mol⁻¹) in early demonstrations²⁴ to ~ 2 GJ t-CO₂⁻¹ (88 kJ mol⁻¹) as validated by recent models and pilot plant studies.^{8,25,26} The high demonstrated thermodynamic efficiency of the stripping process of 50–75 % suggests only limited further energy improvements of the thermal regeneration process are possible.⁸ As amine-based point-source capture has been largely studied in power plants with available stripping steam, the thermal duty is benchmarked by the equivalent work of the amine regeneration, or in other words, by the electricity that could be generated instead of regenerating the amine. For conditions in the 2 GJ t-CO₂⁻¹ regeneration duty case, the equivalent work of regeneration (excluding pump and compressor work) with 90 % Carnot efficiency is 22 kJ_e mol⁻¹ and the total equivalent work is 32 kJ_e mol⁻¹.⁸

Despite the maturity, promise, and research progress of amine-based CO₂ capture, widespread implementation is slower than was anticipated 10 years ago.¹³ High capital costs and a lack of coordinated effort are blamed as the most significant policy barriers,²⁷ and the thermal duty of the stripper, inefficiency of the absorber, and amine decomposition as the most significant technological barriers.⁸ For example, amine degradation at the Boundary Dam project in recent years has been more significant and costly than anticipated.²⁸

An alternative to aqueous amines are supported amines, which offer the advantages of use in membranes and lack of bulk water, thereby eliminating a component of the regeneration energy. In addition, the lower heat capacity of solids requires lower energy input for thermal regeneration compared to aqueous amine solutions, resulting in a lower regeneration temperature.²⁹ Amines supported on carbon, metal-organic-frameworks (MOFs), zeolites, polymers, alumina, and silica have all been studied, as reviewed in ref. 30 and 31.

Supported amines are regenerated thermally above ~ 75 °C. Due to the poisoning effect of flue gas contaminants³¹ and the lack of volatility of the solid adsorbent, supported amines may be more suited to DAC than point-source capture. Several companies, including Climeworks (DAC, Switzerland)³² and Global Thermostat (DAC and point-source, USA)³³ use solid amine technologies.³ Averaging over companies, current energetics for DAC include ~ 35 kJ_e mol⁻¹ for blowers/controls and ~ 240 kJ mol⁻¹ (5.4 GJ t-CO₂⁻¹) heat for regeneration of the solid sorbent from either steam or low-grade waste heat.³

Although a plethora of supported amines have been studied and patented, optimization, techno-economic, and scale-up studies are less available than for aqueous amines. One of the largest concerns is rapid loss of capacity from cycling, severely limiting the useful lifetime of supported amines and increasing the cost.³⁰

2.2. Aqueous and solid alkalis. Both alkaline hydroxides and carbonates are used for CO₂ scrubbing and form carbonates and/or bicarbonates. Hot potassium carbonate solutions have been used since the 1950s as an alternative to amine scrubbing for process gases.³⁴ Potassium carbonate with water captures CO₂ as potassium bicarbonate: $K_2CO_3 + H_2O + CO_2 \leftrightarrow 2KHCO_3$. As carbonates have lower heats of absorption, $-\Delta H_{\text{abs}} \sim 40$ kJ mol⁻¹, a pressure swing is used to regenerate the carbonate and both the absorber and regenerator are operated at “hot” conditions ~ 100 °C.³⁵ Though in the traditional process the bicarbonate stays in solution, purposeful precipitation of KHCO₃ to enable high-pressure stripping has also been explored with promising results.³⁴

Some main advantages of alkaline carbonates include lower toxicity and greater resistance to flue gas contaminants than amines. K₂CO₃ suffers from slow reaction kinetics leading to low CO₂ removal efficiencies and rate promoters, which can include amines, are needed to keep absorber units manageably sized.³⁶ The regeneration duty is comparable to amines, ~ 2 – 4 GJ t-CO₂⁻¹. As an alternative to thermal regeneration, use of the formed bicarbonate as feedstock for bacteria is being explored.³⁷

Aqueous hydroxide solutions are also relatively resistant to flue gas contaminants and react with CO₂ to produce carbonates, $2KOH + CO_2 \leftrightarrow H_2O + K_2CO_3$ with large $-\Delta H_{\text{abs}} \sim 90$ – 100 kJ mol⁻¹.³⁸ After capture there are three steps to regenerate and release CO₂: a) adding Ca(OH)₂ to K₂CO₃ regenerates KOH, yielding solid CaCO₃, b) CaCO₃ is heated at ~ 900 °C to make CaO and to release CO₂, and c) Ca(OH)₂ is regenerated when CaO is mixed with water.^{3,4} A DAC commercial plant using this process is Carbon Engineering (1 Mt-CO₂ year⁻¹, DAC, Canada),³⁹ which recently released a detailed report on the process.⁴ In their facility, partially capturing CO₂ from the air and releasing at 1 bar requires either 5.2 GJ t-CO₂⁻¹ (230 kJ mol⁻¹) heat (from gas) and electricity 77 kWh t-CO₂⁻¹ (12 kJ_e mol⁻¹) or only fuel-based 8.81 GJ t-CO₂⁻¹ (387 kJ mol⁻¹). The negatives of this process are water loss and the need for high-grade heat that is supplied by burning fuel.

2.3 Summary of existing technologies. From the brief survey of technologies above it is apparent that recent improvements in existing CO₂ capture have brought energy requirements and costs down considerably from initial demonstrations. Although it is desirable to continue to bring costs and energetic requirements down and explore alternative options to do so, the main downsides in current capture strategies are the toxicity of components, the need for steam or fuels for high temperatures, and poor cyclability/capacity retention. The loss of capacity stems mainly from reactivity with flue gas contaminants and oxygen, thermal degradation, and volatility.

By contrast, electrochemical swings offer the possibility of isothermal operation and thus may limit thermally catalyzed degradation. As the potential can be set to target a specific reaction, the energy of electrochemical regeneration of the sorbent may be lowered, for example, by eliminating the need to heat the water in an aqueous solution of a CO₂ sorbent. For the case where electricity (from say solar/wind) is available and access to steam, waste heat, or other fuels is not possible, electrochemical means are particularly appealing. The next section introduces electrochemically-mediated CO₂ capture and highlights several methods.

3. Electrochemically-mediated CO₂ capture

Electrochemically-mediated CO₂ capture can be grouped generally into either direct or indirect modification of a CO₂ sorbent and is illustrated in Figure 1. For direct modification, as shown in 1a), the sorbent itself must be redox-active and its nucleophilicity is directly modified electrochemically, activating and deactivating its affinity toward the sorbate, CO₂. This is termed Electrochemically-Mediated Complexation Separations (EMCS)⁴⁰ or Electrochemically Modulated Complexation (EMS).⁴¹ For indirect or competitive, as shown in 1b), the sorbent itself is not redox-active but interacts with a redox-active competitor which, when activated, has affinity for the sorbent and not for CO₂. The competitor activates (deactivates) its affinity toward the sorbent and thereby indirectly turns off (on) the sorbent's ability to bind with the target sorbate, CO₂. This has been called Electrochemically-Mediated Competitive Complexation Separation (EMCCS).⁴² For specifics of possible electrochemically-mediated CO₂ capture systems, see ref. 42–44. For both indirect and direct electrolyzers, CO₂ is captured cathodically and released anodically. Electrochemical methods can be applied to both adsorption and absorption.

