Persistent anthropogenic greenhouse gas emissions, particularly emissions of CO$_2$, necessitate the development of novel mitigation solutions. Global anthropogenic fossil CO$_2$ emissions exceeded a record estimated 37 Gt in 2017. To limit excessive CO$_2$ emissions and to minimize impacts on the climate, a range of technologies including a transition from fossil fuel-based to renewable energy, improvement of vehicle and building energetic efficiencies, and CO$_2$ capture and sequestration must be implemented together. CO$_2$ can be captured from point sources (e.g., coal-fired power plants) or atmospheric air, the latter theoretically allowing for negative CO$_2$ emissions. Although various demonstration projects have come online in recent years, the only CO$_2$ capturing technique that has been utilized at an industrial scale is amine scrubbing. This is a post-combustion process that uses amine-based solvents (e.g., monoethanolamine) that absorb the carbon dioxide contained in the flue gas. The CO$_2$ is then removed from the CO$_2$-containing solvent by means of a regeneration process, driven by a temperature or pressure swing. The solvent is recycled and the captured CO$_2$ is treated for transport and subsequent storage. The main drawbacks of this technology are related to the corrosive nature of the solvent and to the high cost (60–107 USD/ton of CO$_2$ captured).

In this context, considerable research efforts are needed to develop more efficient and, at the same time, less costly CO$_2$ capture technologies. Alternative to amine scrubbing are the capture of CO$_2$ using solid sorbents such as alkaline earth metal oxides, layered double oxides, carbon, or metal organic frameworks but also electrochemical methods. Using solid sorbent-like metal oxides (e.g., CaO) or carbon present the advantage of using cheap abundant materials, less corrosive and potentially more selective for CO$_2$ capture. Electrochemical gas separation was successfully used for H$_2$ separation from gas mixture containing CH$_4$, reformate gas, and N$_2$. The method consists of selectively oxidizing (or reducing) a gas at one electrode to an ion which is further transported through a membrane or liquid electrolyte to the other electrode where is reduced (or oxidized) back to the gas. The advantages of this technology is that the separation occurs at low temperature and pressure and that, in principle, the energy requirements are low.

Moreover, electrochemical methods for CO$_2$ capture can be performed at atmospheric concentration levels. While electrochemical CO$_2$ separation methods have been investigated for almost half a century, recent years have brought a surge of interest and encouraging developments.
19,21 or transport of protons through the CEMs or hydro-electrodialysis, this can occur through electrolysis of water at the electrodes15,27,30 or transport of protons through the CEMs or hydroxide through the AEMs.19 Other loss mechanisms that have been proposed are leakage of protons through the AEM,17,19,21 loss of BPM perm-selectivity,17 and unwanted water electrolysis in AEMs.17 For gas-fed membrane electrochemical cells, the transport of hydroxide instead of (bi)-carbonate ions leads to faradaic losses. Low efficiencies for low concentrations of CO2 in the feed gas exemplify this issue.16 Cells operating at higher voltages (>1.23 V) also have the potential to electrolyze water and evolve O2 and H2.15,27,30

Specific energy consumption, which incorporates voltage across the cell or stack, is negatively affected by activation, ohmic, or mass transport overpotentials. These can arise from slow reaction kinetics at the electrodes, membrane/electrolyte materials with poor conductivities, poor interfacial contact, or insufficient flows of reactants and/or products to or from reaction interfaces. Thus, design aspects such as membrane spacing or electrolyte concentration in electrodialysis can have significant effects.17,19,21 There is no universal solution to optimize both faradaic efficiency and specific energy consumption of an electrochemical CO2 separation cell or stack, and the design of such a system requires careful consideration of the process inputs and constraints.

Electrodialytical regeneration.—In a two-step CO2 capture and electrodialytical regeneration system, an electrolyte solution absorbs CO2 at near-ambient temperatures and pressures before it is pumped to an electrodialysis unit where the CO2 is removed and the solution is regenerated. Stacks of bipolar membranes (BPM), cation exchange membranes (CEM), and/or AEMs are arranged to create alternating acidic and alkaline compartments through a pH swing, allowing for release of CO2 and regeneration of the solution, respectively. Gaseous CO2 is formed by decreasing the pH of the carbonate solution. This is in contrast to the energy-intensive thermal regeneration system of traditional CO2 capture processes. Various architectures of electrodialytical stacks found in literature are shown in Fig. 2. BPMs can be incorporated to split water into hydroxide ions and protons, but they are not necessary for an electrodialytical separation process (as shown in Fig. 2d). While different studies propose different aqueous capture solutions, the generic reaction to acidify the carbonate solution and release the CO2 are:

$$\text{CO}_3^{2-} + H^+ \rightarrow HCO_3^-$$  \hspace{1cm} \text{[1]}

In this way, CO2 is typically released from the CO2 recovery compartment or downstream gas-liquid separator as a pure gas, meaning concentration factors of 2500 are obtainable for DAC and subsequent electrodialytical regeneration. While an electrochemically-driven regeneration process has theoretically low energy requirements, there is a significant gap between the experimental values reported in literature and the ideal energy requirement for recovery of CO2 from alkaline carbonate solution, which has been attributed mostly to reactions in the electrodes and ohmic losses in the cell or stack.19 Most electrodialysis studies use commercially available membrane materials from suppliers like DuPont,20,22 Ameridia (Eurodia),17,18,20 Astom,21,29,33 Tokuyama,39 or Asahi Glass.19,21,33

Liquid electrolyte pumping allows for transport of the ions to the electrodes at a relatively high concentration, in turn allowing for higher current densities to be reached and at higher faradaic efficiencies as compared to direct gas phase separation of a dilute CO2 mixture (e.g., air). This comes at expense of introducing a parasitic energy loss to the system in the form of pump work, additional energy costs associated with the capture step, and technical challenges associated with using a caustic, volatile solution.34 Inclusion of these costs is largely ignored in electrodialysis studies, arguing that the energy and equipment cost contributions for the absorption step are negligible by comparison.21 This, however, depends strongly on the concentration of CO2 being separated and the assumptions of component efficiency. Operational energy estimates for an alkali solution air contactor have ranged from 13 kJ mol−1 CO2 for fan and pump energy in a pilot plant35 up to approximately 100 kJ mol−1 CO2 depending on column design.36 At the prototype scale, values of 190–390 kJ mol−1 have been obtained for a spray-based air contactor.34

Past electrodialytical regeneration studies have primarily focused on potassium17,18,24,33,37 or sodium18–21 (bi)-carbonate as the CO2 capture medium, implying that the CO2 capture step takes place using potassium hydroxide or sodium hydroxide. One study proposing the use of or amino acid salts25 as an electrolyte is a variation of this approach. Although sodium and potassium hydroxide are chemically similar, previous experimental work has determined that potassium hydroxide captures more CO2 and has a higher absorption efficiency than sodium hydroxide in both flue gas38 and air29 contactors.

