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Electrochemical carbon dioxide capture to close the carbon cycle†

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Electrochemical CO_2 capture technologies are gaining attention due to their flexibility, their ability to address decentralized emissions (*e.g.*, ocean and atmosphere) and their fit in an electrified industry. In the present work, recent progress made in electrochemical CO_2 capture is reviewed. The majority of these methods rely on the concept of "pH-swing" and the effect it has on the CO_2 hydration/dehydration equilibrium. Through a pH-swing, CO_2 can be captured and recovered by shifting the pH of a working fluid between acidic and basic pH. Such swing can be applied electrochemically through electrolysis, bipolar membrane electrodialysis, reversible redox reactions and capacitive deionization. In this review, we summarize main parameters governing these electrochemical pH-swing processes and put the concept in the framework of available worldwide capture technologies. We analyse the energy efficiency and consumption of such systems, and provide recommendations for further improvements. Although electrochemical CO_2 capture technologies are rather costly compared to the amine based capture, they can be particularly interesting if more affordable renewable electricity and materials (*e.g.*, electrode and membranes) become widely available. Furthermore, electrochemical methods have the ability to (directly) convert the captured CO_2 to value added chemicals and fuels, and hence prepare for a fully electrified circular carbon economy.

Broader context

The necessity of taking actions to achieve a net zero CO_2 emission has brought up the question "*how to achieve a circular carbon economy?*". To close the carbon cycle, sustainable CO_2 capture and utilization are indispensable. Current technologies for CO_2 capture rely dominantly on absorption of CO_2 from flue gas, regenerated *via* energy-intensive temperature swings, which imply a huge energy consumption when expanding capture towards a net zero CO_2 emission. When also realizing that approximately 40% of the CO_2 emission is decentralized, which may even increase when power plants and industry are transitioning to renewable energy, we are facing a massive challenge for closing the carbon cycle. In that framework, electrochemical technologies for CO_2 capture, from the atmosphere, ocean, and flue gas, can play an important role. The installed renewable electricity generation capacity is increasing each year, with more than 2300 GW in 2018. However, currently, most electrochemical methods are at early stages of development and are still energy intensive. In this contribution, we evaluate each of these technologies while focusing on the pH-swing approach. We establish the current state of the art, describe the major technical barriers and R&D needs, and discuss opportunities for improving electrochemical CO_2 capture.

1 Introduction

To honour the Paris Agreement, a global net zero greenhouse gasses (GHG) emission needs to be realized by the end of this century.[1–3] Among all GHG's, $CO_2(g)$ is accepted to be the main anthropogenic control knob on the climate and has been the focus of many studies.[4,5] To achieve a net zero emission,[6] reducing the total CO_2 emission obtains most impact in the short term.[7] The largest CO_2 emission is due to combustion of fossil fuels and thus can be reduced through fossil fuels phase out. However, although ultimately fossil fuels phase out might be possible for the power industry and transportation sector (through substitution with renewable energy), many sectors (*e.g.*, steel/cement production, intercontinental air transport or non electrical trains) do not have a suitable alternative for carbon based fuels. In addition, due to the current agriculture techniques, the net global deforestation and the growing demand for carbon as a resource, CO_2 will be emitted due to

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many anthropogenic activities. Therefore, to achieve a net zero GHG's emission, in addition to emission reduction, CO_2 capture and utilization is required in the long term. Also, as the long term CO_2 emitters include decentralized emitters, direct capture from CO_2 sinks (*e.g.*, atmosphere and ocean, see Fig. 1 is necessary for effectively addressing the anthropogenic CO_2 emissions.[8,9]

The main challenge that currently available CO_2 capture methods face is a high energy consumption.[13–15] A few mature, non-electrochemical CO_2 capture technologies *e.g.*, absorption, adsorption, membrane separation and cryogenic capture are already available in industrial scales,[16–25] Section 4. These methods often depend on the availability of thermal energy, which makes them less well suited for CO_2 capture from dilute sources *e.g.*, air and ocean. Furthermore, the cost of direct air capture *via* traditional technologies has been estimated in the literature from $100 to $1000 per tonne of captured CO_2.[3,26–28]

Electrochemical processes have the potential to be rather energy efficient as they can target molecules directly (instead of the medium surrounding them).[29,30] Using electrochemistry for CO_2 capture dates back to the late 1960s, when molten carbonates as electrolyte were used for CO_2 control in a manned spacecraft.[31–34] Nowadays, electrochemical CO_2 capture methods can be applied to all CO_2 containing streams with any concentration. Direct capture from air,[35] ocean[8,36] and flue gas[37–39] have been reported. Such capture units can be retrofitted as plug-and-play processes, allow small footprints and are geometrically flexible.[39,40] They do not require external sources of heat or high pressures/vacuum for operation, nor degradation of sorbent material is expected.[40] Although heat integration can be beneficial for power plants in reducing the need for energy, other

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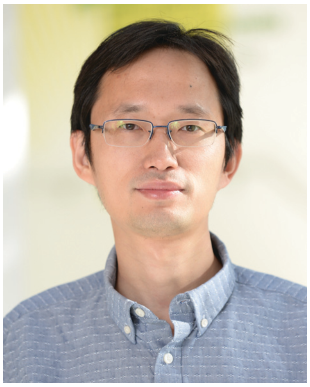

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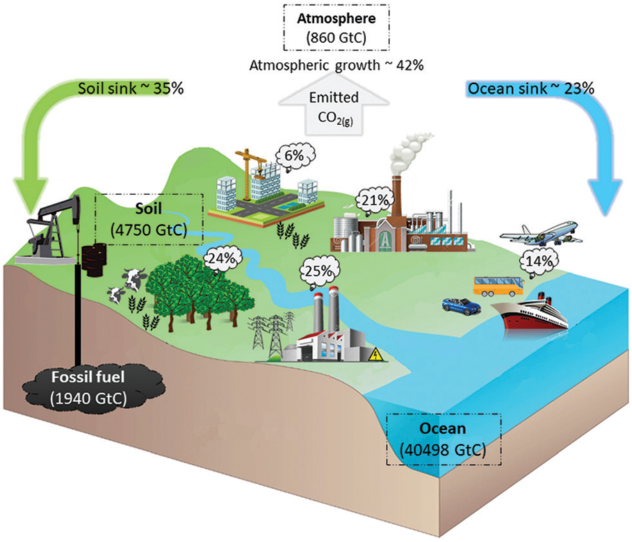

Fig. 1 Schematic of the carbon cycle. The total carbon reserve is shown in gigatonnes of carbon (GtC). The global GHG emissions in CO_2(eq) by economic sectors: 25% electricity and heat production, 24% agriculture, forestry and land use, 6% buildings, 14% transportation, 21% industry and 10% other energy usages. Data extracted from ref. 10–12.

industries (*e.g.*, food and water sector) cannot integrate high heat, rising the need for technologies that can perform under low heat conditions from centralized emitters as well.[14] In electrochemical systems, the electric potential gradient is the main driving force which can be controlled precisely to drive chemical reactions isothermally.[29,30,41] A number of bench-scale capture demonstrations *via* electrochemical pH-swing have obtained CO_2 capture and release at the promising value of $\sim$100 kJ mol^{-1} CO_2.[42,43]

The added advantage of the electrochemical methods is their ability to integrate CO_2 capture and utilization[44] (Section 5). An example is the modular, sequential CO_2 capture and conversion system that uses the pH-swing concept to produce CO electrochemically.[45,46] In addition, reactive CO_2 capture, in which the CO_2 capturing medium pre-concentrates the dilute feed and produces favorable local micro-environments, has become an emerging field for integrated CO_2 capture and conversion using electrochemical techniques.[47,48]

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David is an assistant professor at Delft University of Technology. He obtained his PhD in Chemical Engineering at University of Twente and Wetsus (2014), and started a research group on electrochemical flow systems at Delft in 2016. David's group currently hosts 15 researchers focusing on mass transport and membrane applications in electrochemical conversion, and collaborating in the e-refinery platform with industry and academics to innovate renewable energy technologies. Current projects include (bipolar) membranes for electrolysis, electrochemical CO_2 capture, H_2–Br_2 redox flow batteries, and local transport near gas bubbles and membrane electrode assemblies.

A wide variety of efforts to electrochemically capture CO_2 has been demonstrated in the past 50 years, with an intensification of research activities in the last two decades. In this work we give an overview of such advances. The center of our scope are the electrochemical methods that use a pH-swing concept, as shown in Fig. 2a and b. The swing refers to (electrochemically) shifting the pH of a working fluid (continuously) between basic and acidic pH to influence the CO_2 equilibrium to capture and recover CO_2.

The pH-swing allows absorption and desorption at ambient temperature and does not require use of any special chemicals. Widely available, inexpensive, non toxic/non corrosive/non volatile salt solutions, such as NaCl, KCl, $KHCO_3$ or even seawater can be used for the process. The pH-swing can be applied electrochemically using electrolysis, bipolar membrane electrodialysis (BPMED), capacitive deionization and reversible PCET agents as demonstrated in Fig. 3. In this work, after providing the required theoretical background in Section 2, each pH-swing route is explained and the research of this route is comprehensive reviewed in Section 3. In addition to a pH-swing approach, other electrochemical technologies involve using redox-active carriers[49] (Section 3.3), molten carbonate cells and hybrid methods (Section 3.4) such as electrochemically enhanced absorption/adsorption.[29,30] To enable comparison, we also briefly describe the main conventional capture methods, their drawbacks and advantages, and opportunities to improve these technologies with electrochemical methods, in Section 4. Finally, CO_2 utilization and storage is discussed briefly in section to close the carbon cycle (Section 5).

2 Theory: pH-swing concept and involved reactions

The concept of CO_2 capture *via* pH-swing leverages the responsiveness of the thermodynamic equilibrium of CO_2 to pH changes. A pH-swing is also used for other resource recovery applications than CO_2 capture, but the method is not always explicitly referred to as "pH-swing". For instance, pH-swing is employed to recover ammonia electrochemically from urine[50,51] and to remove phosphate from waste water streams.[52]

2.1 Carbonate equilibrium

The carbonate equilibrium can be described as open or closed based on the contact with an overlying gas and is explained in detail in ref. 53–56. In an open system, the total concentration of the dissolved inorganic carbon varies by changing in the pH; acidification results in CO_2(g) out-gassing, while basification lead to more CO_2(g) absorption, increasing the DIC. In a closed system (*e.g.*, inside of an electrochemical cell), the total DIC

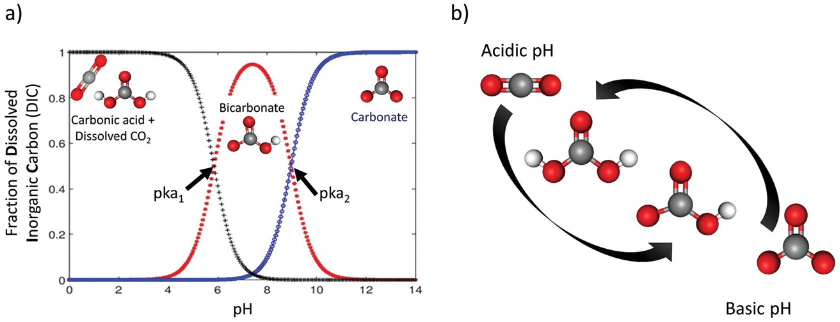


Fig. 2 (a) Effect of pH on the CO_2 equilibrium (for a closed system at temperature of 25 °C and salinity of 35 ppt). The solution is buffered around two pK_a values. (b) Schematic of the pH-swing concept.