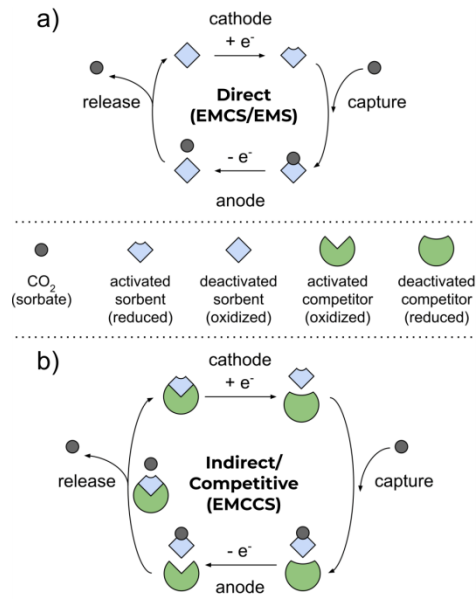


Figure 1. Direct and indirect/competitive CO₂ capture. a) direct capture (EMCS/EMS). In direct capture, the CO₂ sorbent itself is electrochemically active and is turned on/off by reduction/oxidation, respectively. b) indirect/competitive (EMCCS) capture. For indirect/competitive capture, the CO₂ sorbent is itself not electrochemically active and is always “activated.” To drive the release or capture of CO₂, a competitor, which when activated binds more strongly to the CO₂ sorbent than the sorbent binds to CO₂, is electrochemically active and its affinity toward the sorbent is turned on/off by oxidation/reduction, respectively. The competition is directly with the CO₂ sorbent, not with CO₂. For an alternate depiction of these systems, see Figures 2-1 and 2-2 in ref. 42 and for a more detailed description see Figures 2-1 and 2-2 in ref. 44.

For any electrochemical CO₂ capture system, thermodynamic paths can be derived for the full cycle of capture and release: activation/generation of the nucleophile (reductive current), capture of CO₂ (chemical), deactivation/elimination of the nucleophile (oxidative current), and desorption/release of CO₂ (chemical). Instead of free energy, the useful representation in an electrochemical cycle is the potential and the independent variable is the net charge passed in the system, which, for example, can be represented or measured by a concentration change. As the oxidative and reductive charge passed are equal in the ideal case, the loop of capture and release is closed and defines a minimum energy of capture/release for any electrochemical CO₂ concentration system.

Just as for chemical sorption methods, the affinity of the sorbent for CO₂ strongly influences the minimum energy required in electrochemical methods, and there exists a balance between efficiency and driving potential to concentrate CO₂. As derived elsewhere,^{43,44} the general expression for the minimum driving potential to concentrate CO₂ is:

$$\Delta V = \frac{RT}{mF} \ln \left(\frac{1+K_{CO_2}P_a^m}{1+K_{CO_2}P_c^m} \right),$$

Where m is the number of CO_2 molecules per sorbent, P_a is the CO_2 partial pressure relative to standard state at the anode side (release, higher partial pressure), P_c is the relative partial pressure at the cathode side (capture, lower partial pressure), and K_{CO_2} is the equilibrium constant for the sorbent's CO_2 affinity. This holds for both the direct and indirect case, assuming the sorbent preferentially binds with the oxidized competitive agent instead of CO_2 .

For low K_{CO_2} (thereby low $-\Delta H_{\text{abs}}$ or weak absorption), small potential differences are needed leading to inevitably low faradaic efficiencies. For large K_{CO_2} , the higher faradaic efficiencies require larger driving potentials. Faradaic efficiency here is defined as the fraction of the current that captures or releases CO_2 . For example, for direct cathodically-mediated capture the faradaic efficiency is the portion of the total current that generates the target nucleophilic capture sorbent multiplied by the portion of the generated nucleophiles that capture CO_2 . For the same nucleophile-generating current, the CO_2 -capturing current is obviously higher for the electrochemically-generated nucleophile with a larger affinity for CO_2 .

The minimum energy required for the electrochemical systems presented in this review are all similar, $\cong 30 \text{ kJ}_e (\text{mol CO}_2 \text{ captured})^{-1}$ for typical flue gas conditions. However, non-unity faradaic efficiency, non-unity transference numbers, undesired side reactions, membrane crossover, overpotentials, etc. all contribute to the required voltages of electrochemically-mediated CO_2 capture/release in a practical system. The requirements for electrochemical capture and concentration are analogous to those for traditional capture methods. Some of the key requirements include

- high selectivity and high affinity for CO_2
- stability in the relevant potential and pH windows; the electrolyte must be stable at potentials needed to concentrate CO_2
- stability to non- CO_2 gases and particulates in air and flue gas streams
- high capacity for CO_2
- high reversibility/long cyclability
- high faradaic efficiency, avoiding unwanted side reactions
- fast CO_2 uptake/release
- fast electron transfer kinetics
- non-toxic, available materials.

Examples of chemical CO_2 capture described above were mediated by carbamates and (bi)carbonates, and hence were grouped by type of carbon adduct. In the following, we organize the electrochemical methods for CO_2 capture and concentration not by type of carbon adduct, but by method of electrochemically driving CO_2 capture and release.

3.1. Transition metal (TM) redox methods. TM complexes have been explored for both direct capture, with TM centers assisting in (bi)carbonate/carbamate formation, and indirect capture, with the modulation of the TM oxidation state turning on and off competition with CO_2 . Choices

of TMs, oxidation states, and coordinating ligands yield tunability and resistance to oxidation. Purely solvated cationic states or plating/stripping metallic states are possible capture systems.

TM redox centers with nucleophilic ligands may be used to directly capture (release) electrolytic CO₂ by increasing (decreasing) the charge density of the complex through its reduction (oxidation).⁶ For example, biomimetic design of mono- and dinuclear TM complexes with macrocyclic amino and pyridine ligands for enzymatic CO₂ fixation was used to study CO₂ capture.^{41,45–47} Zn, Cu, and Ni compounds with certain bridging ligands allow strong carbonate binding at the metal centers, yielding complexes of the form [M₂(μ₂-CO₃)L]²⁺, which release CO₂ when the complex is reduced.^{41,47} This is the only instance covered in this review where *reductive* currents *release* CO₂ and *oxidative* currents *regenerate* the capture sorbent. In this case, a bridging hydroxyl ligand, μ-OH, immobilized between the TM centers acts as the CO₂ capture moiety. The CO₂ insertion mechanism has some similarity to that of carbonic anhydrase, typically a mononuclear Zn complex,⁴⁸ but instead of bicarbonate as in the case of carbonic anhydrase, in the dinuclear complexes CO₂ is captured as bridging carbonate. The [M₂(μ-OH)L]³⁺ complex captures CO₂ (CO₂ + μ-OH⁻ → μ-CO₃²⁻ + H⁺) as bridging carbonate, μ-CO₃, forming [M₂(μ₂-CO₃)L]²⁺, leading to the release of protons and a decrease in pH. Though the M(II) [M₂L]⁴⁺ complex reversibly reduces to the M(I) [M₂L]²⁺ complex, the negatively charged bridging hydroxyl and carbonate ligands are stable only in the M(II) complex. By reducing M(II) in [M₂(μ₂-CO₃)L]²⁺ to M(I) centers, the carbonate ligand is released and, through controlled protonation steps, subsequently given off as gaseous CO₂.