Potassium (bi)-carbonate.—A few early studies in the 1990s proposed electrodialytical CO2 capture from the atmosphere for the application of renewable fuel production.32,37 Bandi et al.37

$$HCO_3^- + H^+ \rightarrow H_2CO_3$$  \hspace{1cm} \text{[2]}

$$H_2CO_3 \rightarrow CO_2 + H_2O$$  \hspace{1cm} \text{[3]}

\(40\)
Table I. Notable experimental results for electrochemical CO₂ separation. Peak values for the given study are in bold font. Ranges are reported when specific values are not available.

| Method                      | Materials                          | Inlet Gas Composition          | Current Density (mA cm⁻²) | Faradaic Efficiency (%) | Energy Consumption (kJ mol⁻¹ CO₂) | Authors         | References, Year |
|-----------------------------|------------------------------------|--------------------------------|---------------------------|-------------------------|-----------------------------------|----------------|------------------|
| Electrodialysis             | 0.5 M K₂CO₃                         | N/A                            | 100                       | 46                      | 457<sup>3</sup>                   | Eisaman, et al. | 17, 2011         |
| Electrodialysis             | BPM-AEM-CEM stack                   | (release step only)            | 139                       | 87                      | 331<sup>3</sup>                   | Eisaman, et al. | 18, 2011         |
| Electrodialysis             | BPM-AEM-CEM stack                   | (release step only)            | 2.4–9.5                   | 70–75                   | 92–123<sup>3</sup>                | Nagasawa et al. | 19, 2009         |
| Electrodialysis             | BPM-CM-AEM stack, BPM-CM stack, CEM-AEM stack | (release step only) | 19.2                       | 80                      | 504                               | Iizuka, et al.  | 21, 2012         |
| Electrodialysis<sup>b)</sup> | BPM-CM-AEM stack, Methionine, Na₂CO₃ | (release step only)            | 30                        | 87                      | 1109                              | Jiang, et al.   | 25, 2017         |
| Electrodialysis/electrolysis| K₂CO₃, KHCO₃                         | ambient air                     | 2                         | 53<sup>3</sup>          | 383<sup>3</sup>                   | Wang, et al.    | 24, 2013         |
| Electrodialysis/electrolysis| Na₂CO₃, NaHCO₃                       | 100% CO₂ to saturate sorbent   | 50                        | 72                      | 367                               | Mehmood, et al. | 29, 2016         |
| Electrochemical amine regen.| Aqueous amine sol., modified porous separator | 100% CO₂ to saturate sorbent | 2.5                       | 42                      | 94                                | Stern, et al.   | 23, 2013         |
| Electrochemical amine regen.| Aqueous amine sol., modified porous separator | 100% CO₂ to saturate sorbent | 5                         | 64                      | 100                               | Stern, et al.   | 23, 2014         |
| Gas-fed cell                | AEM (Fumasep)                       | 400 ppm CO₂ in synthetic air   | 0.5                       | 23                      | 350                               | Eisaman, et al. | 16, 2009         |
| Gas-fed cell                | AEM (Neosepta)                      | 50% CO₂ in O₂                   | 6                         | 89<sup>3</sup>          | 130<sup>3</sup>                   | Landon & Kitchin Rigdon, et al.  | 15, 2010         |
| Gas-fed cell                | AEM (custom)                        | 50% CO₂ in O₂                   | 1.9                       | 69                      | 208                               | Landon & Kitchin Rigdon, et al.  | 27, 2017         |

<sup>a)</sup> Indicates corrected (lower) value without contribution of electrodes. <sup>b)</sup> Simultaneous methionine synthesis and CO₂ capture. <sup>c)</sup> Calculated based data provided in paper (not directly reported).
performed experiments using a potassium hydroxide solution in a packed column, in which sulphuric acid was used to recover the CO₂, and the solution was subsequently treated using BPMs and CEMs (see Fig. 2a). Total energy demand for such a process of removing CO₂ from air was estimated to be 427 kJ mol⁻¹ CO₂.

Stucki et al.³² developed a similar method of atmospheric CO₂ capture using a potassium hydroxide solution in a microporous membrane and subsequent Na-ion-based electrodialysis membrane stack. The system also generated O₂ and H₂ through the electrolysis of water, with H₂ exiting in the CO₂ stream. Notable findings included that average cell voltage of the system for a constant current density of 100 mA cm⁻² had a linear dependence on potassium bicarbonate anolyte concentration for concentrations above 0.2 mol l⁻¹, and that efficiencies for the regeneration step generally favored more open electrode structures due to enhanced mass transfer.

Eisaman et al. performed BPM electrodialysis studies to investigate the ability of aqueous (bi)-carbonate solutions to separate CO₂ at near-atmospheric and elevated pressures. The system employed AEMs to transport (bi)-carbonate from the basic chamber to the acidic chamber and BPMs to split water and provide protons (see Fig. 2b). Various mixtures of potassium (bi)-carbonate and potassium hydroxide solution were evaluated in terms of CO₂ gas generation rate, efficiency, voltage, and energy consumption. Results indicated an energy consumption as low as 100 kJ mol⁻¹ CO₂ and 200 kJ mol⁻¹ CO₂ to regenerate captured CO₂ from aqueous bicarbonate and carbonate solutions, respectively. Current densities in the study were limited to 100 mA cm⁻² due to difficulties reaching steady state at higher values. Authors performed a follow-up study with a BPM electrodialysis system working at pressures of 10 atm. As a result, they were able to achieve higher current densities of 139 mA cm⁻² and reductions in energy consumption of 29%. They also determined that the improvement in performance outweighs the additional energy costs from pressurization.