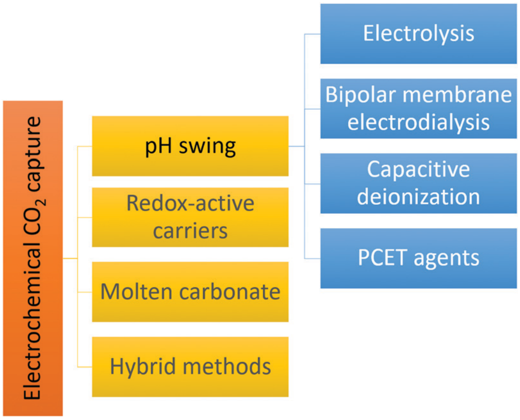


Fig. 3 Summary of electrochemical CO_2 capture methods.

remains constant regardless of any pH changes. If so, the dominant carbonic species alter by changing the pH as demonstrated in Fig. 2a. The equilibrium can be shown through reactions (1)–(4):

$$CO_2(g) \rightleftharpoons CO_2(aq) \qquad (1)$$

$$CO_2(aq) + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2CO_3 \qquad (2)$$

$$CO_2(aq) + OH^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HCO_3^- \qquad (3)$$

$$OH^- + H^+ \overset{K_W}{\rightleftharpoons} H_2O \qquad (4)$$

Reaction (1) is dependent on the fugacity of $CO_2(g)$ and often described through Henry's law (see Section 2.3). It is often assumed to be really fast (*i.e.*, 10^{10} s^{-1} in both directions) in a well-mixed scenario (*i.e.*, only mass-transport limited).[55,57,58] For experimental values of k_1, k_{-1}, k_2, k_{-2} see ref. 57, 59 and 60. As the pH increases, reaction (3) pushes the equilibrium towards HCO_3^-, and it predominates reaction (2) above pH 8.5.[59] See Section 2.2 for more discussion on the kinetics of the reactions. The total dissolved inorganic carbon, DIC, can be described as the summation of the concentration of all present carbonic species:

$$DIC = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \qquad (5)$$

where $H_2CO_3^* = H_2CO_3 + CO_2(aq)$. In multi-ionic systems, additional carbonate species or complexes (*e.g.*, $NaCO_3^-$ and $NaHCO_3(aq)$) are present in the definition of DIC, as well.[61,62]

2.2 Reactions kinetics and how to improve it

To capture and release $CO_2(g)$ through a pH-swing, both thermodynamics and kinetics play a role.[57,59] Assuming thermodynamic equilibrium, the equilibrium ratio of $\frac{[H_2CO_3^*]}{[HCO_3^-]}$ changes by a factor of more than 100 over when using a small pH-swing of only 2 pH-units, see Fig. 2a. However, although such a narrow pH-swing is thermodynamically favourable and enables lower energy consumption, it suffers from slow kinetics. At near neutral pH, the CO_2 hydration rate is $\sim 2.9 \times 10^{-2}$ s^{-1} and the (HCO_3^-) dehydration rate is $\sim 2 \times 10^{-4}$ s^{-1}.[42,60] These reaction rates are a function of *e.g.* temperature and ionic strength of the system.[63–65] To overcome the slow kinetics, (1) a wider range of pH-swing or (2) a reaction catalyst need to be applied. As for a wider pH-swing range, the base promoted hydration rate of the CO_2/HCO_3^- system is reported to be $\sim 6 \times 10^3$ M^{-1} s^{-1} and the acid-promoted dehydration rate is increased to $\sim 4.1 \times 10^4$ M^{-1} s^{-1}.[42,59,60,65] Alternatively, the use of a catalyst such as the carbonic anhydrase (CA) enzyme[66] is suggested for improving the kinetics.[42,67,68] CA is reported to enhance both the CO_2 hydration and dehydration reaction kinetics; hydration rate constant $\sim 10^5$ s^{-1} and dehydration rate constant $\sim 10^6$ s^{-1} near a neutral pH of 7 are reported.[66] However, although initially effective, such enzyme is not stable, and is prone to enzyme loss, deactivation, or degradation. Investigation on improved catalysts is recommended, but until such catalysts are developed, to effectively capture and recover CO_2, a wider range of pH-swing ($pH < pK_{a1}$ and $pK_{a2} < pH$) is needed for capture application.

2.3 Inorganic carbon solubility

In equilibrium, the concentration of free CO_2 in water (*i.e.*, $[CO_2(aq)]$) is proportional to its partial pressure in the gas phase; according to the Henrys law, $[CO_2(aq)] = K_0 \times f_{CO_2(g)}$ where K_0 (in mol L^{-1} atm^{-1}) is the solubility coefficient of $CO_2(g)$ and $f_{CO_2(g)}$ stands for the gas fugacity (in atm), which is close to the partial pressure of $CO_2(g)$ (within 1%). Fig. 4a

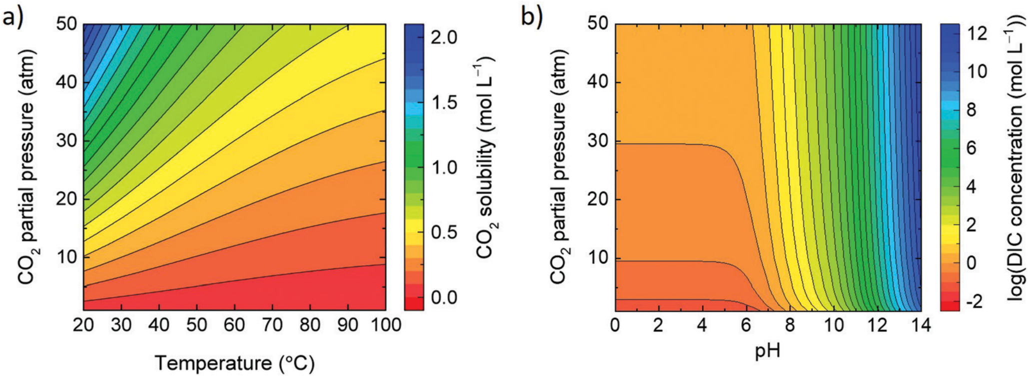


Fig. 4 (a) CO_2 solubility in water as a function of the temperature and CO_2 partial pressure. (b) Logarithmic solubility of dissolved inorganic carbon (DIC) in water at 25 °C as a function of the water pH and CO_2 partial pressure.

shows the solubility of CO_2 as a function of temperature and CO_2 partial pressure. At elevated alkalinity, the total solubility of $CO_2(g)$, and hence DIC (in eqn (5)) increases due to reaction (3) route. Fig. 4b shows the solubility of DIC as a function of the water pH and the partial pressure of CO_2. See the ESI† for the used equations and references.

2.4 Inputs and metrics

Fig. 5 demonstrates input parameters and the metrics of electrochemical CO_2 capture based on a pH-swing. The feed, cell, process and kinetics can be leveraged for the product/output. The main challenge such capture technologies are facing is their (estimated) high Capex, resulted from a high energy consumption and the immaturity of the technology.[3] Data on Capex of electrochemical methods is still scarce, making the energy consumption (at high current density and capture efficiency) the most practical metric of comparison. Thankfully, despite the currently high energy consumption, optimization of the process and cell parameters can significantly decrease the energy loss involved in such processes as explained in Sections 3.2.1 and 3.5.

3 Electrochemical pH-swing concepts

Electrochemically induced pH-swings for CO_2 capture have been demonstrated through (membrane) electrolysis, bipolar membrane electrodialysis, reversible redox couples, capacitive deionization and hybrid processes that combine two or more methods as shown previously in Fig. 3. In this section we introduce each method separately and compare them in terms of feasibility, energy consumption, energy efficiency and technology readiness level (TRL).

3.1 Electrolysis

Electrolysis can enable the pH-swing in the vicinity of (two) electrodes as shown in Fig. 6. (Membrane) electrolysis for CO_2 capture is used for alkali absorbent (re)generation[38,69–73] or simultaneous H_2 production.[36,74–76] H_2 production can (partially) offset the cost of CO_2 capture and is possible when water electrolysis takes place. In the earliest work done by Stucki *et al.*, CO_2 is absorbed from a flue gas in an KOH absorbent, the resulted (bi)carbonate solution is fed into the electrolyser (for alkaline regeneration), where CO_2 is recovered and H_2 is produced *via* the following reaction:

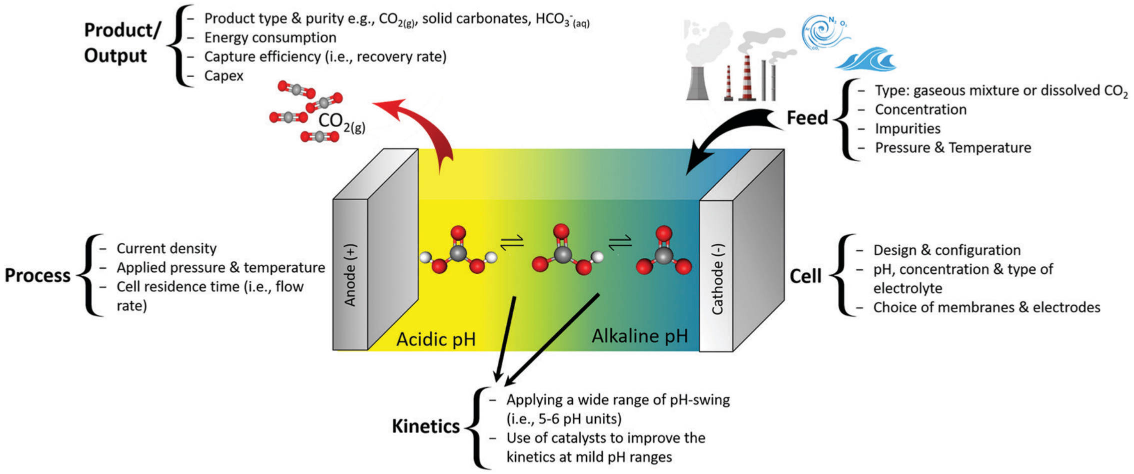


Fig. 5 Input and metrics of electrochemical pH-swing based CO_2 capture and the overall process concept.

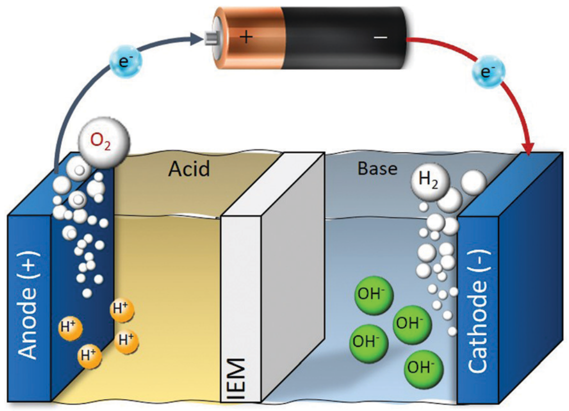


Fig. 6 Schematic of water electrolysis. Depending on the catholyte/anolyte (air, water, *etc.*), applied voltage and the pH of the medium, different half reactions take place.

$$2H_2O + K_2CO_3(aq) \rightarrow 2KOH(aq) + CO_2(g) + H_2(g) + 0.5O_2(g) \quad (6)$$

The KOH can be used as absorbent for capturing CO_2, turning into $K_2CO_3(aq)$, which can be fed again to the electrolysis system.

One downside in such systems is that the cell voltage has, in addition to 1.23 V for water splitting, a contribution from the pH difference between the anolyte and the catholyte, represented by Nernstian potential of $\Phi = 0.059\Delta pH$ (in volts) at 25 °C, as shown in the Pourbaix diagram (Fig. 7).[74] When using an extreme pH gradient (pH 0 at anode, pH 14 at cathode), this would imply a 2.06 V for balancing the free enthalpy of the reaction.

Using the pH-swing in electrolysis, the CO_2 can be either released as (purified) gas (*e.g.*, *via* reaction (6)), or as (bi)carbonate products in the work of Rau and Park *et al.*[70,71,75,78] The latter has been demonstrated for $Ca(HCO_3)_2(aq)$ (Fig. 8a) and[71,75] solid carbonate mineral as shown in Fig. 8b.[70] Natural (mined and crushed) carbonate minerals are used to provide Ca^{2+} in Fig. 8a. Through reaction (7), CO_2 can be removed from an overlying gas mixture (*e.g.*, air or flue gas). The produced $Ca(HCO_3)_2(aq)$ can be diluted and stored in the ocean, water reservoirs or underground:

$$2H_2O + CaCO_3(s) + CO_2(g) \rightarrow Ca(HCO_3)_2(aq) + H_2(g) + 0.5O_2(g) \quad (7)$$

Capture of 1 mole of $CO_2(g)$ for each mole of $CaCO_3$ *via* reaction (7) is possible, while 22 tonnes of CO_2 can be captured per tonne H_2 generated (assuming a 1 : 1 molar ratio).[71] This implies that, depending on CO_2 emission involved in the operation (*e.g.*, for supplying electricity and for limestone/carbonate mining, crushing and transport), the system has the potential of producing carbon-negative hydrogen.[79]

The process efficiency in Fig. 8a can be enhanced *e.g.*, by:

- Improving the mass transfer between the overlying gas and the absorbent (to improve $CO_2(g)$ dissolution).

