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Electrochemical methods for carbon dioxide separations

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Abstract | The build-up of carbon dioxide in the atmosphere is one of the grand challenges facing society. Addressing this challenge by removing CO₂ from the atmosphere or mitigating point source emissions through the separation and concentration of CO₂ from these dilute sources requires reductions in energetic and monetary cost relative to traditional thermal and pressure swing methods. Electrochemical methods of CO₂ separation have drawn increasing attention in recent years as potentially cheap, low-energy, scalable carbon capture technologies. In this Primer, we provide an overview of the experimentation and analysis needed for the study of electrochemical methods for CO₂ separation, including a discussion of the considerations necessary for targeting the application of such techniques. This Primer focuses on ambient temperature techniques such as pH swing and direct redox processes, which utilize similar experimental set-ups. We include considerations on the choice of redox agent and an outlook on this growing body of research. Experimentation to address real-world conditions, particularly at practical oxygen concentrations, and novel system designs that overcome transport limitations or, potentially, couple capture and CO₂ utilization are emerging areas in the field.

The electrochemically mediated separation of carbon dioxide from a dilute feed comprises a growing field of research that shows promise towards reducing the energy requirements of carbon capture processes. The importance of improving carbon capture processes has grown with the worsening climate crisis driven by anthropogenic CO₂ emissions^{1–3}. CO₂ is released into the atmosphere from relatively high concentration (approximately 5–15% CO₂) point sources such as power plants, cement plants and other industrial processes, and distributed sources of CO₂ such as cars, trains and animals⁴. Whereas some processes may be able to replace carbon-emitting fossil fuels to eliminate emissions, other processes cannot be easily replaced due to the chemistry involved (for example, cement and steel plants) and, thus, methods to capture the emitted CO₂ for later sequestration or transformation to other chemicals (utilization) has been the subject of extensive research⁵. Although capture from point sources offers lower theoretical energy and cost requirements given the higher CO₂ concentration, the capture of CO₂ directly from air to mitigate ongoing emissions from distributed sources is also a critical component to solve the climate crisis^{3,6,7}. In either case, the primary goal of a CO₂ separation process is to produce a stream of nearly pure CO₂ with low monetary and energetic costs.

Traditional methods of separating CO₂ from the flue gas of a power plant, from industrial processes or from air rely on thermal or pressure swings to modulate the affinity of a sorbent for CO₂. Such processes, including amine scrubbing, calcium looping and those utilizing solid, supported sorbents, have been studied for decades, with several commercial processes now available⁴. Processes to concentrate CO₂ for later sequestration or conversion, on the scale necessary to substantially reduce emissions, still require significant improvements in cost and energetic penalty. Although advances have been made with process improvements and new chemistries that increase sorbent capacity and reduce the required change in temperature^{8,9}, methods involving electrochemistry could enable revolutionary enhancements.

These electrochemical processes have several potential advantages over traditional methods. Temperature swing processes often face difficulties related to operation at elevated temperature, including accelerated sorbent degradation and equipment corrosion, high evaporative losses and challenges in heat integration with existing plant designs^{10–12}. Electrochemical processes may operate isothermally and without necessarily including heating or cooling, although some designs benefit from faster kinetics at elevated temperatures. Further, electrochemical systems can be designed to combine with renewable power sources (such as

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Amine scrubbing

A carbon separation technique that reacts CO₂ with aqueous solutions of amine-based molecules in an absorption column, followed by release of CO₂ and regeneration of the amine at elevated temperature in a stripping column.

Calcium looping

A carbon separation process that uses high temperatures (>600 °C) to oxidize calcium carbonate to release pure CO₂ and calcium oxide, followed by reaction of calcium oxide with CO₂ (in a dilute stream) to form additional calcium carbonate.

Temperature swing processes

Processes that capture CO₂ from dilute sources at low temperature and release it at elevated temperature to regenerate the sorbent.

Organic redox

An electrochemical process that employs organic molecules that change oxidation state under applied potentials.

Electrophile displacement

A process in which a bound species is replaced by another species with a stronger binding constant.

Bipolar membrane

(BPM). Cation exchange membranes and anion exchange membranes laminated or electro-spun together with a water dissociation catalyst in between.

pH swing

A process that changes the pH of a liquid to induce a change in CO₂ solubility.

wind and solar) directly, and quickly scale to different applications with highly modular units.

Electrochemical methods of separating CO₂ from a dilute feed gas were first studied in the early days of manned spacecraft as a means of cabin air filtration, using carbonate fuel cells. Since then, many other types of electrochemical processes have been described that can operate with the full range of source concentrations (0.04% from air to flue gas concentrations near 15%). As illustrated in FIG. 1a,b, electrochemical methods may fall under two general classes of separations, depending on the type of influence on the sorbent¹³. In a direct process, electrochemistry acts directly on the sorbent, whereas indirect processes act on a secondary aspect of the system to modulate CO₂ loading capacity.

Several example chemistries for electrochemical capture processes are illustrated in FIG. 1c–g, and TABLE 1 summarizes the types and applications of each process. The reader is referred to several recent reviews for a more exhaustive description and tables summarizing further metrics of these processes^{13–17}. Major examples of direct electrochemical capture processes include organic redox¹⁸ with species such as bipyridines^{19,20}, disulfides²¹ and quinones in organic electrolytes^{22–24}, salt-concentrated aqueous electrolytes²⁵ or ionic liquids^{26,27} (FIG. 1c). Certain transition metal compounds also directly react with CO₂ upon reduction or oxidation²⁸. There are many types of indirect electrochemical methods. Electrophile displacement methods such as the electrochemically mediated amine regeneration (EMAR) process²⁹ operate through the introduction and removal of a competitive binding species (FIG. 1d). Many other indirect electrochemical processes leverage the carbonate equilibrium illustrated in FIG. 1e, where acid–alkaline swings in solution pH adjust the balance of carbonate species in solution and, thereby, the overall carbon content. These swings in pH have been generated through proton-coupled electron transfer of organic molecules^{14,30–33} (FIG. 1f), electrolysis³⁴, bipolar membrane (BPM) electrodialysis^{35–37} (FIG. 1g), capacitive deionization³⁸ and H⁺ (de)intercalation from functional electrodes³⁹. Carbonate fuel cells, operating at low temperature with liquid water^{40,41} or at high temperature as molten carbonate fuel cells^{42–45}, can also be considered indirect processes. In such cells, oxygen is split at the cathode, reacting with CO₂ to generate CO₃^{2–} ions that pass across a membrane to the anode where hydrogen is fed and oxidized, producing water and CO₂. Hybrid methods (including electrochemical CO₂ capture and conversion combinations⁴⁶ and battery systems⁴⁷) are also gaining attention.

This Primer provides an overview of relevant experimentation and data analysis of electrochemical CO₂ separation methods, with a discussion of relevant applications. The focus is on organic redox, electrophile displacement and pH swing-based processes that operate under ambient conditions. Molten fuel cells and similar devices are excluded from this discussion. First, the necessary equipment and considerations for electrochemical cell design are introduced. This discussion is grouped by the nature of the cell, either containing a flowing liquid sorbent or cells that utilize supported solid sorbents or

static liquid membranes (static cells). Relevant electro-analytical and characterization techniques are then introduced to discuss the necessary analysis of processes at each stage of technological design. Several limitations and challenges with electrochemical methods are discussed, relating to both laboratory-scale and real-world scenarios. Whereas past reviews have covered in detail the many different types of electrochemical CO₂ separation methods, the focus of this Review is a broad overview of the necessary tools and considerations for new entrants to the field.

Experimentation

In this section, a complete experimental set-up used for the study of electrochemical CO₂ separation is described. The performance of such systems is determined by various factors including the type of input feed (such as gaseous or aqueous) and its CO₂/water/impurity content, temperature, heat/steam availability and energy source. Testing equipment must therefore be able to replicate such process conditions. Typical electrochemical systems for the study of CO₂ separations are illustrated in FIG. 2, showing various possible electrochemical cell configurations. In each case, potentiostats regulating the current/voltage, gas mixing and feed devices, gas concentrations and flow rate measurement devices and pumps for flowing liquid set-ups are necessary. First, important measurement systems are discussed that apply to any type of electrochemical cell. Experimental protocols for small-scale initial testing are then discussed, followed by considerations for operation of bench-scale systems.

Metrics

When analysing electrochemical methods for CO₂ separations, it is important to consider relevant figures of merit, with the most common being the energy consumption, capture rate (such as current density), gas product purity and long-term/cyclic stability. For the energy consumption, expressed in kilojoules per mole of captured CO₂, it is noteworthy that electrical energy is required (for example, from renewable sources), as opposed to traditional methods based on amines or calcium looping, which require heat. Most publications report only the electrical energy consumption of the electrochemical cell, ignoring the (usually much smaller⁴⁸) energy consumption for circulating the liquids or extracting/dissolving gases from the liquid. The energy consumption can be written as:

$$E = \int \frac{IV}{\dot{n}_{\text{CO}_2(\text{g})}} dt \quad (1)$$

where E is the energy consumption (kilojoules per mole of CO₂), I is the current (amps), V is the cell voltage (volts), t is the time (seconds) and $\dot{n}_{\text{CO}_2(\text{g})}$ is the continuous amount of CO₂ captured (moles per second). Although the energy consumption is the most reported figure of merit for electrochemical CO₂ capture methods, a stable process at high current density (allowing high throughput) and a high gas purity are required for a practically relevant process. Commercially relevant current densities are typically on the order of