Taniguchi et al.³³ proposed a similar method of electrodialytic CO₂ capture using CEMs and AEMs to treat a potassium bicarbonate solution (see Fig. 2d), but instead proposed vacuum desorption for the CO₂ recovery step, resulting in theoretically lower energy requirements compared to thermal regeneration. Preliminary thermodynamic calculations were performed showing a potential minimum work of 83 kJ mol⁻¹ CO₂ at a pressure of 6 mbar using commercial membranes. This value, authors claim, could be pushed even lower through the use of membranes with improved ion conductivity, but no bench-scale experimental work was performed.

Wang et al.²⁴ investigated a membrane electrodialysis and electrolysis setup with a single CEM and AEM to capture atmospheric CO₂. Potassium hydroxide was electrochemically generated from O₂ and H₂O reduction to form hydroxide ions at the cathode (see Fig. 3a). CO₂ was then recovered from the solution by reacting the potassium (bi)-carbonate with electrochemically generated sulfuric acid from protons formed at the anode through the oxygen evolution reaction. Using current densities of 2.0 mA cm⁻² and cell...
voltages of 2.1 V, CO₂ was captured from the air and released in a pure stream at an energetic cost of 383 kJ mol⁻¹ CO₂.

Sodium (bi)-carbonate.—The use of BPM electrodialysis for CO₂ capture from flue gas was explored by Nagasawa et al. with three membrane configurations of BPM and CEM (see Fig. 2a); BPM and AEM (see Fig. 2b); and BPM, CEM, and AEM (see Fig. 2c). Units were arranged in stacks of 10, and sodium bicarbonate and sodium chloride solutions were used in the feed and recovery compartments, respectively. Under a constant current density of 17 mA cm⁻², faradaic efficiencies of 40%–50% were observed for the two configurations involving CEMs and a value 30% was observed for the BPM-AEM configuration. Leakage of protons through the CEM and hydroxide ions through the AEM were determined to be significant detrimental factors for efficiency. The BPM-CEM configuration had the best performance in terms of energy requirement per CO₂ recovered. Other findings were that specific energy requirement was reduced with more units in a stack and less distance between membranes. At reduced current densities of between 2.4–9.5 mA cm⁻², higher current densities were associated with higher specific energy requirements and higher CO₂ recovery rates. As can be observed in Table I, the study achieved one of the lowest minimum energy requirements of 92 kJ mol⁻¹ CO₂ at a low current density of 2.4 mA cm⁻².

Further development of the BPM electrodialysis approach was presented in a study by Iizuka et al., which examined the effects of numerous factors on specific power consumption and faradaic efficiency under steady-state conditions. This was in the same membrane arrangement as shown in Fig. 2a. In general, power consumption was favored by higher sodium concentrations in the feed solution, lower current densities, and a higher number of cells. Faradaic efficiency was favored by higher sodium concentrations in the feed solution, higher current densities, and higher flow rates. Both power consumption and faradaic efficiency were favored by higher extents of CO₂ absorption and higher extents of CO₂ recovery. A cost analysis determined electricity cost and membrane cost to dominate the economics of the overall process.

Datta et al. developed an electrochemical pH-swing process for CO₂ capture from flue gas, employing resin-wafer electrodialyzers and a process liquid of monosodium dihydrogen phosphate and disodium hydrogen phosphate. The system contained alternating CEM and BPM in a buffer solution to form diluate and concentrate chambers. This system distinguishes itself from other electrodialysis approaches by including ion-exchange resin beads (resin wafer) in the diluate chambers to promote ion transfer and improve pH control. Up to 80% CO₂ was captured with purity exceeding 98% from a 15% CO₂ in N₂ inlet gas. Enhancement of reaction kinetics was a key challenge in this method of CO₂ capture. A novel membrane electrodialysis and electrolysis system was investigated by Mehmood et al., which examined both a CEM-AEM and a CEM-CEM arrangement to produce sodium hydroxide from aqueous sodium chloride (see Fig. 3). Protons were generated at the anode through the hydrogen oxidation reaction (HOR) and hydroxide ions were generated at the cathode through the hydrogen evolution reaction (HER). Sodium ions combined with hydroxide in the alkaline compartment to form sodium hydroxide, which was used in turn to capture CO₂ as sodium (bi)-carbonate. Recirculation or treatment of the sodium (bi)-carbonate was not explored in this study. In the second arrangement, the AEM was replaced by a CEM to transport protons to the acidic chamber, which granted improved performance due to the generally higher stability and conductivity of CEMs compared to AEMs. Under optimized conditions, cell voltage was 1.25 V at 50 mA cm⁻², leading to a specific energy consumption of 367 kJ mol⁻¹ CO₂.

Another variation of the BPM electrodialysis CO₂ capture process was described by Jiang et al. with the side process of amino acid production. The BPM electrodialysis unit consisted of three repeating BPM, AEM, and CEM units (see Fig. 2c). Experiments were performed under constant current density conditions from 20–50 mA cm⁻² with inlet gas concentrations between 10%–30% CO₂ in N₂. Faradaic efficiencies of up to 87% were reached for the highest inlet concentration of CO₂ case. Reported energy consumption was relatively high at 1109–1505 kJ mol⁻¹ CO₂, but the process simultaneously produced methionine and sodium hydroxide, which are potentially valuable chemical products.