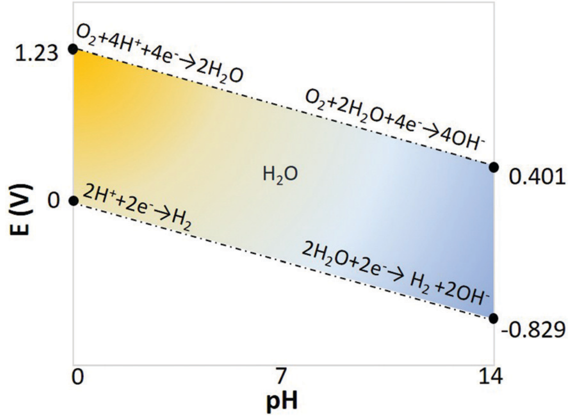


Fig. 7 Pourbaix diagram of water electrolysis.[77]

- Introducing an ion selective membrane between the electrodes (to avoid unwanted secondary reactions).

Alternative to water electrolysis, salt electrolysis, such as NaCl[69] and KCl[38] can also be used for CO_2 capture. If so, only an alkaline pH (at the cathode) is enabled, because at the anode *e.g.*, the reaction $2Cl^- \rightarrow Cl_2(g) + 2e^-$ takes place instead of the oxygen evolution reaction (OER).[70] The produced alkalinity at the cathode can then be utilized to sequestrate CO_2 in the form of carbonate salts. When the capture product is $CaCO_3(s)$, no $CO_2(g)$ desorption step is required. Furthermore, $CaCO_3$ is easier to transport and store compared to $CO_2(g)$. NaCl electrolysis for alkaline absorbent (re)generation follows reaction (8):[69]

$$2H_2O + 2NaCl(aq) \rightarrow 2NaOH(aq) + Cl_2(g) + H_2(g) \quad (8)$$

Using salt electrolysis for CO_2 capture is especially interesting due to salt availability in the seawater, leveraging possible substitution of the electrolyte with abundant seawater.[69] The produced (toxic) $Cl_2(g)$ at the anode can be treated by the produced NaOH solution using a scrubber, or can alternatively be utilized as a feedstock for the synthesis of HCl, Cl containing polymers and bleaching agents.[69] Alternatively, using water electrolysis and by inserting two ion exchange membranes (IEMs) between the electrodes (Fig. 9), produces H_2 simultaneous acidifies seawater to recover $CO_2(g)$.[36,80,81] The use of two IEMs avoids the production of $Cl_2(g)$ and electrode contamination.

When applying electrolysis using a reversible redox reaction – thus no net gas production – saves energy. For example, the production of $O_2(g)$ (or $Cl_2(g)$) can be avoided by recirculating the produced $H_2(g)$ from the cathode to the anode compartment.[72,73] Alternatively, H_2 production can be avoided if O_2 reduction takes place on the cathode, instead of the H_2O reduction.[82] At the cathode, depending on availability of O_2 or H_2, two possible reactions may exist for OH^- production:

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^- \quad (E^0 = 0.401 \text{ V } vs. \text{ SHE}) \quad (9)$$

$$4H_2O + 4e^- \rightarrow 2H_2(g) + 4OH^- \quad (E^0 = -0.83 \text{ V } vs. \text{ SHE}) \quad (10)$$

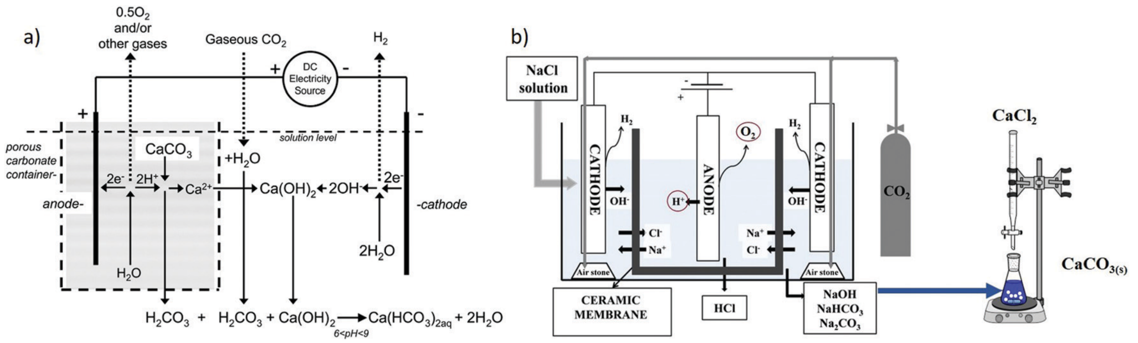


Fig. 8 (a) H^+ ions at the anode dissolve $CaCO_3$(s), the resulted Ca^{2+} ions move towards the cathode, forming $Ca(HCO_3)_2$(aq). Reprinted (adapted) with permission from ref. 71; Copyright (2008) American Chemical Society. (b) NaCl electrolysis, where NaOH is used as the CO_2(g) absorbent and $CaCO_3$(s) is the final capture product, figure from ref. 70. Both approaches use the concept of placing the anode inside of a porous container.

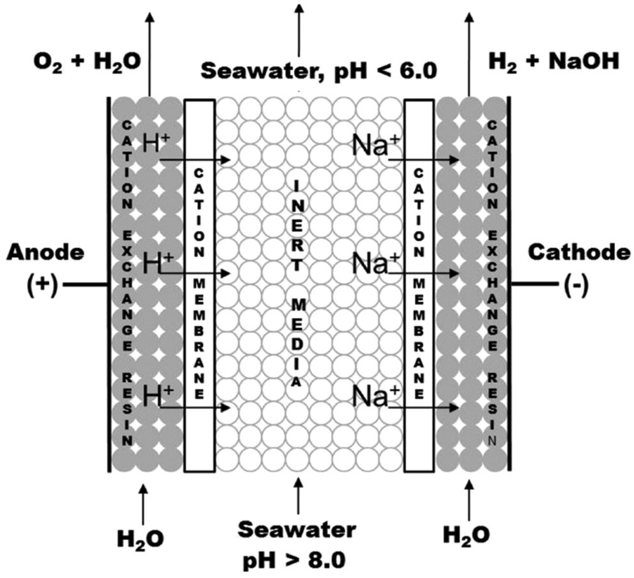


Fig. 9 CO_2 capture and H_2 production *via* sea water acidification and water electrolysis. In the middle compartment, cation exchange resins are used. Reprinted (adapted) with permission from ref. 81; Copyright (2014) American Chemical Society.

When sufficient O_2 is available at the cathode, or sufficient H_2 at the anode, the H^+/OH^- generation can take place in a practical cell voltage range of 1.3 V to 2.2 V through reaction (9). The supply of sufficient gas to the opposing electrode can be assisted by using gas diffusion electrodes.[83] Without recirculating the gaseous products, the cell voltage is typically >2.2 V.[82]

From a thermodynamic point of view, the use of (net) water electrolysis requires a significant thermodynamic minimum energy (1.23 V for water splitting), in addition to the potential required for generating a pH difference (see Fig. 7).[77,84] Considering the necessity of a wide pH-swing to enhance the carbon equilibrium kinetics, and using pH 0 and 14 to favour electrolyte conductivity, a minimum of 2.06 V is required, corresponding to 199 kJ mol^{-1} CO_2. Furthermore, in almost all demonstrated devices/systems, the rate of CO_2 capture is locked with the rate of H_2 or O_2 generation, which sometimes may not be desirable and present additional challenges for multi-stack development of the system. These drawbacks can be addressed using bipolar membrane electrodialysis as explained in the following section.

3.2 Bipolar membrane electrodialysis (BPMED)

A bipolar membrane (BPM) consists of an anion (AEL) and a cation (CEL) exchange layers, laminated together. When a sufficient electric field is applied, the BPM dissociates water into OH^- and H^+, producing a controllable ΔpH over the membrane as shown in Fig. 10a and b.[85–90] Using a bipolar membrane, the thermodynamic minimum voltage required for this water dissociation is 0.829 volts for a produced $\Delta pH = 14$. That is 2.5 times lower than that of water electrolysis at the same $\Delta pH = 14$ (1.23 + 0.829 at minimum), as no gas evolution takes place using a bipolar membrane.[85] The thermodynamic voltages over the BPM are even lower for smaller ΔpH over the membrane.[84,88] The feasibility of using bipolar membrane electrodialysis for pH-swing based CO_2 capture is shown in early studies in 1995;[91] alkaline KOH and acidic H_2SO_4 were regenerated in a two compartment BPMED cell, containing a BPM and a cation exchange membrane. After CO_2 from air is captured in KOH absorbent, it can be recovered through acidification. The produced K_2SO_4 is treated in the BPMED cell to regenerate the desired acid and base again. CO_2 capture *via* BPMED has been further explored by others, and these works are addressed in more details in next sections.

3.2.1 Energy consumption and capture efficiency. In BPMED, a trade off between the energy consumption and the process rate, determined by the applied current density, exists. Operating at very low current densities is not effective due to the higher salt ion leakage through the BPM and hence the lower water dissociation rate.[92] On the other hand, at high current densities, the ohmic voltage losses increase, leading to an undesirable higher energy consumption (see ESI†). As an example, Fig. 11a shows the minimum energy consumption for CO_2(g) recovery from 0.125 M K_2CO_3-rich solution *via* BPMED at a current density around 10 mA cm^{-2}.[3] However, although the energy consumption is the lowest at that current density, production rate favours higher current densities as shown in

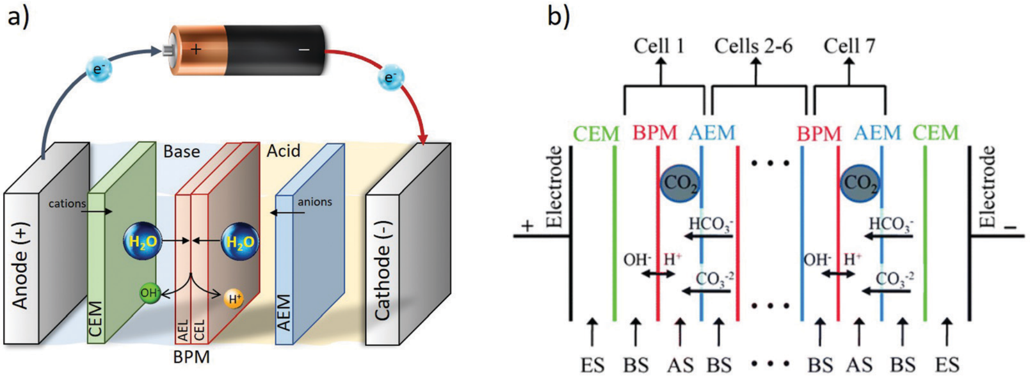


Fig. 10 (a) BPMED schematic. (b) BPMED for CO_2 recovery in ref. 92. (ES) electrode solution = KOH, (AS) acid solution of KH_2PO_4 + H_3PO_4, (BS) base solution of six different mixtures of $KHCO_3$, K_2CO_3 and KOH. Figure adapted from ref. 92.

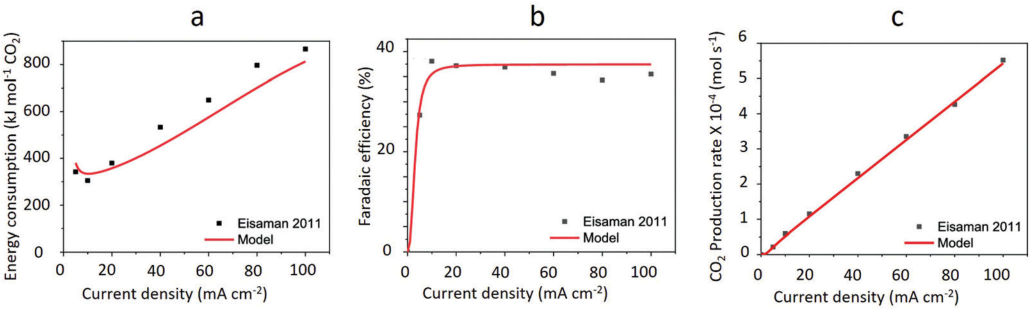


Fig. 11 Trend of energy consumption, faradaic efficiency and CO_2 production rate *vs.* current density in CO_2(g) recovery from 0.125 M K_2CO_3-rich solution *via* BPMED. The black squares are experimentally measured data by ref. 92 while the red lines show the calculated values performed by ref. 3. Reprinted (adapted) with permission from ref. 3; Copyright (2020) American Chemical Society.