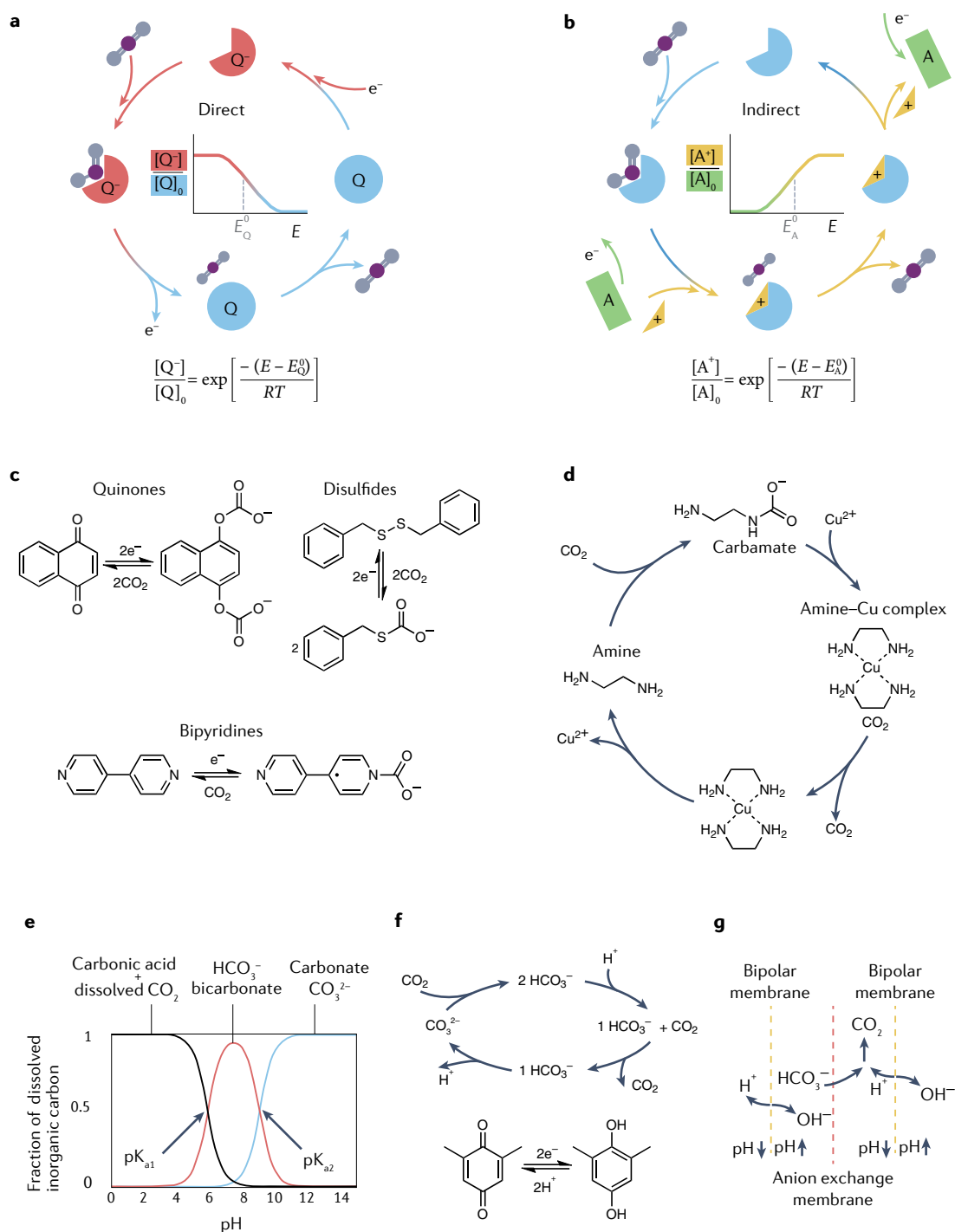


Fig. 1 | Overview of electrochemical methods for CO_2 separations. **a** | Direct processes where a sorbent is reduced or oxidized to modulate CO_2 affinity. **b** | Indirect processes, where electrochemistry acts on a secondary aspect of the system to modulate sorbent affinity for CO_2 . **c** | Several example chemistries for direct redox with CO_2 including quinones, disulfides and bipyridines¹⁸. **d** | Electrochemically mediated amine regeneration (EMAR) process, where amine binding with CO_2 is competitive with copper complexation¹²⁸. **e** | Fraction of dissolved inorganic carbon (DIC) as a function of pH, illustrating the change in CO_2 speciation as a function of solution pH¹⁴. **f** | pH swing process to capture CO_2 at high pH and release it by acidifying the solution, alongside an example proton-coupled electron transfer agent (2,6-dimethylbenzoquinone) that can perform this swing⁷⁹. **g** | Bipolar membrane (BPM) electrodialysis process where pH is modulated across a series of membranes to create a swing that performs CO_2 separation.

100 mA cm⁻², whereas the minimum energy consumption is typically found at a current density an order of magnitude lower⁴⁹. The gas purity is often defined as the molar fraction of CO_2 in the product gas. The achieved

energy consumption and product purity should be reported alongside the feed composition, including the presence of contaminants or oxygen and the concentration of CO_2 . The recovery rate (the fraction of the

Table 1 | Summary of example electrochemical capture processes

Method	Example process	Type	Demonstrated scale	Targeted applications
Direct				
Organic redox	Liquid quinone flow system ⁷⁶	Continuous or cyclic	Bench-scale systems	DAC, point source
Organic redox	Faradaic electro-swing ²⁷	Cyclic	Bench-scale systems	DAC, point source
Transition metal redox	Binuclear copper complexes ²⁸	Process not demonstrated	Small scale	–
Indirect				
Electrophile displacement	EMAR ²⁹	Continuous, but cycle flow direction	Bench-scale systems	Point source
pH — proton-coupled electron transfer	Flow pH swing cycle ³⁰	Cyclic	Bench-scale systems	DAC, point source
pH — electrolysis	Coupled CO ₂ capture and hydrogen generation ²⁴	Continuous	Bench-scale systems	DAC, DOC, point source
pH — BPM electrodialysis	Stacked BPM electrodialysis system ³⁷	Continuous	Bench-scale systems	DAC, DOC, point source
pH — membrane capacitive deionization	Solvent-free system ³⁸	Continuous	Bench-scale systems	Point source
pH — intercalation electrodes	MnO ₂ intercalation system ⁷³	Continuous, but cycle flow direction	Bench-scale systems	Point source
pH — carbonate fuel cells	Fuel cell concentrator ⁴⁰	Continuous	Bench-scale systems	DAC

BPM, bipolar membrane; DAC, direct air capture; DOC, direct ocean capture; EMAR, electrochemically mediated amine regeneration.

entering stream captured) may be an important metric for point source concentrations, although in the case of capture from dilute CO₂ sources, such as water or air, the recovery rate is less relevant, and often not reported.

Measurement systems

Gaseous and dissolved CO₂. Gas measurement systems include infrared sensors, gas chromatography systems and flow meters. Non-dispersive infrared (NDIR) sensors detect the number of CO₂(g) molecules based on the difference between the amount of light radiated by an infrared source and the amount of infrared light received by the sensor's detector. Such sensors are relatively cheap, small, detect concentrations between parts per million levels and pure CO₂, and can be utilized in continuous flow configurations. NDIR sensors can be affected by the length of use, temperature, pressure and presence of any other gases that absorb in the same infrared range^{50,51}. Gas chromatography enables the identification of mixed gas streams by separating substances based on the order in which they elute from the gas chromatography column⁵². Owing to the time required for column elution, gas chromatography cannot sample as frequently as NDIR sensors. Gas flow meters that measure the volume or mass of gas in a stream enable the quantification of captured or released CO₂. Numerous methods of gas flow rate measurement are available, and it is important to verify calibration of the flow meter with the exact composition of entering gas^{53–55}. Selection of the flow meter and gas sensor is dictated by the required sensitivities for a given process. This required sensitivity may be estimated from prior knowledge of the chemistry and expected current.

For example, a process that would ideally operate at 1e[−] per CO₂ captured at 10 mA would expect to capture or release 0.14 ml min^{−1} of CO₂ at 273 K and 1 atm; thus, a flow meter with appropriate sensitivity below 0.5 ml min^{−1} would be required. Similar calculations can be performed for other measurement devices.

In solution, dissolved inorganic carbon (DIC) can be in the form of physically dissolved carbon dioxide CO₂(aq), chemically dissolved carbonic acid H₂CO₃, bicarbonate ion HCO₃[−] and carbonate ion CO₃^{2−}, depending on the pH of the solvent⁵⁶. In multi-ionic, systems the presence of salt ions such as Na⁺ and Ca²⁺ results in salt compounds such as NaHCO₃(aq), Na₂CO₃(aq) and CaCO₃(aq), and they therefore should also be considered as components of the DIC^{57,58}. The DIC content can be measured through solution acidification, followed by gaseous CO₂(g) desorption. This is the principal technique in commercial DIC analysers and total carbon analysers. There are additional commercial sensors for measuring dissolved CO₂ based on the Severinghaus electrode⁵⁹.

The total salt concentration, the pH of the solvent and the detection limit of the measurement devices (for example, 1–100 mg l^{−1} DIC for a total organic carbon analyser and 0–15 g l^{−1} CO₂ for the dissolved CO₂ sensor) can affect DIC measurements. Milli-Q water can be used to reduce the salt concentration, which in turn also reduces the DIC content. However, such dilution allows for a (kinetically rapid^{60–62}) exchange between atmospheric CO₂(g) and dissolved CO₂, particularly in strongly alkaline or acid solutions, reducing the accuracy of the detection methods.

pH measurement. The pH plays a crucial role in determining the carbonate equilibrium because CO_2 reacts with protons in aqueous solutions to form carbonic acid, bicarbonate or carbonate²⁸. In an open carbonate system, increasing the pH increases the DIC content through $\text{CO}_2(\text{g})$ absorption from the overlying gas. However, in a closed system, the pH determines the dominant carbonic species whereas the total DIC remains constant¹⁴, as illustrated in the Bjerrum plot in FIG. 1e. The equilibrium between the carbonic species can be written in terms of the equilibrium constants^{57,58}, which have been measured in various studies as functions of the temperature, pressure and salinity (such as ionic constants) of the solution^{63,64}. The curves for $\text{CO}_2(\text{aq})$, H_2CO_3 and HCO_3^- intersect at $\text{pK}_{\text{a}1}$, and the curves for HCO_3^- and CO_3^{2-} intersect at $\text{pK}_{\text{a}2}$ (FIG. 1e). The values of $\text{pK}_{\text{a}1}$ and $\text{pK}_{\text{a}2}$, and thus the curves in the carbonate Bjerrum plot, change substantially with temperature and salinity⁶⁵. For example, from fresh water to ocean water, pK_{a} values decrease with salinity, shifting the Bjerrum plot to the left⁶⁶. Furthermore, CO_2 solubility in aqueous electrolytes decreases with salinity (for example, a salting-out effect)^{67–71}. As a simplified approach, the carbonate equilibrium can be simulated using software such as PHREEQC, Visual MINTEQ or OLI. pH serves as an indicator of the DIC concentration (due to its buffering attribute), and thus monitoring of the pH is important in any aqueous system. The pH can be measured using calibrated pH meters (high accuracy of approximately 0.02 pH units) or colour change in dyes such as in pH indicator papers (accuracy of approximately 1 pH unit)⁷². In liquid flow systems, it is also possible to connect a semi-micro pH probe to the channel for in situ pH monitoring⁷³.

Electrochemical instrumentation. Potentiostats, galvanostats and power supplies are typically utilized to provide the electrical driving force for the desired chemical reaction. These systems are readily available, with potentiostats typically employed at lower currents, moving to larger power supplies as the system size increases. It can be beneficial to employ potentiostats with electrochemical impedance spectroscopy options to allow monitoring of cell conditions^{74,75}.

Small-scale cells

Many types of electrochemical carbon capture processes are first tested in batch mode at small scale prior to the fabrication of prototypical devices, the exception being processes such as electrodialysis where flow is a necessary component^{14,76}. FIGURE 2a shows a typical cell for initial electroanalytical measurements employing working, reference and counter electrodes. The working electrode can be prepared active material with well-defined geometric area, or can be an inert electrode (glassy carbon, platinum or gold) with the redox-active sorbent molecules dissolved in a supporting electrolyte. Standard reference electrodes such as the silver chloride and saturated calomel electrodes are typically used for aqueous systems, whereas a silver wire with dissolved ferrocene (Fc) as an internal reference is commonly used for non-aqueous systems^{75,77}. This type of cell

can also be purged with defined gas mixtures prior to the measurement. The pH of an aqueous process can be a simple indicator of the time necessary to reach saturation.

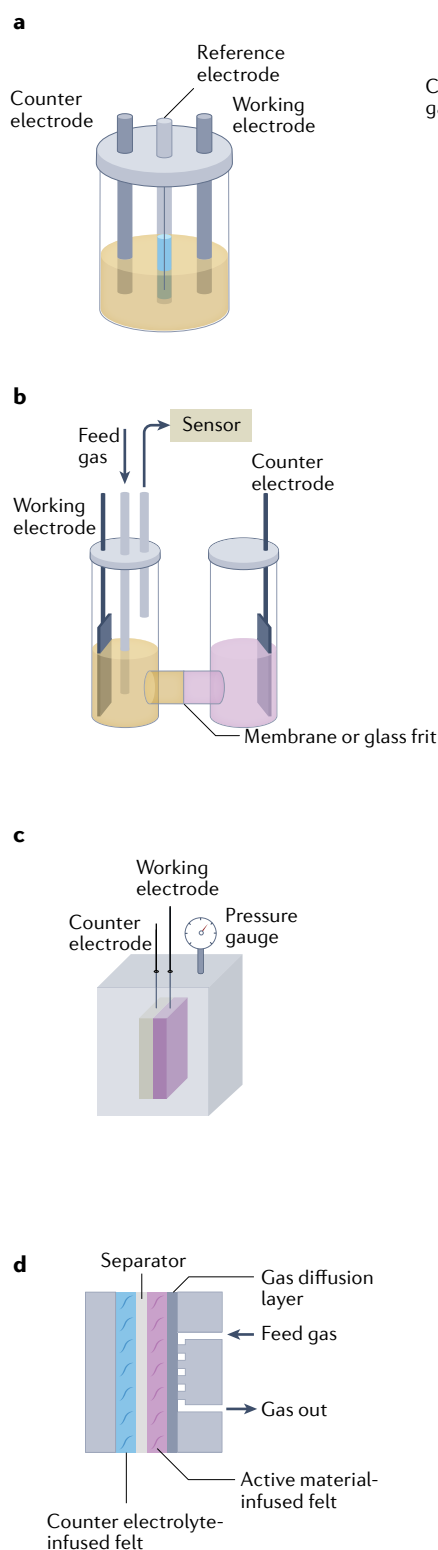
Small cells with larger electrodes to quantify carbon capture capacity are illustrated in FIG. 2b,c. FIGURE 2b shows an H cell that separates two electrodes with a glass frit or membrane. The H cell is kept airtight whereas a CO_2 -containing gas stream continuously flows into the working electrode compartment at a controlled rate. The CO_2 concentration at the gas outlet is monitored with an infrared sensor, gas chromatography system or mass flow meter⁷⁸. The H cell configuration allows quantification of captured CO_2 with the redox-active species of interest, without interference from the counter electrode process. In FIG. 2c, a set headspace gas is introduced and then the cell is sealed completely²⁷. The headspace can be monitored with a pressure transducer or sampled with gas chromatography. These types of cells are amenable to multiple electrode geometries and chemistries, where the example in FIG. 2b illustrates a soluble redox-active species whereas FIG. 2c illustrates active species affixed to an electrode. An alternative configuration is shown in FIG. 2d, where a gas diffusion layer is pressed against the back of an active material-infused electrode and there is no gap between the electrodes and the membrane separator (a zero-gap configuration)⁷⁶. Such a cell enables small-volume testing and separation of the counter electrode from the gas stream.