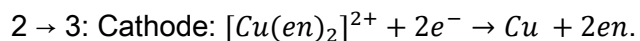
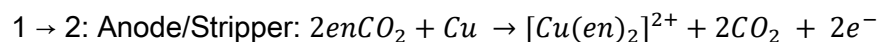
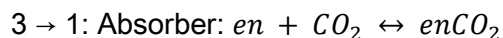
Though the reduction potential of a bimetallic Ni dinucleating carbonate complex was too negative to be useful,⁴⁷ a Cu²⁺/Cu⁺ couple complex demonstrated concentration from 10 to 75 % CO₂ at accessible potentials.⁴¹ This complex with a macrocyclic ligand with amino and pyridyl donors, N,N',N'',N'''-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (tpmc), is air stable, water soluble, and has preferential carbonate coordination in its Cu²⁺ state. During reduction of the complex and release of CO₂, partial precipitation of the Cu⁺ complex limited its feasibility. Other supporting electrolytes or ligands could stabilize the Cu⁺ complex. For example, Cu²⁺/Cu⁺ used in acidic chloride media was used to directly capture and concentrate CO.⁴⁰ With this method of bimetallic complex-mediated capture, CO₂ is fixated as μ-CO₃, which then undergoes protonation steps to be released as CO₂. Control of the pH for capture/release and full consideration of aqueous (bi)carbonate equilibria is critical for the design of any carbonate-adduct based capture process; see section 3.2 on pH swings for further discussion.

Instead of direct CO₂ capture through a Cu²⁺/Cu⁺ couple, other methods employ indirect, that is competitive, capture mediated by Cu²⁺/Cu⁰. The electrochemical regeneration of amines is presented as an alternative to the thermal generation as described earlier. Cu²⁺ in the presence of amines forms complexes with a wide possible range of stability constants^{49–51} which can compete with the amine-CO₂ bicarbonate/carbamate formation. The equilibrium of free Cu²⁺, CO₂-loaded amines, and [Cu(amine)_n]²⁺ complexes is influenced by the choice of the amine and can be shifted by electrochemically plating or stripping Cu. Both monoethanolamine^{52,53} (HOCH₂CH₂NH₂, MEA, -ΔH_{abs} = 71 kJ mol⁻¹),⁵ a common solvent in thermal scrubbing, and

ethylenediamine^{54,55} ($C_2H_4(NH_2)_2$, EDA or written “en” as a ligand, $-\Delta H_{abs} = 81 \text{ kJ mol}^{-1}$)⁵ have been studied with Cu^{2+} -mediated regeneration.

The EDA system has been extensively characterized by the Hatton group for the purpose of flue gas capture and is termed electrochemically-mediated amine regeneration (EMAR).⁵⁴ The EMAR setup as shown in Figure 2a) is an electrolytic flow cell that separates the amine and CO_2 by preferentially forming a $[Cu(en)_2]^{2+}$ complex. In the anode chamber, $[Cu(en)_2]^{2+}$ is formed and CO_2 is released. In the cathode chamber, Cu is plated, freeing amine from the Cu-amine complex for further CO_2 capture. In EDA-excess solutions, $[Cu(en)_2]^{2+}$ complexes are formed. The stability constant of $[Cu(en)_2]^{2+}$, $\log \beta \sim +19$, is orders of magnitude stronger than the CO_2 -en equilibrium constant, $\log K_{CO_2} \sim +3$, ensuring preferentially binding of en with Cu^{2+} , when present. Low-level Cu^{2+} concentrations in the absorber (inevitable in the EMAR process), lowers the CO_2 capacity per amine, however electrochemical instead of thermal regeneration limits the potential for Cu^{2+} -catalyzed *thermal* degradation as seen in traditional amine systems.

Though MEA is a standard CO_2 capture sorbent, early work identified EDA as a better sorbent for EMAR.⁴² EDA binds CO_2 more strongly than MEA but is unstable at the higher temperatures required to access its CO_2 capacity via thermal swings. For a separate absorber and cathode compartment, the relevant reactions are:



A schematic of the EMAR process and the corresponding thermodynamic cycle are shown in Figure 2a) and c). The teal shaded area in 2c) represents the minimum work of capture for the EMAR system. First, carbamates are formed in the absorber from flue gas (10–15 % CO_2) [3 \rightarrow 1 in Figure 2c)] decreasing the pH and raising the potential. In the anode chamber Cu is oxidized and dissolved, preferentially forming $[Cu(en)_2]^{2+}$ and releasing CO_2 , reducing the overall CO_2 loading [1 \rightarrow 2 in 2c)]. Lastly, Cu is plated at the cathode to regenerate the free amine, reducing the potential to the starting point [2 \rightarrow 3 in 2c)]. Cu^{2+} is stabilized by en, note the significant cathodic shift compared to the standard potential of Cu^{2+} . Figure 2b) shows the detected evolution of CO_2 upon applying a cell potential of $\sim 0.4 \text{ V}$. Due to the plating/stripping on the cathode/anode during operation, continuous operation of an EMAR system would require polarity switches.