Alternative approaches using liquid electrolytes.—Novel electrochemical approaches have been proposed based on seawater electrolysis and mineral calcination. Novel ionic liquids or amines paired with a transition metal. proposed the use of a calcium carbonate solution in tandem with electrolysis of a saline water solution (seawater) to capture atmospheric CO₂ as calcium bicarbonate, similar to that process shown in Fig. 3 without ion-selective membranes. This was accomplished through the following electrochemically-driven overall reaction:

\[
\text{CaCO}_3 + 2\text{H}_2\text{O} + \text{CO}_2 \rightarrow \frac{1}{2}\text{O}_2 + \text{H}_2 + \text{Ca(HCO}_3)_2
\]
abundance and low cost. The concept was tested at a laboratory scale, and the electrochemically treated seawater absorbed CO₂ at a rate approximately 3 times that of untreated seawater. However, energy input was orders of magnitude higher than that expected for a commercial electrolyzer. The author noted the additional significant energy penalty of regeneration if concentrated CO₂ is desired as the end product, which would be partially offset by reduced supply and transportation costs if the reactant were recycled. A later study by Rau et al. investigated a similar process using silicates and found an experimental energy expenditure of 426–481 kJ mol⁻¹ CO₂ removed.

Reinhardt et al. wrote a perspective focusing on CO₂ capture using electrogenerated nucleophiles. In such a process, carbon in the CO₂ reversibly binds with an electrochemically reduced quinone (Q) within a liquid electrolyte on the cathode and is released on the anode as a pure gas. One benefit of these novel electrolytes is enhanced tunability of the chemistry, which can theoretically reduce the potential differences between the capture and release step. This can be implemented in a system that either utilizes electrolyte pumping or electromigration across a static liquid electrolyte, with the following generic overall reaction:

\[ Q + 2e^- + 2CO_2 \iff Q(CO_2)_2^2- \]  \[ \text{[5]} \]

Scovazzo et al. developed an aqueous redox active CO₂ carrier in a proof-of-concept batch-type cell and achieved pumping of CO₂ at <1% levels to pure concentrations at atmospheric pressures with a transfer of 0.427 moles CO₂ per electron mole (solution CO₂ release step, 0.5 for the ideal case). Poor stability in O₂ was a critical issue for the system that would preclude operation with ambient air.

Stern et al. developed an electrochemically-mediated amine regeneration system to capture CO₂ from flue gas. The study used polyamines as the CO₂ sorbents and copper electrodes to produce cupric ions that assist in displacing CO₂. The relevant reactions were:

\[ A(aq) + nCO_2 \iff A(CO_2)_m(aq) \]  \[ \text{[6]} \]

\[ \frac{2}{m}A(CO_2)_m(aq) + Cu(s) \iff CuA_{2/m}^+(aq) + 2CO_2(g) + 2e^- \]  \[ \text{[7]} \]

\[ CuA_{2/m}^+(aq) + 2e^- \iff Cu(s) + \frac{2}{m}A(aq) \]  \[ \text{[8]} \]

with A representing a generic amine molecule. Pure CO₂ was used to saturate the sorbent, and the authors achieved a faradaic efficiency of 42% operating at 2.5 mA cm⁻². The authors also reported a specific energy consumption of 100 kJ mol⁻¹ CO₂ for their system. Tuning the chemistry to optimize binding constants for CO₂ and reduce the potential difference between the capture and release process is the subject of ongoing work.

Legrand et al. proposed a membrane capacitive deionization technique to separate CO₂, in which ions in a CO₂-containing deionized water solution are removed via an anion exchange or cation exchange membrane and stored in the electrical double layer of a carbon electrode. The experimental cell operated in batch mode at very low current densities of 0.02–0.06 mA cm⁻² and feed concentrations 15%, 30%, and 100% CO₂ in N₂ were tested. Authors reported low energy requirements of approximately 40 kJ mol⁻¹ CO₂, but also reported low amounts of CO₂ exchange (<9%) and very low capture CO₂ rates of 6 × 10⁻⁶ mol s⁻¹ g⁻¹ carbon. In addition, captured CO₂ was desorbed back to the solution rather than to a concentrated gas stream, making direct comparison with other methods difficult. Authors acknowledged the necessity of an additional membrane contactor for separating liquid and gas phases to generate pure streams of CO₂.

Direct separation from a gas mixture via an electrochemical cell.—Other existing literature in the field describes electrochemical cells that directly separate gas-phase CO₂ via electromigration of carbon-containing ions across a physical barrier. The electrochemical cell approach offers a distinct advantage over conventional membrane separation processes, namely that it allows for high-selectivity concentration from relatively dilute mixtures through active electrochemical pumping of carbon-containing ions and does not require large pressure gradients for operation. In fact, such a method opens possibilities of pumping against concentration gradients (i.e., electrochemical compression), as has already been demonstrated for hydrogen. However, there are still significant challenges in operation when the feed gas is extremely dilute, such as the high energetic costs of delivering large volumes of gas to the cell and limitations in applicable current density.

In the first reported devices for electrochemical CO₂ separation, the electrochemical reactions occur on electrodes separated by an aqueous carbonate solution supported in a thin asbestos matrix. In such a device, water is produced accompanied by the generation of electrical energy (fuel cell-like operation) and the transfer of CO₂ from the cathode to the anode side. The National Aeronautics and Space Administration explored electrochemical methods for separation of CO₂ in the early 1970s to scrub CO₂ from spacecraft cabins. These early studies note a number of benefits an electrochemical process has over a cyclic adsorption process, which include continuous operation, low CO₂ partial pressure capabilities with low system weight, concentrated CO₂ without air contamination, premixed H₂ and CO₂ at relevant ratios for downstream processing, elimination of mechanical CO₂ compressors, and low temperature operation with low flows. The electrochemical reactions hypothesized were:

\[ O_2 + 2H_2O + 4e^- \iff 4OH^- \]  \[ \text{[9]} \]

\[ 2OH^- + CO_2 \iff H_2O + CO_3^{2-} \]  \[ \text{[10]} \]

