

Review

Challenges and opportunities in continuous flow processes for electrochemically mediated carbon capture

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SUMMARY

Carbon capture from both stationary emitters and dilute sources is critically needed to mitigate climate change. Carbon dioxide separation methods driven by electrochemical stimuli show promise to sidestep the high-energy penalty and fossil-fuel dependency associated with the conventional pressure and temperature swings. Compared with a batch process, electrochemically mediated carbon capture (EMCC) operating in a continuous flow mode offers greater design flexibility. Therefore, this review introduces key advances in continuous flow EMCC for point source, air, and ocean carbon captures. Notably, the main challenges and future research opportunities for practical implementation of continuous flow EMCC processes are discussed from a multi-scale perspective, from molecules to electrochemical cells and finally to separation systems.

INTRODUCTION

Climate change caused by anthropogenic greenhouse gas emissions is one of the biggest challenges facing humanity today owing to its profound global impact. The atmospheric concentration of carbon dioxide (CO₂), the most prevalent greenhouse gas, is now 50% higher than before the industrial revolution. To meet the Paris Agreement's goal of limiting the total global warming to less than 2°C above pre-industrial levels with an aspirational target of 1.5°C, carbon capture and storage as well as negative emissions technologies are projected to assume a critical role in all climate change mitigation scenarios (Bui et al., 2018; IPCC et al., 2018). Carbon capture and storage technologies involve capturing CO₂ from stationary emitters (coal and gas power plants, steel, cement, fertilizer productions, etc.) followed by either using this CO₂ as a resource to create valuable products or sequestering it permanently in geological formations (MacDowell et al., 2010; Millar and Allen, 2020). The deployment of carbon capture and storage processes also provides foundational knowledge to enable negative emissions technologies, such as CO₂ removal from biomass combustion or directly from the atmosphere or seawater (Lackner et al., 2012; National Academies of Sciences, Engineering, and Medicine, 2019).

The conventional carbon capture methods, notably amine scrubbing, carbonate looping, and solid adsorbents, rely on thermal or pressure swings to modulate the affinity of sorbents for CO₂ (MacDowell et al., 2010). Despite the broad consensus on the importance of carbon capture technologies, they have not been implemented fast enough to the scale necessary to close the anthropogenic carbon cycle. One major technical barrier is the high energy penalties associated with such processes. For example, post-combustion capture from a coal-fired power plant by amine scrubbing can reduce the power plant's net efficiency by about 30% (Ciferno et al., 2009; Rochelle, 2009). Moreover, amine scrubbing is challenged by high-temperature sorbent evaporation and degradation, process equipment corrosion, and the need to modify steam cycles when retrofitting existing power and chemical plants (Lucquiaud and Gibbins, 2011; Rochelle, 2012). This motivates fundamental research on new CO₂ separation methods that are effective, efficient, easy to deploy, and adaptable to the multi-scale nature of carbon capture applications.

With the accelerated deployment of utility-scale wind and solar power and the consequent plunging cost of electricity from these renewable sources (Haegel et al., 2019), electrochemically mediated carbon capture (EMCC) methods have galvanized increasing research interests in the past decade (Gurkan et al., 2021; Renfrew et al., 2020; Rheinhardt et al., 2017; Sharifian et al., 2021). In a typical EMCC process, the sorbent material is reversibly activated and deactivated for CO₂ capture and release via applying electrochemical

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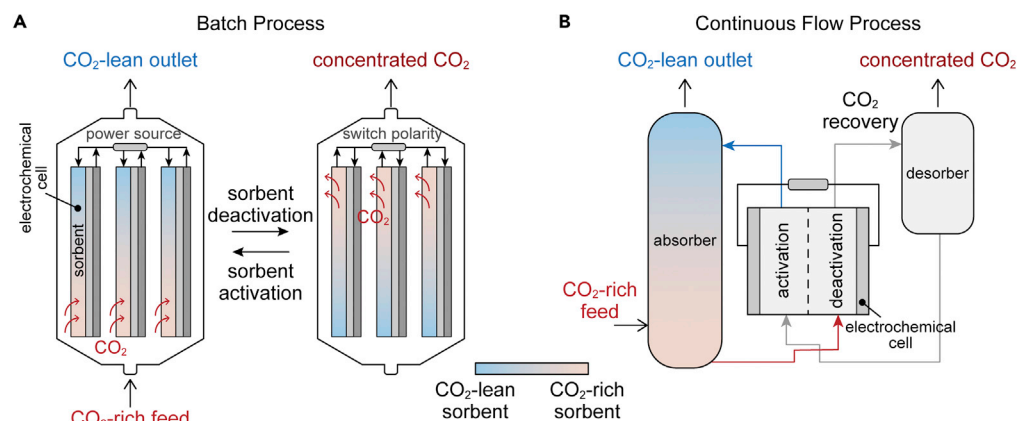


Figure 1. Overview of the two typical process configurations for EMCC

Schematic of the general operation mode for (A) batch-based and (B) continuous flow EMCC processes.

potentials. As a result, EMCC can operate isothermally, desorb concentrated CO₂ at ambient or even elevated pressure, and enable a simple, modular design. Moreover, EMCC processes target directly at the sorbent species not the media, which minimizes the energy cost associated with sensible heat as in the case of temperature swing. Finally, as EMCC is based solely on electricity as an input, it can be turned off and on with minimal efficiency losses compared with temperature or pressure swings, making it ideal for coupling to intermittent renewable energy sources. Such distinct features promise disruptive carbon capture technologies that are cost-effective yet remain flexible enough to address decentralized emissions and accommodate an ever-changing energy landscape.

Several recent reviews have exhaustively surveyed the various mechanisms of EMCC approaches (Renfrew et al., 2020; Rheinhardt et al., 2017; Sharifian et al., 2021), which can have configurations ranging from supported liquid membranes (Gurkan et al., 2015) to heterogeneous sorbent electrodes for cyclic capture and release (Voskian and Hatton, 2019), to flow systems (Diederichsen et al., 2022). In a batch process, sorbent species are fixed inside an electrochemical cell (often as adsorbents immobilized on electrodes, but can also be static liquid sorbents). During capture, the sorbents are electrochemically activated, whereas the system opens toward a CO₂ feed stream; once the sorbent capacity is reached, the feed flow is stopped, and the sorbents are deactivated by reversing the polarity of the electrodes (Figure 1A). One important consideration associated with cyclic EMCC operations is the necessity to scale the electrochemical reactor directly with the gas transfer area. The large area over which the captured gas is released may also present engineering challenges, such as the need for purging between capture and release and for constructing a complex network of distributors and valves. Compared with a batch process, continuous flow EMCC in which liquid sorbents are activated or deactivated in a central electrochemical cell before the fluids are transferred to an absorption or desorption unit (Figure 1B), offers greater design flexibility and the advantage of capturing over distributed areas while releasing at a single-point location. The high electrode area to the reaction volume ratio and the narrow inter-electrode gap in an electrochemical flow cell also add to the appeal of continuous flow EMCC, which can minimize ohmic drop and mass transfer losses for better system energetics. We therefore focus our discussion on continuous flow EMCC processes. We first summarize the general concepts of flow-based EMCC for point source, air, and ocean carbon captures, and then highlight the recent advances. After that, we discuss the main challenges toward practical continuous flow EMCC processes and provide an outlook on opportunities for future research.

EMCC MECHANISMS COMPATIBLE WITH CONTINUOUS FLOW PROCESSES

EMCC via pH swing

The vast majority of continuous flow EMCC processes demonstrated to date employ the concept of pH swing, in which the pH of an aqueous solution is electrochemically shifted between basic and acidic to influence the carbonic acid equilibrium for CO₂ capture and release, respectively (Figure 2A) (Sharifian et al., 2021).

The spontaneous chemical reaction between CO₂ and alkali hydroxide solutions (NaOH, KOH) to form (bi) carbonates is perhaps the most straightforward concept for carbon capture from stationary emitters or the