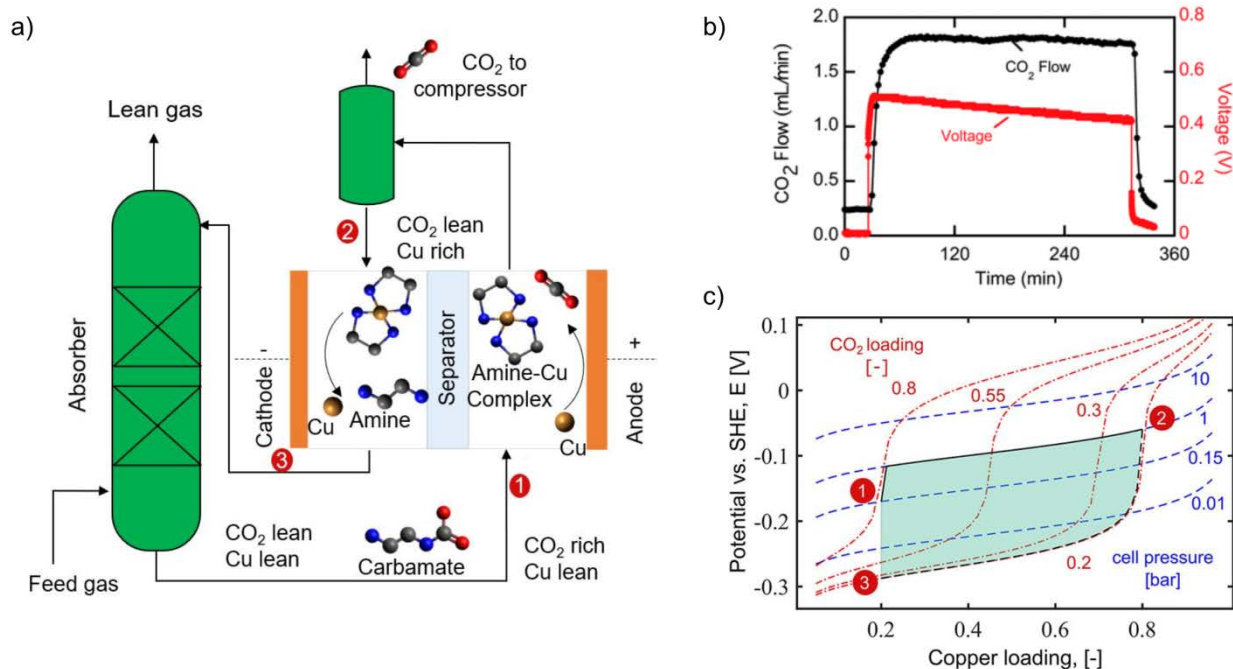


Figure 2. EMAR process. a) schematic of the full EMAR cycle for flue gas capture with formation of carbamate in the absorber, preferential formation of the Cu^{2+} complex in the anode, and regeneration of the lean amine in the cathode. b) CO_2 evolution rate with applied cell potential from a room temperature bench-scale setup. c) thermodynamic paths of the absorber (3→1), anode (1 → 2), and cathode (2 → 3) showing the minimum energy for capture and release shaded in teal. The red numbers in panels a) and c) correspond. b) adapted from ref. 55 under the [CC BY 3.0](https://creativecommons.org/licenses/by/3.0/) license. a) and c) modified with permission from ref. 56 and 57, respectively. Copyright 2020 American Chemical Society.

A membrane separates the anode and cathode compartments and the EMAR electrolyte includes a supporting salt for conductivity. Membrane resistances, membrane cost, and unwanted membrane crossover of active species all could negatively affect operation. As EDA has two amine groups, it captures one CO_2 per EDA and is zwitterionic, thus membrane crossover is not anticipated, but OH^- , H^+ , and (bi)carbonate could all contribute to the current due to membrane crossover. Nitrate, sulfate, and chloride have all been studied as the supporting anion. Nitrate tends to enhance CuO formation on the electrodes while Cl^- provides kinetic enhancement at the expense of faradaic efficiency and also leads to precipitation of powder Cu in the anolyte from cuprous ion stabilization.^{42,44}

Amine degradation pathways for flue gas conditions have been extensively studied and, to be brief, are complex and debated (see section 2.1). Exposure to O_2 and SO_x/NO_x at absorber conditions leads to initial oxidation products that can later decompose at stripper conditions to more unpleasant compounds. It is unclear what decomposition pathways will be present for the electrochemical versus thermal regeneration of EDA. Understanding O_2 and SO_x/NO_x reactivity with EDA and Cu , especially as oxidants and decomposition products accumulate with operation, will be essential for knowing the applicability of the EMAR system. Additional considerations are other potential metal contaminants (from the Cu salt/electrodes or from

corrosion processes) and their effect on electrochemical stability. EDA is a toxic, corrosive solvent that oxidatively decomposes to other amines, expanding possible electrochemical decomposition routes.⁵⁸

The minimum energy of separation for the EMAR cycle for flue gas capture as shown in Figure 2c) is $\sim 16 \text{ kJ}_e \text{ mol}^{-1}$ but overpotentials increase the operating cell voltage to $\sim 300 \text{ mV}$.^{56,59} From initial demonstrations of $\sim 100 \text{ kJ}_e \text{ mol}^{-1}$,⁵⁵ the most recent optimizations point to $\sim 30\text{--}40 \text{ kJ}_e \text{ mol}^{-1}$ for the EMAR process (not including the compression step).⁵⁶ Optimization of the system in the last 7 years has already demonstrated improvements that are energetically on par with the equivalent work of thermal regeneration. Additional energy savings could be realized if the cathode and absorber occurred together.^{42,60} The EMAR system was not explored for DAC and given the oxidative instability of aqueous amines, it is an unlikely candidate for DAC.

Even though more work is needed to show full feasibility as an alternative to thermal regeneration for flue gas scrubbing, EMAR is particularly attractive for low O_2 containing streams without access to steam cycles. It has the possibility to avoid thermally induced amine decomposition and unnecessary heating of the water solvent. Further understanding of the electron transfer kinetics of plating/dissolution of Cu in the presence of EDA and decomposition mechanisms with contaminants may inform other TM-sorbent combinations. Similar strategies could be explored for non-plating TM complexes and other ligands/sorbents.

This section explored methods that altered CO_2 affinity by manipulation of a TM oxidation state. Although modulating the pH was not explicitly mentioned, the pH change accompanying CO_2 absorption/desorption is an important consideration, particularly with Cu electrodes. The next section looks at methods of explicitly modulating the pH to capture and release CO_2 via (bi)carbonate equilibria.

3.2. Electrochemically-mediated pH swings. After capture in an aqueous hydroxide or carbonate solution, CO_2 can simply be released by appropriate acidification of the (bi)carbonate solution and the starting sorbent can be regenerated by appropriate alkalization.^{42,61} Electrochemical methods offer the ability to locally alter the pH and convert (bi)carbonate to dissolved CO_2 while simultaneously regenerating the sorbent capture solution. An effective pH swing will be reversible, switching from high pH capture to low pH release, avoiding pH drifts in operation that decrease the CO_2 capacity.

Electrochemical methods to alter the CO_2 equilibria by generating and/or storing H^+ include direct⁶² and indirect water splitting,⁶³ H^+ (de)intercalation,⁶⁴ capacitive ion storage,⁶⁵ and proton-coupled electron transfer (PCET) of organic molecules.^{66,67} Although organic redox chemistries for CO_2 capture have largely been studied in aprotic media to prevent protonation and thus directly capture CO_2 , for example in quinones,⁶ small organics may also act as pH mediators. Another possible H^+ source is the H_2 oxidation reaction (HOR) at the anode of fuel cells, which is possible at both low and high temperatures. The first efforts of electrochemically-mediated CO_2 separation were based on molten carbonate fuel cells for applications in space.^{68,69} Fuel

cells for CO₂ capture and release have been reviewed elsewhere, see ref. 6 and 70. A notable alternative arrangement employing only oxygen reduction is given in ref. 71.