In any cell, the counter electrode needs to have reversible redox properties (such as an intercalation electrode or redox-active polymers) and should not interfere with the working electrode. For example, redox products from the counter electrode cannot be allowed to diffuse to the working electrode as they will result in unwanted parasitic reactions. A two-compartment electrochemical cell design such as the H cell in FIG. 2b is recommended, separated by ion exchange membranes (IEMs) or salt bridges to minimize crossover on the timescale of interest for batch testing. Nevertheless, bulk electrolysis does not always mimic the real working conditions of electrochemical carbon capture methods (for example, the diffusion kinetics of active species may be slower than in flow systems), and small-scale batch processes tend to generate low amounts of CO_2 that sometimes can make gas quantification challenging⁷⁶. However, small batch cells such as these can easily include reference electrodes to identify the electrode potentials more precisely than in some larger geometries and enable testing with a relatively small amount of active material.

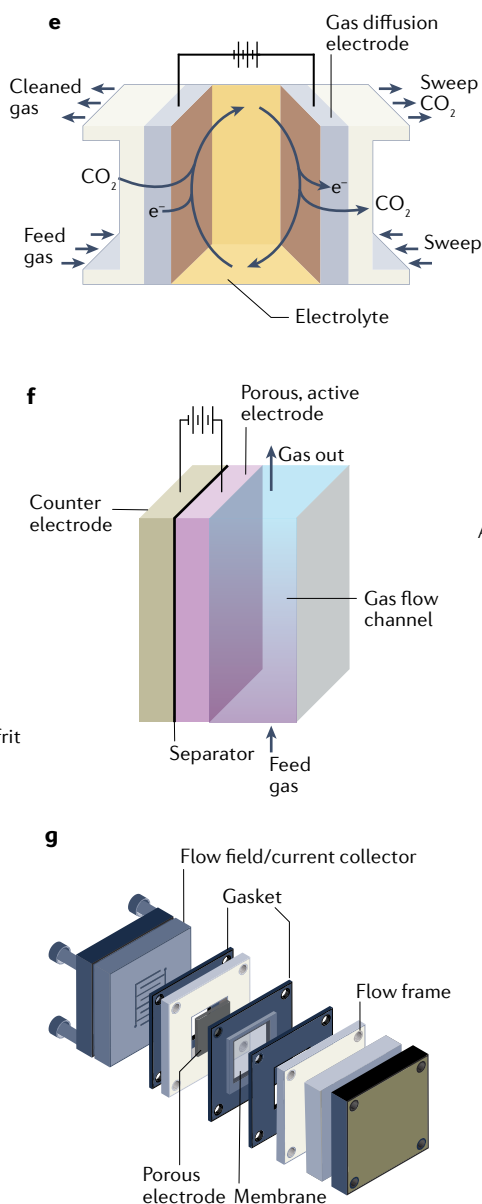
Bench-scale systems

Static liquid cells. Static cells that do not employ a flowing liquid can be categorized into either homogeneous systems^{26,40,79} or heterogeneous systems^{16,27,80}, as depicted in FIG. 2e,f, respectively. Both systems generally employ an anode and a cathode that are contacted with metallic current collectors, but the roles of the electrodes and electrolytes are different. In heterogeneous systems, active materials that react with CO_2 upon electrochemical activation are affixed directly to the surface of the electrodes with an electrolyte present solely to

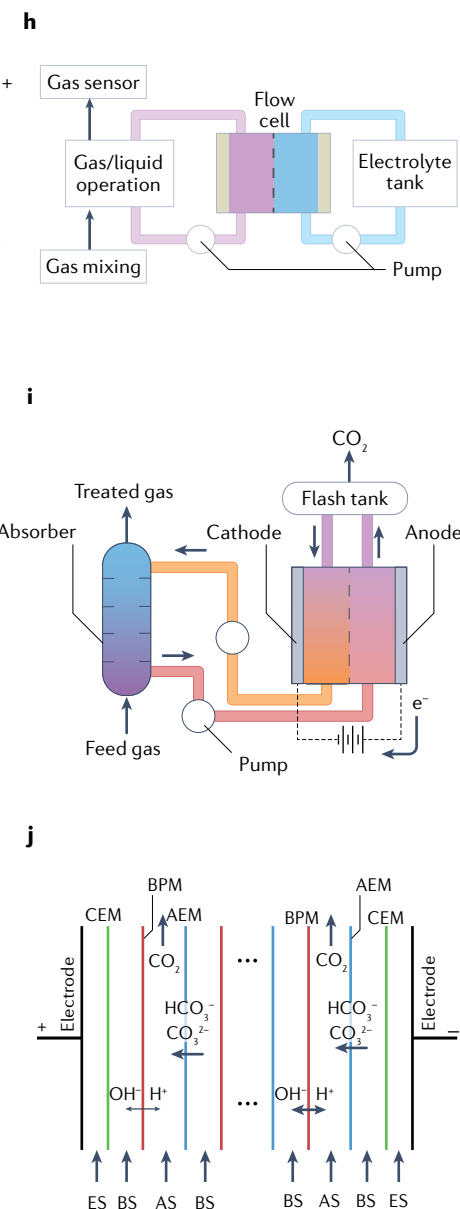
Small-scale cells



Bench-scale cells



System configurations



provide ionic conductivity. In homogeneous systems, however, the electrodes modulate the CO_2 capacity of the electrolyte near the electrode surface to generate a concentration gradient of CO_2 across the cell, selectively pumping CO_2 across the membrane. Such systems may employ redox-active organic species^{26,79} or fuel cell-type

configurations⁴⁰. Homogeneous systems are typically arranged in a continuous capture–release set-up where capture is performed at one electrode at low CO_2 partial pressure and release at the other electrode with a higher CO_2 partial pressure, without changing gas or electrode configurations. Heterogeneous systems,

◀ Fig. 2 | **Overview of several types of electrochemical cells relevant to CO₂ separation studies.** **a** | Typical three-electrode cell for cyclic voltammetry⁷⁷. **b** | H cell with sealed working electrode chamber to measure CO₂ capacity of a solution or electrode⁷⁸. **c** | Sealed chamber containing an electrochemical cell where CO₂ uptake and release is monitored by changes in chamber pressure²⁷. **d** | Zero-gap configuration electrochemical cell for measurement of small liquid volumes or supported species, where the active electrode is contacted by gas through a gas diffusion layer^{25,76}. **e** | Supported liquid membrane cell, where a redox process between two electrodes drives CO₂ separation^{26,79}. **f** | Static heterogeneous electrochemical cell, where active materials are bound to an electrode that is exposed to a gas channel, and sandwiched with a counter electrode and inert separator²⁷. **g** | Representative liquid flow cell showing end plates, a current collector, a flow distribution plate, gaskets, an optional porous electrode to increase surface area and a membrane separator⁷⁶. **h** | Flow cell system that can operate in a cyclic capture–release process, or a batch process if the loop on each side of the cell is broken^{30,39,76}. **i** | Flow cell system that can operate continuously to capture and release a concentrated stream of CO₂ (REF.⁸²). **j** | Stacked flow system for bipolar membrane (BPM) electrodialysis with multiple flow channels separated by cation exchange membranes (CEMs), BPMs and anion exchange membranes (AEMs). Feed locations of the working electrolyte solution (ES), basic solution (BS) and acidic solution (AS) to the stack of cells are shown. Part j adapted with permission from REF.³⁷, RSC.

on the other hand, operate in a cyclic manner where active sorbent species are saturated in a capture step, followed by switching off the gas distribution system to release the captured CO₂ into a separate flow. Further improvements in gas contacting could be achieved by regionally separating the feed and product gas streams, such as the recently reported gas gating membrane that is driven by reversible electrochemical metal deposition/dissolution⁸¹.

In static liquid cells, porous electrodes must be used to facilitate CO₂ entry to the electrochemical cell. The distance between the electrodes is minimized by using a typically inert separator to reduce ohmic resistance and mass transfer resistance. In these systems, the area for gas contacting scales with the electrode size, and thus a long and narrow flow channel or serpentine pattern is often employed, and/or a porous conductive gas diffusion layer (for example, metal or carbon foam) is incorporated. It is also possible to use a stack of the electrode pairs for heterogeneous CO₂ capture, to enable a highly efficient CO₂ uptake capacity with regard to the overall cell volume^{27,80}.

Standards for selecting suitable electrolytes include solubility and diffusivity of CO₂ and other present gases, viscosity and chemical stability. Sorbent material diffusivity and solubility should be maximized in homogeneous systems, whereas sorbents should remain insoluble in heterogeneous systems. In either system, there is an important balance in CO₂ solubility in the liquid electrolyte. CO₂ uptake performance of the sorbent materials is typically improved with higher solubility, but dissolved CO₂ leads to higher back-diffusion in homogeneous systems and higher carrying capacity between cycles in heterogeneous systems, both of which reduce energy efficiency. In either type of static liquid cell, diffusion is the primary mass transfer driving force and, thus, diffusion lengths should always be minimized by maintaining a low liquid volume. Ionic liquids have been used in electrochemical systems due to their low volatility and high conductivity^{26,27,80}. For heterogeneous systems, any redox material that is compatible with the electrolyte and can serve as electron source and sink could be used in the counter electrode.

Liquid flow cells. A representative layout of an electrochemical liquid flow cell^{29–31,39,76} is shown in FIG. 2g. In these cells, sorbent electrolyte flows either next to or through the active electrode. This electrode is typically contacted by a metal or graphite plate on the back side, which will then be connected to the power supply/potentiostat. A membrane separates the flow channels while allowing ions to pass between the compartments, completing the electrochemical circuit. Diffusion lengths are less critical to the design of liquid flow cells as liquid flow creates convection and the system capacity is determined by the liquid volume. Instead, the most important considerations in cell design are maximization of the active electrode area and optimization of the flow path to minimize pressure drop and increase flow distribution^{76,82–84}. Depending on the process involved, additional components in the flow cell stack, including multiple feed flows or membrane channels, may be necessary. The flow cell must then be connected to liquid flow lines, gas contacting apparatus and pumps in an appropriate arrangement for the experiment of interest. FIGURE 2h illustrates a configuration for a cyclic capture–rest–release–rest process, where the active material can either be reduced or oxidized while exposed to gas, although cannot undergo both processes simultaneously^{30,76,85}. In FIG. 2i, the system is configured to continuously reduce and oxidize the active material, enabling continuous capture and release^{39,86}. Some liquid flow systems may also be constructed in stacked configurations analogous to the stacked configurations of static heterogeneous cells. BPM electrodialysis may be stacked with multiple membranes and flow channels and only two electrodes^{37,87}, as illustrated in FIG. 2j, whereas others, such as EMAR, may be stacked in bipolar electrode configurations²⁹. It should be noted that many alternative flow path and cell configurations are possible.