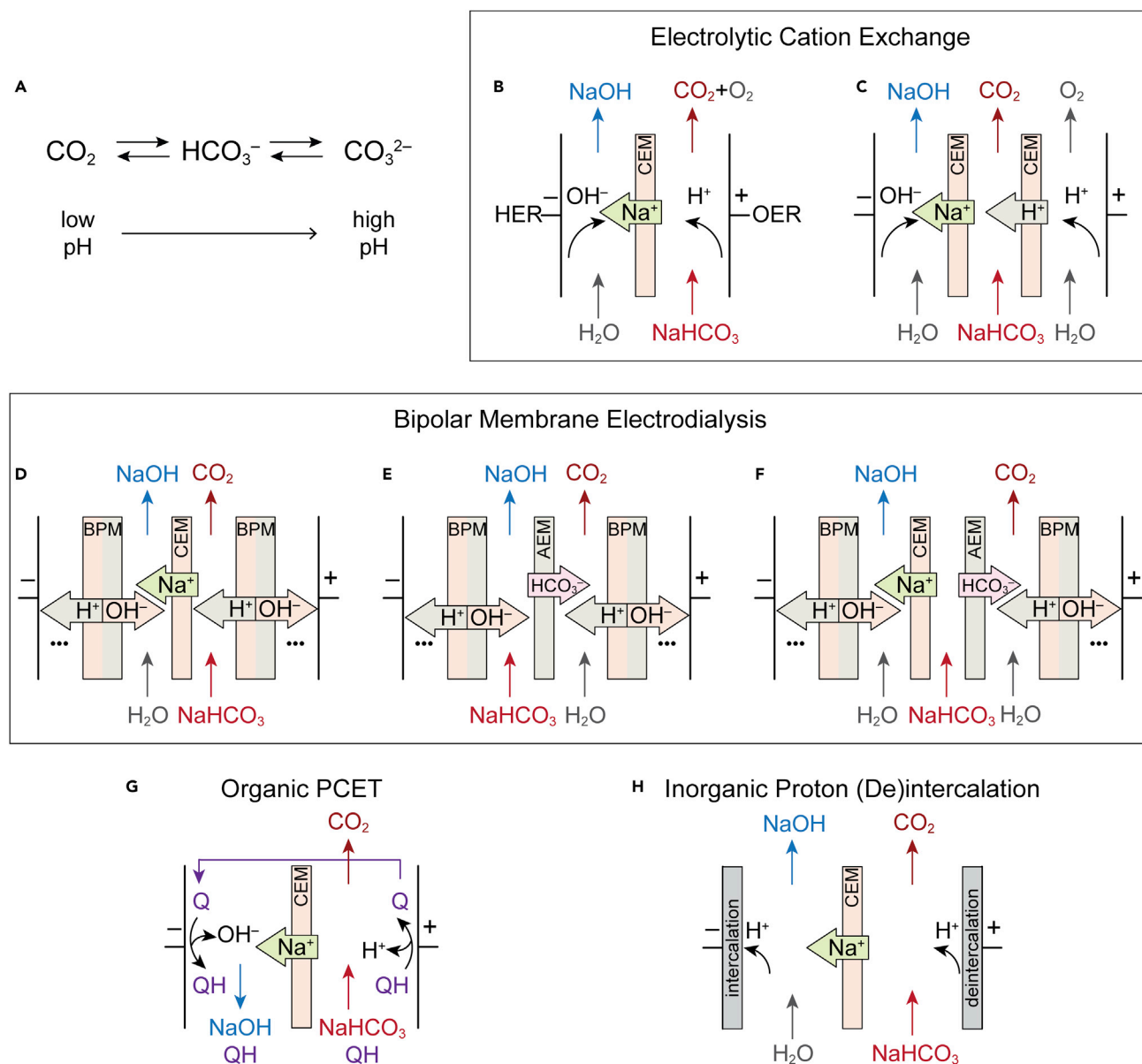


Figure 2. Mechanisms of EMCC via pH swings

(A) The pH swing concept, where the pH of an aqueous solution is electrochemically shifted between basic and acidic to influence the carbonic acid equilibrium for CO_2 capture and release.

(B–F) Electrolytic cation exchange (Stucki et al., 1995; Willauer et al., 2011, 2012, 2014) and (D–F) bipolar membrane electrodialysis cell designs (Eisaman et al., 2011a, 2011b; Iizuka et al., 2012; Nagasawa et al., 2009) for pH swing EMCC using NaHCO_3 as an example CO_2 carrier. The NaHCO_3 can represent spent NaOH sorbent from point-source capture and DAC or the DIC in seawater.

(G) pH swing EMCC with organic PCET molecules (Huynh et al., 2016; Jin et al., 2022; Seo et al., 2022). (H) pH swing EMCC with proton (de)intercalation inorganic electrodes (Rahimi et al., 2020a, 2020b).

atmosphere (Zeman and Lackner, 2004). Compared with aqueous amines, alkaline hydroxides have lower toxicity, lower vapor pressure, and greater resistance to gas contaminants. The conventional method to recover the spent hydroxides involves reacting the (bi)carbonates with $\text{Ca}(\text{OH})_2$ to afford solid CaCO_3 , which can then release CO_2 by heating at $\sim 900^\circ\text{C}$ in a Calcifier. The direct air capture (DAC) company Carbon Engineering optimized this process flow and designed a 1 Mt CO_2 /year pilot plant that could deliver dry CO_2 at 15 MPa with an energy consumption of 5.25 GJ/t CO_2 heat from natural gas and 366 kWh/t CO_2 from electricity (Keith et al., 2018). The negatives of this process are water loss and the need for high-grade

heat supplied by burning fuel. In addition, owing to the slow reaction kinetics between carbonate and CO₂, DAC regenerates the spent hydroxides well before the formation of bicarbonate in the air contactor, whereas point source capture can have more efficient use of hydroxides to form bicarbonates.

In parallel to chemical and thermal methods, alkaline hydroxides can also be regenerated via pH swings induced by electrochemical reactions (typically water splitting). In the earliest work by Stucki et al. (Figure 2B), the (bi)carbonate solution was passed through the anodic compartment of an electrochemical cell where oxygen evolution reaction (OER) acidified the solution to release CO₂ at the anode (Stucki et al., 1995). Simultaneously, alkali cations electromigrated across a cation exchange membrane (CEM) to the cathodic compartment, where hydroxides produced from hydrogen evolution reaction (HER) at the cathode completed the sorbent regeneration. The hydrogen gas can also be recovered as a valuable byproduct. Nevertheless, such an electrolytic cation exchange setup generates a mixed gas output of O₂ and CO₂ that is non-ideal for downstream carbon utilization or sequestration. An alternative cell design that produces CO₂ with higher purity is shown in Figure 2C, where two CEMs separate the OER and HER compartments with spent (bi)carbonate solution flowing in between (Willauer et al., 2011, 2012, 2014). A shortcoming of the design in Figure 2C is that it can only be employed as a single stack.

To overcome the above problem, subsequent bipolar membrane electrodialysis (BPMED) designs with various possible membrane arrangements (liquid flow and ionic transport shown in Figures 2D–2F) have the flexibility to be extended to multi-stack configurations (Eisaman et al., 2011a, 2011b; Iizuka et al., 2012; Nagasawa et al., 2009). Bipolar membranes (BPMs) are a special class of ion-exchange membranes that consist of a CEM layer (or CEL) and an anion exchange membrane (AEM) layer (or AEL) laminated together. Much like a p-n junction, the junction between CEL and AEL allows for the recombination of mobile charges, creating a depletion region and in turn, a large electric field. This electric field, often with the addition of water dissociation catalysts, leads to enhanced water dissociation at the junction of the BPM. H⁺ then migrates selectively through the CEL and OH⁻ migrates selectively through the AEL, developing a pH gradient across the BPM (Oener et al., 2020). As water splitting requires a substantial thermodynamic minimum energy (1.23 V), combining multiple BPMED cells in series is desirable to reduce the voltage penalty associated with the OER and HER reactions at the two terminal electrodes (Nagasawa et al., 2009).

The concept of pH swing and the above-mentioned electrochemical cell designs for regenerating alkaline sorbents can be extended to enable indirect CO₂ capture from seawater. Electrochemical ocean carbon capture extracts the dissolved inorganic carbon (DIC) in oceans (~2.2 mM, primarily in the form of bicarbonate in normal seawater of pH~8.1) by acidifying seawater (Rau, 2011; Zeebe and Wolf-Gladrow, 2001). CO₂ gas is then vacuum stripped from the acidified stream, and the CO₂-lean seawater is recombined with a basified solution cogenerated in the electrochemical cell to restore the pH of decarbonized seawater, which can further equilibrate with air over a longer timescale (2–4 months depending on the discharge locations) to capture more atmospheric CO₂ (Jones et al., 2014). Ocean capture provides an interesting alternative to DAC, as oceans are massive sinks for CO₂ with a concentration about 140 times higher than that in the air on a weight per volume basis (Willauer et al., 2014). The concept was pioneered by Willauer et al., 2011, 2012, 2014 and Eisaman et al. (2012) with flow cell designs shown in Figures 2C and 2F, respectively.

Digdaya et al. improved the energetics of BPMED ocean capture by replacing the HER and OER reactions at the terminal electrodes with a reversible reaction (the potassium ferro/ferricyanide redox couple) that has minimal thermodynamic and kinetic losses (Digdaya et al., 2020). Figure 3 shows the corresponding process flow diagram. First, the simulated seawater input stream was vacuum degassed using hollow fiber membrane contactors before entering the acidification compartment of the BPMED cell. After acidification, the CO₂ gas was vacuum stripped using another series of membrane contactors, and the acidified seawater was subsequently fed to the basification compartment of the BPMED cell to produce decarbonized oceanwater with elevated pH and the same alkalinity for the subsequent atmospheric CO₂ drawdown. Recently, built on the configuration shown in Figures 2C and 2A hydrogen-looping concept for ocean capture was proposed, where OER at the anode was replaced by hydrogen oxidation using products generated at the cathode (Yan et al., 2022). The proposed concept eliminated the use of bipolar membranes for acid and base generation and significantly improved the energy efficiency. However, the large quantity of seawater that needs to be processed through the electrochemical cell presents practical challenges.

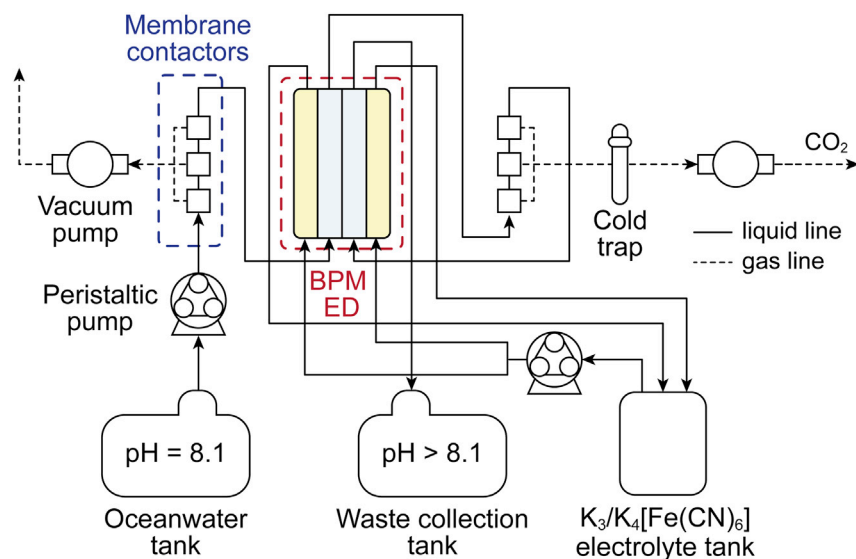


Figure 3. Process flow diagram of the experimental setup for continuous flow CO₂ capture from seawater via BPMED (Digdaya et al., 2020)

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In addition to electrodialysis, the pH of aqueous solutions can also be modulated using dissolved redox-active organic molecules that undergo proton-coupled electron transfer (PCET, Figure 2G) (Huynh et al., 2016; Jin et al., 2022; Seo et al., 2022). In this scheme, electrochemical reduction of PCET molecules (symbolized as Q, $Q + H_2O + e^- \rightarrow QH + OH^-$) raises the electrolyte pH for CO₂ capture, and the subsequent electrochemical oxidation of the reduced molecules ($QH \rightarrow Q + H^+ + e^-$) acidifies the electrolyte for CO₂ release. Classic PCET molecules such as quinone and phenazine derivatives have been demonstrated for flow-based EMCC (Jin et al., 2020; Watkins et al., 2015; Xie et al., 2020). Some inorganic materials, such as manganese dioxide (MnO₂) (Rahimi et al., 2020a, 2020b) and titanium dioxide (TiO₂) (Makivić et al., 2021), are also capable of reversible proton (de)intercalation (Figure 2H). However, given the finite capacity of these immobilized proton intercalation electrodes, continuous flow processes are only achievable if the polarity of the electrodes and the liquid flows are reversed periodically with respect to the sides of the electrochemical cell.