Electrodialysis capture. Electrodialysis (ED) has been explored in several configurations for aqueous CO₂ capture and release, including concentration of KHCO₃ from K₂CO₃ capture sorbents to enable more efficient vacuum regeneration.^{72,73} In the specific case of hydroxide capture and ED regeneration, early ED configurations suffered from prohibitively high resistances that led to energy inputs that were not competitive with chemical methods.⁷⁴ ED can be operated by evolving H₂ and forming OH⁻ at the cathode and evolving O₂ and forming H⁺ at the anode.

An alternative approach splits water not at the electrodes but at bipolar membranes (BPMs), often called BPMED. Within a bipolar membrane, water molecules are subject to a large electric field and, often with the help of a water dissociation catalyst, split into OH⁻ and H⁺. The OH⁻ migrates toward the anode and the H⁺ migrates toward the cathode, developing and maintaining a pH gradient. A generalized simple scheme for BPM-aided CO₂ capture and release is shown in Figure 3a). Although only bicarbonate ions are written, it holds as well for carbonate ions, which instead need 2H⁺ for CO₂ recovery.

BPMs maintain pH gradients and for this reason are gaining particular interest in the field of CO₂ reduction, where designer catalysts at each electrode benefit from the different pH conditions.⁷⁵⁻⁷⁷ For a single BPM between two electrodes, water splitting will occur at a cell voltage of 1.23 V yielding ~ 120 kJ_e mol⁻¹ for the bicarbonate pathway. The membrane potential drop across the BPM is itself dependent on the pH gradient at low currents, 0.0591·ΔpH, increasing with increasing pH change, but is also dependent on the current applied, typically reaching 0.83 V at higher currents regardless of the pH gradient.⁷⁸ Although at the terminal electrodes H₂ and O₂ evolution will still occur, “stacks” of many BPM cells put in series between the terminal electrodes decrease the relative portion of the current lost to H₂/O₂ evolution.⁶³ Design of BPMED for CO₂ capture will involve optimizing the ideal pH values of the capture and release electrolytes, taking into account the membrane potential, non-ideality of the membrane, the CO₂ capacity, and the kinetics of capture and release. Fundamental studies on the nature and the conditions of non-ideality and co-ion transport in BPMs are a current topic of research.^{78,79}

Electrodialysis employs stacked cells that, in addition to BPMs, employ either or both anion (AEM) and cation exchange membranes (CEM). Figure 3b) shows an ED setup with both AEM and CEM compartments that converts a salt to its acid and base forms and purifies the inlet feed. For the purposes of CO₂ capture, there is no need to purify the feed and the feed compartment can be combined with another compartment to reduce cost, membrane resistance, and cell potential.⁸⁰ BPMED with either cationic or anionic transport are shown in Figure 3c) and 3d), respectively. In principle, CO₂ capture can occur within⁸¹ or before⁶³ the ED stack, labeled as “feed” in Figure 3.

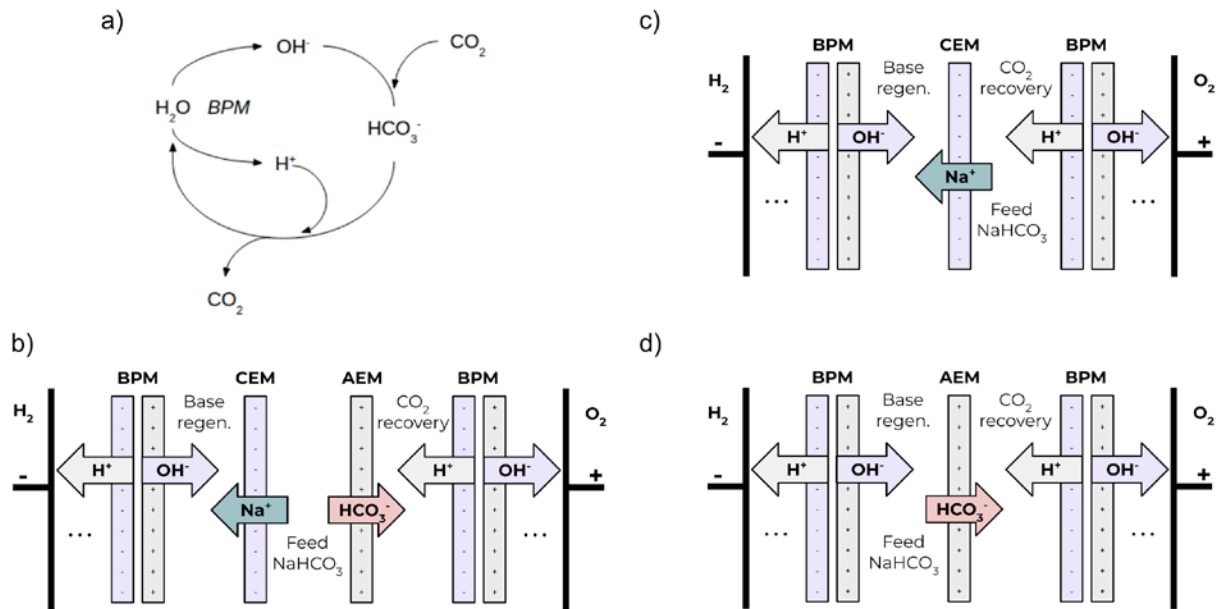


Figure 3. Bipolar membrane (BPM) NaOH-based CO₂ capture and release via electrodialysis (ED). a) a general CO₂ capture and release scheme for water splitting from BPMs. b) ED CO₂ capture with base regeneration and feed purification. c) a simplified ED process with only cationic flux with CEMs. d) a simplified ED process with only anionic flux with AEMs. This Figure is largely based on descriptions from ref. 80.

Areas of low ionic conductivity increase resistance, and thus solutions need to be appropriately buffered. Leakage current and imperfect membrane permselectivity reduce the pH gradient and lead to particularly low efficiency at lower currents.^{63,80} Higher currents can, however, lead to CO₂ bubbling within the ED cell that limits contact, increases resistance, and leads to short membrane lifetimes.⁶³ In early iterations of BPMED, these deficiencies lead to unsustainable energy requirements that did not compete with traditional regeneration methods. Process optimization and design choices to control pH have included incorporation of ion exchange resins,⁸¹ operating at high pressure to decrease CO₂ bubbling,⁸² elevated temperature (~ 75 °C),⁸³ and increasing the total number of ED stacks to increase the total device efficiency.^{80,84}

A recent analysis⁸⁵ calculated total energetic and cost requirements of the DAC setup of Carbon Engineering⁴ as described earlier with a BPMED process^{63,82} instead of the caustic calcium high temperature recovery loop to regenerate the hydroxide capture sorbent. Projected energetics for a BPMED regeneration unit for DAC were 236 kJ_e mol⁻¹ for compression to 150 bar.⁶⁴ While this compares favorably to the energetics presented by the plant calculations by Carbon Engineering,⁴ BPM and ionic membrane costs and short membrane lifetimes make BPMED prohibitively expensive in current markets.