Liquid flow devices including the pumps, tubing, temperature/pressure control and liquid flow measurements are an important part of the system design. Several types of pumps are available, although at the laboratory scale peristaltic pumps are most frequently used due to their ease of implementation and simplicity. To access higher pressures, piston pumps such as those used in high performance liquid chromatography systems can be employed⁸⁷. When selecting pumps and tubing, it is important to consider material compatibility in case of possible corrosion, chemical degradation or seal wear. With either type of pump, the possible impact on gas measurements must be considered, especially in sealed systems where the pump can cause a substantial disturbance to the gas headspace above the liquid.

The delivery of gas to the active sorbent and subsequent removal after sorbent regeneration are an important consideration. For continuous operation, absorption columns that allow larger-area gas–liquid contact are recommended. In the laboratory, these columns may be packed with glass, plastic or metal beads or alternative structures to provide appropriate wetting to distribute liquid without causing column flooding⁸⁸.

For some electrochemical processes, particularly those based on organic redox molecules, the location of gas delivery is important. The redox potential of these

Ohmic resistance

Resistance to the flow of electrons that follows Ohm's law, typically related to current flow through a metal or the ionic conductivity of an electrolyte.

Column flooding

Flooding that occurs when liquid covers the full cross section of the column, leading to gas bubbling through the liquid with reduced overall mass transfer and increased pressure drop.

species can depend on the solution CO_2 concentration, so it may be important to maintain a high CO_2 concentration inside the electrochemical cell^{89,90}. CO_2 is consumed in the cell during the activation step, ideally far beyond the liquid saturation limit. This means that to maintain CO_2 concentration inside the cell, devices must be designed to deliver gas to the cell itself as opposed to in a separate contacting process. On sorbent deactivation to release CO_2 , a mixed stream of bubbles and deactivated sorbent is typically sent to a vapour–liquid separating tank following the electrochemical cell, but removal of evolved gas during sorbent deactivation may be prudent because bubbles of gas may block the electrode and increase the cell potential⁷⁶. An alternative would be to operate the cell at a higher pressure to reduce bubble formation, and then flash the stream in a tank prior to regeneration of the sorbent. Such a process would require careful consideration of changes in CO_2 physical solubility in the sorbent with pressure, and changes in the electrochemistry of the process.

Membranes. Membranes used to separate the anode and cathode can include dense, charged IEMs and porous barriers, which are selected based on the desired transport properties between the anodic and cathodic chambers of the electrochemical cells. IEMs include negatively charged cation exchange membranes (CEMs), positively charged anion exchange membranes (AEMs) and BPMs^{91,92}. The choice of the IEM determines the dominant ion carrier (cation, anion or H^+/OH^- from water dissociation, respectively). In addition to the membrane cost and lifetime, controlled by fouling and stability, their permeation selectivity and ionic resistance are the main consideration for use in industry^{48,49}.

Electrodes. The choice of electrode geometry is dependent on the type of electrochemical process and the choice between flow and static cells. In any process, maximization of the electrode–electrolyte contact area within the cell is important for process efficiency, and in the laboratory to enable operation within a large enough range to obtain clean measurements of the CO_2 separation process. Expected capture rates can be calculated directly from the current with knowledge of the reaction stoichiometry and the Faraday constant. Capture rates should be compared with the sensitivity of available sensors. Completely flat, planar electrodes are typically only utilized in liquid flow systems as they provide minimal resistance to fluid flow, although typically with baffling or other flow distribution mechanisms to distribute current across the plate evenly⁸². In all other bench-scale systems, different types of porous electrodes are employed.

Porous electrodes filled with liquid enable large surface areas within a small volume and can be utilized for both static liquid cells and flowing liquid cells where flow is directly through the pores^{30,32,76,85}. Porous materials are often placed adjacent to a conductive backing plate and pressed down during cell assembly, combining the electrode and any necessary flow field. Good electrical contact with low electrical resistance between the backing plate and the porous material is important to ensure even distribution of current throughout

the porous material. Porous carbon materials include cloths, papers and foams with varying levels of porosity and mechanical strengths. Metal mesh and felt materials are also available. Rigid materials provide consistent cell sizes because they do not compress when the cell is tightened but can lead to membrane punctures during assembly. In flow systems, ensuring even liquid flow is also important. Liquid can be fed directly into the porous material, but distribution across the material requires a flow distribution header or plate⁸⁴. These either spread the internal flow across the entering section of the porous material or distribute the flow across the backing plate. Flow dead spots can often be visually identified inside cells through the presence of material build-up or excessive reaction, because in these areas the sorbent conversion or stripping/plating of metal would be the highest⁷⁶.

Porous electrodes may also facilitate gas distribution within the electrochemical cell by allowing gas flow on one side of the cell with liquid held in place by capillary forces or pressure on the other. The choice of appropriate electrodes to facilitate gas–liquid contact depends on the wetting properties of the system, ensuring that liquid does not flow out of the cell. Gas diffusion electrodes for this purpose have been studied extensively for CO_2 electrolyzers⁹³.

Electrode material choice is dependent on the type of electrochemical reaction. Redox sorbents such as quinones have most frequently been studied with carbon electrodes³³. Processes involving stripping and plating of metals such as EMAR employ metal plate electrodes²⁹, whereas pH swing processes can make use of these or intercalation materials^{30,73}. Flat, graphitic carbon electrodes are available with prefabricated flow patterns. They can typically be reused between experiments by cleaning with appropriate solvents and light mechanical polishing, but the possibility of contamination and surface reactions should be considered⁹⁴. Porous carbon electrodes are known to have complex morphology and surface chemistry dependent on pretreatment conditions, although the full effects of these conditions have not been studied generally for carbon capture applications⁹⁵. Metal electrodes where the surface is stripped or plated during the experiments should generally not be reused unless the surface is completely refreshed by sanding and repolishing.

For electrodes involving active materials, including CO_2 -active redox centres and pH swing materials, fabrication is carried out by casting a solvent-dispersed mixture of active materials, conducting agents and binders in an appropriate ratio on a conductive substrate followed by drying of the solvent^{27,73}. Various types of carbon black can be used as the conducting agents whereas polyvinylidene fluoride is mostly employed as the binder^{25,73}. Carbon-based sheets, cloths and felts are suitable substrates. The performance of the electrodes depends on their microstructure, which affects the mass transfer properties, such as accessibility, of the liquid and CO_2 . In addition, the operation potential should be maintained within the range where oxidation of carbon substrates is negligible⁹⁶. For heterogeneous CO_2 capture systems, the use of binder and conducting additive

Baffling

Liquid flow directing devices within channels.

should be minimized as this can result in a thick stack of deposited materials, causing a significant mass transfer resistance for CO₂ in the electrolyte⁸⁰. This effect can be less important in other cell configurations.

Material characterization

Before testing the CO₂ separation performance, detailed characterization of prepared materials or electrodes is necessary. Such characterization can be coupled to post-experiment analysis to identify problem points. Scanning electron microscopy (SEM) and transmission electron microscopy are typically used to obtain microstructural and nanostructural/atomic information of materials, respectively. For example, FIG. 3a shows the SEM image of calcium carbonate crystals formed during a BPM electrodialysis process, which slowly foul the membrane⁹⁷. Coupled with energy dispersive spectroscopy, SEM can also map and quantify elemental composition. FIGURE 3b shows the corresponding energy dispersive spectroscopy map of the crystallite in FIG. 3a, showing the distribution of calcium, oxygen and carbon in the crystal that verifies that the type of crystallite is CaCO₃. These characterization tools are particularly important when using redox sorbents and intercalation electrodes as electrode uniformity is critical to ensure consistent separation performance. FIGURE 3c includes an SEM micrograph of a porous carbon electrode with a conformal coating of poly(anthraquinone),

demonstrating electrode uniformity²⁵. NMR and Fourier transform infrared spectroscopy are frequently used to analyse the molecular structure of the redox sorbents, before and after adduct formation, and analyse the potential material degradation products^{98,99}. X-ray diffraction and X-ray photoelectron spectroscopy are the standard techniques to probe the crystal structure and surface chemistries, respectively, of inorganic intercalation materials used for pH swing processes. FIGURE 3d shows example X-ray photoelectron spectroscopy spectra of an MnO₂ electrode before and after application of an electrochemical potential, confirming a change in the manganese oxidation state³⁹.

Results

In this section, relevant electroanalytical and characterization techniques are introduced to discuss the necessary analysis at each stage of technological design. Typical results obtained at small scale through initial experiments with the cells depicted in FIG. 2a–d are first discussed, highlighting some of the most common experiments of interest. The results obtained from larger bench-scale systems such as those in FIG. 2e–j are typically highly system-dependent, but can be classified by operation principle in batch, cyclic and continuous modes.

Initial or small-scale experimentation

Electroanalytical techniques can be employed to probe the fundamental electrochemical properties of prepared electrode materials before testing the carbon capture performance in a prototypical device, such as the three-electrode cell in FIG. 2a. Common techniques include cyclic voltammetry, linear sweep voltammetry and galvanostatic or potentiostatic charge–discharge, which will provide key information such as the onset potential of electrochemical reactions and the capacity and reversibility of the electrode materials. For carbon capture using organic redox sorbents, cyclic voltammetry is recommended as an initial technique for the screening of potential candidate compounds, as changes in cyclic voltammetry responses in the presence of CO₂ are often a good indicator of chemical interactions between the compound and CO₂ (REFS.^{26,100–102}). For example, FIG. 4a shows the cyclic voltammetry curves of anthraquinone²⁵. The experiment was conducted using a three-electrode set-up with anthraquinone dissolved in a supporting organic electrolyte, glassy carbon as the working electrode, platinum wire as the counter electrode and silver wire as the reference electrode. Fc was added into the electrolyte as an internal reference. Under N₂, the electrochemical reduction of anthraquinone follows the typical stepwise two-electron transfer process, where the two reduction peaks correspond to the formation of semiquinone radical anion and quinone dianion, respectively. However, in the presence of CO₂, only one broadened reduction peak with increased current is observed, which is attributed to the chemical reaction between reduced quinone and CO₂ following an ECEC mechanism (where E is electron transfer and C is chemical reaction)¹⁰⁰. It was suggested that the formed semiquinone radical anion reacts rapidly with CO₂ via

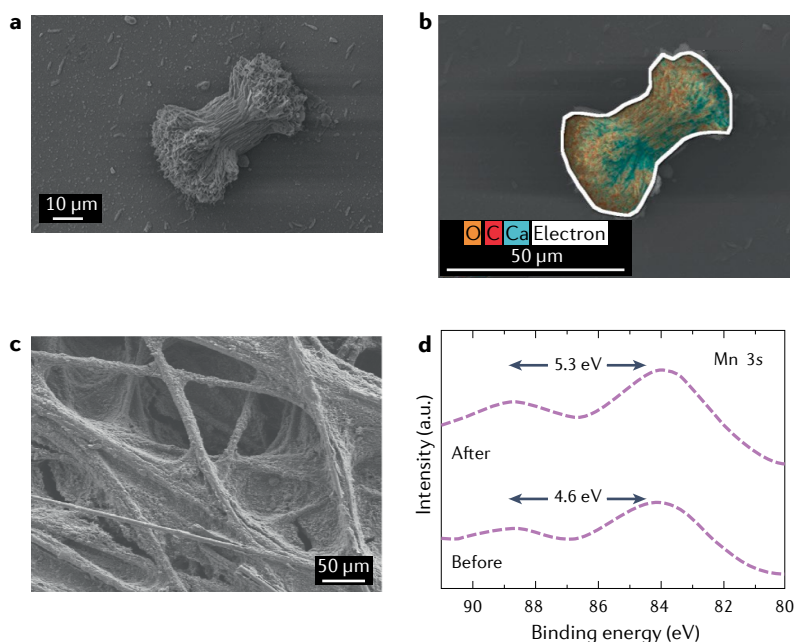


Fig. 3 | Material characterization examples. **a** | Scanning electron microscopy (SEM) image of calcium carbonate crystallites that foul a bipolar membrane (BPM) during an electrodialysis experiment⁹⁷. **b** | Energy dispersive spectroscopy map of the crystal in part **a** showing the distribution of calcium (blue), carbon (red) and oxygen (orange). **c** | SEM image of a poly(anthraquinone) thin film drop cast on a carbon felt electrode, showing uniform coating of the substrate²⁵. **d** | X-ray photoelectron spectroscopy spectra (manganese 3s) of MnO₂ deposited on carbon electrodes before and after a reduction experiment, supporting a change in manganese oxidation state³⁹. Parts **a** and **b** adapted from REF.⁹⁷, CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>). Part **c** adapted from REF.²⁵, CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>). Part **d** adapted with permission from REF.³⁹, RSC.

