

**Direct Ocean Capture: The Emergence of Electrochemical Processes for Oceanic Carbon Removal**

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Broader Context Statement

In the context of increasing concerns over climate change and the urgent need for effective mitigation strategies, emerging electrochemical direct ocean capture (eDOC) offers an attractive approach as a negative emissions technology (NET) that could help address this global challenge. As the first comprehensive review of its kind, this paper highlights the potential of eDOC in oceanic carbon removal and emphasizes the rapid advancements in electrochemical processes that make this technology a promising candidate for large-scale deployment. By examining various eDOC approaches, discussing their limitations, and suggesting potential improvements, valuable information is provided for researchers, policymakers, and industry stakeholders working on climate change mitigation strategies. Furthermore, the need for further research to enhance system efficiency, address design bottlenecks, and reduce overall costs is emphasized. As such, this paper serves as both a catalyst for future research in the field of oceanic carbon removal and as a guide for the broader research community and industries seeking to develop and implement innovative carbon capture solutions. Ultimately, the successful realization of eDOC as an economically viable and environmentally sustainable NET will have far-reaching consequences in the global fight against climate change.

Direct Ocean Capture: The Emergence of Electrochemical Processes for Oceanic Carbon Removal

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Abstract

The urgent need for effective climate change mitigation has spurred exploration of various negative emissions technologies (NETs). Here, we investigate recent advancements and challenges in electrochemical direct ocean capture (eDOC) of carbon dioxide (CO₂), a promising NET for oceanic carbon removal. We analyze different eDOC strategies, focusing on pH swing as the primary mechanism for ocean dissolved inorganic carbon removal, and examines techno-economic challenges, such as achieving industrially preferred current densities and reducing overall costs. Early designs have relied on bipolar membrane electrodialysis, while recent developments have eliminated the need for membranes entirely. We compare different approaches, highlighting the limitations of current eDOC systems. Our study provides insights into the optimization of eDOC systems, suggesting further research is needed to improve system efficiency and address design bottlenecks for large scale deployment. Ultimately, these advancements will play a crucial role in realizing the full potential of eDOC as an economically viable and environmentally sustainable NET for mitigating climate change.

Keywords: Climate change, Carbon removal, Direct ocean capture, Electrochemical methods

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1. Climate Change Mitigation and the Need for Carbon Removal

Global average temperatures have risen by 1°C (1.8°F) since pre-industrial times [1]. Experts have unanimously attributed this change to be mainly driven by the anthropogenic emission of carbon dioxide (CO₂) into the atmosphere. Further warming to 2°C could potentially result in an array of catastrophic and irreversible damage to our planet. The Intergovernmental Panel on Climate Change (IPCC) reported that we have about 420, 770, and 1270 gigatons of CO₂ (GtCO₂) left in the emissions budget as of 2020 to limit global warming to 1.5, 1.7, and 2.0°C, respectively, at 50% likelihood [2, 3]. For perspective, the total global emission in 2021 was a little over 36 GtCO₂ [4]. Despite international efforts to fulfill the commitments laid out in the historic Paris Agreement in 2015, global CO₂ emissions still rose by 4.1% from 2015 to 2021 [2]. Researchers estimate that with the current trajectory, the 1.5°C and 2°C-scenario budget will be surpassed in less than 10 and 25 years, respectively if things remain unchanged [4].

1.1. Technological Mitigation Options

The need for carbon dioxide removal has never been direr. It has since been emphasized by the IPCC in their sixth assessment report in 2022 that CO₂ removal is essential in meeting our emission targets [5]. There are three broad climate change mitigation approaches being considered: (1) decarbonization technologies, (2) negative emissions technologies (NETs), and (3) alteration of the earth's radiation balance [6]. For this paper, the third option will not be discussed as these technologies are still currently theoretical and are not considered within any existing policy frameworks [7, 8]. Decarbonization technologies have been our first line of defense because it includes mitigation strategies that are focused on reducing our direct input of carbon dioxide into the atmosphere. This includes shifting to more renewable sources of energy and decarbonization of fossil fuel energy [9-11]. However, attempts have, so far, been proven insufficient in decreasing our overall global footprint. Despite the efforts of many countries to invest in green energy sources, more efficient industries, and decarbonization, global net CO₂ emissions are still rising.

At the core of decarbonization technology is carbon capture and storage (CCS), which involves the separation of CO₂ from a gas mixture from large single sources such as fossil-fueled power plants and other CO₂-emitting industrial operations (such as cement) and its subsequent storage (e.g., underground sequestration) [12-16]. Despite the maturity of the technology, global-scale CCS has not been sufficient at curtailing global carbon emissions as was expected decades before [17, 18]. One speculated reason for the slow deployment of CCS is the increasing pressure to shift toward renewable sources of energy, diminishing the demand and political support for CCS [18]. Following the roadmap laid out by the International Energy Agency (IEA) in 2009, over 40 CCS projects were proposed since then up until 2021, but only half came to fruition [19]. Although there is no doubt that CCS will play an important role in the march to reach net zero by 2050, the fact remains that its potential is limited to emissions from point sources which account for only 58% of total annual emissions [5]. With the rapidly dwindling CO₂ budget, capturing legacy carbon dioxide is expected to be a crucial component of the strategy to reach our carbon emission goals [3, 20-23].