As a product of the following two reactions:

\[ CO_2 + OH^- \iff HCO_3^- \]  \[ \text{[11]} \]

\[ HCO_3^- + OH^- \iff H_2O + CO_3^{2-} \]  \[ \text{[12]} \]

\[ H_2 + 2OH^- \iff 2H_2O + 4e^- \]  \[ \text{[13]} \]

\[ H_2 + CO_3^{2-} \iff H_2O + CO_2 + 2e^- \]  \[ \text{[14]} \]

with reactions 9–12 taking place on the cathode side and reactions 13–14 taking place on the anode side. Wynveen et al. designed and fabricated a one-man, self-contained electrochemical system for CO₂ separation and concentration, capable of removing 1.9 kgCO₂/day from air. Humidified CO₂ and O₂ were fed at the cathode and H₂ was fed at the anode, which were separated by a cesium carbonate electrolyte at 21 °C–29 °C. The authors also tested rubidium carbonate and cerium carbonate electrolytes with less success. The electrolytist used was platinum, which exhibited better performance than palladium. The primary figure of merit for system performance was transfer index, or mass of CO₂ removed over mass of O₂ consumed, which was affected by current density and CO₂ partial pressure. In typical operation, 50% or more of the inlet CO₂ stream was transferred to the H₂ stream, and the system showed no signs of deterioration after 260 d of operation.

A follow-up study by Winnick et al. furthered the concept with a scale-up of the technology. The system was tested with one, three, and 90 cells, each with an aqueous carbonate solution (either potassium or cesium carbonate) suspended in an asbestos matrix with platinum catalyst at the electrodes. The system operated in the same configuration as described previously. Partial pressures of CO₂ up to 12 mbar and current densities up to 32 mA cm⁻² were
tested. Important findings were that CO₂ transfer rate increased with increasing inlet CO₂ concentration and increasing current density. At a given current density, there was a peak effective inlet CO₂ concentration beyond which the transfer rate was unaffected. Other results were that performance was unaffected by cell temperature and the scaled-up system performed as predicted based on the single cell system. Chin and Winnick⁵¹ also developed a steady-state numerical model for the aforementioned system and found good agreement between the simulations and experiments.

Further studies by Winnick et al. developed CO₂ separation from air using a molten carbonate electrochemical cell operating at high temperatures (>500 °C). This approach benefits from its insensitivity to relative humidity and fast reaction kinetics. Experiments were run in both a hydrogen mode (i.e., fuel cell) and a driven mode feeding only N₂ at the anode. In the driven mode, the reaction at the anode was oxygen evolution from the oxidation of carbonate or bicarbonate, i.e.: 

\[
2CO_3^{2-} \leftrightarrow 2CO_2 + O_2 + 4e^- \quad [15]
\]

\[
4HCO_3^- \leftrightarrow 4CO_2 + O_2 + 2H_2O + 4e^- \quad [16]
\]

A more recent study by Spinelli et al. used thermodynamic system modeling to examine the possibility of retrofitting natural gas and coal power plants with molten carbonate fuel cells for CO₂ capture. The study estimated a specific primary energy consumption of approximately 57 kJ/LHV/mol CO₂ avoided, which was significantly lower than conventional amine scrubbing methods.

Li and Li⁵² investigated the use of an electrochemical membrane cell to remove CO₂ from breathing gas mixtures. Authors employed a 1-mm porous polyamide sheet saturated with potassium bicarbonate between two nickel screens. The feed gas, consisting of 4% CO₂, 56% O₂, and 40% N₂ was fed to the cathode side, resulting in mostly CO₂ with some O₂ collected at the anode. Current densities of up to 25 mA cm⁻² were tested, at which point the CO₂ removal rate became relatively independent of current density. A follow-up study by Xiao and Li⁵⁶ used the same experimental setup to separate a humidified mixture of 4.8% CO₂, 17% O₂, and 78.2% N₂ on the cathode side with humidified N₂ on the anode side and modeled its performance. Experiments found the CO₂ removal rate to be independent of feed and carrier gas velocities within the range of 0–1.5 m s⁻¹. Based on simulation and experimental results, transfer of CO₂ was mainly controlled by resistances in the electrolyte solution (i.e., adsorption of CO₂ at the cathode, migration as carbonates, and evolution at the anode).

As described previously, electrochemically-mediated quinones can be used as redox-active CO₂ carriers in an electrochemical cell configuration. Gurkan et al.⁵⁶ characterized potential ionic liquids for their quinone solubility and stability in the presence of CO₂. This operated through the same principle as that shown in Eq. 5. The high polarity of the examined quinone enabled more effective CO₂ separation by mitigating diffusive back-transport. Watkins et al.⁵⁶ investigated an electrochemical separation cell containing a quinone liquid-soaked membrane to separate CO₂ from a simulated flue gas mixture. The quinones, represented as Q, were used to transfer protons in the overall reaction:

\[
2HCOO^- + QH_2 \leftrightarrow 2CO_2 + 2H_2O + Q + 2e^- \quad [17]
\]

leading to the net transfer of CO₂ from the cathode to the anode side. Platinum was found to be the most effective catalyst in terms of CO₂ transport, while palladium and ruthenium catalysts showed significant O₂ due to water splitting at higher potentials.

Eisman et al.⁶ developed an electrochemical method of CO₂ separation using an ion-conducting membrane. The proof-of-concept study employed either 390-μm-thick cellulose paper saturated with a cesium carbonate solution or a 500-to-600-μm-thick AEM saturated with a potassium carbonate solution. Ideal faradaic efficiencies for pure bicarbonate and pure carbonate transport are 100% and 50%, respectively, and ionic current carried by hydroxide and hydrogen ions negatively affects this parameter. In the experiments, higher inlet CO₂ concentrations led to higher faradaic efficiencies, but lower fractions of CO₂ separated. Using an AEM, air containing 400 ppm CO₂ was separated with an energy consumption of 350 kJ mol⁻¹ and 23% faradaic efficiency. Water management was an issue when operating with fully humidified gases, prompting experiments with a room-temperature ionic liquid electrolyte solution containing cesium bicarbonate, which achieved comparable but slightly lower efficiencies.