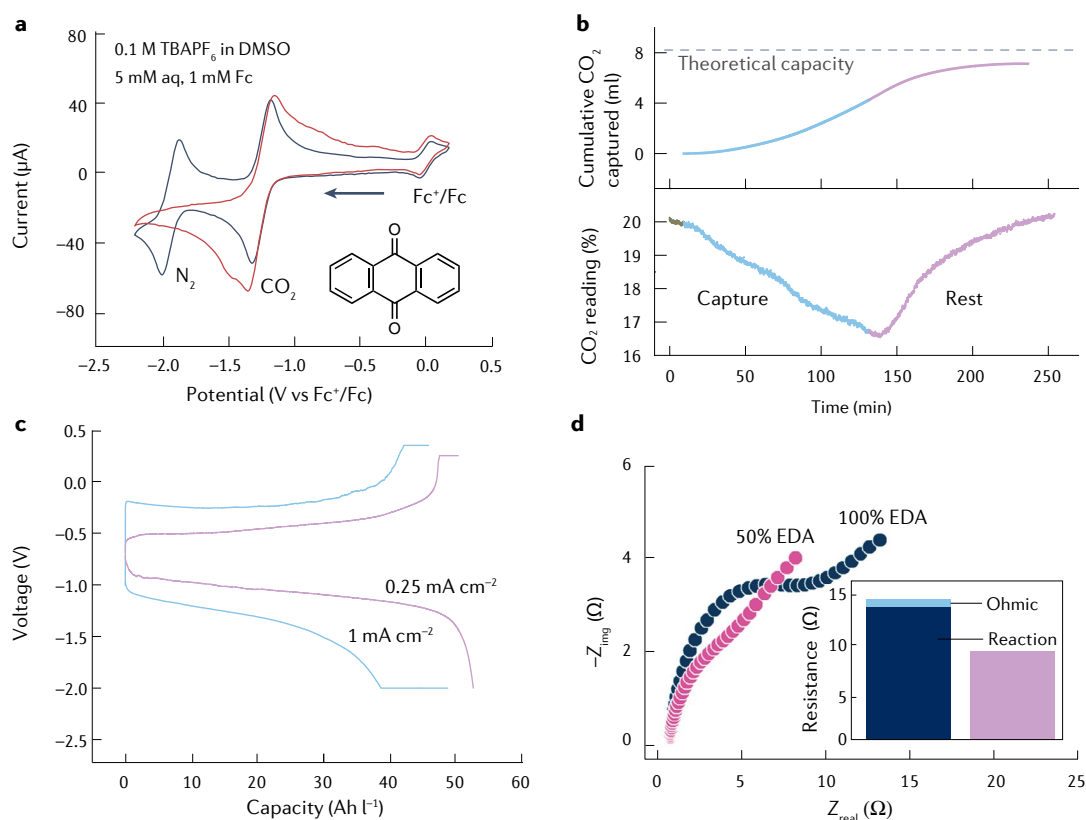


Fig. 4 | Example results from small-scale systems. a | Cyclic voltammogram of anthraquinone dissolved at 5 mM in DMSO with 0.1 M tetrabutylammonium hexafluorophosphate as supporting salt, and 1 mM ferrocene (Fc) as internal standard. Curves shown for N₂ and CO₂ headspaces²⁵. **b** | Example result for a bulk electrolysis experiment, where the CO₂ reading from a non-dispersive infrared (NDIR) sensor as a function of time is shown. CO₂ at 20% in N₂ continuously flows through the cell. During capture, the reading decreases, and during rest the reading will slowly return to baseline. Integration of this curve (shown in the top panel) allows calculation of the total CO₂ captured and comparison with the theoretical amount⁷⁶. **c** | Example electrochemical result for a zero-gap cell, showing a charge and discharge curve at constant applied current plotted as potential versus capacity. Achieved capacity as a function of current density and cyclic stability can be investigated in this configuration⁷⁶. **d** | Example electrochemical impedance spectroscopy experiment, utilizing a copper/copper symmetric cell and amine sorbents with copper salts. Data plotted as a Nyquist diagram of the imaginary versus real impedance. Spectra for ethylenediamine (EDA) in water with CuSO₄ and EDA mixed with aminoethylethanolamine are shown. Inset shows the reaction and ohmic resistance components derived from the spectra⁹⁹. Part **a** adapted from REF.²⁵, CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>). Parts **b** and **c** adapted with permission from REF.⁷⁶, Elsevier. Part **d** adapted with permission from REF.⁹⁹, ACS.

nucleophilic addition, causing a positive shift in the second reduction potential. Subsequently, the second electron transfer generates one additional nucleophilic oxygen for CO₂ attachment.

A simple bulk electrolysis set-up can be used as a first step to test the carbon capture/release behaviour. Bulk electrolysis is more frequently used when validating redox sorbents, EMAR and intercalation electrodes^{73,76,82}. The sorbent materials can be electrochemically oxidized or reduced to capture or release CO₂ in a cell such as that illustrated in FIG. 2b or 2c. For example, FIG. 4b shows bulk electrolysis for quantifying the carbon capture capacity of a quinone-based redox sorbent⁷⁶. This experimental set-up included quinone dissolved in a supporting electrolyte, a carbon felt working electrode and a zinc foil counter electrode connected to a potentiostat. As the quinone was electrochemically reduced, the CO₂ reading detected at the outlet dropped. Integration of this reading gave the amount of captured CO₂.

The cell illustrated in FIG. 2d can also be utilized to test the theoretical electrochemical capacity of sorbent materials and material stability. For example, FIG. 4c shows charge–discharge curves for a quinone-infused carbon felt electrode paired with an Fc-infused counter electrode⁷⁶. At low current, a greater cell capacity is achieved due to concentration polarization at higher current. Repeated charge–discharge cycles could then investigate changes in capacity over time to assess electrochemical stability⁷⁶.

Electroanalytical measurements and bulk electrolysis studies provide the opportunity to estimate the process energetics, which dictate the feasibility of any carbon capture methods. It is critical to evaluate the energetics of the system at early stages of technological development and pinpoint the bottleneck components for improvements. As cells are scaled up and full devices assembled, electrochemical impedance spectroscopy can be a useful tool to probe different contributions to

Nyquist plot

A representation of an electrochemical impedance spectroscopy experiment in which the negative of the imaginary component of the impedance is plotted against the real component of the impedance over a range of frequencies.

the cell resistance by applying an oscillating current or potential at a range of frequencies. In FIG. 4d, for example, a Nyquist plot of imaginary versus real impedance at a range of applied frequencies from an electrochemical impedance spectroscopy experiment is shown⁹⁹. Here, a full electrochemical cell from the EMAR process that incorporates amine solutions and copper plates was used. From the diagram, it is possible to determine the ohmic resistance of the cell from the lower-left intercept at zero imaginary impedance, corresponding to resistance from the wires, electrodes, solution conductivity and membrane resistance. The size of the semicircle can be related to the copper stripping and plating reaction in the cell. Here, a mixture of ethylenediamine (EDA) and aminoethylethanolamine has a lower reaction resistance than pure EDA alone.

Bench-scale experiments

Prototypical cells constructed in the laboratory at bench scale are used to examine the capture/release efficiency and capacity of sorbent materials, investigating the current–voltage behaviour of cells over the full capacity range and demonstrate operation in continuous set-ups^{37,39,79,86}. There are several different possible modes of operation, depending on the process type and experimental goals. For heterogeneous static liquid cells, operation is necessarily in cyclic capture–release steps, whereas homogeneous static liquid cells are typically operated in a continuous capture–release process. Flowing cells can operate in cyclic or continuous modes, or in an intermediate batch configuration that

continuously separates CO₂ but does not recycle the liquid back to the electrochemical cell. Example results for each type of process are illustrated in FIGS. 5 and 6. In any type of operation, the cell current under an applied voltage (or vice versa) and the CO₂ concentration leaving the cell may be monitored, alongside other relevant variables such as pH. In all cases, integration of the gas flow rate and concentration together with knowledge of the current and expected capture fraction yields estimates for the process efficiency and, with integration of the voltage as in Eq. 1, the energetic requirement for separation.

In FIG. 5a, typical results are illustrated as a function of time for cyclic operation, such as in the schematic in FIG. 2h utilizing the cell in FIG. 2g, or for cyclic operation of the heterogeneous cell in FIG. 2f. The experiment begins with a feed of CO₂ at some concentration. At time $t=0$ a voltage is applied, causing an initial spike in current as there is a large concentration of active species to react at the electrode surface, and over time this spike decays. The exiting gas concentration decreases as CO₂ is captured. When the cell is shut off, the gas concentration returns to the baseline because CO₂ is continuously fed to the cell. The captured CO₂ can then be released into the same entering stream, or the configuration can be adjusted to release CO₂ into a different headspace. The cell performance under different release conditions and the cyclic operation of the cell can also be investigated. This type of operation can be seen in the results for a pH swing-type process operated in a cyclic manner in FIG. 5b, where extended cycling was used to illustrate system stability³⁰.

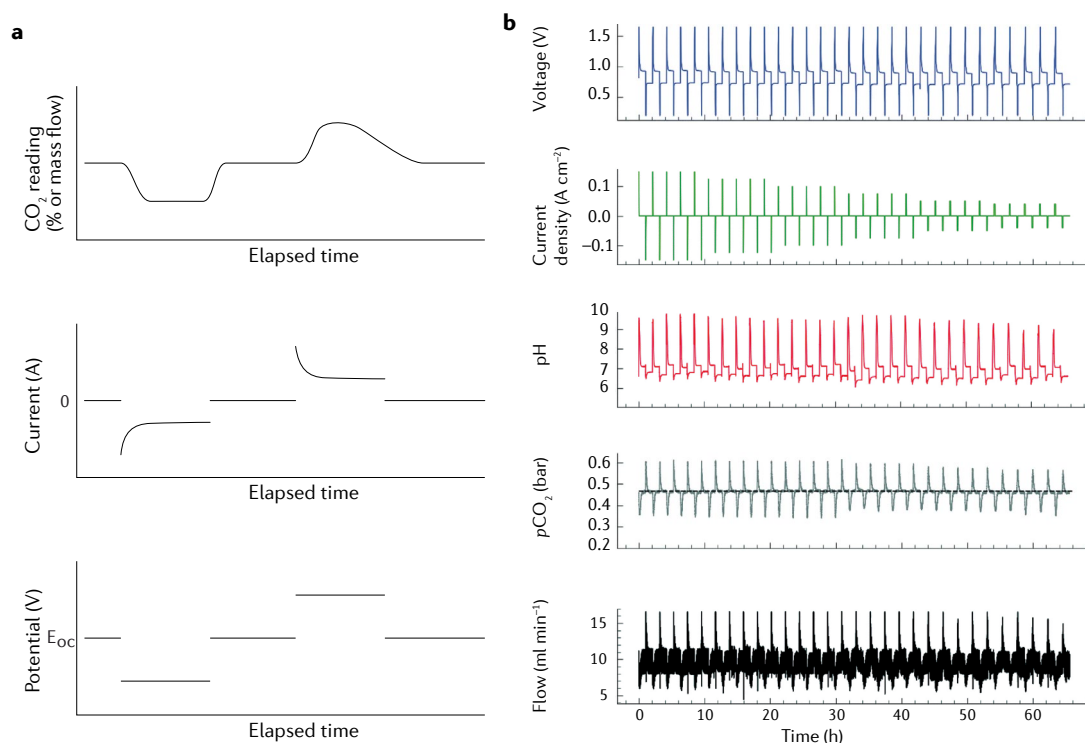


Fig. 5 | **Cyclic bench-scale results.** **a** | Typical results from bench-scale electrochemical capture systems operated in a cyclic manner, moving between capture and release states. **b** | Long-term, repeated cycling of an electrochemical CO₂ separation set-up, showing the cycling voltage, current density, pH, CO₂ partial pressure (pCO₂) in the headspace and gas flow rate³⁰. Part **b** adapted with permission from REF.³⁰, RSC.