The main advantages of BPMED are the ambient temperature operation and simpler processing that reduce the potential for high temperature decomposition and water loss. As the process is powered by electricity, fuels required for high temperature decomposition of CaCO₃ are not

needed here, which is advantageous as long as cheap and carbon-free electricity is available. This cost analysis, however, brings to light issues that are needed to make BPMED a viable alternative.

When the capture sorbent is OH^- , BPMED is most efficient with lower pH HCO_3^- regeneration (1 H^+) instead of higher pH CO_3^{2-} (2 H^+).⁶³ However, the rate of capture of CO_2 in a sorbent decreases as the pH decreases, indicating competing interests for efficient capture and efficient BPMED-mediated regeneration.^{63,85} This indicates that future optimization of BPMED should be focused on both capture and regeneration together.⁸¹ As membranes are cost prohibitive, the challenges are to increase the operating current density, increase the efficiency of water splitting, and increase membrane lifetime. In ref. ⁸⁵ a number of possible improvements in membranes are suggested, including segmented bipolar membranes, which both split water and transport ions. BPMs themselves may find applications in all-in-one CO_2 capture and reduction electrolyzers.

PCET of organics. In proton-coupled electron transfer-mediated CO_2 capture/release, H^+ is stored on a water soluble organic and the organic is oxidized to decrease the pH and release CO_2 from solution or reduced to increase the pH and regenerate the CO_2 capture sorbent.^{42,61} A general scheme of a redox-active molecule Q that is cycled between $Q + 2\text{H}^+ + 2e^- \leftrightarrow \text{QH}_2$ and mediates CO_2 capture by production of OH^- is shown in the top of Figure 4a).

Covered in another review,⁶ organic redox electrochemistry for CO_2 capture has largely been studied in aprotic media for direct reduction and capture of CO_2 , though recent work enabled direct capture with highly concentrated aqueous electrolytes.⁸⁶ Indirect capture through pH swings is relatively less studied. A general methodology and thermodynamic cycle for pH swings using PCET of small redox-active organics is given in ref. 87. Within this work, the theoretical minimum for flue gas capture was calculated at ambient conditions to be 16–75 $\text{kJ}_e \text{ mol}^{-1}$ and for DAC 30–75 $\text{kJ}_e \text{ mol}^{-1}$; the redox potential of the cycle is plotted in the bottom of Figure 4a). Similarly to the EMAR cycle, the potentials of the oxidation ($\text{QH}_2 \rightarrow Q$, generation of H^+) and reduction ($Q \rightarrow \text{QH}_2$, generation of OH^-) paths as a function of charge passed (measured here by concentration of Q), define the electrochemical cycle and are integrated to calculate the minimum energy of capture and release.

A proof-of-concept of PCET-mediated CO_2 separation was demonstrated as a membrane with TM catalysts deposited on carbon electrodes separated by a polypropylene separator and NaHCO_3 electrolyte with 5mM benzoquinone or 2,6-dimethylbenzoquinone. CO_2 gas was introduced to the negative electrode, captured at high pH, transported through the pH gradient of the electrolyte, released at low pH, and finally detected at the positive electrode.⁸⁸ Undesired water splitting yielding H_2 and O_2 , low solubility of the quinones, and low throughput limited this configuration.

In another demonstration, a CEM was used to separate the catholyte and anolyte to maintain the pH gradient and the redox agent was the more soluble tiron (1,2-dihydroxybenzene-3,5-disulfonic acid). In an aqueous K_2SO_4 electrolyte with 0.1–0.7 M quinone, CO_2 was successfully

released on oxidation, however pH drifts let to difficulties in reducing the quinone to regenerate the capture sorbent, OH^- .⁶⁶ A recent bio-inspired approach used a biological proton carrier, 25 mM riboflavin 5'-monophosphate (FMN), to enable CO_2 capture and release and reported $\sim 10 \text{ kJ}_e \text{ mol}^{-1}$ for 15 % CO_2 at 60 °C.⁶⁷

To enable effective CO_2 capture with PCET of an organic molecule, Q, the catholyte must reach and be stable at a high pH to better capture CO_2 , which is controlled in part by concentration (solubility), pKa, and buffering capacity of the electrolyte.⁸⁷ Ion selective membranes are also needed to maintain the pH gradient, keeping the catholyte at high pH and the anolyte at low pH. While in theory either AEMs and CEMs could be used with a supporting salt, inevitable undesired transport of acidic/basic species will decrease the pH gradient.⁶⁶ Alternate membrane and cell designs could limit this effect.⁸⁷ The redox kinetics of Q and the dynamics and transport of active species at the electrodes will also be critically important. The localized concentration gradients and pH at the electrode will impact the concentration overpotential; the study of which will be aided by experience from the CO_2 reduction community.⁸⁹ Also importantly, the system must be stable in the presence of O_2 and other flue gas contaminants.

pH swings mediated by small molecule redox is a budding area of research, and the possibility of ambient or near ambient operation and potentially less toxic and cheaper redox mediators make it an attractive area for electrochemically-mediated CO_2 capture and release.

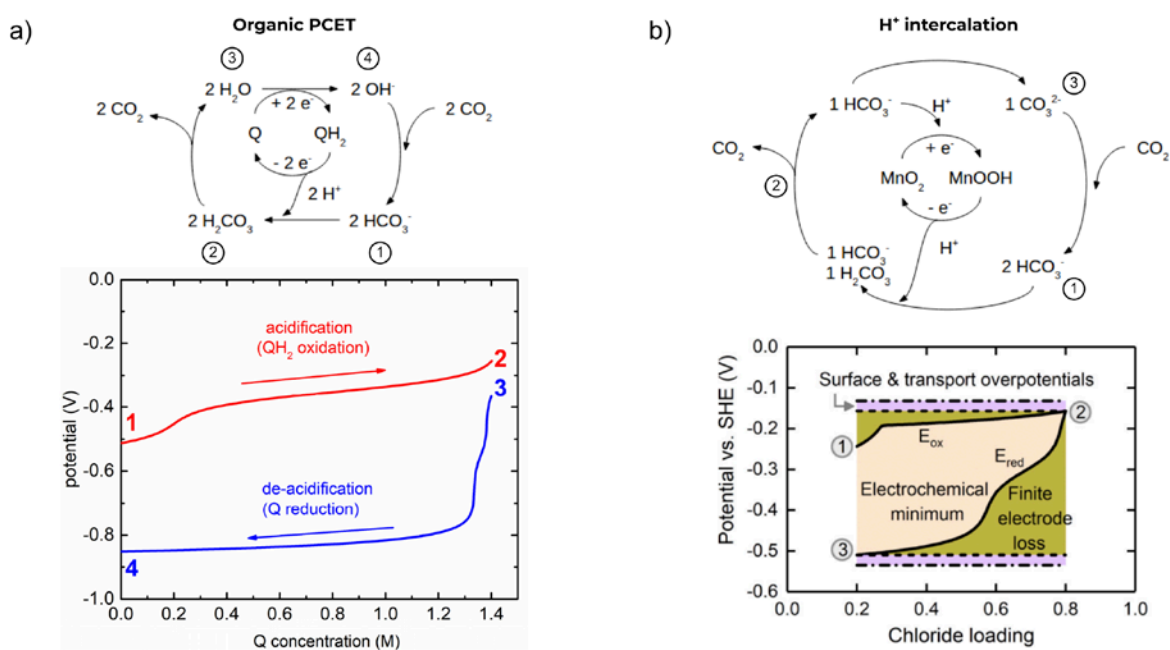


Figure 4. pH swings with organics and metal oxides. a) sketch of PCET cycle and thermodynamic cycle of an organic redox-active molecule, Q, mediating CO_2 capture via OH^- and H^+ generation. b) sketch and thermodynamic cycle for K_2CO_3 -based CO_2 capture and regeneration mediated by H^+ intercalation into MnO_2 . a) plot reprinted from ref. ⁸⁷ under the [CC BY-NC-ND 4.0](https://creativecommons.org/licenses/by-nc-nd/4.0/) license. b) plot reprinted from ref. ⁹⁰ under the [CC BY-NC-ND 4.0](https://creativecommons.org/licenses/by-nc-nd/4.0/) license.