EMCC via redox-active CO₂ carriers or competitors

Electrochemically mediated capture and release of CO₂ can also be achieved, either directly or indirectly, by regulating the oxidation state of redox-active sorbents or competitors, respectively.

For direct modulation, the sorbent species must be redox-active, and its CO₂ binding affinity is reversibly tuned via an electrochemical reduction and oxidation cycle (Figure 4A). Redox-active organic CO₂ carriers fall into this category (Rheinhardt et al., 2017). Mizen and Wrighton first observed that the electrochemical reduction of quinones in aprotic media generates nucleophiles that can form adducts with the electrophilic CO₂; the adducts can be subsequently oxidized to regenerate the parent quinone while liberating pure CO₂ (Mizen and Wrighton, 1989). Figure 4B shows a stepwise scheme of the capture and release mechanism using anthraquinone as an example. Other electrogenerated nucleophiles based on bipyridine and disulfide chemistries have also been explored (Ishida et al., 1994; Ranjan et al., 2015; Singh et al., 2017). Whereas reports on proof-of-concept EMCC with redox-active organic carriers are primarily batch processes (Hemmatifar et al., 2022; Liu et al., 2020a, 2020b; Scovazzo et al., 2003; Voskian and Hatton, 2019) or supported liquid membranes (Gurkan et al., 2015), the first flow-based prototype was demonstrated recently (Diederichsen et al., 2022). In that study, a naphthoquinone derivative was synthesized, which is a liquid at room temperature (“liquid quinone”). By combining this liquid quinone with low volatility glymes as a diluent for salt dissolution, the researchers formulated a redox-active liquid sorbent with high active material concentrations (above 1 M, 1 equiv of quinone captures 2 equiv of CO₂). In their constructed flow EMCC setup, the sorbent was activated (reduced) in an electrochemical flow cell, contacted with CO₂ in an absorber column, then deactivated (oxidized) in a second flow cell, and allowed to release CO₂ in a desorption tank before being cycled back to the first cell (Figure 5A). In addition to reversible

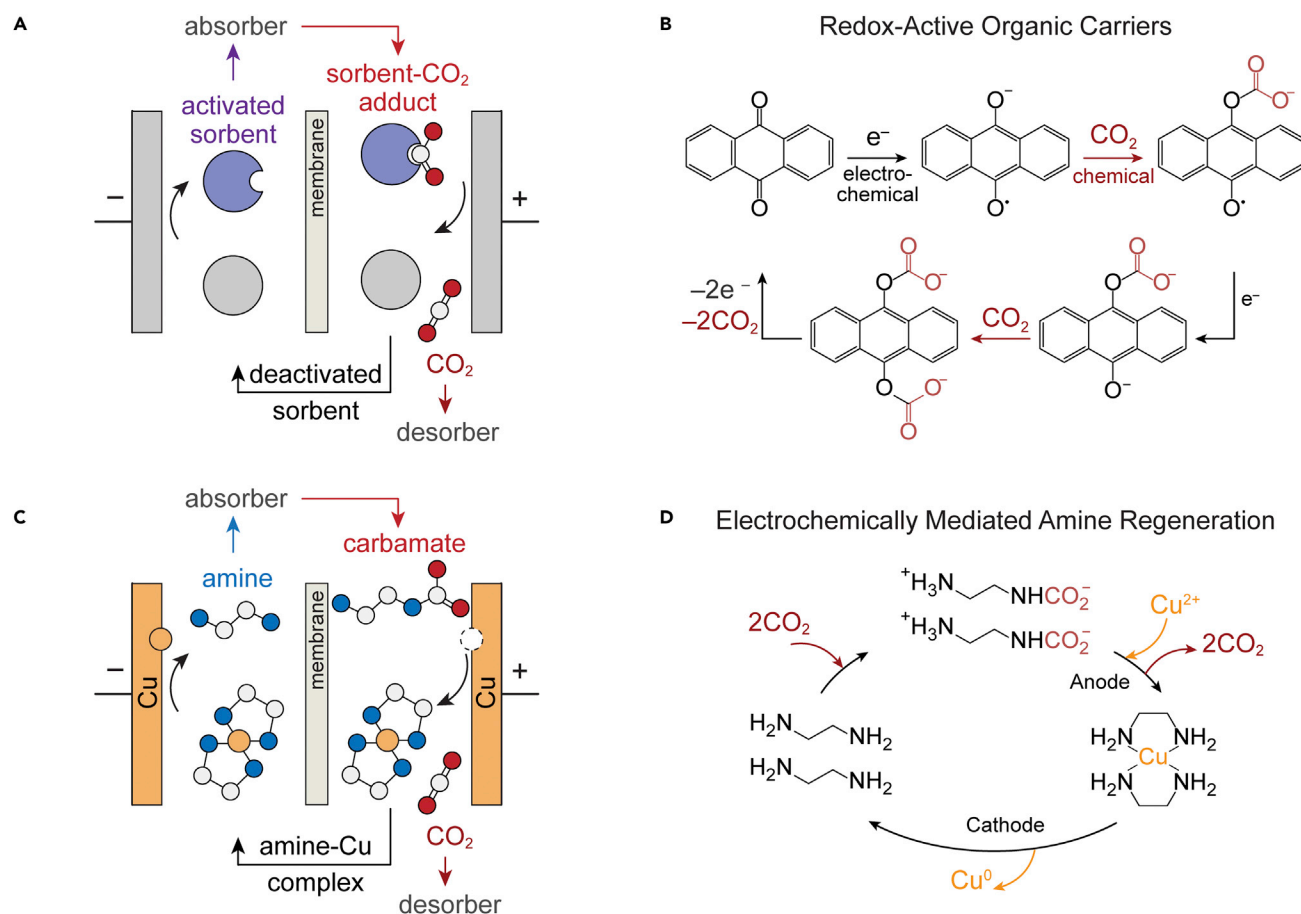


Figure 4. Mechanisms of EMCC via redox-active CO₂ carriers or competitors

(A and B) Schematic and (B) the mechanism of reversible CO₂ adduct formation using redox-active organic CO₂ carriers. Anthraquinone is used as an example to show the chemistry of the capture-release process.

(C) Schematic and (D) the mechanism of the capture-release cycle in EMAR.

CO₂ complexation with redox-active organic carriers, several transition metal clusters have also been reported to bind carbonate ions triggered by changes in the oxidation state of the metal centers (Appel et al., 2005; Newell et al., 2005), although no flow EMCC process has been demonstrated yet.

For indirect modulation, the sorbent itself is not redox-active. However, the system contains a redox-active competitor species that, when electrochemically activated, competes with CO₂ for sorbent binding and thereby desorbing the CO₂. The competitor can then be electrochemically deactivated to regenerate the sorbent. One prominent example of indirect EMCC is the electrochemically mediated amine regeneration (EMAR) process pioneered by Hatton and co-workers (Stern et al., 2013; Stern and Hatton, 2014; Wang et al., 2019a, 2019b, 2020b), in which cupric ion (Cu²⁺) serves as the competitor for amine complexation (Figures 4C and 4D). In a typical continuous flow EMAR system (Figure 5B), CO₂ is captured by conventional aqueous amine solutions to form carbamate in an absorption column. In lieu of thermal regeneration, the solution is sent to the anodic chamber of a parallel plate electrochemical flow cell, where the oxidation of the metallic Cu⁰ electrode generates Cu²⁺, affording amine-Cu complexes to displace CO₂. CO₂ can then be disengaged in a flash tank, and the CO₂-lean, Cu²⁺-rich amine solution will be pumped to the cathodic chamber of the same electrochemical cell to reduce Cu²⁺ back to Cu⁰, thus regenerating the free amine for another absorption cycle. The polarity of the electrodes and the liquid flow needs to be switched periodically in EMAR owing to the finite capacity of the metallic Cu⁰ electrodes.

Some other EMCC concepts that are potentially compatible with continuous flow processes are also being actively investigated in the research community, such as electromigration-assisted carbon capture driven