Direct air capture (DAC). The separation of CO₂ from air.

Direct ocean capture (DOC). The separation of CO₂ directly from ocean water to indirectly capture CO₂ from the atmosphere.

In continuous operation, more than one gas stream must be monitored at a time, corresponding to the feed and separation product. In the example illustrated in FIG. 6a, a continuous feed of gas enters the cell, whereas the product side is swept with pure CO₂ at a known flow rate. For homogeneous static liquid cells, the feed and product sides correspond to the two porous cell electrodes (see FIG. 2e), whereas for flowing liquid cells the feed and product correspond to the absorption column and flash tank, respectively (see FIG. 2i). At time $t=0$ the electrochemical process is switched on. The product stream flow rate increases, whereas the exiting concentration of CO₂ in the feed decreases. These changes should reach a steady-state value, which corresponds to the capture rate determined by the applied current/potential. The time to reach a steady state can give information about the system kinetics, whereas the fraction of the expected capture/release based on the applied current will determine the faradaic efficiency of the process^{76,82}. It should be noted that alternative configurations are possible, including flow systems with absorption/desorption through porous electrodes, liquid flow in heterogeneous systems or multiple electrochemical cells, but the primary changes to the results illustrated in FIG. 6a in such cases will be in the timescale of approach to steady state. Changes to the steady-state value over time can be the result of sorbent material or electrode stability, whereas deviations from the theoretical value may be due to parasitic side reactions, material purity or mass transfer considerations.

The special case of batch operation in flow cells will appear qualitatively similar to the results illustrated in FIG. 6a. Here, pre-made sorbent solutions under simulated conditions flow through the cell to approximate a certain operation condition. In the batch process, these pre-made solutions would not be connected except

within the electrochemical cell, and thus the flowing liquid does not complete a full circuit. This operation mode has been utilized in the EMAR system to study electrolyte formulations without concern for composition shifting as a result of liquid mixing in the full system loop^{99,103}.

For continuous systems, a critical metric for investigation is the energy consumption as a function of the current density. This can be directly related to the flux of CO₂ captured, and thus achieving high capture rates at low cost necessitates high current densities¹⁰⁴. To probe this, experiments such as those in FIG. 6b can be performed, where a continuous set-up was operated at a range of different applied currents and multiple liquid flow rates⁷⁶. In this case, two electrochemical cells were utilized to achieve a continuous operation. The plateau values at each applied current can be compared against the expected amount of CO₂ captured or released to assess system performance.

Applications

In studying electrochemically mediated carbon capture, it is important to deeply consider the end application and baseline feasibility of the envisioned technique at all stages of the research process. Example calculations include the necessary volume of feed gas to fully saturate the sorbent liquid and estimations of expected evaporation rates at relevant temperatures. These early calculations will dictate where a given electrochemical technique would prove most useful.

Sources for electrochemical separations

There are many different sources of CO₂, with opportunities to apply electrochemical capture techniques in point source capture, direct air capture (DAC) and direct ocean capture (DOC)¹⁴ (FIG. 7). From the total

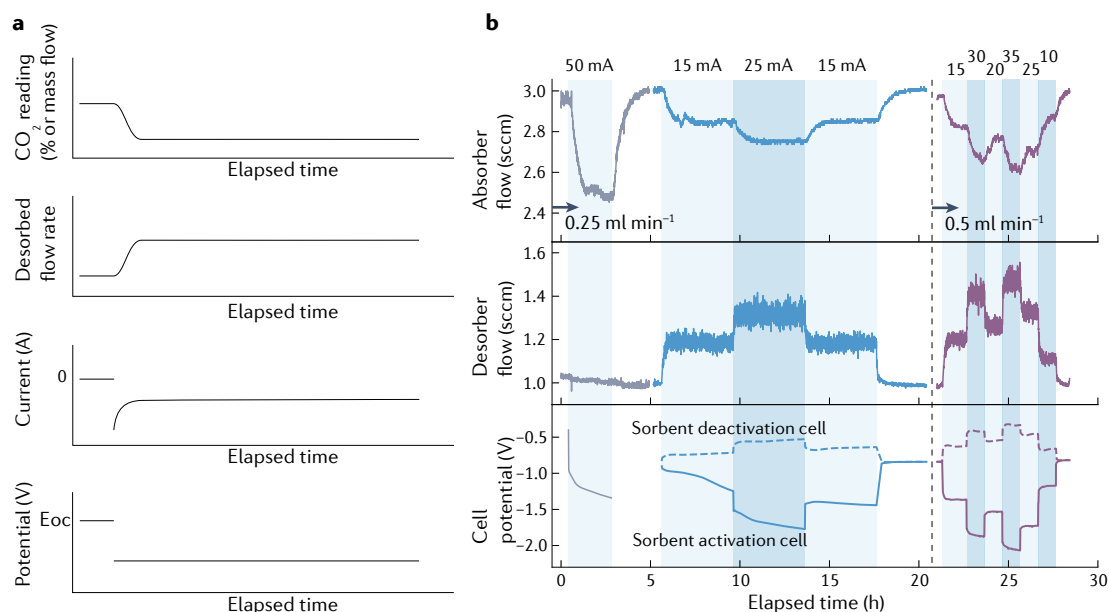


Fig. 6 | Continuous or batch results at bench scale. a | Typical results from a bench-scale continuous capture–release process. **b** | Extended operation of a continuous capture–release process based on quinone chemistry, operated at several applied currents and different flow rates to investigate system performance⁷⁶. sccm, standard cubic centimetres per minute. Part b adapted with permission from REF.⁷⁶, Elsevier.

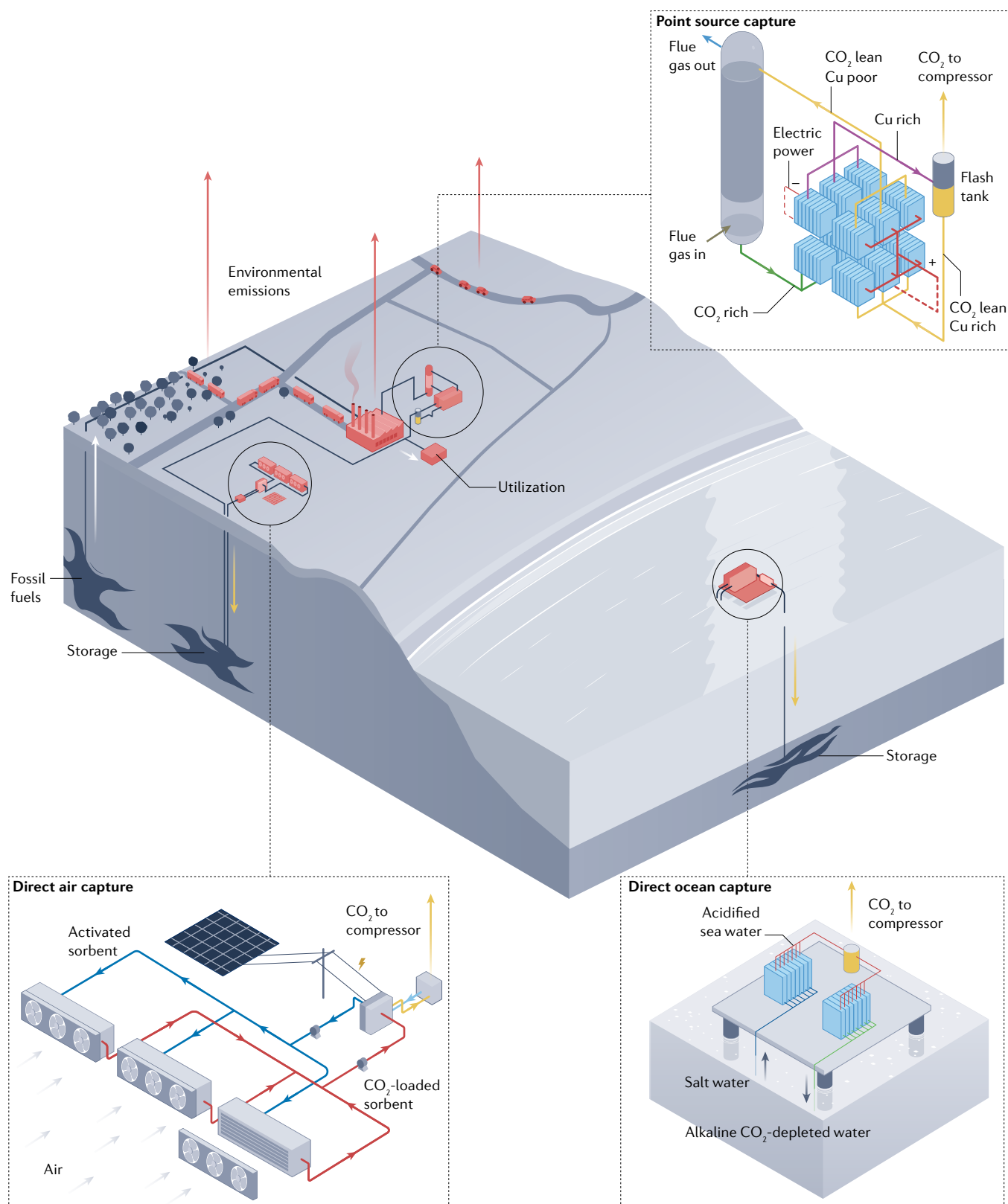


Fig. 7 | **Illustration of the carbon cycle and electrochemical capture processes.** CO₂ is released from point sources and various distributed sources. It can be captured from these point sources, through direct air capture (DAC), direct ocean capture (DOC) or biological methods and bioenergy with carbon capture and storage. Representative systems for point source capture of electrochemically mediated amine regeneration (EMAR)⁴⁸, DAC using large air contactors and DOC using an ocean water feed and membrane contactor to release CO₂ are illustrated. Whereas DOC and DAC can be applied nearby sequestration opportunities, point source capture would more likely require pipelines to transport the CO₂, either for sequestration or utilization. Top right adapted with permission from REF.⁴⁸, ACS.

annual carbon emission (approximately 37 Gt per year), more than 58% is from point sources in the form of flue gas¹⁴ with a carbon dioxide concentration $p\text{CO}_2$ around 0.03–0.15 atm and high feed temperatures of between 150 and 1,200 °C (REFS.^{105,106}). Several impurity gases such as SO_x , NO_x and H_2O are present in flue gas¹⁰⁷. These impurities can complicate the capture process by unwanted reactions with the absorbent/adsorbents^{107,108}. CO_2 capture from point sources, given the high CO_2 content, has been the main focus in carbon capture research¹⁰⁹. However, the capture of CO_2 directly from air or the ocean should be considered to achieve negative emissions in the long term¹¹⁰.