Fig. 11c. The experimentally measured current efficiency (*i.e.*, faradaic efficiency) in Fig. 11b shows – in addition to its low values at $i < 10$ mA cm^{-2} due to salt cross-over – a slight decreases at $i > 20$ mA cm^{-2}. It is hypothesized that current densities above the optimum value, reduce the BPM's permselectivity[93] or enhance the water splitting reaction in the AEM's,[94,95] leading to a lower efficiency.[92] The current efficiency also decreases if the current is carried by an undesired ion through the membranes. For example, in Fig. 10b, the (bi)carbonate ions are the desired current carriers. However, if (as a result of high pH) OH^- ions become the main charge carrier through the AEM, the current efficiency decreases. On the other hand, when capturing CO_2(g) from flue gas or in DAC, a high pH (*i.e.*, high $[OH^-]$) is favoured in the outlet of the same compartment, because CO_2(g) absorption capacity and rate increase in a solution with high pH. Adopting monovalent-ion-selective AEM's that favour the transport of HCO_3^- ions over OH^- ions then could improve the efficiency when such process is intended.[3,96]

As opposed to what is shown in Fig. 11b, the current efficiency of BPMED can reach as high as 95% if *e.g.*, a 0.5 M $KHCO_3$ is used instead of the 0.125 M K_2CO_3 for CO_2(g) recovery through acidification. In fact, both in BPMED and (membrane) electrolysis, in addition to the current density, the anolyte and catholyte concentrations and the operation temperature affect the current efficiency, as demonstrated in Fig. 12[38] and summarized in Table 1.

The (slightly) positive effect of temperature on improving the faradaic efficiency of electrochemical methods has been reported.[38,69] Higher temperatures improve the electrochemical reaction rates. In the case of BPMED, the kinetics of water dissociation in BPM is also enhanced at elevated temperatures.[97,98] However, in addition to the extra energy needed for heating up the electrolytes, the thermal stability of the ion exchange membranes poses a limitation on high temperature processes. For instance, the commercial bipolar membranes are cannot withstand temperatures higher than 40–60 °C for a long duration.[99] Moreover, CO_2 solubility decrease at higher temperatures (up to 100 °C).[100–102] This means that operating at high temperature is not yet practical.

A breakdown of energy consumption and comparison for (membrane) electrolysis and BPMED is provided in Section 3.5 and the ESI.†

3.2.2 Cell configuration.

The cell configuration defines the number of membranes, membrane cell pair arrangement, electrolyte flow path and the thickness of the compartment/membrane. The design of the cell is the most important factor to minimize the cell resistance.[74] As opposed to the BPMED for traditional acid and base production (*i.e.*, BPM–CEM–AEM–BPM), the pH-swing process for CO_2 capture allows a simplified

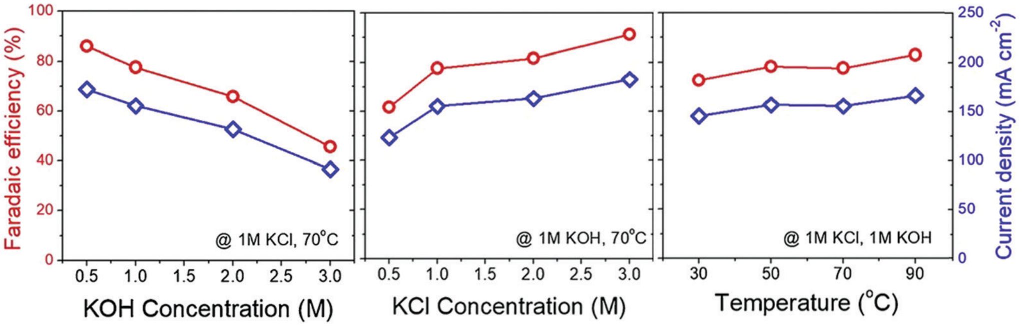


Fig. 12 Change of the measured current density (blue diamond line) and faradaic efficiency (red circle line) with regards to the change in catholyte concentration, anolyte concentration and the applied temperature in an electrochemical KOH (absorbent) production *via* KCl electrolyser. Reprinted from ref. 38, Copyright (2019), with permission from Elsevier.

Table 1 Electrochemical CO_2 capture

Capture method	Feed	Energy-consumption[a] (kJ mol^{-1} CO_2)	Current-efficiency	Product	Current-density (mA cm^{-2})	Remarks
Fuel-cell[35]	Air + H_2	350	23%	CO_2(g)	0.5	Upscaling unfeasible (low current-density)
Electrolysis[74]	Air	290–350 (kJ mol^{-1} KOH)	>95%[b]	CO_2(g) + H_2(g)	100	KOH/K_2CO_3 electrolysis at 70 °C
Electrolysis[71]	Air + mined $CaCO_3$(s)	1 267 200[c]	Not reported	H_2(g) + CO_2(g)	Not reported	Water electrolysis. Fig. 8a
Electrolysis[38]	Synthetic flue gas + cement kiln dust	>634–1276 (kJ mol^{-1} $CaCO_3$)[d]	60–90%[b]	$CaCO_3$(s)	100–200	KCl electrolysis. Fig. 12
BPMED[91]	K_2SO_4	~308	Not reported	CO_2(g)	50	Produces KOH + H_2SO_4
BPMED[106]	$NaHCO_3$/NaOH	160–500	65–80%	CO_2(g)	5–20	
BPMED[92]	$KHCO_3$/K_2CO_3	100–450[e]	95% ($KHCO_3$), 50% (K_2CO_3)	CO_2(g)	5–100	Fig. 10b for cell design & Fig. 11 for cell performance
BPMED[43]	$KHCO_3$	200–500	70–90%	CO_2(g)	22–139	High pressure BPMED enables 30% energy win. See Section 3.2.3
BPMED[113]	Artificial seawater	250–400	<70%	CO_2(g)	1–3	59% of DIC from seawater was removed using *ca.* 242 kJ mol^{-1} CO_2
BPMED[8]	Artificial seawater + NaCl	390–640	60–95%[f]	CO_2(g) or $CaCO_3$(s)	100	Cost of membrane contactors is avoided *via* the base route
BPMED[107]	Artificial seawater + CO_2(g)	1080–2880 (kJ mol^{-1} $CaCO_3$)	Not reported	$CaCO_3$(s)	Not reported	CO_2(g) absorption in basified seawater followed by crystallization
EDI + BPMED[42]	Synthetic flue gas	Not reported	Not reported	CO_2(g)	2–16	At near neutral pH, the slow kinetics can be enhanced using CA enzyme
EDI + electrolysis[36,76,81,194]	Natural seawater	2775–6940[g]	Not reported	CO_2(g)/H_2(g)	20–61	Fig. 9
MCDI[156]	Synthetic flue gas	40–50	60–80%	CO_2(g)	0.02–0.06	Using IEM's improve efficiency[37]
Redox-active carriers + pH-swing[140]	Synthetic flue gas	106[h]	90%	CO_2(g)	18	Aqueous tiron (Na_2Q) is used as pH mediator/active carrier to capture CO_2
Redox-active carriers[147]	Synthetic flue gas	56	>75%	CO_2(g)	0.5	

[a] Only for the electrochemical step, defined as in eqn (11). [b] For KOH electrochemical regeneration. [c] Although the theoretical work requirement for the reaction is only 266 kJ mol^{-1} CO_2. [d] Calculated from data on energy consumption for KOH production, assuming 2 moles KOH delivers 1 mole $CaCO_3$. [e] Plus 200 for CO_2(g) capture into hydroxide solutions.[193] [f] Only for the production of HCl and NaOH, not for CO_2 capture and recovery. [g] Calculated based on data from ref. 76: R = 0.5–1.8 Ω, i = 20.4–61.2 mA cm^{-2} and recovered CO_2 rate of 0.004 mol min^{-1}. [h] Only for the CO_2 desorption step.

membrane sequence due to the limited pH-range (*i.e.*, pH 3–9 instead of 0–14).

In choosing the optimised configuration, the (co-)ionic leakage of the membranes is crucial. When using multi-ionic CO_2 feed, such as seawater, carbonic species should be rejected to obtain a maximum capture efficiency. Carbonic species are neutral (*e.g.*, CO_2(aq) and H_2CO_3) or negatively charged and hence are rejected better by a CEM than by an AEM. In addition to higher selectivity, the use of CEM's instead of AEM's have proven to increase conductivity and mechanical stability in a BPMED cell for CO_2 capture[72]).[103]

For further reducing co-ionic cross-over, a trade off between the permselectivity of IEM's and their resistance should be considered, which is controlled by the membrane thickness. In general, thicker membranes have higher resistivity but show a better selectivity.[72] Applying a reinforced structure to a thinner membrane can improve its selectivity while maintaining its resistivity to a certain extent.[72,104]

Depending on the charge carriers in the cell, the flow mode (*i.e.*, one-way pass *vs.* batch mode) and feed concentration, each BPMED process asks for a different cell configuration. While BPM–CEM might be the choice of some researchers for CO_2 recovery from carbonate solutions,[105,106] others chose a BPM–AEM[43,92] for the same purpose. That is while novel configurations as BPM–AEM–AEM are also emerging for minimizing BPM fouling when extracting $CaCO_3$ from seawater,[107] see Section 3.2.4.

3.2.3 High pressure BPMED.

In a closed system (such as the one created inside of an electrochemical cell), acidification increases the concentration of dissolved CO_2. This concentration can lead to the formation of $CO_2(g)$ bubbles inside of the cell. Theoretical models, suggest the trapped CO_2 in the acid solution dominate the cell resistance and increase the energy consumption.[108] Trapped gas bubbles lower the effective membrane surface area, cause high voltages and shorten the membrane lifetime (due to localized ''hot spots'' of high current density). To avoid gas production inside of the cell, Eisaman *et al.*[43] proposed a high pressure BPMED process using a similar cell as shown in Fig. 10b where the entire stack is kept at high pressure, *i.e.*, there is no pressure difference across the membranes in the stack. The authors observed that by increasing the pressure, the total cell voltage decreases due to the avoided CO_2 gas bubbles production in the cell; the electrochemical energy required at 6 atm (333 kJ mol^{-1} CO_2) was seen to be 29% less than that of 1.5 atm (471 kJ mol^{-1} CO_2) at a current density of 139 mA cm^{-2}.

3.2.4 BPMED for CO_2 extraction from seawater.

The ocean is a massive sink for CO_2.[11,109,110] The higher carbon content of the oceans compared to that of the atmosphere[8,54,111] makes the ocean an interesting source for CO_2 capture.[109] Moreover, as opposed to the separation of CO_2 from a gas mixture that involves two steps (*i.e.*, capture and release), in CO_2 capture from seawater, a separate $CO_2(g)$ adsorption/absorption step is not required, because the ocean already acts as CO_2 absorbent leveraging its gigantic surface. The ocean contain DIC of $\sim$2.3–2.5 mM, mainly in the form of HCO_3^- ions, in normal seawater of pH $\sim$ 8.1.

The product of seawater CO_2 capture can be (1) gaseous CO_2,[8] (2) solid carbonates,[107] or (3) dissolved bicarbonates and carbonates ions (to be subsequently stored in the ocean).[71,75,78,112] To extract the CO_2 as gas, the bi-/carbonate ions present in the seawater can be converted into $H_2CO_3^*$ in the acidic compartments adjacent to the BPM.[113] Subsequently, through vacuum stripping of the acidified stream using membrane contactors, $CO_2(g)$ can then be produced.[8,113] Alternatively, at alkaline pH $> pK_{a_2}$, HCO_3^- converts to CO_3^{2-} and can subsequently precipitate through reaction with dissolved Mg^{2+} or Ca^{2+}.[8,107] When the partial pressure of CO_2 remains unchanged, the pH determines which mineral is obtained *e.g.*, the precipitation of $CaCO_3$ (in synthetic seawater) is favoured in $9.3 < pH < 9.6$.[8,114] Considering that the Ca^{2+} and Mg^{2+} concentrations in seawater are respectively ×4 and ×25 higher than that of DIC, mineralization has the potential to remove all DIC, theoretically.[115] In addition, mineralization eliminates the expenses of using a membrane contactor.[116,117] In the third option, converting CO_2 to dissolved alkaline bicarbonates and carbonates enables carbon sequestration. This is a long-term carbon storage which also helps against ocean acidification by increasing the ocean alkalinity.[71,75,78,112] However, further research is required for understanding the full range and capacity of such approach.