H⁺ intercalation/PCET of metal oxides. In another method of CO₂ capture/release, the pH is controlled by intercalating and storing H⁺ into an oxide electrode, e.g., MnO₂, contrasting it to the storage in the form of hydrogenated organics or hydrogen gas in the previous sections. Though based on TM redox chemistry, this technique is grouped with pH swings as the H⁺ storage capability of MnO₂ is specifically taken advantage of. This technique has been explored as an alternative to pressure/thermal swing regeneration for K₂CO₃ based absorption for flue gases.^{64,90} A sketch and thermodynamic cycle of the MnO₂-mediated capture/release are shown in Figure 4b).

Manganese dioxide, MnO₂, is commonly used as a cathode in lithium and alkaline primary batteries and exists in many different polymorphs, some of which contain stable tunnel structures that allow reversible intercalation of H⁺/Li⁺.^{91,92} Mn(IV)O₂ can be reduced and intercalate protons to form manganese oxyhydroxide, Mn(III)OOH: $MnO_2 + H^+ + e^- \leftrightarrow MnOOH$. Applied for a pH swing, or alternatively called a proton concentration process, protons are either de-intercalated (Mn is oxidized) to decrease the pH and release captured CO₂, or protons are intercalated (Mn is reduced) to increase the pH and regenerate the capture sorbent. In the setup of ref. 64 an AEM is used to separate the anode and cathode. Taking the transference number of Cl⁻ as one, the Cl⁻ loading can be used to indicate bulk pH changes and define the (electro)chemical cycle as shown in Figure 4b). Cl⁻ concentration increases as the solution is acidified to release CO₂, and decreases as the CO₃²⁻ is regenerated. The theoretical minimum energy for the capture and release cycle for 15 % CO₂ was calculated to be 23 kJ_e mol⁻¹.⁹⁰ The use of MnO₂ as a proton host for CO₂ release and regeneration of K₂CO₃ is a new concept that has been validated on the bench scale.⁶⁴

As mentioned earlier, K₂CO₃ capture suffers from low rates of CO₂ absorption, which are usually compensated by higher temperatures and rate promoters; future development of a H⁺ intercalation process for K₂CO₃ would require consideration of these factors. An additional consideration is the long-term stability and reversibility of the MnO₂ electrodes, i.e. the reversible capacity. MnO₂ has poor electrical conductivity and thus high charge transfer resistance and can dissolve, particularly in acidic environments. MnO₂ electrodes are often prepared thin, doped, and stabilized with polymer binders;⁹² the relative sizing of the electrodes to the capacity of the CO₂ capture system would be important. An additional consideration is the permselectivity of the AEM on the overall energetics of the system, as multiple anions are present in the system: Cl⁻, CO₃²⁻, HCO₃⁻, and OH⁻. As mentioned in the organic PCET section, consideration of the local pH at the electrodes, particularly important for MnO₂, and the stability with O₂ and other gaseous components of flue gas is critical for future development.

Capacitance based capture. Another pH swing system uses deionized H₂O and membrane capacitive deionization (MCDI) to store and release CO₂. A sketch of a MCDI cell is shown in Figure 5 and consists of one carbon electrode covered by an AEM and another carbon electrode covered by a CEM. When an appropriate potential is applied between the electrodes, cations are stored in the double layer of the negative electrode, and anions in the positive electrode, thereby desalinating the aqueous electrolyte. Reversing the current releases the ions into solution.⁶⁵

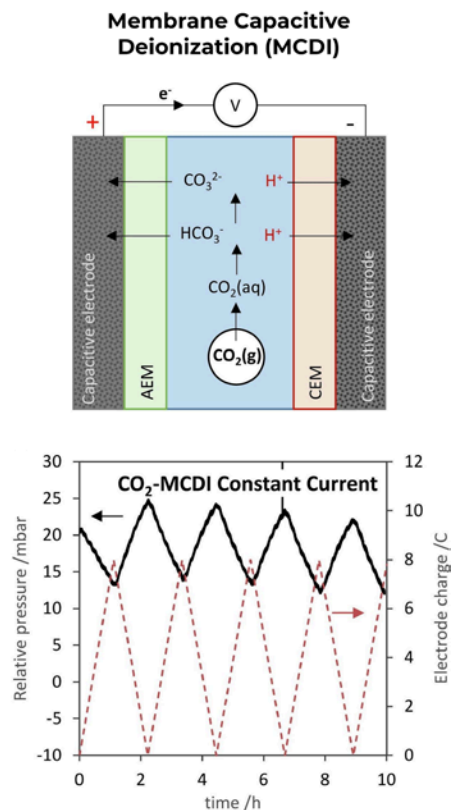


Figure 5. Capacitive-based CO_2 capture. The top sketch shows the MCDI setup and illustrates the CO_2 capture process. The bottom plot shows the cyclic capture of CO_2 (dip in pressure) as the electrodes are charged and release of CO_2 (increase in pressure) as the electrodes are discharged. Both graphics reprinted from ref. ⁹³ under the [CC-BY](#) license.

When CO_2 is absorbed, it is in equilibrium with all of its forms: $\text{CO}_2(\text{aq}) \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-}$. For CO_2 capture, MCDI works by separating $\text{HCO}_3^-/\text{CO}_3^{2-}$ and H^+ in deionized water, storing CO_2 as adsorbed bicarbonate/carbonate at the electrode as shown in the top of Figure 5.⁶⁵ By trapping the ions on the electrode surfaces, the equilibrium is shifted and more CO_2 can be absorbed into solution. The amount of stored CO_2 is dictated by the electrode charge. Upon reversal, desorption of the ions in solution shifts the equilibria and CO_2 is desorbed and released. MCDI is a mixed method where capture proceeds via absorption and storage via adsorption. A related capture system is supercapacitive swing adsorption (SSA).^{74,75}

The efficiency of the capacitor is measured by the charge efficiency, the sum of the charged (bi)carbonate species over the total charge passed, and has an ideal value of 1 if only HCO_3^- is present. Co-ion expulsion and undesirable faradaic reactions reduce the charge efficiency. As in other methods, HCO_3^- is more efficient for storing CO_2 than CO_3^{2-} and is controlled by the local pH. As in CO_2 reduction, the local pH in the pores/surface of the electrode dictates the observed behavior rather than the bulk pH in solution. A locally high pH at the positive electrode will shift the equilibria of the absorbed CO_2 to CO_3^{2-} , thus reducing the capacitor's efficiency.