1.2. Negative Emission Technologies (NETs)

Negative emission technologies (NETs) are carbon capture and removal methods that are designed to remove the carbon dioxide already in the atmosphere [21, 24]. As a response to decarbonization approaches falling short of reaching our earlier emissions goals, NETs have been pushed into the center stage as an essential tool in our climate mitigation toolset. In every global warming mitigation scenario laid out by the IPCC assessment reports, NETs were highlighted to be necessary [3, 25, 26]. Between 100 and 1,000 GtCO₂ will have to be removed from the atmosphere by the end of the century to limit warming below 1.5°C [3]. Of all the NETs, bioenergy with carbon capture and storage (BECCS), direct air capture (DAC), and afforestation and reforestation (AR) are reported to currently have the greatest potential in terms of annual CO₂ removal at 12, 10, and 6 GtCO₂ per year, respectively [24, 27]. Currently, BECCS and DAC remove 0.002 and 0.00001 GtCO₂ per year, respectively [28, 29]. From an economic standpoint, in order for NETs to be a competitive and practical option, the cost will have to be reduced to less than \$100 per tCO₂ by 2050 [27, 30-32]. Currently, the cost of BECCS and DAC reported in the literature range from \$15 to \$400, and \$60 to \$2,770 per tCO₂, respectively [31-45]. To put these costs into perspective, existing and mature decarbonization options such as shifting to photovoltaics (PV) and wind power cost between \$25 and \$29 per tCO₂ avoided, respectively.

In order to meet the target of limiting global warming to within 2°C by 2100, substantial efforts are necessary to enhance the world's capacity for negative emissions. Projections indicate that

negative emissions must reach at least 0.7 GtCO₂ annually by 2030, 13.8 GtCO₂ by 2070, and 20 GtCO₂ by 2100 (Figure 1A) [46]. While DAC, BECCS, AR are promising methods for negative emissions, relying exclusively on these approaches would prove challenging in our pursuit of climate change mitigation goals. DAC stands out for its higher cumulative carbon removal potential compared to AR, with a smaller environmental footprint. It can be constructed and operated at full capacity within a relatively short time frame. On the other hand, AR takes years to achieve maximum sequestration rates and has limited permanence, while BECCS faces challenges related to the availability of sustainable biomass. Although AR offers benefits such as lower costs and positive environmental effects, it competes with bioenergy and food production for land use. Both AR and BECCS have significant land and water footprints [47, 48], potentially causing environmental and societal harm by disrupting natural ecosystems and displacing agricultural land. BECCS, for instance, requires 41 hectares of land to capture 1 MtCO₂ per year when using dedicated high-productivity energy crops assuming a land intensity of 24.4 tCO₂ ha⁻¹ y⁻¹ [48]. If we were to rely solely on BECCS, we would need to dedicate additional land the size of Brazil. For AR, it will be double that size.

In contrast, DAC has a much smaller land footprint and can be deployed anywhere, operated continuously, and designed for efficient CO₂ retention [27, 28, 49]. However, it does face challenges, with cost being a primary concern that hinders widespread deployment. The high cost of DAC is primarily attributed to the energy-intensive sorbent regeneration and CO₂ concentration steps following CO₂ sorption. In some DAC system designs, the process requires significant amounts of water during regeneration and concentration, further adding to its operational limitations [50, 51]. Currently, there are only 18 operational DAC facilities worldwide, with a total capacity of 0.00001 GtCO₂ per year. To meet the required negative emissions targets, DAC will need to be significantly scaled up.

According to the Net Zero Emissions scenario outlined by the IEA, DAC's annual capacity must reach 90 MtCO₂ by 2030 and 985 MtCO₂ by 2050 [52]. Assuming a linear increase in capacity, the estimated annual capacities of DAC by 2070 and 2100 would be 1.9 GtCO₂ and 3.2 GtCO₂, respectively. The fractions of the projected DAC capacity at the end of each decade relative to the needed negative emissions in the 2°C scenario is illustrated in Figure 1. Furthermore, achieving these targets comes with substantial economic challenges. Considering a commonly assumed learning curve of 10% for DAC [36] and a capture cost of \$300 tCO₂⁻¹ in 2030, the projected cumulative cost of capturing the required CO₂ by 2100 in the 2°C scenario would be equivalent to the projected GDP of Belgium in 2100 [53, 54]. [Based on these projections, the average cost of DAC per decade is estimated to be \\$70 billion, equivalent to the GDP of Bulgaria](#)

in 2020. Though these costs may appear minuscule in comparison to world GDP, they represent substantial financial commitments in the context of climate mitigation efforts.

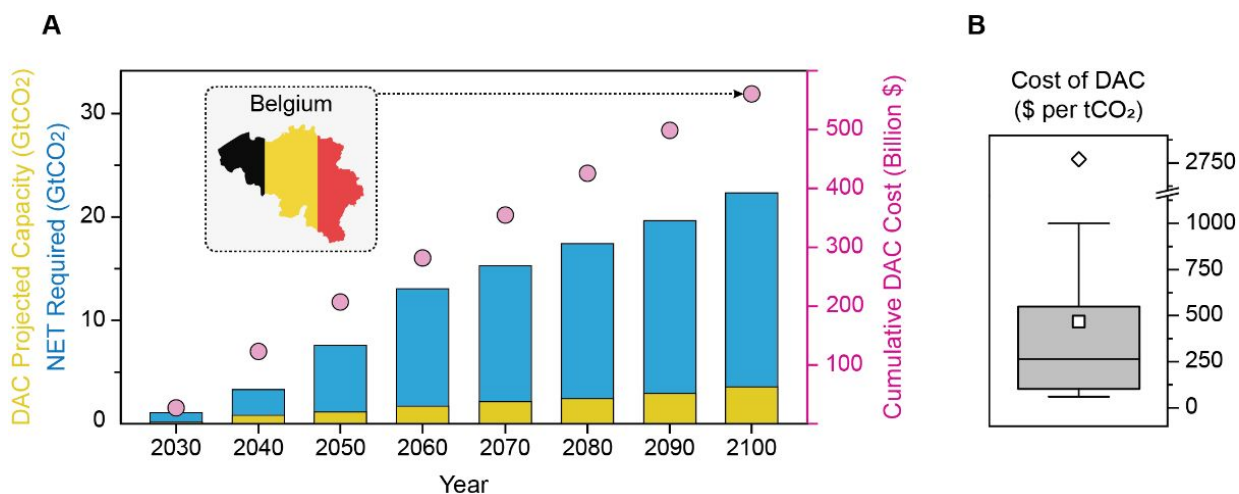


Figure 1. Projected Capacities and Costs of DAC for Achieving Negative Emissions Targets. (A)