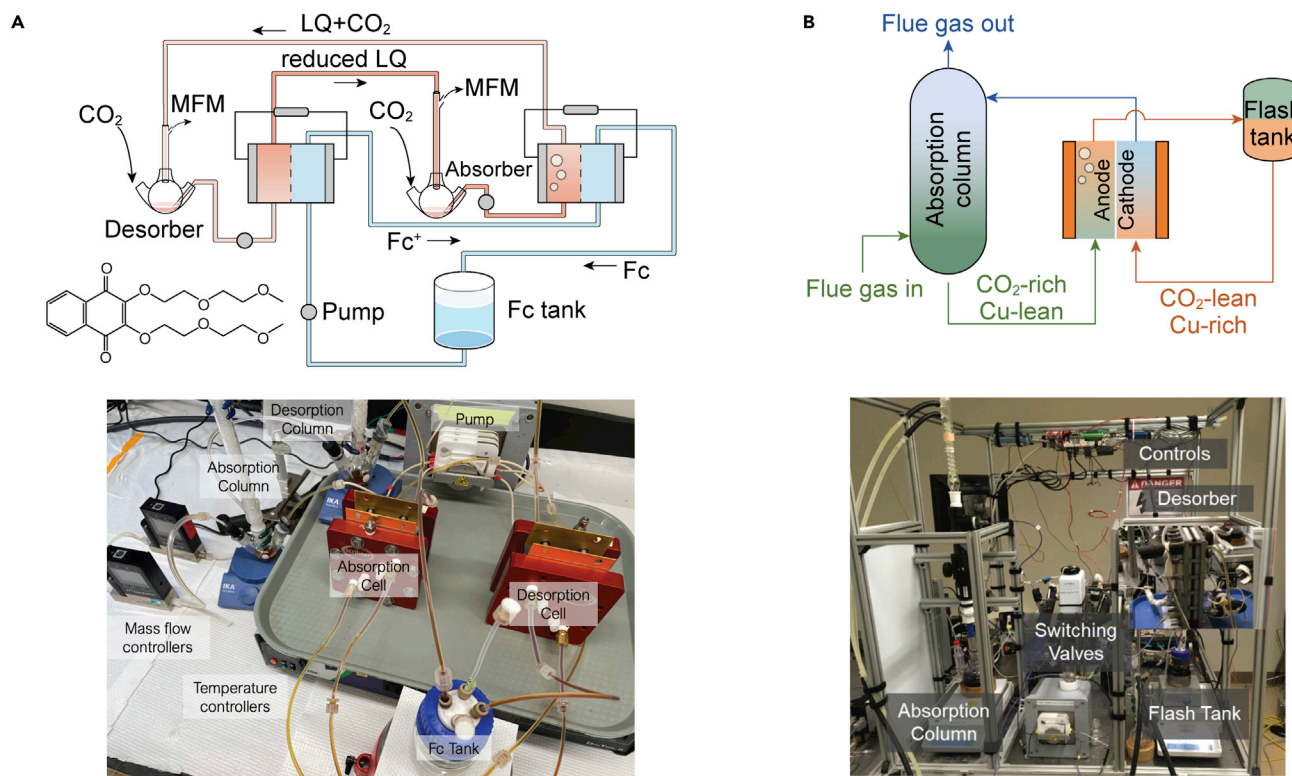


Figure 5. Schematic and photograph of bench-scale systems using (A) liquid quinone (LQ) as a redox-active CO₂ carrier (Diederichsen et al., 2022) and (B) EMAR (Wang et al., 2019b)

(A) Adapted and reprinted from Figures 6A and S14, respectively, with permission from Diederichsen et al. (2022). Copyright 2022, Elsevier. (B) Reprinted from Figure 3C with permission from Wang et al. (2019b). Copyright 2019, Elsevier.

by a moisture gradient (Prajapati et al., 2022), electrolytic carbonate mineralization (La Plante et al., 2021), electrolytic dissolution of minerals for enhanced weathering (House et al., 2007; Rau et al., 2013), and coupled carbon capture and conversion via a bicarbonate electrolyzer (Li et al., 2019b).

CHALLENGES AND OPPORTUNITIES TRANSFORMING FROM BATCH TO CONTINUOUS FLOW SYSTEMS

Chemistries of redox-active species

The physicochemical and kinetic properties of redox-active species are critical to the performance of EMCC processes in which they are used. Therefore, this section discusses the design of redox-active species at the molecular level for continuous flow EMCC, which is the most relevant to pH swing processes enabled by reversible redox couples or organic PCET molecules and processes with redox-active CO₂ carriers or competitors.

Sorbent solubility

The solubility of redox-active species is critical for continuous flow EMCC, as it dictates the carbon capture capacity as well as the size and cost of the infrastructure. For example, Figure 6A shows the minimum concentration of PCET molecules required to convert 99% of carbonate/bicarbonate to CO₂ at a fixed DIC concentration under a headspace of 0.1 bar or 400 ppm CO₂ (Jin et al., 2020). Moreover, sufficient CO₂ carrier solubility is required to overcome the partial pressure difference between capture and release owing to the physical solubility of CO₂ in electrolytes. This is particularly important when using organic electrolytes (e.g., redox-active organic carriers) owing to the relatively high CO₂ solubility in organic solvents. Figure 6B shows the minimum organic carrier concentration in representative organic electrolytes at different desorber pressures with a 0.1 bar CO₂ feed. To increase the active material concentration, inspiration can be drawn from research on redox flow batteries, where strategies such as molecular engineering, electrolyte engineering, and slurry-based flow systems are employed (Ding et al., 2018; Luo et al., 2019). Along this

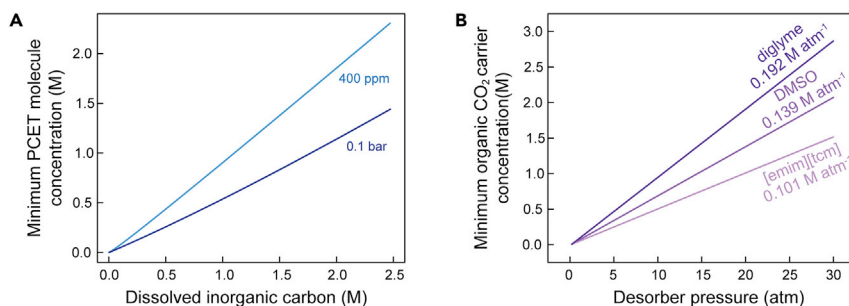


Figure 6. Minimum sorbent solubility requirements for continuous flow EMCC

(A) The minimum concentration of PCET molecule required to convert 99% of DIC into CO₂ under 0.1 bar or 400-ppm CO₂ feed, assuming two protons can be released per molecule (Jin et al., 2020).

(B) The minimum concentration of organic CO₂ carrier required to overcome the partial pressure difference between capture and release owing to the physical solubility of CO₂ in organic electrolytes. The plot assumes capturing at 0.1 bar CO₂, and two CO₂ molecules can be captured per organic carrier. Three representative organic solvents with different Henry's law constants are shown, which are diglyme, dimethyl sulfoxide (DMSO), and an ionic liquid 1-ethyl-3-methylimidazolium tricyanomethanide ([emim][tcm]) (Diederichsen et al., 2022).

line, highly-soluble quinone-based organic CO₂ carriers (Diederichsen et al., 2022) and phenazine-based PCET molecules (Jin et al., 2020, 2022) were successfully realized via rational side-chain design. It is worth noting that PCET species compatible with pH swing EMCC do not have to be organic. For example, highly soluble polyoxometalates can be promising candidates if they are PCET-active in alkaline electrolytes (Jin et al., 2020).

Redox potential

The parasitic reaction between redox-active species and molecular oxygen (O₂) is a key source of inefficiency in EMCC processes. The standard reduction potential of O₂ is 1.23 V vs standard hydrogen electrode in aqueous electrolytes and approximately -1.2 V vs ferrocene/ferrocenium (the oxygen/superoxide redox couple) in aprotic electrolytes (Vasudevan and Wendt, 1995). Thus, redox-active species with more negative potentials to these values may be chemically oxidized by atmospheric or dissolved O₂ in their reduced form (although the reaction kinetics needs to be evaluated), leading to losses in the Coulombic efficiency. Furthermore, if a counter electrode is employed, the cell will eventually go out of balance over repeated capture and release cycles (Jin et al., 2022).

Redox potentials of organic molecules can be modified through molecular engineering. The general principle is that introducing electron-withdrawing groups to the molecular structure can increase the electron affinity of molecules, leading to increased redox potentials (Ding et al., 2018). Nevertheless, it is essential to note that, in the case of redox-active organic CO₂ carriers, sufficient nucleophilicity (or Lewis Basicity) is required for CO₂ complexation. Electron-withdrawing substituent groups can weaken the CO₂ binding, and CO₂ adduct formation will not occur if the electron-withdrawing groups are too strong. It shall also be noted that the redox-active organic carriers generally show a higher oxidation potential after CO₂ binding, making the adducts more resistant to parasitic oxidation. Electrolyte engineering is another possible method to address the challenge of O₂ sensitivity. For example, adopting supporting salts with stronger Lewis acid cations or controlling the hydrogen bonding environment in nonaqueous electrolytes can positively shift the redox potentials of certain organic molecules (Barlow and Yang, 2022; Diederichsen et al., 2022; Luo et al., 2019).

Besides solubility and redox potential, the pK_a (or Brønsted basicity) of the redox-active species is also crucial in some EMCC applications. For example, in pH swings by PCET, the maximum achievable pH of the sorbent solution increases with the pK_a of the reduced PCET molecules. In addition, for redox-active organic CO₂ carriers, a reduced form pK_a smaller than that of water can lower their susceptibility to protonation, which is a competing process with CO₂ adduct formation. There is generally a strong correlation between redox potential, Lewis basicity, and Brønsted basicity of redox-active organic molecules (introducing electron-withdrawing groups to the molecular structure tends to positively shift the redox potential with a concomitant reduction in Lewis and Brønsted basicities) (Zhang et al., 2022). Therefore, the possibility of breaking such a scaling relationship to design ideal sorbents for EMCC remains an open question.

Reversibility

The reversibility of the redox-active species warrants close examination when designing continuous flow EMCC processes. Knowledge can be learned from the electrochemical energy storage and electrodeposition community, where extensive efforts have been made to understand and mitigate the degradation pathways involving redox-active molecules, metal plating/stripping, and intercalation electrodes (Kwabi et al., 2020; Lin et al., 2017). For example, the reversibility and uniformity of Cu plating/stripping remain challenges in EMAR. Thus far, only planar Cu⁰ electrodes with limited current densities have been demonstrated owing to difficulties in realizing stable electrochemical cycling of porous Cu⁰ (Stern and Hatton, 2014). Recently, anionic surfactants were introduced to the EMAR electrolyte, which achieved a much smoother plating/stripping morphology and suppressed Cu⁰ pulverization (Rahimi et al., 2020c). Moreover, gas streams for carbon capture, especially at point sources, typically have a complex composition with various reactive impurities (e.g., nitrogen oxides and sulfur oxides). Thus, it is also imperative to evaluate the reversibility of redox-active species under more realistic mixed gas environments.

(Electro)chemical reaction kinetics

Redox-active species with rapid intrinsic charge transfer kinetics are desirable for EMCC processes. The kinetic parameters of redox reactions, such as the standard rate constants, can be determined by various electroanalytical techniques (Wang et al., 2020a). Opportunities exist to employ electrocatalytic surfaces to enhance the kinetics of outer-sphere electron transfer reactions (Sawant et al., 2021). For example, HER and OER electrocatalysts can be a natural choice to overcome the sluggish kinetics of water splitting in pH swing EMCC.