Other studies by Landon and Kitchin⁵⁵ and Pennline et al. used an AEM in an electrochemical cell to separate mixtures of approximately 50% CO₂ in O₂ (Eqs. 9–12, 15–16). Only humidified argon was used as a carrier gas on the anode side, resulting in oxygen evolution and CO₂ formation from primarily bicarbonate. Both studies employed nickel and platinum as electrocatalysts, and cell potentials of up to 1.2 V were used in order to stay below the water-splitting potential of 1.23 V. The cell setup of Landon and Kitchin⁵⁵ reached current densities up to 6 mA cm⁻² with an average ratio of 3.56:1 CO₂:O₂ measured at the anode. Authors determined that the investigated membrane conductivity and stability were too low and electrocatalysts were not active enough for practical application in coal power plants. In addition, the gas mixture examined was not analogous to an air-combustion flue gas mixture, but the results compared favorably with previous studies of electrochemically separating CO₂ from breathing gas mixtures.

Rigdon et al. examined the use of AEM to separate mixtures of CO₂ and O₂ in an electrochemical cell (Eqs. 9–12, 15–16). Platinum was used as the electrocatalyst for both the anode and cathode, and the polymer membrane was approximately 57 μm thick. Humidified N₂ was supplied to the anode side of the cell, and humidified 50% CO₂ in O₂ was supplied to the cathode. Similar to the study by Landon and Kitchin, CO₂ was transported via membrane carbonation and evolved at the anode along with O₂. Cell potentials of up to 1.5 V were reached at current densities of approximately 2 mA cm⁻² with a resulting transference of approximately 0.67 CO₂ molecules per electron, indicating a CO₂ transport across the membrane via a mixture of carbonate and bicarbonate ions. The dominant transport pathway shifted from carbonate to a carbonate/bicarbonate mixture as the cell potential increased.

There are important implications about the quality of CO₂ at the outlet of an electrochemical concentration cell system depending on the methodology used. While water can be easily separated from the gas mixture through condensation, gas phase separations are more difficult and costly to address. Inert carrier gases are often used to facilitate gas analysis, but other options would be more practical in a scaled-up system, e.g., recirculation of the anode gas. If carbonate and bicarbonate are neutralized at the anode in an inert atmosphere, the highest ratio of CO₂ to O₂ possible is 4:1 based on the stoichiometry of Eq. 16. Authors have proposed using the resulting gas mixture for oxy-combustion, resulting in a pure CO₂ stream. If the cell is operated in a fuel cell mode (H₂ at the anode), hydrogen oxidation produces a mixture of CO₂, water, and residual H₂. Running the cell at low stoichiometries would in theory allow for higher concentrations of CO₂ to be obtained, although this would also approach an upper limit due to mass transport limitations and lead to possible degradation in the cell. In spite of this limitation, mixtures of H₂ and CO₂ could be useful chemical feedstocks, for example, in reverse water gas-shift reactors or methanol synthesis. Use of quinones could theoretically produce a pure stream of CO₂ in the same way that electrodialysis methods do, although O₂ evolution is still possible.

Energy consumption of CO₂ pumping with AEMs is still relatively high in the pioneering studies, but may be decreased below the state of the art for absorption through advancements in the catalyst and membrane materials, as well as cell engineering. As with most AEM fuel cell studies, the majority of electrochemical cell studies reviewed in this work use platinum as the electrocatalyst, but cheaper, platinum-group-metal-free catalysts will need to be
employed to obtain significant reductions in stack cost. Cheaper membrane materials with high conductivities will also be critical in providing a scalable system, especially if the applicable current densities remain low. If current densities can be increased by an order of magnitude while limiting cell overpotentials and maintaining reasonable faradaic efficiencies, this will lead to an order of magnitude reduction in stack cost for a given production rate of CO₂.

Table II summarizes some of the pros and cons for electrochemical methods of CO₂ capture.

### Point-Source vs Direct-Air Capture

Point-source (e.g., flue gas) capture of CO₂ is a more thermodynamically advantageous approach compared to DAC. Capture of CO₂ from fossil fuel combustion is primarily performed in one of three configurations with different corresponding CO₂ concentrations: oxy-fuel post-combustion capture (>90% CO₂), pre-combustion capture (e.g., partial oxidation, 30%-35% CO₂), and air post-combustion capture (5%-25% CO₂). Minimum work to separate CO₂ depends logarithmically on the concentration; the minimum work to separate CO₂ from flue gas (15% CO₂ in N₂) at 300 K is 7 kJ mol⁻¹ CO₂. Given practical limitations to process efficiency, 32 kJ mol⁻¹ CO₂ represents a roughly lower limit of energetic cost for amine scrubbing,⁴ with literature showing energetic inputs to be 4-5 times higher.³¹,³⁸

Membrane separation is typically discussed in reference to post-combustion gases, as it generally requires gas mixtures containing 10% or more CO₂.⁴⁷,⁵⁹,⁶⁰ Two key parameters that require optimization for such systems are membrane permeability and selectivity, as the pressure gradient through the membrane provides the driving force. A number of reviews on non-electrochemical, membrane-based methods of CO₂ capture from combustion gases have been published, focusing on conventional polymeric membranes,⁴⁷ facilitated transport membranes,⁵⁹ mixed matrix membranes,⁶¹ organosilica membranes,⁶² and membrane contactors as compared to membrane gas separators.⁶⁰ In terms of an electrochemical separation process, the chief benefit of point source capture is that the relatively high concentration of CO₂ allows for higher current densities to be reached at higher faradaic efficiencies in a direct gas separation cell. For a liquid electrolyte absorption step, less gas would need to be flowed through the absorber to saturate the solution, reducing energy costs. However, common flue gas contaminants (e.g., NOₓ, SO₂, soot) would potentially pose additional challenges such as electrocatalyst poisoning or electrolyte degradation.