Losses in the system are generally grouped into ohmic (solution resistance) and non-ohmic (concentration polarization and faradaic reactions). MCDI suffers from low rates of capture and high solution resistances at low CO₂ uptake.⁶⁵ However, initial calculations from proof of concept demonstrations estimated ~ 40–50 kJ_e mol⁻¹ for capture and release of 15 % CO₂ in N₂, showing competitiveness with other electrochemical methods for flue gas capture. The concept of MCDI for CO₂ capture is quite novel and thus basic research on the fundamental understanding of the nature of the surface charges and the dissociation of the weak acids present in the system is needed.⁹³ The complexity will inevitably increase in the presence of reactive species like O₂ and other components of air and flue gases.

4. Conclusions and future research and development opportunities

Traditional CO₂ capture is typically mediated by thermal or pressure swings of carbonates, hydroxides, and/or amines. In this review, we covered alternative electrochemical CO₂ capture systems employing TM-redox couples and pH swings with either direct or indirect/competitive capture. These systems included dinuclear Cu complexes, electrochemically-mediated amine regeneration (EMAR) utilizing mononuclear Cu-amine complexes, bipolar membrane electrodialysis (BPMED), PCET of small organics, H⁺ (de)intercalation of TM oxides, and membrane capacitive deionization (MCDI). For (nearly) all systems, CO₂ is captured cathodically and released anodically. Electrochemically-mediated CO₂ capture methods are appealing due to the possibility of ambient operation, the ability to control the applied potential, and the low theoretical energy penalties of capture/release. The pH swing systems discussed are also appealing due to their use of less toxic materials. In a number of the reviewed systems, bench- and lab-scale operation has already demonstrated proof of concept and feasibility.

The recent advances in the engineering and the theoretical foundations of the principles of electrochemically-mediated CO₂ capture and separation are impressive and have laid the groundwork for future work. Continuing advances and knowledge from CO₂ reduction, bipolar and anion exchange membranes, intercalative batteries, bio-mimetic/inspired design of the biological processes of PCET and CO₂ uptake, and, as discussed in ref. 87, redox-flow batteries, will all accelerate improvements in electrochemically-mediated CO₂ capture. Future work in the field will include fundamental research on new redox-active sorbents and competitors, fundamental research on surface processes and electron/charge transfer kinetics, studies of reactivity with O₂ and flue gas contaminants, engineering of advanced device architectures and scale-up, and coupling CO₂ capture/concentration with subsequent CO₂ reduction.

To fully realize the low theoretical energy penalties of electrochemically-mediated CO₂ capture, further work is needed to increase CO₂ uptake rates and improve electron and charge transfer kinetics by a fundamental understanding of the elementary reaction steps. Further improvements are needed in terms of CO₂ capture/release configurations (i.e. absorb at the cathode, desorb at the anode) and membrane permselectivity that can be achieved by a more comprehensive molecular understanding of the interaction of the membrane chemistry with ions and solvents. Additionally, future electrochemically-mediated CO₂ capture systems need

increased operable current rates and more molecular understanding of the evolution of their cycling performance coupled with insight into their decomposition pathways. Particularly unexplored are short and long-term (electro)chemical reactivity to O₂, SO_x/NO_x, and other flue gas contaminants, which are required for any practical CO₂-capturing system. Future work must focus on the possible detrimental cross-coupling effects of contaminants on the CO₂ capture (electro)chemistry.

Of particular importance will be new strategies to combine CO₂ capture and subsequent reduction to useful products, that is, valorization of CO₂. Specifically, the aim will be, on a molecular level, to couple in space and time the interfacial release of captured CO₂ and immediate subsequent interfacial CO₂ reduction. If direct electrocatalytic reduction of CO₂ could be realized using feeds of CO₂-loaded capture media, expensive process steps related to CO₂ separation and pressurization could be eliminated, raising the overall energy efficiency of the process chain. In other words, the goal is to couple the cathodic processes of CO₂ release and reduction. For example, the electroreduction of CO₂ from bicarbonate feeds can be considered a trivial case of such a coupling scheme, where local pH gradients and acid-base equilibria play a key role in the release and local supply of CO₂.

Electrochemically-mediated CO₂ capture will particularly benefit from closer ties to the surface and interface science communities investigating electrocatalytic CO₂ reduction. Specifically valuable will be the techniques that focus on a deep atomic-scale understanding of the interfacial electrochemical processes and molecular-level insights into the charge and mass transport across membranes, which will provide valuable guidance for material development and device optimization. To achieve the necessary level of atomic-scale understanding of the interfacial electrochemical processes, the application of *in-situ* and *operando* characterization techniques to understand the chemical state and morphology of the active catalyst, the rate and selectivity of the elementary reaction processes, and the nature of reactive and spectator species inside the electrochemical double layer as well as Nernst diffusion layer will prove useful.^{94–96}

X-ray based *operando* electrochemical analysis techniques, such as WAXS,⁹⁷ XANES,^{98–100} EXAFS,^{101–103} XPEEM,¹⁰⁴ and XPS^{105–110} will provide time- and space-resolved information about the chemical states of the catalyst surface and its bulk. Of particular interest is the recent development of ambient pressure X-ray photoelectron spectroscopy with tender (hard) X-rays (AP-HAXPES).^{111–113} Its ability to operate at pressures exceeding the vapor pressure of water at room temperature (25 mbar) combined with the increased information depth of the measurement afforded by the kinetic energy of the photo-emitted electrons allow for the in-situ investigation of solid/aqueous electrolyte interfaces with bulk-like liquid films at ambient conditions. These measurements allow for direct correlation between chemical transformations at the interface and experimental conditions (e.g., applied potential) and promise to provide deep insight into the mechanisms of chemical transformations at electrochemical interfaces.^{114,115}

Differential Electrochemical Mass Spectrometry (DEMS)^{116–118} coupled to *inline* electrochemical inductively coupled plasma (ICP)-MS analysis^{119–127} will offer insights into individual reaction rates and selectivities, onset potentials of metal dissolution and deposition, as well as formation and consumption rates of intermediates and products. In select cases, *operando* electrochemical UV-vis spectroscopy of the electrochemical interface can serve as a time-resolved analytical technique to follow the time trajectories of chemical redox states of metal centers in the catalyst or in the electrolyte.¹²⁸ Furthermore, vibrational *operando* electrochemical techniques such as FTIR or Raman spectroscopy provide insight in the rate of accumulation or consumption as well as the chemical structure of surface-adsorbed intermediates or species in the bulk electrolyte.^{129–132}

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