As above-mentioned, continuous flow EMCC can decouple the electrochemical activation of sorbents from their chemical reaction with CO₂. Therefore, another vital consideration is the chemical reaction kinetics between sorbents and CO₂. For example, Carbon Engineering chooses NaOH over KOH for a higher absorption rate. Whereas the reaction between CO₂ and alkali hydroxide solutions is generally rapid at high pH values (the second-order rate constant is of the order of 10³ M⁻¹s⁻¹ at 25°C) (Wang et al., 2010), CO₂ adduct formation with amines or redox-active organic carriers tends to occur on a longer timescale. Mizen and Wrighton measured the bimolecular rate constant between CO₂ and 9,10-phenanthrenequinone radical to be 96 M⁻¹s⁻¹ at room temperature in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting salt (Mizen and Wrighton, 1989). The reported reaction rate constants of some typical amines for carbon capture are 6.71, 412, and 5,939 M⁻¹s⁻¹ for methyl diethanolamine, diethanolamine, and monoethanolamine, respectively (Sema et al., 2013). Fundamental studies are needed in the future to understand how factors such as sorbent chemistry and electrolyte environment influence the adduct formation kinetics.

The formulation of redox-active liquid sorbents for continuous flow EMCC is a multi-parameter optimization problem. Other factors such as viscosity, ionic conductivity, diffusivity of redox-active species, and cost should also be considered to strike the right balance.

Electrochemical cell design

The electrochemical cell is the core of EMCC systems. An efficient EMCC flow cell calls for materials innovation and optimization of each component. This section discusses key electrochemical cell design considerations owing to several challenges unique to continuous flow EMCC.

Sorbent flow rate and single-pass conversions

In continuous flow EMCC processes, the conversion of species of interest and the efficiency of the system largely depends on the liquid residence time in the electrochemical cell (residence time = volume of the electrochemical cell/liquid flow rate). Depending on the mechanism employed for EMCC, one could expect to design systems with either extremely high or low flow rate requirements.

For pH swing, a limiting operating current exists depending on the ionic composition of the input solution, which is defined as the current for the depletion of (bi)carbonates. Whereas a certain degree of over acidification can provide a stronger driving force for CO₂ desorption, operating significantly beyond the limiting current compromises the system efficiency by generating excess protons and higher

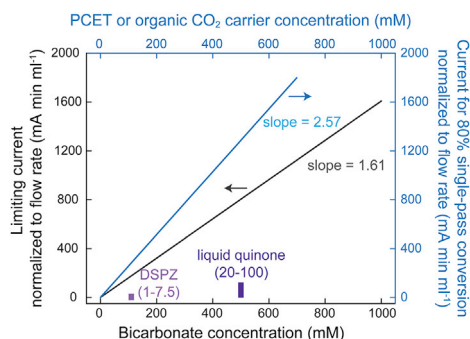


Figure 7. Relationships between current density and liquid flow rate under various EMCC conditions

Flow rate normalized limiting current in pH swing EMCC as a function of bicarbonate concentration, and flow rate normalized current required to achieve 80% single-pass conversion of PCET molecules or redox-active organic CO₂ carriers (assuming two active sites per molecule) (Diederichsen et al., 2022; Jin et al., 2020, 2022).

electrochemical overpotentials. On the other hand, too low of an operating current will lead to insufficient sorbent regeneration and higher capital expenditures (CAPEX) by requiring larger cell sizes. Figure 7 estimates the limiting current normalized to liquid flow rate using bicarbonate-based solutions as an example, assuming 1:1 stoichiometric regeneration of HCO₃⁻ by electrons and the membranes are 100% selective toward species of interest (HCO₃⁻ or H⁺). Digdaya et al. observed that the near-optimal operating conditions for their ocean capture BPMED cells (2.69 mM HCO₃⁻ and 0.408 mM CO₃²⁻) yielded a normalized operating current of 5.71 mA min mL⁻¹, which agrees with our limiting current estimation (Digdaya et al., 2020). When operating at a current density of 3.3 mA cm⁻², their ocean capture system demonstrated an energy consumption of 155.4 kJ_e mol⁻¹ of CO₂. Efficiency is lost owing to the fact that there is still significant co-ion crossover at low currents. Better Faradaic efficiencies toward H⁺ and OH⁻ transport are achieved above 10 mA. For low (bi)carbonate concentrations (e.g., ocean water), high liquid flow rates are expected so that the system can operate at practically relevant current densities. As a result, balancing the pressure among all the compartments in the flow cell is crucial to avoid mechanical damage to the membrane stack and the unwanted mixing of different solution streams (Eisaman et al., 2012). In addition, liquid pumping energy can be a significant fraction of the overall system operation, especially for electrochemical devices operating at low current densities (Moreno et al., 2018; Pärnamäe et al., 2020; Vermaas et al., 2011). The trade-offs between reducing the CAPEX (higher operating current density) and minimizing the operation expenditures (OPEX) (lower operation voltage and lower pumping energy) are highly system-dependent and remain an active research topic for many EMCC approaches.

Similar calculation applies to continuous flow EMCC involving reversible redox couples, organic PCET, as well as redox-active CO₂ carriers and competitors (Figure 7, assuming two protons or CO₂ binding sites per redox-active molecule). A practical continuous flow process requires a high single-pass conversion of redox-active species. However, the demonstrated systems so far involving such chemistries are not genuinely continuous flow processes but are instead conducted in a semi-batch mode. That is, the sorbent solution is recirculated through a reservoir to enable better conversions. For example, in a recent pioneering study on pH swing EMCC with organic PCET (3,3'-(phenazine-2,3-diylbis(oxy))bis(propane-1-sulfonate), DSPZ), the electrolyte was circulated at a high flow rate of 100 mL min⁻¹ with an operating current in the range of 100–750 mA (normalized current marked in Figure 7) (Jin et al., 2020, 2022). The system demonstrated with liquid quinone can be regarded as an actual continuous flow process as the liquid sorbent was translated sequentially between capture and release (Diederichsen et al., 2022). Nevertheless, the single-pass conversion remained low. The bench-scale prototype operated at a liquid flow rate of 0.25–0.5 mL min⁻¹, but the current was limited to 10–35 mA owing to the higher resistance of organic electrolytes.

Both above-mentioned systems adopted electrochemical cells used for redox flow batteries, where a flow field distributes the liquid electrolyte into a porous carbon electrode. Subsequently, the redox-active species permeate through the pores to react at the carbon surface. A high single-pass conversion can be achieved by reducing the liquid flow rate or increasing the operating current. However, the mass transport losses at a high degree of conversion caused by the reduced thermodynamic driving force for reactant delivery to the electrode surface will increase the cell overpotential and thus the energy consumption of the system. Moreover, it was observed that the non-uniform flow patterns at low flow rates could result in pockets of static sorbent trapped inside the porous carbon electrode, leading to inefficiency in sorbent capacity utilization (Diederichsen et al., 2022). Therefore, precise engineering of the surface chemistry and microstructure of porous electrodes is urgently needed to optimize fluid distribution and species transport.

Instead of employing commercially available, monolithic porous carbon materials, enormous opportunities exist to explore electrodes with architected porosity leveraging advances in additive manufacturing and computational design (Beck et al., 2021).

Bubble formation

In EMCC processes, gaseous CO₂ evolution often occurs inside the electrochemical cell. Trapped gas bubbles can block the electrode or membrane surface, leading to increased overpotential and localized hot spots of high current density that can compromise the stability of the electrode or membrane. As the amount of gas soluble in liquid increases with increasing pressure, Eisaman et al. demonstrated CO₂ desorption from aqueous bicarbonate solutions using a high-pressure BPMED stack, which avoided bubble formation inside the electrochemical cell (Eisaman et al., 2011b). The solution was depressurized downstream of the membrane stack to liberate gaseous CO₂. Their results showed that at a high current density (139 mA cm⁻²), a reduction in energy demand up to 29% can be achieved by operating at pressures above 6 atm. Smaller bubbles are also obtainable by reducing the surface tension of liquid sorbents using surfactants. This concept has been successfully applied in EMAR to improve system stability and energetics (Rahimi et al., 2020c).

Bubble management strategies explored in electrochemical gas evolution reactions (Zhao et al., 2019), such as textured superhydrophobic electrodes with weakened bubble adhesion or active flow-through configurations in gas diffusion electrodes, have not yet been applied to EMCC processes. Moreover, as supersaturation of dissolved gas is a pre-requisite for bubble nucleation and growth (German et al., 2018), electrodes with ample gas-solid-liquid triple-phase contact lines can expedite CO₂ transport to the gas phase and avoid bubble formation in the electrolyte. Strategies that involve suitable pore or surface microstructures and chemistries are commonly used to construct these electrodes, such as alveolus-like polyethylene (Li et al., 2019a) and rationally designed gas diffusion layers (Dinh et al., 2018). Such concepts can be explored for bubble mitigation in EMCC in the future. It is important to note that creating a sustained triple-phase boundary can be especially challenging for EMCC involving nonaqueous electrolytes, owing to their lower surface tension than water. In these scenarios, omniphobic surface coatings or high-pressure-gradient electrodes may be adopted (Lazouski et al., 2020; Pan et al., 2018).

Membrane permselectivity

In continuous flow EMCC, ion-exchange membranes play a critical role in compartmentalizing electrolytes of varying compositions inside the electrochemical cell and selectively transporting species of interest across the different compartments. Therefore, the ionic conductivity, selectivity, stability, and cost of membranes are pivotal in determining the performance metrics of EMCC.

Membranes with high ionic conductivity are necessary to operate EMCC at high current densities. Whereas the state-of-the-art AEMs and CEMs have good ionic conductivity in aqueous electrolytes (area-specific resistance <1 Ω cm²), commercial BPMs require relatively high operating voltages owing to the greater thickness and the kinetic limitation of water dissociation (Blommaert et al., 2021). Digdaya et al. showed that the voltage loss across BPM dominates the energy penalty in BPMED cells (Digdaya et al., 2020). Other important failure mechanisms for BPMs are membrane delamination at the AEL-CEL junction and catalyst deactivation. Therefore, there is a strong research driver to develop better water dissociation catalysts for BPM, better membrane morphology and adhesion to overcome water transport limitations at high flux, as well as overall electrochemical cell re-design to accommodate high current density operation (Krol et al., 1998; Oener et al., 2020). Importantly, it must be pointed out that the ionic conductivity of ion-exchange membranes in nonaqueous electrolytes is at least two orders of magnitude lower than in aqueous systems, which presents a significant hurdle to EMCC processes using redox-active organic CO₂ carriers (Gong et al., 2015). In the flow EMCC prototype demonstrated using liquid quinone with Nafion membrane (Diederichsen et al., 2022), the operating currents were limited to <2 mA cm⁻². Therefore, designing membranes specifically tailored for nonaqueous electrolytes shall be prioritized in future research.