High energy requirements are the primary detriment of DAC compared to point-source capture. Due to the extremely dilute concentration, at least 2500 tons of air need to be processed in order to capture one ton of CO₂, so a minimal pressure drop is desired. There are therefore implications for duration of the capture step and methodology to effectively deliver air to the capture medium and sufficiently saturate it with CO₂. Lackner et al.⁶³ reviewed the state of the art and challenges in CO₂ capture from ambient air. Some of the critical requirements the authors note for air capture are the thermodynamic limits associated with the free energy of mixing CO₂ in air at 300 K and the mechanical work required to compress CO₂ from 1 to 60 bar isothermally, 22 and 11 kJ mol⁻¹ CO₂, respectively. The minimum theoretical separation work for the range of CO₂ partial pressures between 0.1 mbar and 1 bar is shown in Fig. 4, with the partial pressure of CO₂ in air indicated. However, there are also significant advantages to air capture, namely, that it allows for geographical decoupling from the emission source. This is of particular relevance to the transportation sector, which is still heavily reliant on carbon-based fuels. DAC can also reduce the need to transport CO₂ over long distances and enable the production of synthetic fuels in a closed carbon cycle. An additional benefit is the significantly reduced scrubbing requirement of air vs flue gas.⁶⁴

Electrochemical methods that operate isothermally at low temperatures can approach the theoretical separation work shown in Fig. 4 due to removing the inefficiencies associated with thermal cycling,²³,²⁷ although overpotentials and faradaic losses present barriers to reaching those limits. Other important thermodynamic limits are set by the absorption reaction enthalpy between CO₂ and the aqueous sorbent solution. When an alkaline capture solution is used, e.g., NaOH or KOH, the enthalpy of the exothermic absorption reaction is 109.4 or 95.8 kJ mol⁻¹ CO₂, respectively. The enthalpy of absorption/desorption of a typical monoethanolamine solution has been estimated to be approximately 80 kJ mol⁻¹ CO₂.⁶⁵ For the AEM electrochemical cell methods described in Refs. 15, 27, 30, the minimum energy consumption as dictated by the standard electrode potentials of the half-reactions⁶⁶ is 35.1 and 56.2 kJ mol⁻¹ CO₂ for a cell operating fully in the bicarbonate and carbonate mode, respectively. Although theoretically low energy consumption is obtainable using electrochemical approaches, it is also important to consider how a practical system would operate and the energy associated with mass transport (e.g., pumping of the capture solution, delivery of the feed gas mixture).

Sorption-based methods are the only commercialized approach for DAC, mainly due to the large volumes of air that need to be processed. Methods based on aqueous sorbents typically regenerate the sorbent using a causticization/thermal regeneration process. The cost of DAC is the subject of much debate, and has been estimated to be $30–1000 per ton of CO₂ captured.⁶⁶ A techno-economic analysis by Fasih et al.⁶⁷ based on estimates from companies commercializing DAC technology gave a value of 243–317 kJ mol⁻¹ CO₂ for combined electrical and thermal energy requirements, although current values are likely to be higher. According to a thermodynamic analysis of DAC performed in 2011, an energetic cost of greater than 400 kJ mol⁻¹ CO₂ was considered potentially counterproductive due to the CO₂ intensity of fossil-based electricity sources in the United States at the time.⁶⁸ However, this value will shift upwards as adoption of renewable energy becomes more widespread.

### CO₂ Transport in Alkaline Membranes

Ion-conducting membranes are of great interest in electrochemical separation processes, as they allow for selective transport of species through a physical barrier. AEMs are particularly relevant for CO₂ separation because of their active transport of (bi-)carbontate. As the name implies, AEMs use negatively charged ions (e.g., hydroxide) as the charge carrier, as opposed to PEMs, which use hydrogen cations (see Fig. 5). In general, AEMs are a more nascent technology than PEMs; commercial implementation of PEMs in automotive fuel cell applications has already begun, albeit with some challenges that still need to be overcome.⁶⁹ The past decade has brought a significant level of interest in alkaline polymer membranes, a subgroup of AEMs, for fuel cells or co-electrolysis of CO₂ to form CO as a fuel or chemical precursor. Developments in AEMs for electrochemical applications are discussed in a perspective by Varcoe et al.⁷⁰

Alkaline membranes in fuel cells.—Alkaline membranes enable the use of non-noble metal catalysts in fuel cell applications, but face complications when air is used as the oxidant, as there is a significant negative influence due to CO₂. CO₂ neutralizes hydroxide in the membrane via Eqs. 9–12 and reduces catalytic activity and ion conductivity. However, bicarbonate in the membrane will be converted to carbonate and hydroxide and transported out of anode side as CO₂ during power generation via Eq. 14. Early studies describe the so-called “self-purging mechanism” in alkaline exchange membrane fuel cell systems.⁷¹–⁷³ Under some conditions, almost all of the CO₂ fed from ambient air can be absorbed, transported, and released on the anode side of the alkaline membrane, and a higher degree of self-purging is observed at higher current densities.⁷²,⁷⁴,⁷⁶–⁷⁸

A modeling study by Krewer et al.⁷⁸ found that temperature has an unclear effect on membrane carbonation during AEM fuel cell operation, and that carbonate formation is heavily favored over bicarbonate at current densities of 0–1500 mA cm⁻². The same
Table II. Pros and cons of various electrochemical methods.