This figure shows the required annual NET capacities at the end of each decade to stay in line with the 2°C warming scenario by 2100. Here, the predicted capacity of DAC at the end of each decade [36] (shown as yellow bars) is contrasted with the target annual NET capacities under the 2°C warming scenario (shown as blue bars). Additionally, shown here is the predicted cumulative cost of DAC based on its projected capacity at the end of each decade. It is estimated that at the end of the century, the total cumulative cost would be equivalent to the projected GDP of Belgium in 2100 [53, 54]. (B) Based on values for the cost of capture using DAC per ton of CO₂ reported in the literature [31-45], the mean DAC cost is approximately \$467 per ton of CO₂, represented by the square. Most of the values reported fall below \$500 per tCO₂, with the median at about \$250 per tCO₂ (represented by the horizontal line). An outlier exists at \$2,770 per tCO₂, which represents an experimental technology that utilizes nanoparticles [45].

This underscores the need for exploring and implementing a diverse range of mitigation strategies and technologies to effectively address climate change. While existing NETs like DAC and BECCS show promise, relying solely on them presents challenges that necessitate a diversified portfolio and exploration of additional avenues. One such avenue that holds immense potential is the ocean, which serves as a major carbon sink with a remarkable storage capacity and a higher concentration of CO₂ compared to the atmosphere. This makes the ocean a compelling target for carbon capture. With CO₂ concentrations approximately 140 times higher (in mass per volume) than in the atmosphere [55, 56], the ocean plays a significant role in regulating carbon. Its immense potential has gained momentum, making it a prime focus for

advancing negative emissions technologies. As the largest carbon sink on Earth, the ocean presents promising opportunities that have yet to be fully realized. This paper aims to thoroughly examine the technological options for harnessing the ocean's capacity for negative emissions. It will assess their potentials and challenges, shedding light on the untapped opportunities for carbon capture from the ocean. By delving into these advancements, we can better understand how to leverage the ocean's vast potential and enhance our efforts to mitigate climate change.

2. Ocean-Based Options to Supplement Climate Change Mitigation

In our efforts to address climate change, it is crucial to recognize that the atmosphere is not the sole repository for the carbon dioxide generated on Earth. There exists a complex network of carbon sinks that play a role in maintaining the balance of CO₂ in the air and other media. Carbon, being a fundamental element for life, undergoes continuous cycling among the various systems that comprise our planet. This global carbon cycle encompasses not only the land and its diverse ecosystems but also extends to the air and the vast expanses of the ocean [57]. While the land, through both biotic and abiotic processes, absorbs an estimated 13.9 GtCO₂ annually, it is the ocean that stands as one of the largest carbon sinks. With a staggering carbon storage capacity of approximately 37,300 GtC, the ocean surpasses the atmosphere by a factor of 50 and absorbs an equivalent of about 7.3 GtCO₂ each year [57]. To complement our climate change mitigation efforts, it is essential to explore and harness the potential of ocean-based options. While much attention has been given to land and air as avenues for NETs, the ocean, with its immense capacity, has been relatively overlooked. Fortunately, there have been significant strides in this area, with dedicated companies founded to explore and develop ocean-based carbon capture solutions (discussed more in Section 4.2). By leveraging the vast potential of the ocean as a carbon sink, we can supplement existing NETs and further enhance our climate change mitigation efforts. The following sections will delve into the mechanism, potentials, and challenges associated with ocean-based options.

2.1. Oceanic Carbon Cycle

The ocean plays a crucial role in the global carbon cycle, much like terrestrial ecosystems. Within the ocean, CO₂ is essential for supporting marine life, driving primary productivity, and maintaining the balance of carbon. In fact, approximately half of the Earth's total primary productivity occurs in the oceans [58]. Marine algae, similar to plants on land, are key primary producers that use photosynthesis to convert CO₂ into biomass. They form the foundation of the marine food chain, with CO₂ being recycled through respiration and returned to the atmosphere.

However, the ocean also acts as a carbon sink through a process known as the marine biological pump. When marine organisms reach the end of their life cycles, organic matter is either recycled back into the food chain or sinks to the deep ocean layers, where it is stored as sediments [59]. This process, in combination with the exchange of CO₂ between the atmosphere and the ocean, forms the central mechanism of the oceanic carbon cycle, a vital component of the global carbon cycle. Annually, the ocean absorbs approximately 80 GtC (equivalent to 290 GtCO₂), maintaining an equilibrium between atmospheric and dissolved CO₂ [60]. The active uptake of dissolved CO₂ by photoautotrophic organisms in the surface ocean layer, along with the marine biological pump, leads to a net influx of CO₂ into the ocean from the atmosphere, estimated to be around 7.3 ± 2.2 GtCO₂ per year. This complex exchange is depicted in Figure 2, which illustrates the different sources and sinks for CO₂ in the atmosphere in GtCO₂ y⁻¹, including the contribution from volcanism, rock weathering, land fluxes, and anthropogenic activities.