For electrodialysis involving AEMs (such as configurations shown in Figures 2E and 2F), the current efficiency is defined as the ratio between the number of CO₂ transported across the membrane over the charge transported. The maximum achievable efficiency is 1 for solutions containing exclusively HCO₃⁻ (one electron is required to release one CO₂) and 0.5 for solutions containing exclusively CO₃²⁻ (two electrons are required to release one CO₂). As the rate of CO₂ capture decreases substantially with decreasing

pH, highly alkaline sorbent solutions are often employed such that the concentration of HCO_3^- in the spent solution is usually much lower than CO_3^{2-} . Therefore, a trade-off exists between capture and regeneration efficiencies. On the other hand, the transport of CO_2 -free anions (e.g., OH^- from the incomplete reaction during absorption) will be detrimental to the current efficiency (Nagasawa et al., 2009; Sabatino et al., 2020). In typical AEMs, (bi)carbonates are less mobile than OH^- , and as a rule of thumb, ion-exchange membranes strongly prefer counterions of higher valence (CO_3^{2-} is preferred over HCO_3^-) (Kiss et al., 2013). Therefore, developing AEMs with high permselectivity toward HCO_3^- is desirable. Elevating the membrane permselectivity between monovalent and multivalent ions is being explored mainly based on the Donnan exclusion effect and the hydration energy effect. The Donnan exclusion effect can be realized by creating a strong negative charge layer on the membrane surface to hinder multivalent anions from entering the membrane matrix (Gao et al., 2018). Another method for developing permselectivity toward monovalent ions is by regulating the membrane hydrophobicity and/or the degree of cross-linking, as divalent ions have a larger hydration shell and hydration energy (Irfan et al., 2019). For electrochemical cells with CEMs in Figure 2, the competing transport of protons over alkali metal ions into the alkaline compartment will also compromise the current efficiency (Nagasawa et al., 2009). Note that whereas these monovalent ion-selective membranes can be used to minimize divalent cation crossovers and prevent undesired precipitation in the alkaline chamber of BPMED cells, these membranes often have much higher resistances.

In addition to ion selectivity, low permeability of redox-active species is also required for certain EMCC processes. The failure to effectively block active species crossover can compromise the separation efficiency and lead to irreversible sorbent capacity loss, which is a particularly severe issue in nonaqueous electrolytes. Some recent membranes developed for battery applications, such as those based on microporous materials (Bai et al., 2021; Ma et al., 2018; Peng et al., 2018) and polymers with intrinsic porosity (Doris et al., 2017), can be interesting candidates for EMCC.

Separation system and process design

Careful design choices and rigorous optimization on the process level are needed when transitioning EMCC concepts from laboratory-scale demonstrations with simulated gas/water feed conditions to actual flue gas, air, or marine environment.

Electrode and membrane fouling

Electrode and membrane fouling should be seriously evaluated when designing EMCC processes involving brine or seawater (e.g., ocean capture, electrolytic dissolution of minerals for enhanced weathering, etc.). Magnesium and calcium ions in brine or seawater can precipitate on cathode or membrane surfaces over time in the form of hydroxides or carbonates under high pH conditions. The mineral deposits will block the active surface area to increase the resistance across the electrochemical module and irreversibly damage bipolar membranes. For electrode-based electrochemical cells, scaling can be mitigated by cyclically reversing the polarity of the electrodes, but this complicates the process by requiring additional flushing of the electrolyte compartments between switches (Willauer et al., 2014). For membrane-based electrochemical cells, such as electrodialysis, it is important to reduce the dication concentration to <1 ppm to ensure the longevity of the membrane and overall electrodialysis operation. However, for ocean carbon capture, it is crucial to restoring the alkalinity of the decarbonized effluent before discharging it back into the ocean to ensure the subsequent atmospheric CO_2 drawdown and avoid potential negative impacts on ocean chemistry or the global carbon cycle (La Plante et al., 2021).

Absorber and desorber

One distinct feature of continuous flow EMCC is the ability to decouple electrochemical sorbent activation/deactivation from CO_2 capture/release. Therefore, the absorption and desorption units are paramount in determining the efficiency and kinetics of the separation process.

As CO_2 capture inside the absorber involves only chemical reactions, conventional chemical engineering wisdom in optimizing gas-liquid contact for reactive absorption can be utilized. For point source capture with relatively high CO_2 partial pressures, traditional counterflow-packed columns are generally sufficient (Diederichsen et al., 2022; Wang et al., 2020b). In practice, an absorption column is typically sized to achieve an optimum just below flooding for a designed gas-to-liquid ratio to reduce pressure drop while minimizing mass transfer resistance on the gas side (Kister et al., 2019). The configuration, sizing, and material choice of the absorption unit are nontrivial to the techno-economic aspects of EMCC systems (Wang et al., 2020c).

For DAC, large volumes of air must be processed to capture a meaningful amount of CO₂ (a plant with a capture rate of 1 Mt yr⁻¹ needs an air throughput of at least 46,000 m³ s⁻¹). Therefore, the absorption unit for DAC necessitates dedicated development to contact the sorbent most efficiently with air. As discussed by [Stucki et al. \(1995\)](#), DAC requires a high air flux and a very slow fluid flux, yet the gas-to-liquid ratio can only be varied in a narrow range in conventional packed columns if flooding or running dry is to be avoided. As a result, a high liquid recirculation rate would be necessary to achieve good CO₂ absorption from air, which can incur high energy losses for pumping. Carbon Engineering uses a cross-flow falling film contactor adapted from cooling-tower technology and cyclic-pulsing solution flow to minimize pumping energy while maintaining good packing wetting, which is promising for cost-effective DAC process design ([Keith et al., 2018](#)). Alternatively, membrane contactors such as hollow fibers offer greater design flexibility to enhance mass transfer rates. However, they would require materials design and engineering optimization to prevent membrane wetting, especially when handling nonaqueous fluids ([Ibrahim et al., 2018](#); [Stucki et al., 1995](#)).

As discussed earlier, for the electrodialysis regeneration of alkaline hydroxides, the current efficiency is higher with lower pH bicarbonate solutions than higher pH carbonate solutions. Although many EMCC studies used bicarbonate solutions for proof-of-concept demonstrations, we shall bear in mind that concentrated hydroxide solutions (>1 M) are usually used for carbon capture and the rate of capture decreases with decreasing pH, which poses a more stringent requirement on the absorber design to achieve a high conversion of hydroxides to bicarbonates. For example, the CO₂-rich solution after the air contactor in the Carbon Engineering pilot plant still has a significant presence of KOH. Carbonic anhydrase (CA), a zinc-containing enzyme ubiquitously found in all kingdoms of life, can rapidly hydrate/dehydrate CO₂ with a catalytic efficiency approaching the diffusion limit ([Alvizo et al., 2014](#)). Therefore, CA could be beneficial in accelerating the kinetics of CO₂ capture, but the high alkalinity of sorbent solutions imposes a considerable challenge to the activity and stability of CA.

For CO₂ desorption, special attention needs to be paid to ocean capture. The ~2.2-mM DIC in surface seawater translates to an equilibrium CO₂ partial pressure of 65 mbar after acidification. Therefore, vacuum stripping is required to produce a concentrated CO₂ stream (e.g., via membrane contactors, as illustrated in [Figure 3](#)) ([Digdaya et al., 2020](#); [Eisaman et al., 2012](#)).

The purity of the CO₂ product gas is critical. The CO₂ gas is usually concentrated by a factor of 2–4 in studies reviewed using redox-active species, which means a single stage is insufficient to produce the purity required for CO₂ storage. Moreover, the product stream from aqueous EMCC systems often has a high water content ([Digdaya et al., 2020](#); [Eisaman et al., 2012](#)), whereas CO₂ desorbed from nonaqueous electrolytes may contain organic vapors. Other gaseous species physically dissolved in the electrolyte (e.g., O₂, N₂, etc.) can also degas into the product stream. As a result, the gas mixture needs to be further dehydrated and purified for downstream applications, such as compression to supercritical CO₂ for pipeline transportation, which requires a water level of <50 ppm to protect the pipes against corrosion ([Herzog, 2018](#)). If the captured CO₂ is used for subsequent conversion into chemicals or fuels using electrochemical or thermochemical approaches, the pressure and purity requirements will likely differ. In one example, a coupled electrochemical capture and conversion concept from seawater was demonstrated by [Digdaya et al.](#), where an additional electrochemical cell for oxygen reduction was required before CO₂ electrolysis to eliminate the O₂ impurity from the concentrated CO₂ stream ([Digdaya et al., 2020](#)).

Evaporative solvent loss during absorption and desorption may burden continuous flow carbon capture systems with substantial solvent makeup rates and costs. For example, the Carbon Engineering process requires 4.7 tons of water per ton of CO₂ captured (at 20°C and 64% relative humidity) ([Keith et al., 2018](#)). EMCC processes using nonaqueous electrolytes with low vapor pressures would have slower (still non-negligible) evaporative rates. Nevertheless, the toxicity and environmental impact of such fugitive organic solvent emissions need to be carefully evaluated.