| Electrodialytical Regeneration | Electrochemical Cell (Direct Separation of Gas Mixture) |
|--------------------------------|--------------------------------------------------------|
| +Decouples capture and release steps, making it more viable for low CO₂ concentrations | +Allows for separation of a gas mixture in a single-step process |
| +Allows for higher current densities to be reached, improving scalability | +Polymer electrolytes are rapidly improving in terms of conductivity and stability |
| +Can generate streams of pure CO₂ | -Low concentrations of CO₂ lead to low faradaic efficiencies |
| -Large ohmic losses due to membrane stack and electrolyte solution | -Limited current densities in experimental literature |
| -Requires the use of a caustic solution with evaporative losses | -Difficulties in generating a pure CO₂ stream |
| -Gas bubbling creates localized high current densities | |
study determined that at current densities greater than 500 mA cm\(^{-2}\), the carbonate builds up in the membrane at the anode in an enrichment zone less than 2 \(\mu\)m thick that is critical to transport and release of CO\(_2\). Other studies found that the ability to flush (bi)-carbonate from the anode side efficiently as CO\(_2\) is a key challenge.\(^{74,79}\) The buildup of carbonate at the anode catalyst layer has also been identified as a source of the high anode overpotential in anion-exchange membrane fuel cells.\(^{75,76,80,81}\) While the introduction of CO\(_2\) on the cathode side leads to a clear degradation in performance of the cell due to increased ionic and reaction resistance,\(^{82}\) experiments show that the effect is at least partially reversible.\(^{75}\) Zheng et al.\(^{83}\) demonstrated that reducing the cathode gas flowrate and increasing hydration can reduce CO\(_2\)-related voltage losses in AEM fuel cells. St. John et al.\(^{84}\) investigated the effects of carbonate on the oxygen reduction reaction (ORR) and the HOR for ruthenium/platinum catalysts in alkaline fuel cells. For the HOR and ORR on platinum, authors observed no dependence on the presence of carbonate, indicating the role of water/hydroxide as the primary proton acceptor for the HOR in potassium hydroxide. Various studies have modeled the ion exchange process in alkaline membranes,\(^{76,79,85,86}\) and water management is a key issue.\(^{79,87}\) As shown in Fig. 5, AEM fuel cells have two reactions involving water compared with one for a PEM fuel cell, and sufficient water must be supplied to the cathode to produce hydroxide. A recent review by Ziv et al.\(^{88}\) comprehensively details the developments in understanding the effect of CO\(_2\) on AEM fuel cells.

Some studies have examined the use of carbonates to transport charge in AEM fuel cells (i.e., carbonate cycle) in contrast to the more common hydroxide.\(^{89-92}\) In this case, CO\(_2\) is fed intentionally on the cathode side at relatively high concentrations to maintain the membrane in (bi)-carbonate form. This potentially allows for higher power densities and improved stability in long-term operation.\(^{82}\) In such a configuration, an increase in the CO\(_2\) at the cathode can actually improve cell performance due to an increase in kinetic current.\(^{91}\) One challenge with this route is the reduced ion mobility of carbonate and bicarbonate as compared to hydroxide.\(^{80,85}\) Another area that requires improvement is the selection of catalysts that promote carbonate formation over hydroxide formation.\(^{91}\)

**Alkaline membranes for CO\(_2\) reduction.**—A number recent of CO\(_2\) co-electrolysis studies also contain relevant information on CO\(_2\) transport in alkaline membranes. The main drawback of using liquid electrolytes instead of polymer electrolyte membranes in electrochemical CO\(_2\) reduction is the poor solubility of CO\(_2\), which limits applicable current densities and potential scale-up. Polymer electrolyte membranes have lower gas permeability than electrolyte-impregnated porous media, and thus can be made thinner to reduce ohmic losses.\(^{91}\) Indeed, faradaic efficiencies of CO of >90% have been reported in literature for alkaline membrane CO\(_2\)-splitting.\(^{94-96}\) Liu et al.\(^{94}\) performed a CO\(_2\)-electrolysis study using imidazolium-functionalized polymer membranes with silver catalyst at the cathode and iridium dioxide catalyst at the anode, and achieved very high CO selectivity (>95%) and current densities up to 600 mA cm\(^{-2}\). A potassium bicarbonate solution was fed to the anode to assist ion conduction, and water management was identified as a key issue in effective operation. The ratio of CO\(_2\):O\(_2\) at the anode was close to 2, suggesting carbonate as the charge carrier. Yin et al.\(^{96}\) reported on a cationic polymer membrane co-electrolyzer with gold catalyst at the cathode and iridium dioxide catalyst at the anode that operated with pure water. Unlike the setup by Liu et al.,\(^{94}\) no alkaline solution was fed during operation, but the duration of the experiment was limited to 100 h as opposed to 4000 h. The cell was capable of maintaining current densities of 500 mA cm\(^{-2}\) and CO\(_2\) crossover was low (<1 \(\mu\)l min\(^{-1}\)·cm\(^{-2}\)), suggesting that hydroxide was the main charge carrier.
CO₂ transport through the membrane is an undesirable side-process in CO₂-splitting applications, as it is a parasitic loss for the system and reduces CO₂ utilization efficiency. Pâtru et al. evaluated cell designs for gas-phase CO₂ reduction using CEM, AEM, BPM, and a novel BPM-like configuration. Authors also quantified CO₂ production at the anode of the various cell configurations. In alkaline membrane co-electrolysis of CO₂, carbonate membrane introduced significant enhancements to make electrochemical CO₂ separation commercially interesting. As shown, CO₂ separation is relevant for a wide range of applications, and will only become more critical in the coming years due to the ubiquity of CO₂ emissions. Current industrially-implemented methods of CO₂ separation have significant drawbacks—sorbent regeneration requires large heat inputs and/or pressure swings, and cryogenic distillation is very inefficient. Electrochemical membrane separation could maintain the desirable aspects of membrane separation, such as high modularity, continuous operation, and relatively low energy intensity, while improving aspects such as selectivity and ability to operate with low CO₂ concentrations.

While early studies show interesting possibilities for electrochemical CO₂ capture, there is still significant research and development work required to reduce costs and increase performance. Critical to these cost reduction pathways are the catalyst and membrane contributions. Research efforts should move towards platinum-group-metal-free catalysts and higher current densities. If the applicable current densities remain restricted to the 0–10 mA cm⁻² range, very large membrane/electrode areas will be required to separate appreciable amounts of CO₂, incurring high capital costs. The importance of faradaic efficiency will depend strongly on the price and CO₂ intensity of electricity used to drive the process. For example, a relatively low faradaic efficiency process may become attractive if capital costs are low and off-peak renewable electricity can be utilized. Another topic that needs to be investigated further is system durability across long operation times, and this should be reported on in future studies. The parallel advancements in AEM fuel cell and electrolyzer technology may allow further improvements to the state of the art in electrochemical CO₂ separation.

### Acknowledgments

The authors would like to acknowledge Shell’s New Energy Research and Technology (NERT) Program for providing the funding for this work. We would like to acknowledge NERT’s Dense Energy Carriers team (DEC) for their useful inputs and discussions during the course of this work.

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