Recent estimates suggest that the ocean CO₂ sink has reached approximately 10.6 GtCO₂ per year since 2021 and has been increasing since the early 21st century [2]. Since the industrial era, the ocean has absorbed about 25% of the CO₂ produced from the burning of fossil fuels [61, 62]. This absorption is evident in the stable carbon isotope composition of carbon in the ocean, with the ratio between ¹³C and ¹²C decreasing over time, indicating an increase in fossil fuel-derived CO₂ that lacks ¹³C [63]. The ocean's surface layer accumulates approximately 147 GtCO₂ per year, a significant portion of which is consumed by marine biota. Over time, this marine biomass descends into the intermediate and deep sea layers, transitioning about 7.3 GtCO₂ per year into dissolved organic carbon [64]. Overall, there is a net annual accumulation of 6.6 GtCO₂ within the intermediate and deep-sea layers. In the deep ocean, approximately 0.7 GtCO₂ is permanently sequestered each year.

The ocean's natural capacity to sequester CO₂ presents an opportunity to develop ocean-based NETs that can enhance its potential for absorbing more CO₂ from the atmosphere. These approaches can also help restore the ocean's alkalinity, mitigating the adverse effects of increasing ocean acidity [65]. Although various processes have been explored and researched [66-68], to date, none have achieved the same level of technological maturity as other well-established NETs like DAC [69]. In the pursuit of effective climate change mitigation, it is essential to further investigate and develop ocean-based NETs. By leveraging the ocean's natural carbon sequestration abilities, we can unlock its untapped potential for capturing and storing CO₂. The subsequent sections of this paper will delve into the exploration of these technologies, examining their possibilities and challenges in harnessing the ocean's capacity for negative emissions.

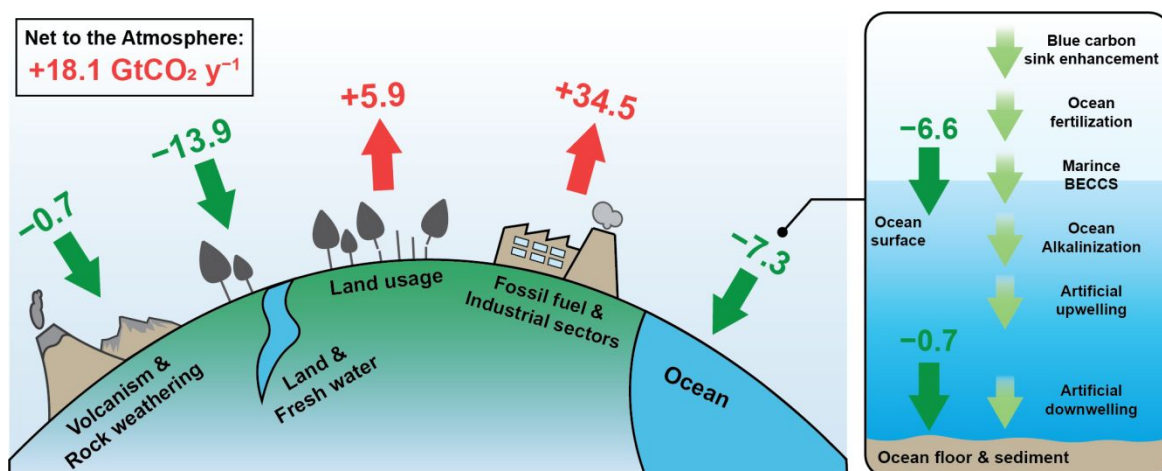


Figure 2. The Ocean Carbon Cycle. The concentration of CO₂ in the atmosphere is contributed by multiple factors. This figure shows the different sources and sinks for CO₂ in the atmosphere in GtCO₂ y⁻¹. Volcanism and rock weathering fixate around 0.7 GtCO₂ y⁻¹. The net natural influx from land including contributions from freshwater is about 13.9 GtCO₂ y⁻¹. The net anthropogenic outflux caused by land use change, i.e., deforestation, is approximately 5.9 GtCO₂ y⁻¹. Fossil fuel and industrial sectors contribute about 34.5 GtCO₂ y⁻¹. The ocean absorbs around 7.3 GtCO₂ y⁻¹, of which 0.7 GtCO₂ is eventually stored in the deep ocean permanently. Overall, the net influx of CO₂ into the atmosphere is 18.1 GtCO₂ y⁻¹. The underlying data was adopted from the IPCC AR6 report. Shown on the right side are the ocean-based NET illustrating how each of them can potentially contribute to negative emissions.

2.2. Ocean-based NETs

Recent advancements have brought attention to ocean-based NETs, which harness the natural CO₂ absorption capacity of ocean systems. Alongside established land-based NETs like BECCS and DAC [65], innovative solutions in the field of ocean-based NETs have emerged as viable addition to our climate change mitigation portfolio. These technologies have gained recognition through extensive research and implementation in various contexts. While land-based NETs have advantages and drawbacks, such as land requirements and costs, ongoing research and exploration focus on developing ocean-based NETs as viable alternatives. In recent years, significant progress has been made in several ocean-based NET technologies, leading to successful commercialization by various start-up companies which are discussed further in Section 4.2.