From the total emission that enters the atmosphere ($p\text{CO}_2$ around 0.0004 atm), approximately 23% will end up in the ocean (for example, atmospheric growth of 42% and soil sink of approximately 35%)¹⁴. The ocean contains 2.3–2.5 mM DIC ($p\text{CO}_2$ around 0.072 atm) at low temperatures of –5 to 35 °C (REF.¹⁴), meaning that the carbon content of the ocean (in the dissolved mode) is 147 times higher than that in the air for the same volume. Therefore, via DAC a volume of air 147 times larger than the volume of seawater must be processed to capture the same amount of CO_2 (REF.¹¹¹). However, DAC sorbents typically have higher CO_2 loadings than seawater and pumping seawater uses more energy than pumping the same volume of air. Electrochemical processes are available in point source capture, DAC and DOC, with several representative systems illustrated in FIG. 7.

Feasibility benchmarks

Analysis and benchmarking of electrochemical capture methods to determine practicality in given applications is most common via the energy consumption, current density, product purity and long-term/cyclic stability. The theoretical minimum work to drive CO_2 up a partial pressure gradient from the initial pressure P_i to final pressure P_f can be calculated from Eq. 2:

$$\Delta G = RT \ln \left(\frac{P_f}{P_i} \right) \quad (2)$$

where ΔG is the energy, R is the gas constant and T the temperature. The theoretical minimum energy to remove CO_2 from air via DOC is equal to that of DAC because the overall process performs the same increase in concentration¹¹¹. Depending on the location, there are conditions where DOC is economically favoured relative to DAC and vice versa; land-based implementations might favour DAC, whereas DOC implanted on a ship or floating platform is favoured¹¹¹.

At a minimum, the energy required for CO_2 capture must be lower than the energy produced when this CO_2 is emitted. The CO_2 capture target proposed by the US Department of Energy (DOE) is 90% of emitted CO_2 captured, while maintaining less than 35% impact on the cost of electricity¹¹². In the United States, the average emission factor from electricity is approximately 0.46 kg CO_2 -eq kWh_e^{-1} (IEA Emissions Factors 2021), which translates to an emission of 1 kg of CO_2 per 2.17 kWh_e of electrical energy. Therefore, to achieve the goal of less than 35% impact on the cost of electricity,

energy consumption must be lower than 0.76 $\text{kWh}_e \text{ kg}^{-1}$ of CO_2 (121 $\text{kJ}_e \text{ mol}^{-1} \text{ CO}_2$). However, in countries where electricity is mainly generated from renewable sources such as Iceland, Norway or France (approximately 0–0.05 kg CO_2 -eq kWh_e^{-1}), much higher values for energy consumption of the carbon capture are tolerated. Some laboratory-scale electrochemical $\text{CO}_2(\text{g})$ captures have been demonstrated using less than 121 $\text{kJ}_e \text{ mol}^{-1} \text{ CO}_2$ (REFS.^{27,113}), proving the potential of electrochemically induced CO_2 capture to achieve the economic goal. Such energetics must, however, be proven at industrially relevant current densities (larger than 100 mA cm^{-2})⁴⁹ with practical feed concentrations of CO_2 . In the laboratory, proof of concept can be achieved through multiple experiments when demonstration of a full process may be beyond feasible laboratory scale. To achieve full saturation of a liquid from a low feed concentration of CO_2 , large absorption units with large volumes of liquid may be required which is not practical for early experimentation. Instead, the process may be broken into parts where capture from low feed concentration is demonstrated and, then, a separate experiment demonstrates release into a concentrated headspace. Such an approach was utilized with the faradaic electro-swing process, as well as the EMAR process^{27,86}.

The design of any new process requires consideration of feasibility at multiple scales to account for other relevant necessities for a given implementation (feed water, power source). For point source capture, relative to traditional thermal swing processes, electrochemical methods offer the ability to design the system independently of the point source itself. The electrochemical process can be modelled based on known inputs of gas to determine optimal arrangement of cells, gas contacting and required resources. Integration with existing plant designs can then be investigated for possible benefits such as available waste heat to increase process kinetics⁴⁸. Important considerations include the rate of replacement for cells, sorbent materials and solvents, and opportunities for recycling or regeneration steps. The design of cell stacks to limit complicated external connections to cells may be considered for advanced processes^{29,37,80}. System modelling that includes cost considerations at earlier design stages can help target research and identify early bottlenecks. For example, within the EMAR process, thermodynamic modelling reveals a shift in plating potential as a function of copper loading, which in turn dictates the CO_2 capacity shift⁸³. In the flow cell, the overpotential would thus shift as the solution moves through the cell, indicating that energetics may be reduced with segmented electrodes. Segmented electrodes, or a train of cells operating at different potentials, have significant implications for cost. Early identification of such considerations for any new process may reveal similar concerns, which may spur innovation or further proof-of-concept work such as small-scale segmented cells to verify their feasibility.

Fate of separated CO_2

Once separated, CO_2 can be injected, typically in a supercritical state, into deep geologic formations (such as in underground saline aquifers); mineralized by injection

into suitable mineral-rich formations (for example basalt, yielding magnesium or calcium carbonates); or further utilized in downstream processes such as renewably driven electrosynthesis of chemicals or fuels. Permanent storage is optimal as utilization pathways ultimately release CO₂ back to the atmosphere, often on short timescales of months to years. Thus, utilization as chemicals or fuels cannot achieve net carbon removal, although they can achieve some emission reductions by supplanting conventional CO₂-intensive production⁷. Consequently, the main argument for utilization has been to provide cost offsets for adoption of capitally intensive capture systems, encouraging early-stage adoption in industry. Critical analyses have examined the potential for utilization pathways, specifically electrochemical reduction pathways, to contribute to net reductions in emissions and have identified extensive challenges regarding realistic environmental impact at scale. Given the high energy requirements to drive selective electrochemical CO₂ reduction and current electrical grid intensity, a recent analysis indicated that only lesser-reduced products (carbon monoxide and formic acid, corresponding to the simplest two-electron pathways) can be electrosynthesized with net reduction in emissions, when compared with current fossil-based synthesis, under an optimistic scenario of 70% energy efficiency and 0.11 kg CO₂-eq kWh_e⁻¹ grid intensity or lower (compared with current grid intensity of 0.295 kg CO₂-eq kWh_e⁻¹)¹⁴. Unfortunately, projected emission reductions for these relatively low-volume chemicals (5 Mt per year associated CO₂ emissions) are negligible on the global scale considering current production levels. Electrosynthesis of further-reduced products with larger market size and higher CO₂ intensity such as ethylene (approximately 800 Mt per year emissions), even under optimistic conditions, cannot reach net reductions given the high overpotentials required to drive adequate selectivity. Post-capture electrochemical CO₂ utilization may be competitive with electrochemical separation for renewable energy in a grid-constrained world. Consequently, there is heated ongoing debate regarding whether utilization merits serious consideration or is a distraction in the larger task of CO₂ mitigation.

Reproducibility and data deposition

Laboratory-scale experimentation to obtain the energy consumption, capture rate, product purity and cycling stability reveals important information about the real-world relevance, although there are several considerations in the design of such experiments to ensure that the obtained values translate beyond the laboratory. First, many laboratory processes are operated with idealized gas feed streams without possible contaminants such as SO_x, NO_x or even oxygen⁷⁶. Oxidative degradation of amines is a significant challenge for the traditional swing process¹¹⁵, thus electrochemical processes that can maintain performance under long-term cycling in the presence of appropriate oxygen concentrations are important. Such long-term cycling must also be performed under realistic operating conditions³¹. This includes a large sorbent capacity swing and utilization

of full sorbent concentrations. For static electrode cells an equivalent consideration is electrolyte and counter electrode lean cells, as opposed to initial fabrications which often employ an oversized counter electrode for heterogeneous systems and excess electrolyte for homogeneous systems, to ensure minimal influence from the inactive components.

Laboratory measurements should also demonstrate reproducibility on fully independent experiments. It can be easy to repeat experiments on a single cell to produce error ranges, but this does not fully account for reproducibility. Common sources of irreproducibility include material and electrode uniformity and purity during fabrication steps as well as measurement calibrations. NDIR-based CO₂ sensors must be calibrated before every measurement because they can drift over extended terms with water or other solvents present, or with changes in pressure. Measurement of DIC is sensitive to exchange with the atmosphere; thus, care must be taken with measurement set-up design. It should be noted that many mass flow meters report flow at standard conditions (for example, as standard cubic centimetres per minute (sccm)), but these standard conditions may vary depending on the manufacturer. Care should be taken to verify each definition of standard conditions and report the values utilized for a given work.

Metric reporting should also be carefully standardized to discuss which components of the process are included. Energetics typically exclude peripherals such as pumps and fans because those devices would scale quite differently in true implementations. However, if the process requires vacuum or downstream separation steps to remove CO₂ from the system, this exclusion can substantially distort the true process metrics.

There is currently no standard of deposition and data sharing for this field. As a minimum we suggest details should include dimensions of cells, and include the morphology, chemical composition and detailed preparation methods for electrodes and electrolytes to enable reproducibility between research groups. Full characterization of materials and electrodes should be reported including, as appropriate, associated SEM, NMR, transmission electron microscopy, energy dispersive spectroscopy, X-ray photoelectron spectroscopy and X-ray diffraction spectra. Details on the methods of CO₂ quantification, including associated gas flow rates, calibrations and the presence of condensers should be reported.

Limitations and optimizations

Although electrochemical CO₂ separation methods show great promise to solve many of the challenges associated with existing processes, there are some limitations in their use¹⁴. Electrochemical processes require an electrolyte to carry ionic current between the active electrodes, something that is not required with solid supported metal organic frameworks and amines¹¹⁶. Ionic liquids and water-in-salt systems have lower vapour pressure, but other systems based on water may require significant water feeds to allow for water evaporation from the gas contacting process^{25,76,117,118}. The solubility of CO₂ in the electrolyte solvent is an important consideration in many processes. For organic redox processes, this solubility

must be enough to provide rapid mass transport of CO_2 to the active species, but any solubility translates to a carrying capacity that must be captured and released during every cycle, reducing process efficiency²⁶.

The presence of contaminants in true feed gases is likely, such as SO_x and NO_x in power plant flue gas that frequently react with sorbents, and laboratories are often not equipped to test such species given their acute toxicity⁴. SO_x is known to bind reversibly to some redox-active organics, whereas the impact of NO_x has generally not been considered in electrochemical processes¹¹⁹. The stability of systems in the presence of these gases will be important to establish implementation at existing power plants. The sensitivity of materials to oxygen is also a current limitation, with many organic redox molecules known to deactivate with oxygen. The choice of electrochemical redox pairs offers one potential optimization to mitigate material sensitivities.

Redox potential landscape

In direct CO_2 separations, a redox-active molecule is first reduced prior to chemical binding of CO_2 . Consequently, the individual electrode potential is pinned by the inherent redox properties of the molecular species. Selection of an appropriate molecule reflects several design considerations; the capture molecule must have a reversible redox-active site that can be modulated at an electrode; its binding affinity for CO_2 must change significantly between reduced and oxidized states, allowing for effective capture and release; and the molecule must be non-reactive towards surrounding solvents and contaminants while exhibiting high selectivity and kinetics of CO_2 uptake. Binding with CO_2 requires the presence of a nucleophilic site with sufficient electron density to activate CO_2 via its acidic carbon. Attention thus far has largely focused on a subset of redox molecules that yield nucleophilic oxygen, sulfur or nitrogen sites upon reduction such as quinones, thiolates and 4,4'-bipyridine, respectively^{15,18}.