Feed stream pre-treatments

Analogous to chemical scrubbing, feed stream pre-treatments are often essential for point source EMCC to remove potential impurities such as particulate matter, sulfur oxides, and nitrogen oxides ([James et al., 2019](#)). Little information regarding the durability and chemical tolerance of EMCC processes is available, primarily because the concepts are in the early stages of development. Therefore, the possible

parasitic reactions between gaseous impurities and redox-active species (e.g., organic CO₂ carriers, PCET molecules, and amine electrolyte formulations in EMAR) need to be scrutinized with sensitive analytical tools in the future to inform rational mitigation strategies. Sulfur dioxide (SO₂) is more electrophilic than CO₂ and will likely bind to the nucleophilic centers of redox-active organic carriers, which will lead to either irreversible adduct formation or a higher overpotential for sorbent regeneration. Highly oxidized species such as O₂ and nitrogen dioxide (NO₂) could oxidize the reduced redox-active species to afford superoxide and nitrite, respectively. Water management is also critical for EMCC processes using nonaqueous electrolytes. Flue gas contains roughly 10% water, and nonaqueous electrolyte components tend to be hygroscopic (James et al., 2019). Water may protonate the CO₂-binding moieties of redox-active organic carriers, making them less effective toward carbon capture. Preliminary results on liquid quinone indicate that added water does not significantly change its redox behavior through at least ~8% water by volume, yet more systematic analyses are needed in the future (Diederichsen et al., 2022).

The seawater feed for ocean capture needs to be filtered to remove algae, organic particles, sands, and other particulate matter and sterilized before feeding to the electrochemical module to ensure minimum biofouling. As water has a higher density than air, more pumping energy is required. The estimated cost of seawater intake, pre-treatment, and outfall in a land-based, stand-alone system is prohibitively high, primarily owing to the high total dynamic head (TDH). Whereas this cost can be largely avoided by co-location with a desalination plant, the CO₂ removal capacity would be limited by the size of the plant (<100 kt CO₂/year) (Digdaya et al., 2020; Eisaman et al., 2018). Alternative approaches also include siting the large-scale oceanic CO₂ removal system in near-shore/off-shore locations, such as off-shore mothballed gas and oil platforms, where the TDH can be minimized and the permeant CO₂ sequestration can benefit from the co-location with depleted gas/oil reservoirs. If pure CO₂ is the desired product, an additional degassing stage must be implemented before the electrochemical module. According to the study by Digdaya et al., the captured gas would contain >30% of N₂ and O₂ without a vacuum degassing stage (Digdaya et al., 2020). The O₂ impurity can be undesirable for downstream applications such as conversions to chemicals and fuels.

Energetics and costs

Table 1 summarizes selected flow EMCC methods based on their theoretical and demonstrated work of CO₂ separation. The values are compared with plant-scale amine scrubbing using piperazine with an advanced flash stripper (Lin and Rochelle, 2016). Although most EMCC mechanisms possess attractive minimum work, the energy consumption of the demonstrated bench-scale prototypes remains much higher than the theoretical value. This is partly because most EMCC processes are still in their infancy, such that heavy research and development are required to lower the energetics.

Sabatino et al. performed a techno-economic assessment (Sabatino et al., 2020) based on the experimental investigation of potassium (bi)carbonate regeneration via BPMED performed by Eisaman et al. (2011a). The authors evaluated the cost of a DAC plant with a carbon capture capacity of 1 Mt/yr. Assuming an electricity cost of \$0.06/kWh, the energy demand and the corresponding levelized OPEX present an optimum with respect to current density owing to the trade-off between the current efficiency and the voltage drop across the electrochemical cell stack (Figure 8A). Although low current density manifests more favorable energetics, a larger membrane area is required to meet the target CO₂ production rate, which translates to a higher CAPEX (Figure 8B). Moreover, the higher membrane area requirement at low current densities also increases the operating costs, as membrane replacement was found to account for almost half of the levelized OPEX. It is important to note that the state-of-the-art, commercially available BPMED units operate at relatively low current densities, e.g., between 500 and 800 A m⁻². Under these cost assumptions and current-voltage characteristics of BPMED (Sabatino et al., 2020), the study shows that the ideal operating current density of BPMED (Figure 8C) is not too far away from the existing off-the-shelf units. However, different electricity cost assumptions as well as improved membrane resistance and cell architecture would yield very different cost scenarios and optimal operating regimes for BPMED. New EMCC chemistries with lower energy consumption in demonstrated bench-scale prototypes could bring the cost down, but detailed techno-economic analyses are needed. Further sensitivity analyses indicate that future reduction in the cost of membrane and renewable energy and membrane lifetime can make this EMCC process more competitive (Figures 8D–8F). Similarly, membrane cost was determined to be the dominant capital cost of the electrochemical desorption unit in EMAR (Wang et al., 2020c). At a membrane unit price of less than \$10 m⁻², the cost for point source capture via EMAR is projected to fall below \$50/t CO₂ with optimized process conditions.

Table 1. Summary of selected flow-based carbon capture methods

Method	CO ₂ Source	Minimum Theoretical Work of Separation (kJ mol ⁻¹) ^a	Demonstrated Energy Consumption (kJ _e mol ⁻¹) ^b	Current Density (mA cm ⁻²)	Description	Ref.
Aqueous Amine Piperazine with Advanced Flash Stripper	Point source	7.3 (Isothermal minimum work at 313K, 12% CO ₂ to pure at 1 bar)	~38	/	Compression to 150 bar. Calculated by converting thermal equivalent work to electrical equivalent work, assuming a Carnot efficiency (0.25). The value is the lower bound as heat losses are not included in the calculation.	(Lin and Rochelle, 2016)
BPMED	KHCO ₃ /K ₂ CO ₃ solutions		~588–4,714 0.5 M K ₂ CO ₃ +0.1 M KOH	5–100	pH swing driven by water electrolysis, seven-cell stack with 200 cm ² electrode area	(Eisaman et al., 2011a)
			~232–604 0.5 M K ₂ CO ₃	5–100		
			~144–325 0.5 M KHCO ₃	5–80		
	Synthetic ocean water	39.6 (pH swing between 4.6 and 10.6)	155.4 (93% CO ₂ product stream)	3.3	pH swing driven by ferro/ferricyanide redox couple, 64 cm ² electrodes	(Digdaya et al., 2020)
PCET Derivatized Phenazine	10% CO ₂	50 (four-stage separation with 0.1 bar inlet and 1 bar outlet)	~61–145	20–150	5 cm ² electrodes separated by a CEM, high liquid flow rate of 100 mL min ⁻²	(Jin et al., 2020, 2022)
EMAR	15% CO ₂ at 50°C	15.6 (60% swing in Cu loading, 0.88 bar desorption)	~40–120	3–13	110 cm ² copper electrodes separated by AEM	(Wang et al., 2019a, 2020b)
Redox-Active CO ₂ Carrier Solubilized Quinone	1 bar pure CO ₂	~19 (0.2-V capture-release voltage gap in 0.1 M NaTFSI propylene carbonate)	~35–220	0.4–1.4	25 cm ² electrodes separated by CEM	(Diederichsen et al., 2022)

^aMinimum theoretical work to concentrate CO₂ to ~1 bar.

^bElectrical work for CO₂ capture and release only.

OUTLOOK

The past decade has seen a growing body of research on developing electrochemical methods as potentially efficient and scalable carbon capture technologies. Compared with batch-based capture and release, continuous flow EMCC decouples electrochemical and chemical reactions and therefore features greater flexibility in optimizing each component of the system. Nevertheless, as most EMCC concepts are still at

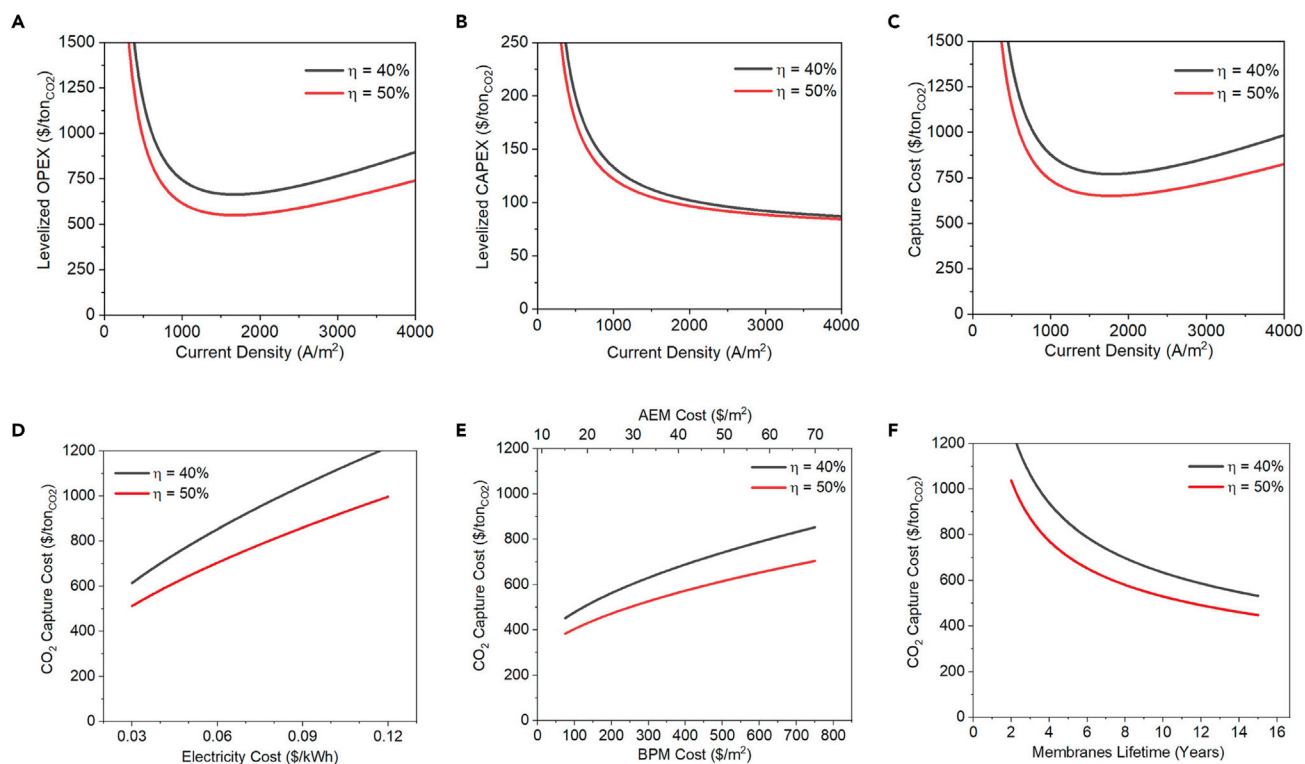


Figure 8. Techno-economic assessment of a BPMEC carbon capture process

(A–F) Levelized OPEX, (B) levelized CAPEX, and (C) capture cost as a function of the current density for potassium (bi)carbonate regeneration using BPMEC. And sensitivity analysis of the capture cost to (D) electricity cost, (E) membranes cost, and (F) membranes lifetimes (Sabatino et al., 2020). Reprinted under the Creative Commons Attribution Non-Commercial No Derivative Works (CC-BY-NC-ND) 4.0 license.

very early stages of development, the field shall continue to explore both operational modes. The ultimate choice will likely be decided by the specific redox chemistries, process constraints, retrofitting requirements, and many others. System modeling at earlier design stages, including rigorous techno-economic and life cycle analyses, can help target research and identify bottlenecks.