Broadly speaking, the technologies described here can be classified into biological and non-biological. Biological methods take advantage of the life forms that thrive in the ocean environments, such as coastal vegetation and marine primary producers that uptake dissolved CO₂ in the surface ocean for growth, as discussed previously. Under this category would be marine BECCS, artificial upwelling, blue carbon sink enhancement, and ocean fertilization. These

technologies achieve negative emissions by supporting the growth of these CO₂-fixating organisms, thereby increasing the ocean's net CO₂ uptake. Non-biological methods, on the other hand, attempt to alter the chemistry and hydrodynamics of the ocean itself, specifically the CO₂-water equilibrium, in order to increase its capacity to absorb more CO₂ from the atmosphere. This includes artificial downwelling and ocean alkalization. The technologies are discussed briefly in the following sections.

Marine BECCS. Of all the NETs to date, BECCS is considered the most mature, reported to capture 2 MtCO₂ per year globally [29, 70] which is about 200 times greater than the overall global capacity of DAC. As the name suggests, marine BECCS utilizes marine biomass as feedstock to produce biofuel. In a similar manner as in conventional BECCS, negative emission is achieved by the utilization of marine biomass, particularly algae, as feed to produce biofuels for energy generation with subsequent capture and storage. The utilization of biomass, particularly micro- and macroalgae, as alternative energy sources have been continuously researched and developed for decades [71-75]. Microalgae, also known as phytoplankton, are microorganisms that inhabit much of the surface ocean layer and are considered the base of the marine food web. Macroalgae, on the other hand, are multicellular forms of algae and are often plant-like. These biomass sources can subsequently be converted into energy by anaerobic digestion, fermentation, transesterification, thermochemical liquefaction, and pyrolysis to produce biogas, bioethanol, biodiesel, or bio-oils [76-81]. To the authors' knowledge, studies involving BECCS have exclusively utilized terrestrial biomass sources and marine biomass has yet to be developed.

Artificial Upwelling and Downwelling. In artificial upwelling, the growth of surface ocean phytoplankton is enhanced by upwelling nutrients from the nutrient-rich deeper layers of the ocean. Beyond negative emissions, artificial upwelling is also a means to replenish fish stocks in response to declining fish populations due to overfishing [82]. Although existing experimental data on the efficacy of artificial upwelling on aquatic ecosystems have shown improvement in primary production, the research is still considered limited in order to assess if this technique is practical in achieving negative emissions in the gigaton levels economically [83-86]. Artificial downwelling, as the name would suggest, works opposite to that of upwelling. In the marine carbon cycle, the CO₂ fixed by surface ocean organisms is eventually transported into the deep ocean as organic debris (e.g., dead cells, excrement). Hence, there is a net uptake of carbon that is permanently stored in the deep ocean. Artificial downwelling attempts to accelerate this natural process by pumping surface ocean waters that are rich in sequestered carbon into the deep ocean for

permanent storage [87, 88]. Research on this technique, however, is largely lacking and currently almost purely conceptual.

Blue Carbon Sink Enhancement. Blue carbon is a term for organic carbon fixated by marine and coastal ecosystems, primarily by mangrove forests, tidal marshes, and seagrass meadows [89, 90]. In addition to fixating carbon, these ecosystems are also environmental hubs for biodiversity. Estimates of the current combined sequestration capacity of blue carbon ecosystems (BCEs) report between 0.5 and 1.8 GtCO₂ per year, accounting for 1 – 5% of anthropogenic emissions [91]. Studies show that an additional 0.62 – 1.1 GtCO₂ can be sequestered by BCEs per year upon extensive restoration of these ecosystems worldwide, an extra 1.7 – 3% of the annual CO₂ emissions avoided [90]. The Blue Carbon Initiative was launched by the International Oceanographic Commission of UNESCO, Conservation International, and the International Union for Conservation of Nature as an international platform on which to promote the preservation and restoration of BCEs to mitigate the effects of climate change [92]. Due to the nature of this approach, actions are taken at the national level. In the International Partnership for Blue Carbon launched at the UN Framework Convention on Climate Change COP21 in 2015, there are only 54 partner countries that officially recognize its importance [93]. Despite international efforts, there have been limited concrete national policies implemented in these countries that specifically support BCE strategies.

Ocean Fertilization. Like terrestrial plants, phytoplankton growth requires sunlight and nutrients. Early studies of marine ecology and biogeochemical cycles have shown that the iron deficiency of the ocean significantly limits phytoplankton growth [94]. Iron enrichment experiments have indisputably confirmed that this iron deficiency limits about one-third of the ocean's overall productivity [95]. Similar in concept to artificial upwelling, ocean fertilization attempts to increase CO₂ uptake by phytoplankton by artificially supplying iron from an external source. However, some have questioned the ethics of such methods that involve the artificial introduction of substances for the purposes of remediating pollution of another substance [96].

Ocean Alkalinization. Ocean alkalinization achieves negative emissions by facilitating the absorption of more CO₂ into the ocean by increasing its alkalinity [97]. The natural uptake of CO₂ by the ocean is an acidic process, i.e., the reaction between CO₂ and water generates H⁺ ions, hence reducing its natural alkalinity. Therefore, in theory, artificially increasing the alkalinity of the surface ocean will increase its capacity to absorb more CO₂. Early proposals involve the

introduction of alkaline minerals, such as olivine and calcium carbonate, across the surface ocean to increase the pH, thereby increasing the solubility of CO₂ in the ocean [98]. This effect occurs due to the pH dependence of the carbonate buffer system in the ocean. More recent proposals have called for alkalization via electrolysis [99] to achieve the same result. However, studies have thus far been limited to laboratory-scale experiments.

Figure 3 shows a plot of the number of publications related to ocean alkalization, as an example, based on data from the Web of Science since the 1990s. While research output on the topic has steadily increased, the focus has been largely on marine biology, oceanography, and environmental science, with limited attention given to ocean chemistry in relation to climate change mitigation applications. This trend, however, is expected considering that the ocean is inherently tied to these themes. Although it is not shown here, similar trends are observed for other ocean-based NETs. One other ocean-based approach has gained attention in recent years with the potential to compete with more mature NETs in performance and cost. This technology is analogous to DAC in that it directly captures the dissolved CO₂ in the ocean and its derivatives. The following section discusses these technologies.