The main bottlenecks in using *in situ* BPMED for this mineral crystallization are the risk of membrane contamination (*i.e.*, fouling) in the stack and the slow kinetics of the carbonate precipitation. To avoid the fouling, pure NaCl (instead of seawater) can be used in the BPMED for NaOH and HCl production.[8] The produced NaOH is then added to the seawater stream in a controlled crystallizer to initiate the precipitation. In order to improve the kinetics of the precipitation, use of a seeded crystallizer unit is suggested.[107,118] Although seawater CO_2 capture through mineralization is shown feasible, debates on the environmental impacts of reducing Ca^{2+}/Mg^{2+} concentration of the ocean are in progress.[115,119]

3.2.5 Electrodeionization (EDI).

Electrodeionization (EDI) combines ion exchange membranes technology with ion exchange resins.[120–125] Ion exchange resins are solid cross-linked polymers that contain fixed charged groups typically based on acrylic or styrene monomers. When filling the flow compartments with beads or 3D structures of ion exchange resins, the polymer–electrolyte interface area is increased.[126] The combination can help overcome the concentration polarization losses associated with electrodialysis and electrolysis. The major application of electrodeionization (EDI) includes the removal/recovery of heavy metals and organic acids for pure water production.[127–131] The combination of BPMED with resin wafer electrodeionization (RW-EDI) is demonstrated in the lab-scale, where porous, solid matrix of ion-exchange resin beads are incorporated in between of the CEM's and BPM's in the cell.[42] However, unfortunately, data on the energy consumption and current efficiency of the system is not reported. The combination of electrodeionization (EDI) with electrolysis is shown feasible as demonstrated in Fig. 9.[76,81] However, as shown in Table 1, the process still requires further optimization (in terms of production of $H_2(g)$ and cost/stability of resins) to decrease its significant energy consumption. Furthermore, the (bio)fouling of the resin beads due to the contact with seawater decreases the overall efficiency of the method and needs yet to be addressed.

The pH-swing based EDI application for CO_2 capture has only been explored at a basic level.[127] More work has been done on the use of amine based ion exchange resins as adsorbent for CO_2 capture, through thermal swing. Such resins are reported to show good stability after repetitive adsorption–desorption cycles with only a small reduction in capture capacity, and require relatively mild desorption conditions.[126,132,133] Recently, wafer enhanced electrodeionization for conversion of CO_2 into HCO_3^- feed for algae cultured photobioreactors is reported.[134] Suggestions for further research on EDI technology are producing inexpensive ion exchange resins, reducing possibility of resin fouling (*e.g.*, for the case of seawater feed[76]), and maintaining long-term resin stability.[127]

3.3 Redox-active carriers and electrode reactions

An alternative to BPMED and electrolysis for CO_2 capture, is the more classical electrochemically-mediated separation strategies that perform absorber/desorber cycles using specific redox-active sorbent carriers.[39,49] These redox-active carriers can be used for separation of $CO_2(g)$ from a gas mixture through (1) binding route Fig. 13a and (2) pH-swing route Fig. 13b. Both routes have been demonstrated feasible in the lab-scale.[135,136]

As for the "binding route", the suitable carrier is activated at the cathode and can bind with the target species at its reduced state. The target species in this case is the CO_2 molecule. Subsequently, the captured CO_2 can be released at the anode through oxidation of the carrier while the carrier is regenerated. This process is also referred to as "electrochemical CO_2 pumping",[135,137] see Fig. 13a. The cycle can be broken down into four steps:[41]

- Sorbent activation through oxidation or reduction.
- $CO_2(g)$ capture on the activated sorbent.
- Sorbent deactivation through the reverse electrochemical process.
- $CO_2(g)$ release.

Alternatively, in order to decrease the required electrical energy, these steps could be integrated in a two or three-stage process[40,41] by *e.g.*, enabling CO_2 capture or release to be performed simultaneously with electrochemical reduction or oxidation of the carrier.

In order to improve the kinetics of CO_2 capture and release, the "pH-swing route" can be integrated, where the chemistry of redox-active carriers are designed to undergo proton coupled electron transfer (PCET) reactions,[135,136,138,139] as shown in Fig. 13b.[135,136,140] If so, an "electrochemical H^+ pumping" takes place that enables an acidic and a basic pH on the anode and the cathode, respectively.

Although redox-active systems have yet to achieve industrial utility, they have the potential of producing a pure CO_2 stream even from dilute gas mixtures, such as air.[141] Among different classes of redox-active compounds that have been explored, such as bipyridines,[142,143] disulfides[49] and copper/amine systems,[29,30] the quinone species[141,144–146] are of particular interest,[40] owing their strong binding affinity for CO_2 in their reduced form compared to that of their neutral state.[39,147] Quinones are organic compounds derived from aromatics, through conversion of an even number of –CH= groups into –C(=O)– groups.[148] Quinones have also gained great interest as potential ideal candidates for PCET mechanism[138,139,149–153] inspired by their role in biological systems.[154] These redox reactions are (ideally) reversible, and can operate within the water splitting window.[135]

The choice of catalysts on the surface of the electrodes to facilitate the electron transfer together with the type and concentration of the electrolyte are important in determining the process efficiency in terms of capture, transport and release of CO_2, and kinetics.[136] Furthermore, the local pH shown in Fig. 13b is not the same as the bulk pH.[155] While the high pH at the cathode determines the CO_2 absorption and the lower pH at the anode drives CO_2 desorption, only the bulk pH can be controlled in a practical process. That makes the choice of an appropriate average pH that enhances both reactions, challenging. Alternatively, the local pH can be maintained by inserting (1) an

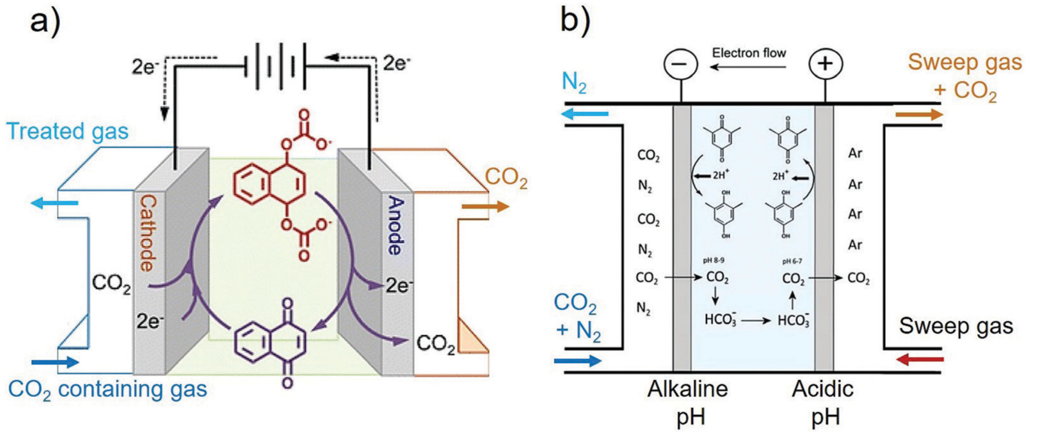


Fig. 13 (a) Electrochemical CO_2 separation using gas diffusion electrodes (GDE) through binding with quinone redox-active carrier (*i.e.*, no pH-swing is created). Reprinted (adapted) with permission from ref. 144; Copyright (2015) American Chemical Society. (b) Combination of pH-swing with the chemistry of redox active carriers through (PCET) reaction using mixture of hydroquinone, quinone, and sodium bicarbonate. Reprinted (adapted) with permission from ref. 136; Copyright (2015) American Chemical Society.

anion-exchange membrane (AEM) or (2) an extra salt compartment sandwiched between an AEM and a cation-exchange membrane (CEM) between the electrodes.[147]

Despite its progress in the lab-scale, CO_2 separation using redox active carriers is not yet practically implemented because of the limitation it faces in terms of both solvents and carriers. It is difficult to find a solvent that is inexpensive, safe, electrochemically stable and allows high solubility of the redox species.[49,147] Possible improvements in terms of solvents can be achieved by using ionic liquids as electrolytes[39,144] or using salt-concentrated aqueous electrolytes.[147] As for the carriers, the solubility, chemical stability and kinetics of the redox molecule can pose limitations on the process.[49] To address these drawbacks, electrochemically mediated amine regeneration can be employed, using a similar concept, but by employing amines rather than quinones as described in Section 4.1.3. Alternative to using dissolved carriers in an electrolyte – where the transport of both the electrolyte and the carrier molecules between the two electrodes is required, the active carriers can be immobilized between the opposite electrodes.[39] The latter is explained further in Section 4.2.1. Recently, solid polymerized quinone (formed into a composite with carbon nanotubes to confer electronic conductivity) is employed.[39] This so called "electro-swing" process exhibits a high faradaic efficiency and a low energy consumption (40–90 kJ mol^{-1} CO_2 captured) compared to the thermal or pressure swings for sorbent regeneration. However, it needs to be improved in terms of capacity and kinetics.

3.3.1 Electrode induced pH-swing. Another electrochemical based CO_2 capture concept utilizing local pH near electrodes is the (membrane) capacitive deionization (MCDI) method.[37,156] Capacitive deionization is mainly used for water treatment, but its application has recently expanded to energy harvesting and CO_2 capture.[157–165] The motivation to capture CO_2 *via* such system is that deionized water can be used without the need of any other chemicals, using inexpensive carbon based electrodes.[37,156]

MCDI cells consist of activated carbon electrodes and ion-exchange membranes. When a current is applied in the charging step of MCDI, HCO_3^- and H^+ ions are adsorbed into the porous electrodes inside of the cell (causing a local low pH at the cathode and increasing pH in the bulk). As the electrolyte is being depleted from ions, more $CO_2(g)$ can be absorbed in the deionized water due to the shift in the CO_2 equilibrium, to make up for the depletion. It has been proposed to use a gas–liquid contactor spiral glass tube outside of the cell for *in situ* absorption. When the current direction is reversed (*i.e.*, discharging step), the subsequent desorption of H^+ and HCO_3^- (plus a small amount of CO_3^{2-}) ions from the carbon electrodes drives the chemical equilibrium in the opposite direction. As the concentration of $H_2CO_3^*$ will exceed the solubility, $CO_2(g)$ is formed from the electrolyte. $CO_2(g)$ absorption and desorption can be controlled through shifting the current direction. CDI can also be used in combination with NH_3-based CO_2 capture.[166]

In addition to the carbon based capacitive electrodes, other metals can also be used. For example, CO_2 can be captured through intercalation/deintercalation of protons on the manganese dioxide (MnO_2) based electrodes. The electrodes can host protons (*i.e.*, intercalation) during reduction and release them (*i.e.*, deintercalation) during oxidation, creating the required pH-swing for CO_2 absorption and desorption, respectively.[167] In such methods, periodic electrode polarity and the switching fluid flows ensure a continuous process.

3.4 Molten carbonate cells and hybrid electrochemical capture methods

Electrochemical methods can benefit from a pH-swing approach but are not limited to it. Examples are using (high temperature) molten carbonate cells or the hybrid methods that integrate CO_2 capture and conversion.

High-temperature molten carbonate cells are early electrochemical CO_2 capture examples.[32,168] In such process, a CO_2 containing (flue) gas is fed to the cathode side of an electrochemical cell, where electricity is used to drive CO_2 and O_2 (in form of CO_3^{2-}) across a molten carbonate salts electrolyte (sandwiched between ceramic membranes in contact with the electrodes). At the anode, carbonate ion will be reduced to CO_2 and O_2 again. An alternative design enables a molten carbonate fuel cell, where CO_2 is captured while H_2 is produced.[169–171] Involved challenges are difficult operating conditions due to the high temperatures, corrosion and sensitivity to the presence of SO_x in the gaseous mixture.[20,24,172] Research for developing dense molten carbonate CO_2 selective membranes at high temperatures (> 723 K) is still in progress.[173–175]

Examples of electrochemical hybrid capture and utilization is the electrochemical seawater battery system,[176] the alkali metal-based CO_2 batteries (*e.g.*, lithium–CO_2 batteries[177,178]) and electrochemical CO_2 capture and conversion combinations.[25,179–183] The absence of pH-swings, and the lack of further development of these proposed electrochemical capture routes, categorizes these concepts beyond the scope of this review. The broader context in terms of CO_2 utilization is discussed in Section 5.