For fundamental research, an in-depth understanding of the reaction and transport phenomena across multiple lengths and time scales can critically inform materials design, reveal degradation mechanisms, and promote rationally motivated improvement strategies. As flow-based electrochemical setups are typically enclosed systems where only the inputs and outputs can be readily measured, an integrated experimental and modeling approach must be adopted to build foundational knowledge in continuous flow EMCC.

Advanced *in-situ* and *operando* characterization techniques, such as UV-Vis spectrophotometry (Tong et al., 2017), nuclear magnetic resonance (NMR) (Zhao et al., 2020), and electron paramagnetic resonance (EPR) (Zhao et al., 2021), can be used to interrogate the chemical states of redox-active species during EMCC operations. In a recent study, *online* NMR was used to probe redox-active anthraquinone-based electrolytes using a flow-through apparatus (Figure 9A) (Zhao et al., 2020). The technique allowed the quantification of key reaction rate parameters and enabled electrolyte decomposition to be monitored in real-time. For pH swing EMCC processes, microscale information on the pH distribution in space and time in operating flow cells can shed light on opportunities to improve system performance. Whereas several techniques are available to perform localized pH measurements (Monteiro and Koper, 2021), the authors would like to highlight fluorescence microscopy as a versatile platform to unravel the dynamic and heterogeneous environment with high spatiotemporal resolution in electrochemical systems. Figure 9B shows an example of quantitatively visualizing the pH gradient in a stagnant electrochemical water-splitting cell using a fluorescence pH sensor foil placed between the anode and cathode (Obata et al., 2020). In another example, by introducing a small amount of ratiometric pH-sensitive dye into the

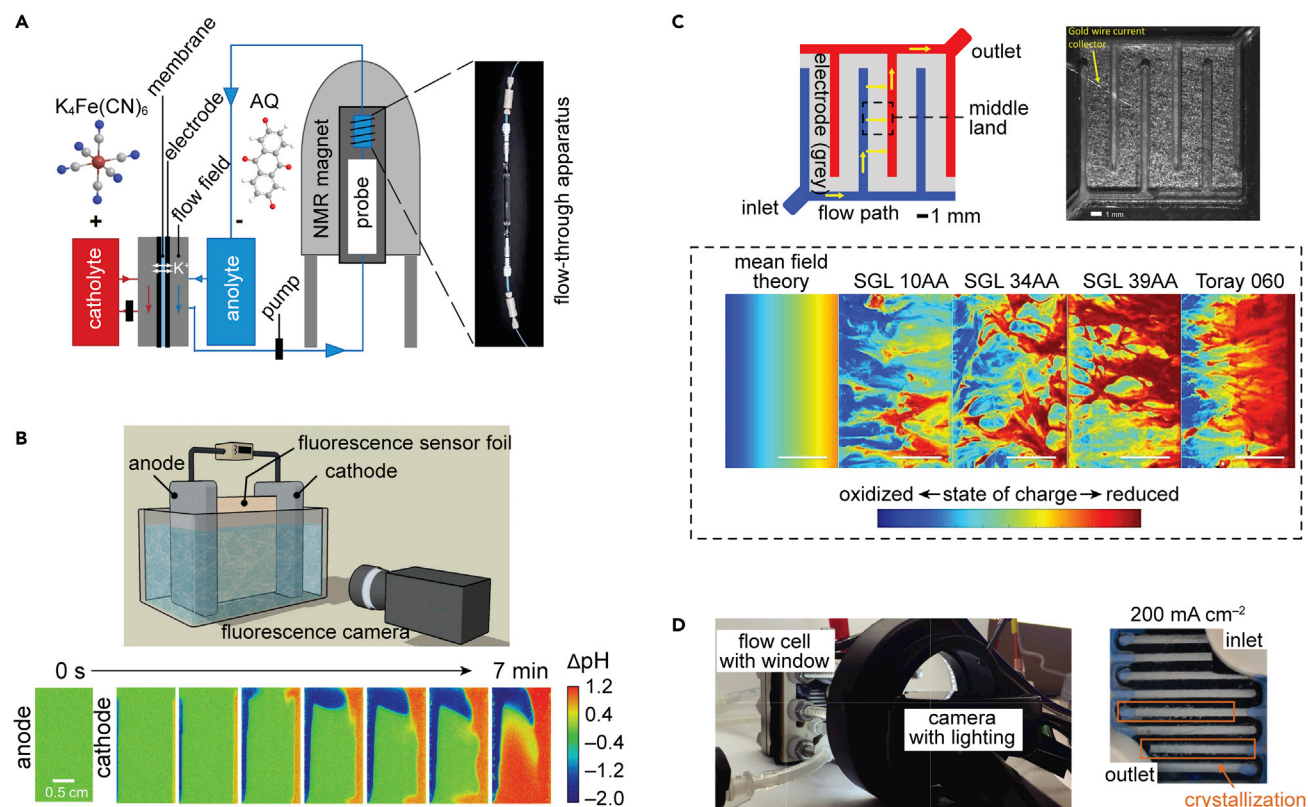


Figure 9. Characterization techniques applicable to fundamentally understand continuous flow EMCC systems

(A) Schematic showing the setup for online NMR studies of electrochemical systems. The electrochemical flow cell is positioned outside the NMR magnet, and one electrolyte solution is pumped through a flow apparatus in the NMR probe, enabling the study of either the catholyte or the anolyte (Zhao et al., 2020). Adapted with permission from Zhao et al. (2020). Copyright 2020, Springer Nature.

(B) Schematic of an *in-situ* fluorescence pH monitoring setup (top) and the measured pH distribution in an electrochemical cell during water splitting (bottom) (Obata et al., 2020). Reprinted under the Creative Commons Attribution 3.0 Unported license.

(C) Schematic and optical image of the flow field used for *operando* fluorescence imaging of quinone reaction and flow in porous electrodes (top). Spatial distributions of reduced and oxidized quinone across various porous carbon electrodes at the middle land region compared with the mean field theory calculation (bottom). The quinone was reduced at a constant voltage during a peristaltic pump pulsed flow (Wong et al., 2021). Scale bars are 1 mm. Reprinted under the Creative Commons Attribution Non-Commercial No Derivative Works (CC-BY-NC-ND) 4.0 license.

(D) Experimental setup of a modified flow cell with a transparent viewing window to observe salt crystallization and flooding on the electrode (Wheeler et al., 2020). Adapted with permission from Wheeler et al. (2020). Copyright 2020, Royal Society of Chemistry

electrolyte, Welch et al. mapped the local pH near the gas diffusion electrode during electrochemical CO₂ reduction using confocal fluorescence microscopy with micrometer spatial resolution in three dimensions (Welch et al., 2021). Moreover, fluorescence imaging has proven powerful in characterizing fluid transport in porous media. By taking advantage of the redox-dependent fluorescence properties of quinones, Wong et al. reported the reaction-transport heterogeneities of quinones within porous carbon electrodes (Figure 9C) (Wong et al., 2021). With an optically transparent flow field, the state-of-charge distribution of the electrolyte at steady-state was found to be substantially heterogeneous, characterized by localized stagnant zones and hydraulic electrolyte channeling. This observation challenged the conventional assumption that transport in porous electrodes can be approximated by a homogeneous Darcy-like permeability, calling for more sophisticated reaction-flow models and novel electrode or flow field architectures to better understand and control the transport phenomena in electrochemical flow cells. Finally, optical microscopy can also be used to observe important electrode behaviors such as salt precipitation (Figure 9D) and bubble generation during continuous flow EMCC operation (Wheeler et al., 2020).

Modeling of the (electro)chemical reactions, mass transport, and fluid dynamics inside the flow reactor as well as the absorber and desorber units is essential to optimize laboratory tests required for performance

evaluation and to scale this performance to larger form factor separation systems. Fuel cells, redox flow batteries, and water electrolyzers provide the closest reference points to continuous flow EMCC as they follow similar configurations. Progress on multi-scale modeling of these more widely studied electrochemical systems can serve as a valuable basis for EMCC modeling. Moreover, modeling can also inform how specific design variables impact separation performance and offer insight into favorable combinations of sorbents, electrochemical devices, and operating conditions. We want to direct the readers' attention to a recent study by Brushett et al. that utilized a thermodynamic modeling approach to estimate the upper performance bounds of EMCC with soluble, redox-active organic CO₂ carriers (Clarke et al., 2022). The authors considered four system configurations and observed competing trends between the thermodynamic and faradaic efficiencies. Therefore, a new metric, the combined efficiency (thermodynamic efficiency × faradic efficiency), was defined and used to highlight sorbent properties that could adequately balance the efficiencies trade-off. Such a framework can be further adapted and extended to other EMCC approaches, such as pH swings and EMAR.

In summary, translating continuous flow EMCC technologies from lab to real-world, large-scale implementations requires innovations in redox-active sorbent chemistries, fundamental knowledge of thermodynamics, kinetics, and transport properties of elementary separation steps, advanced reactor architectures and system components, and rigorous process evaluations under realistic operating conditions. The outlook for this field is strong, with encouraging developments in new start-up ventures for direct air and ocean capture.

LEAD CONTACT

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Yayuan Liu (yayuanliu@jhu.edu).

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AUTHOR CONTRIBUTIONS

All authors jointly conceptualized the paper and contributed to the writing of the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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