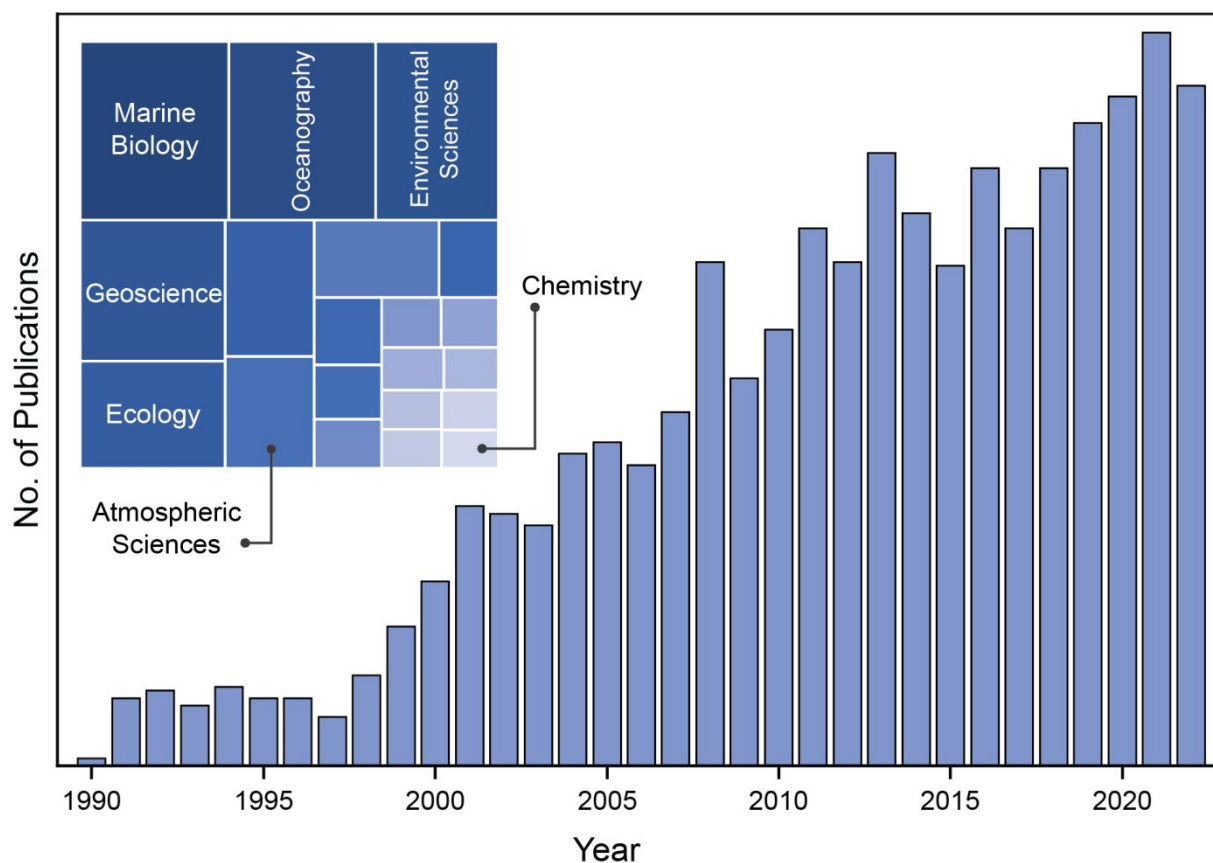
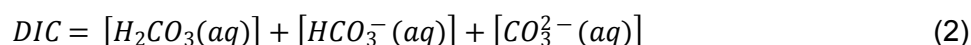
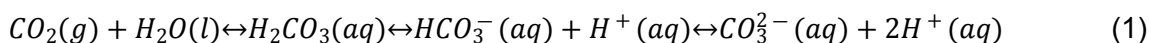


Figure 3. Trends in Ocean-based NETs Research with Ocean Alkalinization as Model. Depicted here is a sample trend in the number of publications related to ocean alkalization since the 1990s, using data gathered from the Web of Science. While the amount of research on this topic has increased over time, it has mainly focused on marine biology, oceanography, and environmental science, with little emphasis on ocean chemistry in relation to climate change mitigation applications.

3. Direct Ocean Capture: An Alternative Ocean-Based NET

Direct ocean capture (DOC) is an emerging NET that has gained increasing attention over the past few years. DOC relies on the natural tendency of CO₂ gas in the air to react with water in the ocean to form carbonic acid (H₂CO₃), which further dissociates into bicarbonates (HCO₃⁻) and carbonates (CO₃²⁻) (Eqn. 1). These technologies apply non-biological methods to increase the ocean's capacity to absorb more CO₂ from the atmosphere by directly removing the dissolved inorganic carbon (DIC) (i.e., carbonic acid, bicarbonates, and carbonates; Eqn. 2) from seawater. Reducing the total DIC concentration in the surface ocean drives the reaction forward, consequently allowing the ocean to dissolve more CO₂. The general principle is analogous to that of DAC in that there is an intake of CO₂-containing media to separate the CO₂ and subsequently discharge the CO₂-depleted stream back into the environment. Hence, discharging the CO₂-depleted seawater is an important step in the overall process to achieve negative emissions.