3.5 Which electrochemical method to use?

A comparison of the metrics of electrochemical pH-swing based CO_2 capture methods is given in Table 1. These capture methods have often energy consumption >300 kJ mol^{-1} CO_2. As a comparison with conventional methods, the energy consumption of CO_2 capture (from flue gas) *via* aqueous monoethanolamine (MEA) using a thermal swing, currently the most mature capture method, is between ∼170–300 kJ mol^{-1} CO_2.[184–190] Approximately ∼80% of this energy is the contribution of the thermal regeneration,[13] included in the reboiler heat duty.[191] Most conventional and electrochemical captures are energy intensive, when compared to the combustion energy of various fuels and the emitted CO_2 per mole of the fuel. From an economic point of view, CO_2 capture is only interesting if the energy consumption of the capture is <66 kJ mol^{-1} CO_2.[42,192]

Renewable sources would be preferred over fossil fuels for driving electrochemical CO_2 capture to (1) maximize the reduction in net carbon emission and (2) leverage the advantage of electrifying the CO_2 capture process. At the same time, the absence of flue gas from power plants in renewable sources would make diffused CO_2 sources (*e.g.*, atmosphere and seawater) the most logical feed for electrochemical CO_2 capture technologies. This is also reflected in Table 1, where most research has focused on capture from air, seawater or (low concentrated) bi(carbonate) solutions.

At present, (membrane) electrolysis and BPMED are the most studied electrochemical capture approaches. Fig. 14a shows the estimated energy consumption of both methods (see ESI† for calculations). This electrical energy consumption, E (in kJ mol^{-1} CO_2), is calculated *via*:

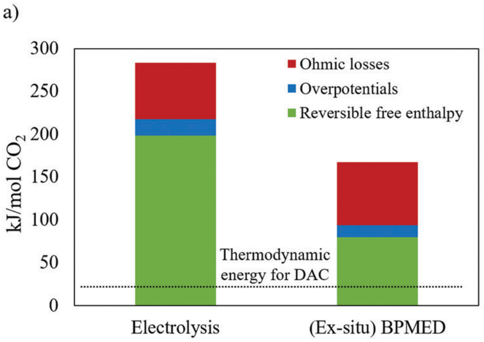
$$E = \frac{i \cdot A \cdot V}{r_{CO_2(g)}} \tag{11}$$

where i is the current density (A m^{-2}), A is effective area of the electrodes (m^2), V is the total cell voltage (volts) and r_{CO_2} is the recovery rate of the captured $CO_2(g)$ in mol s^{-1}. To put the energy consumption of Fig. 14a in perspective, the energy produced per mole of fuel (through combustion) and the associated emitted CO_2 are shown in Fig. 14b. This emphasizes the energy-intensive nature of the capture process: capturing 1 mole of CO_2 *via* BPMED consumes 25–60% of the energy obtained from combustion of hydrocarbon fuel per mole of CO_2, dependent on the fuel type. For conventional methods and electrochemical capture *via* electrolysis, this figure is even larger.

Fig. 14a shows that the ohmic losses cover a significant part of the energy losses,[77] and bring in a lever to reduce E. In electrochemical cells, such losses can appear as *e.g.*, heat and/or unwanted chemical byproducts. For example, losses caused by product recombination, such as recombination of produced H^+ and OH^- in BPMED or the recombination of $O_2(g)$ and $H_2(g)$ in water electrolysis to form water again. Membrane co-ion leakage is another common loss often involved in membrane based electrochemical processes.[93] The limitations and areas of improvements of each electrochemical CO_2 capture method can be summarized as:

(1) It is obvious from Fig. 14a that the energy consumption for BPMED is lower than that of electrolysis when targeting CO_2 capture. In case hydrogen is an aimed product as well, the energy difference between these two methods (which is equivalent to 1.23 V) can be justified, and can be lower than the energy for two separate systems making acid/base and hydrogen. However, in more detail, the combination of these two products in electrolysis complicates the optimal current density, which is not necessarily the same for hydrogen and acid/base production. Moreover, most hydrogen catalysts are geared towards acidic environments, and earth abundant oxygen catalyst are available for alkaline environments, while the opposite environments are present in the combined electrolysis/acid–base production.[196] That limits the options for electrocatalytic material (*e.g.*, platinum and ruthenium), which can pose resource limitations as a relatively large electrode area is required. On the contrary, up scaling can be done easily for BPMED capture method by repeating multiple cell pairs within a single electrode pair.

(2) When using BPMED, despite its uncomplicated up scaling, the typical energy consumption in Table 1 is still 2–3 times more than theoretically expected in Fig. 14a. These losses are due to the involved non-idealities in charged membranes (*e.g.*, high resistivity, co-ion leakage, low chemical stability), the high over potential of water dissociation in BPM, or carbonate feed (requiring 2 H^+ per molecule to acidify to H_2CO_3) instead of bicarbonate. Thankfully, achieving a lower energy consumption is possible both through process optimization and material engineering. Process optimizations can be done by *e.g.*, controlling the applied current density (i), feed flow rate (residence time in the cell), electrolyte conductivity/pH, cell configuration, flow path/mode, and operation pressure/temperature, while water dissociation can be improved through material engineering.[197,198] The current minimum economic cost of BPMED is at least twice of the cost of the wet-scrubbing rival.[3] However, the cost can significantly decrease if improvements in the cost of renewable energies, cost and availability of ion exchange membrane, membrane life time and membrane selectivity is achieved. Finally, the total capture cost does not only depend on the method, but also on the source of the capture. For example, depending on the pumping facilities and plant location, indirect ocean capture (IOC) can be



b)

Fuel type	Combustion energy (kJ/ mol fuel)	Energy vs. emission (kJ/ mol $CO_{2(g)}$)
CO	283	283
H_2	286	0
Coal (100% on Cs)	393	393
Methane (CH_4)	890	890
Ethanol (C_2H_5OH)	1367	683.5
Gasoline (octane)	5450	681.25

Fig. 14 (a) Electrical energy consumption for direct air capture (DAC) through (membrane) electrolysis. Current density of 20 mA cm^{-2} and ΔpH = 14 is assumed for both cases. See Section S2 of the ESI† for detailed calculations. The thermodynamic work required for DAC (assuming 400 ppm $CO_2(g)$) is 20 kJ mol^{-1} CO_2.[15] (b) The combustion heat of common fuels and their $CO_2(g)$ emission, obtained from ref. 195 and stoichiometric combustion reactions.

economically favored relative to direct air capture (DAC), or *vice versa*.[199]

(3) The reversible free enthalpy in Fig. 14a is based on a ΔpH = 14. Using lower ΔpH, a lower reversible free enthalpy is involved.[84] Although it is theoretically possible to perform a pH swing between pH 4–7, potentially reducing the energy consumption to values close to the thermodynamic limits, this low energy consumption is not obtained in practical BPMED at medium to high current density.

(4) Membrane capacitive deionization (MCDI) is recently demonstrated to capture CO_2 from a $CO_2(g) + N_2(g)$ mixture, using only demineralized water[37,156] with the lowest capture energy among other methods ($\sim$40–50 kJ mol^{-1} CO_2), see Table 1. However, the obtained current density is extremely low ($\sim$0.02–0.06 mA cm^{-2}) and there is a long way to go before (M)CDI becomes a competitive means of CO_2 capture as the stability and performance of the large-scale CDI applications are yet unknown. Future work is suggested to investigate the physical and chemical effects of weak electrolyte solutions in CDI.[156]

(5) Only a few works on CO_2 capture through electrodeionization (EDI) show lab scale feasibility[76,121,200] as summarized in Table 1. However, no data on the energy consumption of those systems is available. CO_2 capture through EDI is limited due to the cost of ion exchange resins, their poor stability and their sensitivity to fouling.[127]

(6) Electrochemical methods that use redox-active carriers are shown to be less energy intensive ($\sim$100 kJ mol^{-1} CO_2). However, these results have been only obtained using synthetic flue gas. Quinones, used as binding agents for CO_2, are highly sensitive to water and oxygen, making the applications for real flue gas (or direct air capture) impractical. Moreover, most redox carriers need organic solvents electrolytes that suffer from a low ionic conductivity which limit the current density. When using quinones as carriers, the total CO_2 carrying capacity is limited by the solubility of quinone in the solvent, the applied electrode potentials, evaporative solvent losses and consequent drying of the electrodes.[144] Luckily, the efficiency of the CO_2 absorption and desorption in such systems can be increased by combining a pH-swing through electrochemical reactions,[136] where proton coupled electron transfer (PCET) takes place. However, the practicality of this approach still awaits the improvement of electrochemical redox kinetics. The low solubility of PCET organics limits its capture capacity.[135] Furthermore, PCET carriers are also very sensitive to gasses such as O_2 and sulfur, posing again challenges for (real) gas CO_2 capture application.[135] Upscaling can be done by using a larger electrode surface area.

All electrochemical CO_2 capture methods are still under development (TRL 5 to 6), although they enable high CO_2 recovery rate (>80%). In order to provide a framework of comparison between these methods and the conventional (non-electrochemical) processes – which have already been commercialized – the conventional processes are described further in the next section.

4 Combining electrochemical methods with conventional capture technologies

Conventionally, the capture industry only targeted CO_2 capture from centralized CO_2 emitters such as fossil fueled power plants, iron, steel, and cement industries. However, this approach is impotent to achieve a net zero CO_2 emission because, as shown in Table 2, decentralized sources still constitute a large part of the total emission (total GHG emission of 55 Gt CO_{2eq} in 2019 [201]). Therefore, currently DAC and IOC are gaining attention (Table 3). For achieving climate targets, CO_2 removal within a gigaton order of magnitude is needed.[202,203]

The (centralized) capture technologies are often grouped in main categories of;[18] (1) oxy-fuel combustion, (2) pre-combustion, (3) post-combustion and (4) chemical looping (combustion) as discussed in Table 4. In addition, capture by algae,[214–220] biochar[221–226] and charcoal[227] are recently demonstrated. While there are many CO_2 capture methods, introducing all of them are out of scope of this work and we refer the reader to various available literature on this topic.[13,17–25,228,229] For an overview of the current state-of-the-art of CO_2 capture, transport, utilisation and storage see ref. 230. Among the available methods, most research focus has been given to the post-combustion methods as they can be retrofitted more easily to the existing industrial units, compared to the oxy-fuel and pre-combustion methods.[229] Traditional post-combustion capture methods are absorption,[18,19,231–236] adsorption,[13,18,237–239] membrane gas separation,[240–246] calcium looping[19,247–249] and mineral carbonation,[110,250–260] see Table 4. These methods are combined

Table 2 Thermodynamically required energy, properties and the scale of main capture feeds

Source	Thermodynamic properties & required energy	Emission & capture scale
Centralized	• **Flue gas**: – 150 $< T <$ 1200 °C, $p_{CO_2} \sim$ 0.03–0.15 atm[204,205] – 7 kJ mol^{-1} CO_2 for 13% flue gas[206]	• >58% of total emission, see Fig. 1 • Current post-combustion capture >2.4 Mt CO_2 per year[207]
Decentralized	• **Direct air capture (DAC)**: – Ambient T, $p_{CO_2} \sim$ 0.0004 atm ($\sim$400 ppm) – 20 kJ mol^{-1} CO_2[15,206,208] • **Indirect ocean capture (IOC)**: – 5 $< T <$ 35 °C, $p_{CO_2} \sim$ 0.072 atm ($\sim$2.5 mM DIC) – Same thermodynamically required energy as DAC[199]	• <42% of total emission, see Fig. 1 • Current DAC capture shown in Table 3, but no large scale IOC, yet[209]

Table 3 Large scale DAC companies

Company	Process mechanism	Capacity (tonne CO_2 per year)
Carbon Engineering[210]	(KOH) absorption + high temperature calcination	1 000 000
Global Thermostat[211]	(Amine based) adsorption + thermal & pressure swing regeneration	4000
Climeworks[212,213]	(Amine based) adsorption + thermal swing regeneration	900

Table 4 Dominant non-electrochemical CO_2 capture methods (continued)