Experiments have shed light on coupling between the redox potential of redox-active molecules used in direct capture processes and CO_2 affinity, showing a correlation between more negative reduction potential and higher affinities or rate constants^{100–102}. In cells employing fully symmetric electrodes, the absolute potentials of the individual redox processes do not factor into the separation energetics given that the total cell voltage polarization is about 0 V regardless of individual redox potentials. However, the selection of absolute electrode potential is significant in avoiding electrolyte and contaminant redox processes, and, frequently, addition of CO_2 to the system will create asymmetric redox behaviour^{29,100}. As depicted in FIG. 8, chemical design of redox-active sorbents has so far led to a versatile energetic landscape with redox potentials spanning approximately –0.4 to –1.4 V versus standard hydrogen electrode (SHE), almost to the point of direct $\text{CO}_2/\text{CO}_2^-$ reduction in non-aqueous media at exceptionally negative potentials (–1.9 V versus SHE)¹²⁰. Sorbent reduction potentials are often shifted positively in the presence of CO_2 compared with the innate redox properties of the sorbents without CO_2 present¹⁰⁰. By necessity, many of these redox processes must operate

in non-aqueous media to avoid the water reduction window. Such processes often employ non-volatile ionic liquids or other solvents, to help facilitate solubility of many redox species. Although non-aqueous media uniquely offer access to highly nucleophilic redox couples, such low reducing potentials generate high driving forces for parasitic reduction of trace water and, especially, O_2 , with a reduction potential pinned significantly higher (–1 to 0 V versus SHE in non-aqueous media depending on the presence of electrolyte salt cations)¹⁰⁰. Future efforts are needed to examine mechanisms to break coupling between CO_2 binding affinities and O_2 reactivity for practical separation systems.

In indirect separations, the electrode potentials are pinned by the proxy electrochemical reactions used to modulate the pH of either a solution or a complexing agent used to chemically displace CO_2 from a sorbent such as an amine. Some pH swing processes, for instance employing BPMs, exploit the water electrolysis reaction, which varies as a function of pH^{17,121} (FIG. 8, top panel). Alternatively, quinones and other molecules can be electrochemically cycled between protonated and deprotonated states^{30,32,79,122} (such as Q/QH₂ in FIG. 8). Redox potentials for this are higher than nucleophilic addition (approximately 0.1–0.3 V versus SHE), although the solubility of active species in aqueous electrolyte can be an issue^{30,79}. Note also that trace water in non-aqueous media employing quinones can compete with CO_2 for binding sites.

EMAR processes exploit direct redox of a metal electrode such as copper, with electrode potentials pinned instead by the metal potential, which must be selected to lie within the water stability window for a given pH²⁹. As with direct redox, electrode potentials in practice will often vary from the standard potential due to complexation with additional species, such as with amines in the case of EMAR. For example, when employing Cu/Cu²⁺, the presence of the amine was found to suppress copper reduction potentials (standard potential of 0.345 V versus SHE) by approximately 500 mV, pushing potentials closer to the hydrogen evolution reaction²⁹. Such shifts need to be considered in future development of electrode-mediated processes and emphasize why three-electrode characterization (with a well-defined reference) is important prior to symmetric cell testing, which can obscure such considerations.

For the design and selection of appropriate redox mediators in pH swing processes, aqueous solubility and chemical stability are the main criteria to consider. Recent works employing disodium 4,5-dihydroxy-1,3-benzenedisulfonate (tiron)¹²² and sodium 3,3'-(phenazine-2,3-diylbis(oxy)) bis(propene-1-sulfonate) (DSPZ)³⁰ addressed solubility to some extent through sulfonate moieties, whereas chemical instability and oxygen sensitivity are yet to be fully resolved. A recent report on nanoparticles coated with polymeric quinones for carbon capture indicates potential new avenues to design redox-active mediators for a pH swing with suspended active material¹²³.

Inorganic materials with the capability to store and release protons inside the lattice by intercalation and deintercalation can be used as electrodes in liquid

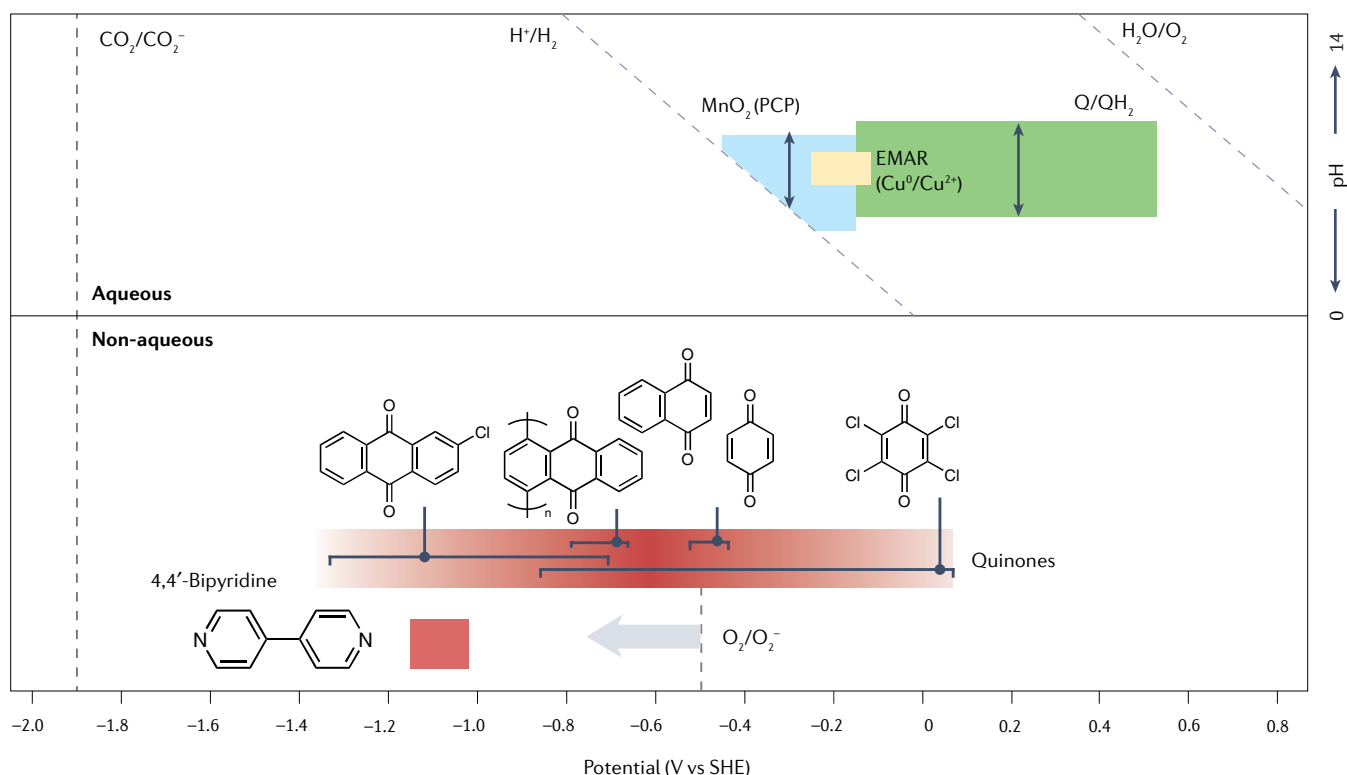


Fig. 8 | **Redox potential landscape for aqueous and non-aqueous electrochemical capture systems.** In aqueous capture systems, reactions vary with pH. Anode and cathode reactions are indicated by slanted lines. MnO_2 -based proton concentration process (PCP; blue), electrochemically mediated amine regeneration (EMAR; yellow)²⁹ and Q/QH_2 (green) denote redox between unprotonated and protonated sorbents, including proton-coupled electron transfer. Ranges given in the vertical direction for aqueous systems denote representative pH ranges spanned in those processes designed for this purpose, whereas horizontal ranges denote redox species variations within a process class (such as proton-coupled Q/QH_2) or Nernstian potential changes as a function of state of charge within a singular process (such as EMAR). In non-aqueous media (bottom section), several organic species have been investigated with a wide potential range. Quinone redox potentials investigated for CO_2 separations span several volts depending on the structure. Many other structures exist. SHE, standard hydrogen electrode.

flow cells for heterogeneous pH swing of the alkaline sorbents. The parameters for choosing the active materials include gravimetric/volumetric capacity, intercalation/deintercalation kinetics and chemical stability in the relevant pH region, estimated to be within pH 6–10, depending on the CO_2 concentrations³⁰. Proton-storable electrodes with fast kinetics have been studied widely for electrochromic devices, but they exclude materials such as WO_3 and MoO_3 that are not stable in alkaline conditions. The first successful demonstration of heterogeneous pH swing was made by using MnO_2 (REF.⁷³), but any other materials that meet the aforementioned standards could be promising candidates for an electrochemically mediated pH swing. In all these systems, competition with hydrogen evolution remains a consideration for selection and engineering of electrode potentials and often places constraints on electrolyte design (namely pH).

Outlook

The growing imperative of environmental CO_2 reduction has led to increasing interest in the development of new capture technologies such as isothermal, electrochemically modulated systems that can, in principle,

rely solely on renewable electricity sources. The number of publications in this area has increased dramatically over recent years and is continuing to grow. These technologies can be manifested in many different configurations and rely on different electrochemical processes such as redox-active organic nucleophiles and intercalation-type sorbents, as well as electrodialysis and other water-splitting processes for pH modulation. The outlook for this field is strong, with significant opportunities for the development of robust new sorbent materials and morphologies with greater capture capacity, selectivity, uptake rates and stability, all the while reducing parasitic losses and other ohmic resistances that degrade unit performance. The promise for these technologies is evident in new start-up ventures for DAC (for example, Verdox) and DOC (for example, Captura).

An emerging area of work in electrochemical capture includes strategies for alternative regeneration, or direct adduct conversion, to couple CO_2 utilization to the capture process. Such combined capture and conversion has been demonstrated for CO_2 adducts of amines (direct carbamate electroreduction to C1 products)¹²⁴ and ionic liquids¹²⁵, although these combined capture and conversion routes are all in their early phase of

development. CO₂ conversion combined with capture routes of organic redox carriers or (bi)carbonate has only been limited to a two-step mechanism, where the CO₂ is first liberated from the carrier and then converted (in a single device or in multiple stages). Specifically for the case of organic redox carriers, CO₂ release occurs at the anode whereas CO₂ is reduced at the cathode, which typically limits the combined capture and conversion to a multistep capture–release concept⁴⁶. CO₂ conversion in bicarbonate solutions, obtained from CO₂ capture, has been demonstrated effectively using BPM-facilitated bicarbonate electroreduction¹²⁶, although this reaction is mechanistically a two-step process. Nevertheless, such combined technology avoids the necessity to regenerate the CO₂-loaded (bicarbonate) solution via a separate energy-intensive process. Precipitation of solid carbonates has also been targeted as a means to couple capture and CO₂ storage, while generating other valuable products¹²⁷.

As the field continues to grow, the development of new electrochemical capture and conversion technologies will rely on having robust experimental capabilities

to enable assessment and optimization of the processes. There are several innovation opportunities that would substantially improve experimentation in electrochemical CO₂ separations. Most clearly, reliable, inexpensive CO₂ concentration sensors that could operate with relatively small amounts of gas or low flow rates would aid early experimentation and allow more rapid screening of new sorbent molecules. There remains substantial opportunity to develop novel redox mediators with enhanced stability towards oxygen and expanded solubility in electrolyte solvents. It would be important for such design to also consider the redox potentials, and to reduce the minimum capture work for a capture–release process. At the same time, transport and reaction rate limitations and ohmic resistances must be reduced, which calls for improved cell design and electrode morphologies. In tandem, membranes that separate anolyte and catholyte chambers in electrochemical cells or catalyse water dissociation in BPM processes are frequently cited as limiting existing processes both in performance and in cost¹⁴.

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Author contributions

All authors researched data for the article. All authors contributed substantially to discussion of the content. All authors contributed towards writing the article. K.M.D. and T.A.H. reviewed and edited the manuscript before submission. Introduction (K.M.D., R.S. and D.V.); Experimentation (R.S., K.M.D., Y.L., J.S.K. and S.K.); Results (Y.L. and K.M.D.); Applications (R.S. and B.M.G.); Reproducibility and data deposition (K.M.D.); Limitations and optimizations (K.M.D.); Outlook (T.A.H. and D.V.); Overview of the Primer (K.M.D. and T.A.H.).

Competing interests

T.A.H. is a co-founder and Scientific Advisory Board member of Verdox, Inc. D.V. and R.S. co-founded SeaO2 and are involved as advisor and CTO, respectively. The other authors declare no competing interests.

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