In conventional CCS and DAC, CO₂ in the gas streams is either physically or chemically sorbed using liquid or solid phase sorbents, commonly amine-based solvents. These methods subsequently require a thermal or chemical desorption step to separate and concentrate the sorbed CO₂ [100, 101]. The main hurdles of these methods are the slow kinetics of the sorption step and the high energy cost of the desorption [102]. Generally, the cost related to sorbents, particularly their lifetime, factors considerably to its limitations [34]. DOC, on the other hand, capitalizes on the fact that the ocean naturally performs the CO₂ absorption step from the atmosphere, thereby only necessitating a desorption step. This is potentially significant considering that the sorption step typically counts for 20–30% of the overall cost in conventional CO₂ capture [103, 104]. Generally, the DIC is extracted from seawater either as gaseous CO₂ or mineral carbonates. In methods that gasify the CO₂, acidification of the seawater is a requisite to shift the equilibrium from dissolved bicarbonates to CO₂. On the other hand, mineralization of the

DIC requires increasing the pH to shift the equilibrium to more carbonates that can precipitate in the presence of cations such as calcium (Ca^{2+}) and magnesium (Mg^{2+}) in seawater. At the core of both methods is controlling the speciation of the DIC, which is dependent on the pH.

In theory, an optimum pH range to achieve DIC removal for either method can be calculated given the composition of seawater. In the case of DIC precipitation, the precipitate species can also be predicted. To explore this, we developed a rigorous thermodynamic framework based on the speciation of the DIC in seawater in a preliminary study. In this model, four types of equilibrium reactions were included, namely gas-liquid, acid-base, complexation, and precipitation reactions. Figure 4A represents a comprehensive diagram of the thermodynamic model speciation of the simulated solution. The equilibrium and precipitation constants at 25 °C were taken from the Visual MINTEQ software, a comprehensive chemical equilibrium database. The model was written in Python and solved using the SciPy package. Figure 4B summarizes the relative concentrations of the ionic species present in the simulated ocean water which was used as the input into the thermodynamic model.

Based on the simulated concentrations of DIC species across the entire pH range shown in Figure 4C, DIC is completely removed from the aqueous phase at pH values lower than 4 and higher than 10. This means that for the acidification process, starting from typical seawater pH of 8, 100% of the DIC converts to dissolved CO_2 at pH 4. On the other hand, complete carbonate precipitation is predicted to be achieved at pH 10, predominantly in the forms of $\text{CaMg}(\text{CO}_3)_2$ (dolomite) and $\text{Mg}_2\text{CO}_3(\text{OH})_2$ (artinite). Interestingly, this contradicts previous literature that assumed the precipitation of CaCO_3 at this pH range [105-107] when in fact precipitation of CaCO_3 is only achievable if calcium is the only metal available in the solution. In the case that CaCO_3 precipitation is desired, the seawater will have to be treated to remove the competing metals, i.e., Mg^{2+} , from the solution prior to the mineralization process. This further highlights the importance of establishing a theoretical framework whenever possible to avoid erroneous oversimplifications.

The pH sensitivity of the speciation of DIC in water presents a wide pathway to develop processes to reduce its concentration in seawater thereby replenishing its capacity to absorb more CO_2 . Ocean alkalinization, as described earlier, achieves negative emissions in a similar mechanism. However, a more powerful alternative approach has recently emerged that involves the use of electrochemical techniques to achieve pH control. The effectiveness of these methods hinges on their capability to more precisely manipulate the thermodynamic equilibrium between DIC and CO_2 due to pH dependence of the associated reactions. This stands in contrast to thermally driven methods, which operate on a fundamentally different mechanism, relying on the

formation of carbamates from CO₂ via absorption. The following section describes the most recent developments in these technologies.