Capture method	Process mechanism	Challenges
Oxy-fuel[261–263]	Instead of air, pure O_2(g) or a CO_2(g)/O_2(g) mixture is used for fuel combustion. 75–80% CO_2 is produced as opposed to combustion in normal air where 3–15% CO_2 is produced	• High oxygen production energy costs (*ca.* 200–220 kW h per tonne of oxygen generated by cryogenic air separation[263]) • High sensitivity to air leakage into the system • Although an efficient capture method,[264] difficult to retrofit compared to post-combustion method • Special materials are needed to resist the high flame temperature (*ca.* 3500 °C). Although, the recycled CO_2 can be used to moderate this temperature[18]
Pre-combustion[265–268]	CO_2 is separated from H_2-rich fuel before combustion. For example, synthetic gas is produced from fossil fuel by adding steam or pure oxygen at high temperature and pressure (1400 °C and 25–55 atm) and a subsequent water–gas shift reaction.	• Retrofit to existing plants is costly and more difficult compared to oxy-fuel and post-combustion • Reaction CO + steam $\leftrightarrow$ $CO_2 + H_2$ produces 15–40% CO_2 at 14–40 atm. The produced H_2 can be used for power generation, but CO_2 needs to be removed using a subsequent separation technique
Post-combustion:		
Absorption[18,19,231–236]	CO_2(g) (from flue gas or air) is absorbed (*i.e.*, chemically or physically) in an absorbent. Pure CO_2(g) is subsequently recovered through temperature swing desorption while the absorbent will be regenerated. Currently, amine based capture is the most mature method for CO_2 capture	• Limited CO_2 absorbing capacity resulted from the reaction stoichiometry and dependent on the absorbent type (*e.g.*, low capacity as 0.4 kg CO_2 per kg-MEA or higher as 1.2 kg CO_2 per kg-NH_3[18,269]) • High absorbent regeneration (*i.e.*, CO_2 desorption) energy • Solvent losses caused by volatility or thermal/chemical degradation, the subsequent equipment corrosion & negative environmental impacts of solvent emissions • High sensitivity to flue gas temperature, pressure and presence of impurities, such as NO_x, SO_x and oxygen (*i.e.*, oxidative degradation)[270]
Adsorption[13,18,237–239]	CO_2(g) is adsorbed on solid materials and will be recovered through temperature, pressure or vacuum swing desorption	• When used for flue gas, pre-treatments to remove impurities, such as NO_x, SO_x and H_2O and to decrease gas temperature are needed • Possible loss in the adsorption capacity of the adsorbent after desorption step (*e.g.*, 4–9% loss for amine immobilized onto solid silica) • Sorbent degradation in cyclic operation
Membrane gas separation[13,240,241,244,246,271,272]	Process is driven by partial pressure difference of the gas molecules to be separated. Gas molecules permeate according to their size, diffusivity, or solubility through the membrane.	• Not feasible for streams with low CO_2 partial pressure and concentration • To accommodate the high flow rate of industrial flue gas, high membrane surface area is required • Sensitivity to presence of moisture (*i.e.*, lower selectivity) • On-going research on new membranes with high selectivity and permeability[273–275]
Calcium looping[13,248,276]	A variant of chemical looping (combustion) that involves carbonation and calcination. Metal oxides *e.g.*, CuO, Mn_2O_3, NiO, and Fe_2O_3 are used instead of O_2(g) in oxy-fuel combustion	• Rapid decrease in the limestone (*i.e.*, sorbent) capacity after a number of cycles of reaction with CO_2 • Environmental concerns caused by limestone mining, the waste from Ca-looping (*i.e.*, the spent CaO) and the need for high temperatures for the operation • Need for air separation unit to obtain pure O_2 for calcination

with thermal swing, pressure swing or vacuum swing for CO_2 desorption.

The conventional absorption and adsorption based captures can be combined with electrochemical methods to decrease (or eliminate) the required thermal energy for the regeneration step as discussed in Sections 4.1.3 and 4.2.1. No available work have been found on electrochemical enhancement of the other conventional methods.

4.1 Absorption (wet scrubbing)

CO_2 is a weak acid. Therefore, substrates that contain basic moieties such as amine groups (*e.g.*, alkanolamines) are efficient absorbents for CO_2 capture.[277] Amines are derivatives of ammonia (NH_3), containing a basic nitrogen atom, where one ($R–NH_2$) or more hydrogen atoms have been replaced by a substituent. Amines act as a nucleophiles (*i.e.*, electron pair donors also known as Lewis bases), reacting with CO_2 at the electrophilic (*i.e.*, electron pair acceptor) carbon center to form a carbamate (derivatives of carbamic acid H_2NCOOH where one or more hydrogens are replaced by other organic functional groups).[49,167,278] Although the amine capture processes are extensively studied, the reaction mechanism is not yet fully understood. For a detailed description see ref. 279.

The post-combustion CO_2 capture is dominated by amine-based absorption, using aqueous solutions of mono-, di-, tri-ethanolamine or hindered amines to absorb CO_2 in gas form.[232,278,280–283] Aqueous solutions are often used in order to control the density, viscosity, surface tension, and the thermal expansion coefficient of the pure amines.[284–286] This is while. the energy consumption for solvent regeneration decreases substantially with increasing the amine concentration (due to an improved CO_2 reaction rate and absorption capacity[287]). However, such high concentrations also increase the degradation rate, viscosity and the involved environmental concerns, posing challenges on the overall capture process.[285,287] In addition to aqueous solutions, both non- and low-aqueous solvents (*i.e.*, water–lean solvent) are viable.[284,288,289] These alternatives are not well studied yet although they have gained interests recently. All currently assessed water–lean solvents have shown lower CO_2 solubilities than aqueous monoethanolamine (MEA). However, because the heat of absorption is not much affected, solvents with the lower volatility than water could potentially offer opportunities for processes with overall less reboiler heat duties than that of ordinary aqueous MEA.[284]

Amines have been used for CO_2 capture since 1930.[278] Monoethanolamine (MEA) scrubbing technology is seen as a benchmark technology for CO_2 capture from flue gas of large-scale power plants.[187,190,290,291] In this method, $CO_2(g)$ is chemically absorbed at low temperatures ($\sim$40 to 60 °C) in the absorbent and is extracted in a desorber column later, generally *via* a temperature swing at high temperatures ($\sim$120 °C), where the absorbent is also regenerated.[186,292] The energy consumption of CO_2 capture (from flue gas) *via* aqueous monoethanolamine (MEA) thermal swing is between $\sim$170–300 kJ mol^{-1} CO_2.[184–190]

To address the drawbacks discussed in Table 4, for CO_2 capture *via* chemical absorption, other inorganic solvents, such as aqueous potassium and sodium carbonate,[167] ammonia solution and alkali hydroxide solution have been investigated.[293,294] When using alkaline or carbonate based solution, hydration of CO_2 takes place rather than carbamate formation.[167] However, CO_2 absorption in carbonate is very slow compared to that of amines.[270] Increasing the absorbent pH (*i.e.*, applying a wide range pH-swing), can enhance the kinetics substantially.

4.1.1 pH-swing *vs.* thermal swing. All available large-scale CO_2 capture processes rely on heating or using a combination of heat and vacuum to release the captured CO_2.[27,294] Given the initial focus was to capture CO_2 from flue gas of fossil fuel power stations, heat integration is relatively straightforward. However, as an alternative to this thermal swing, an (electrochemical) pH-swing approach can be applied for CO_2 recovery and absorbent regeneration.[3]

In a thermal swing absorption process, the energy performance is dominated by (1) absorbent absorption capacity, (2) absorption rate, (3) heat of absorption and (4) thermal degradation.[270] The required thermal energy is often exacerbated due to use of aqueous solutions in which the capturing agent is contained (*e.g.*, water for the case of MEA[270]).[49] Furthermore, the required heat is normally generated from combustion of fossil fuels, decreasing the net captured CO_2 in the conventional processes.[108]

Alternatively a pH-swing can be used, to absorb and desorb CO_2. The cost of absorbent regeneration through pH-swing *via* BPMED in wet scrubbing (using KOH absorbent) is estimated to be $\sim$773 \$ per tonne CO_2. That is more than three times of the cost of the thermal swing rival. However, the cost can significantly decrease if the cost of renewable energy decreases (*e.g.*, from 0.06 to 0.018 \$ per kW h), cost of membrane decreases (to lower than 100 \$ m^{-2}), membrane life time increases from around 3 years[295] to 15 years and the process is optimized.[3]

4.1.2 Physical absorption. The advantage of the physical absorption to chemical absorption explained above is its lower heat consumption in the solvent regeneration step.[21,22] Solvents, such as methanol, poly(ethylene glycol) and dimethyl ether can be used to absorb $CO_2(g)$ physically. Recently, ionic liquids have been proposed as alternatives to the conventional absorption solvents.[296–298] Ionic liquids are molten salts that exist as liquids near room temperature, often composed of an organic cation with an inorganic or organic anion and featuring polar properties.[25] Ionic liquids are referred to as green solvents due to their low volatility, exceptional thermal stability, non-flammability and environmentally benign character.[299] The capture using ionic liquids is often based on physisorption although some ionic liquids react with CO_2 in a chemisorption mechanism.[22]

4.1.3 Electrochemical enhancement of amine based absorption. Electrochemical methods provide alternative routes to the conventional thermal regeneration step in absorption based capture. Such electrochemical enhancements are shown feasible through (1) pre-concentrating the CO_2 rich amine stream, (2) substituting CO_2 with suitable metallic species or (3) pH-swing. These three routes are explained below.

For pre-concentrating the CO_2 rich amine stream, a capacitive deionization unit (CDI) can be used. Inside the CDI cell, when current is applied, ionic species (*i.e.*, $MEAH^+$ and $MEACOO^-$ in case of monoethanolamine absorption) are adsorbed at the electrodes, creating an ion-free solution (mainly water[270]) that can be sent back to the absorber column without the need to undergo the thermal desorption step. Subsequently, when power is switched off or reversed, the adsorbed ions will be released back from the porous electrodes, creating a carbon rich stream that can then be sent to the stripper column. When applying thermal regeneration, the concentrated solution from the CDI unit then requires 50% lower solvent regeneration heat energy because of its high CO_2 loading.[300]

As an alternative approach, the conventional temperature swing step in the amine absorption process can be replaced by metal ion substitution in an electrochemical cell.[29,30,301] Such a cell consists of multiple anode and cathode chambers made of copper. At the anode, Cu^{2+} reacts with the amines, displacing the CO_2 as shown in Fig. 15. CO_2 is subsequently removed in flash tanks after the anode chambers and the amines are regenerated by subsequent reduction of the Cu^{2+} to Cu in the cathodes. The process allows for higher CO_2 desorption pressures, smaller absorber columns and lower energy demands.

There are few works available on using a pH-swing to regenerate amine based absorbents; The early work of Zabolotskii *et al.* shows the feasibility of a low-temperature BPMED for regeneration of aqueous monoethanolamine (MEA) sorbent.[303] Huang *et al.* demonstrated a pH-swing for amine based absorbents, doing so electrochemically (for flue gas desulfurization)[304] and Feng *et al.* by simply adding a (weak) acid to the rich amine stream (for CO_2 capture).[236] Such addition of acid is reported to have the potential to increase the volume of the released CO_2 and to decrease the absorbent regeneration heat energy. Both contributing to a higher energy efficiency.[236]

4.2 Adsorption

CO_2 can be adsorbed on solid porous materials, where CO_2(g) is subsequently recovered and the adsorbent is regenerated through a temperature, pressure,[305] vacuum[306–315] or electric swing desorption.[316] Previous work has shown CO_2 adsorption on metal–organic frameworks (MOF's), silica, zeolites, immobilized amine, alumina, polymeric resins, molecular sieves and activated carbon. Adsorption is possible through both physical (*e.g.*, on zeolite, graphene, MOF's, silica) and chemical (*e.g.*, amine and calcium based materials) bonding with CO_2.

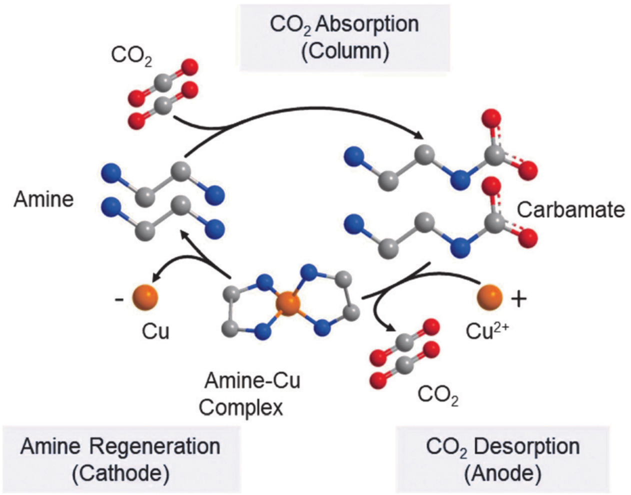


Fig. 15 Electrochemically-mediated amine regeneration (EMAR) using copper. Reprinted from ref. 302, Copyright (2019), with permission from Elsevier. The conventional thermal swing is replaced with an electrochemical step. In addition to Cu/Cu^{2+}, many possible chemistries can be utilized in such separation processes as discussed further in ref. 29, 30 and 301.

An advantage of adsorption based capture is that using solid adsorbents (instead of the mature aqueous monoethanolamine (MEA) technology) in capturing systems reduce the regeneration heat (due to the much lower heat capacity of solid adsorbents and the avoidance of water evaporation in the regenerator).[187] The (calculated) regeneration heat for polyethyleneimine (PEI)/silica adsorbent based capture is reported to be around 2.46 GJ per tonne CO_2, which is much lower than the value of 3.3–3.9 GJ per tonne CO_2 for a typical aqueous MEA system.[187] In general, adsorption also has higher CO_2 adsorption capacity compared to that of absorption *e.g.*, *ca.* 88–176 kg CO_2 per kg adsorbent[305] *vs.* 0.4–1.2 kg CO_2 per kg absorbent.[18,269,317]

4.2.1 Electrochemical enhancement of adsorption.

Similar to absorbents, the CO_2 capture and recovery of recent adsorbents has been assessed *via* electrochemical swings instead of the conventional pressure or temperature swings.[39,318] As an example, the redox active carriers described in Section 3.3 can be employed as solid adsorbents, immobilized on surface of electrodes. Such electro-swing systems normally operate in charge/discharge cycles where changing the cell polarity regulates the activation and deactivation of the carrier.[39] The significant advantage of the electro-swing process with respect to pressure swing adsorption (PSA) and temperature swing adsorption (TSA) is that the CO_2 capacity of these solid adsorbents does not depend on the feed concentration, making them suitable for CO_2 capture even from very dilute streams.[39] Moreover, up-scaling is easily achievable in electro-swing adsorption by using multiple anode and cathode chambers repeating within one cell.

Alternative to the electrochemical electro swing approach described above and in ref. 39, the electrochemical process can induce a temperature swing. In that case, a low voltage passes through a conductor to change the sorbent temperature *via* Joule heating (*i.e.*, resistance turning electric energy into heat).[318–322]

5 CO_2 utilization

After CO_2 is captured, it can be stored or utilized, see Fig. 16. CO_2 is an inexpensive, non-toxic, renewable commodity.[323,324] The market for CO_2 use is projected to grow from 0.23 gigatonnes (Gt) per year today to 7 Gt per year by 2030.[325]

In addition to fuels, chemicals such as ethylene, alcohols, formic acid (or formate), syngas, urea and other organic materials can be produced from CO_2, electrochemically, thermo-chemically or by other approaches.[323,329–337] Such organic chemicals are often more expensive than fuels and may offer advantages in the techno-economic analysis. However, the global demand for them are much lower than fuels as shown in Fig. 17.

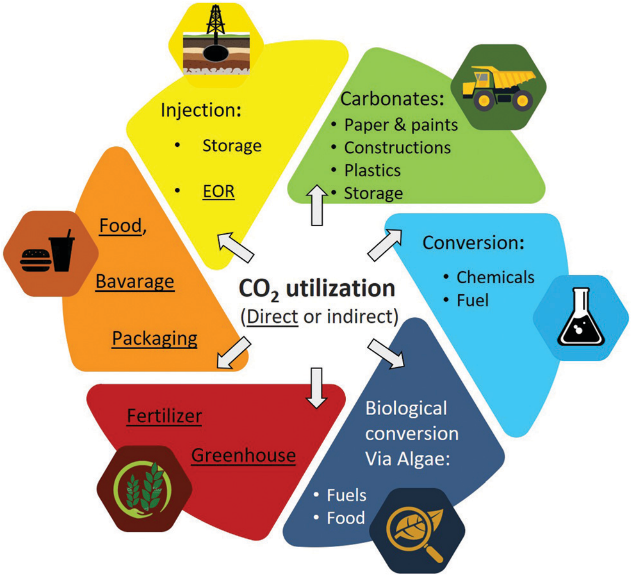


Fig. 16 Schematic of direct and indirect (*i.e.*, *via* conversion) utilization of CO_2. Alternative to gaseous CO_2, carbonate minerals (*e.g.*, $CaCO_3$) can be utilized[326] in paper industry, coating, plastics,[327] paints, adhesive/sealants, rubber, cement and construction materials.[328]

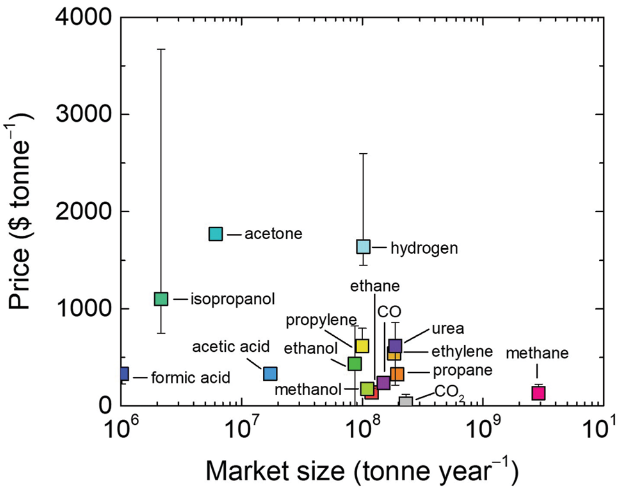


Fig. 17 Average price of CO_2 utilization products as a function of their market size. Error bars indicate anomalies in some regions (see the ESI,† Table S1 for values). CO_2 and H_2 are included for reference.

For instance, the global demand for one of the largest chemical markets, ethylene, is 184 Mt per year.[338] Ethylene manufacture also stands as the prime contributor for CO_2 emissions among carbon-based chemicals, with a CO_2 emissions rate of 184.3–213 Mt in 2015, which could reach 1.34 Gt per year by 2030.[339]

Production of synthetic hydrocarbon fuels and chemicals often requires high purity CO_2 feeds. Many CO_2 capture facilities using centralized sources simultaneously capture sulfur containing compounds, such as hydrogen sulfide (H_2S) that must be removed upstream to avoid catalyst poisoning.[340] The process of desulfurization typically involves liquid phase oxidation to promote H_2S oxidation to sulfur, followed by sulfur separation from the gas stream.[341] Chemical adsorption using high surface area ZnO-based adsorbents may be used in sequence to further eliminate H_2S prior to pipeline transmission.[342,343] Alternatively, CO_2 conversion can take place *via* biocatalytic routes with both natural and engineered microorganisms[344,345] that generally have higher tolerance for impurities.[346] CO_2 capture from dilute sources, such as from air and seawater, usually contains non-negligible amount of O_2 and N_2.[28,45] While N_2 is an inert gas and may not negatively impact the CO_2 conversion, a trace amount of O_2 may lower the catalytic turnover through the unwanted reaction with hydrogen in the thermochemical process,[347] or through the preferential reaction of oxygen reduction in the electrochemical process.[45] Strategies for O_2 removal from CO_2 stream include catalytic oxidation of hydrogen[348] or methane[349] on noble metal catalysts such as Pt or Pd,[350] chemical adsorption of O_2 on Cu surfaces at elevated temperatures,[348] and electrochemical reduction of O_2 on Ag catalysts.[45]

A pressurized CO_2(aq) stream is beneficial for a subsequent CO_2 conversion step. In a CO_2 electrolyser for methanol production, when the produced CO_2 remains dissolved due to an applied pressure, the avoided typical gas regeneration step and CO(g) compression step save more than 150 kJ mol^{-1} CO_2.[46] High pressure electrolyser (up to 40 bar) is also reported to increase the current efficiency of CO_2 reduction to formic acid/formate.[351,352] Moreover, a high pressure CO_2(g) is required for the transportation in the pipes, enhanced oil recovery or geological CO_2 sequestration for underground injection. Supercritical CO_2 (above its critical temperature 31.0 °C and pressure 72.8 atm) with its low density and viscosity plays a significant role in the extraction of oil.[353–355] Furthermore, supercritical CO_2 can be used in the enhanced geothermal system for heat exchange.[247,356]

The electrochemical CO_2 conversion lacks studies that demonstrate the capability of the technology at scales large enough for industrial implementation.[357] As an alternative, CO_2 can be converted biologically to organic carbon in plants or microalgae, through photosynthesis, resulting in various products, such as biofuel or animal feed.[358,359]

Gaseous CO_2 can be stored (*i.e.*, sequestrated) in deep geological layers or in the ocean.[19,360–362] In 2019, from the 19 in operation large-scale carbon capture & storage (CCS) facilities, 33.2 Mt per year of CO_2 were captured and stored[363] (*i.e.*, less than 0.1% of the total global emissions).[364] By addition of the already in constructions facilities, this value is estimated to be doubled, within the coming years. Most of this storage is done through enhanced oil recovery (EOR) application (*i.e.*, over 260 Mt of anthropogenic CO_2 by 2019).[363]

As an alternative to sequestration of gaseous CO_2, CO_2(g) can first be converted to bicarbonate ion and, subsequently, be stored as already abundant forms of ocean alkalinity, through electrogeochemistry.[71,75,78,112]

There are social concerns associated with the gas sequestration including fear of CO_2 leakages, lack of suitable locations, required site monitoring, unknown impacts on living organisms and limitations involved with CO_2 transportation and injection to storage sites. Alternatively, solid (carbonates) storage can be used. Such mineral carbonate sequestration is permanent, safe, has a large worldwide storage capacity and is less subject to social opposition.[328,365,366]

6 Conclusions

Electrochemical CO_2 capture methods are undergoing a renaissance as their applications expand due to their higher energy efficiency, flexibility and sustainability compared to the conventional approaches. Electrochemical CO_2 capture is classified into four categories; (1) methods that apply a pH-swing to capture and recover the CO_2, (2) methods that rely on the binding affinity of CO_2 molecules to redox-active species, (3) molten carbonate cells and (4) hybrid electrochemical processes that combine CO_2 capture and *e.g.*, direct conversion. Among the electrochemical capture methods, pH-swing based approaches, leveraging the carbonate equilibrium, are most widely studied, due to their straightforward operation and the absence of toxic or expensive chemicals. In theory, a mild pH-swing over *ca.* 2–3 pH units would allow to capture $>98\%$ of the CO_2. However, in practice, to improve the slow kinetics associated with such a mild swing, either a wider pH range (*ca.* 5–6 pH units) or catalytic enzymes (*e.g.*, carbonic anhydrase) need to be applied.

An electrochemical pH-swing is induced *via* electrolysis, bipolar membrane electrodialysis (BPMED), redox active molecules that undergo proton coupled electron transfer (PCET) or capacitive deionization. Among all, electrolysis is the earliest method (used for alkaline absorbent regeneration), but is still rather energy intensive due to the intrinsic irreversibility of the gas evolution redox reactions. However, the produced $H_2(g)$ (through water electrolysis) can be used to offset the total energy consumption. Capture *via* PCET active agents enable high current efficiencies, but are at the moment limited by slow electrode kinetics, low solubility of PCET organics and the sensitivity of the process to impurities in the flue gas such as O_2, water and sulfur. Using (membrane) capacitive deionization (MCDI) enables capture with an electrical energy consumption as low as 40 kJ mol^{-1} using only deionized water. However, (M)CDI capture is so far only applied at very low current densities, is still in the very early stage of the lab-scale research (TRL of 3) and its large scale applications await more performance studies. All electrochemical capture methods can be used easily as plug-and-play units. Among the four technology for electrochemical pH-swing, BPMED has the advantage of keeping a small footprint upon up scaling. At present, the cost of using BPMED for CO_2 desorption and alkaline (re)generation in alkaline wet scrubbing is estimated to be 2–3 times more than the conventional thermal swing desorption rival. However, the cost can significantly decrease if improvements in the cost of renewable energies and ion exchange membranes, membrane life time and their permselectivity and resistivity are achieved.

Despite of the successful lab-scale demonstrations, both CO_2 capture *via* electrolysis and BPMED have achieved TRL of 5–6 and are not yet commercialized. This is while, the conventional post-combustion CO_2 capture methods, such as absorption, adsorption, membrane separation and chemical looping have found their way to industrial applications. As opposed to the electrochemical captures, conventional methods are mainly designed to capture CO_2 from centralized emitters such as fossil fueled power plants. These methods have a larger footprint and are not geared for efficient decentralised emitted CO_2. However, in the last decade, to benefit from the high efficiency and selectivity of the electrochemical processes, conventional methods are also promoted to be combined with electrochemical process. Substituting the temperature or pressure swings with an electrochemical swing in an amine based absorption capture is shown to halve the energy consumption of the CO_2 desorption step while decreasing the footprint of the unit. The framework established in this paper can be the basis for future studies on the energetics of electrochemical CO_2 capture processes, not only for flue gas separations, but also for a range of other applications, such as seawater CO_2 capture and direct air capture.

Conflicts of interest

There are no conflicts to declare.

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