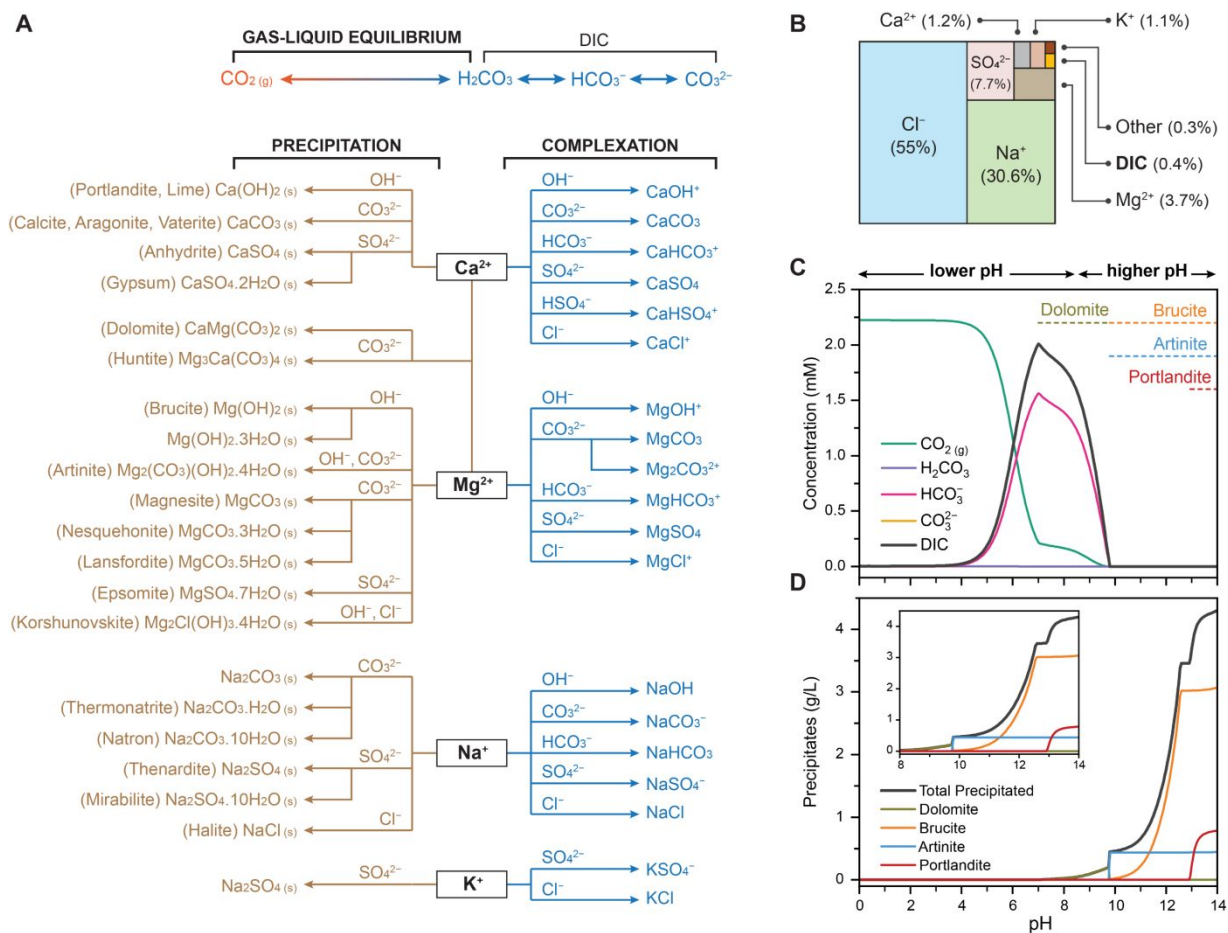


Figure 4. Complete Thermodynamic Analysis of DIC Speciation and Removal. For an aqueous solution reflecting typical ocean water concentrations, a rigorous thermodynamic framework based on speciation analysis was developed. (A) The thermodynamic model was developed to predict the speciation of DIC in the presence of the major ions present in seawater as a function of pH. There are four types of equilibrium reactions that are included in the model, gas-liquid, acid-base, complexation, and precipitation. Ocean-atmosphere CO₂ equilibrium is shown on the upper left. (B) The relative proportions of each major ion in seawater are shown. (C) As seen here, the DIC concentration and the relative proportions of each DIC species is a function of pH. (D) At higher pH, precipitation is predicted, beginning at pH 8. It is clearly shown that a variety of carbonate and hydroxide precipitates are possible. Dolomite (CaMg(CO₃)₂) precipitation dominates until pH 9.7, beyond which precipitation is dominated by artinite (Mg₂CO₃(OH)₂) and brucite (Mg(OH)₂).

4. Electrochemical Processes for Direct Ocean Capture

Electrochemically mediated methods for ocean-based NETs utilize reduction and oxidation (redox) reactions to control the pH of seawater to achieve DIC removal. Electrochemical carbon capture methods have been recently researched, particularly for conventional point source CCS. These approaches have increasingly gained traction over recent years due, in part, to their operability at ambient temperatures and capability to be entirely powered by renewable energy. Although conventional thermal processes can generate steam from renewable sources, such as geothermal energy or resistive Joule heating from renewable electricity, electrochemical systems may offer advantages in certain contexts. Mature carbon capture technologies that rely on physical or chemical means of absorption of CO₂ employ thermal or pressure-swing processes to facilitate the release of the absorbed CO₂ from the sorbents (desorption), which can be energy-intensive and costly to scale [108]. In contrast, electrochemically facilitated carbon capture methods utilize redox reactions to concentrate CO₂ from CO₂-rich sources for eventual permanent storage [109]. This means that these processes only require electricity which can be solely from renewable sources and avoid the need for additive chemicals such as amine absorbents and alkali. This gives them a substantial advantage over conventional systems because it allows them to be more easily retrofitted into existing facilities without major disruptions due to being entirely electrically driven. This benefit is especially valuable for facilities that are already in full operation, as it avoids the downtime associated with remodifying the facility for thermal processes that require additional infrastructure to generate substantial amounts of steam or other sources of heat. For the same reason, electrochemical systems also benefit from being more modular in nature, i.e., capable of being scaled by running units in parallel, owing to the relative flexibility in their design and simplicity of their operation [110]. While the entirely electrically driven operation of these systems does not inherently give them an advantage over conventional thermal systems, the integration of electrochemical systems with specific renewable energy sources, the adaptability to different contexts, and ongoing technological advancements may enable optimizations that yield environmental and operational benefits.

While not suggesting a definitive superiority over conventional systems, the unique attributes of electrochemical systems—including being entirely electrically driven, offering more modular implementation possibilities, and operating at lower temperatures [110]—highlight their potential value. In certain scenarios, these characteristics may align well with operational needs and sustainability objectives, making them an appealing option to explore. These systems, while promising, are not without their complexities and may require careful consideration to fully realize

their potential. This subject will be explored in more detail in sections 4 and 5. As a complementary approach, the value of electrochemical systems lie in their ability to integrate with existing technologies, enhancing the broader toolkit for carbon capture and reduction. This nuanced approach to understanding electrochemical systems does not present them as a universal solution but emphasizes their specific applications where they may offer distinctive advantages. As the field continues to evolve, a well-rounded perspective that acknowledges both the potentials and challenges will be essential in guiding future research and technological development.

Electrochemical CO₂ separation methods can be grouped into four broad classes according to the mechanism that drives the separation of CO₂: (1) electrochemical generation of nucleophiles [111-113], (2) electrochemical modulation of proton concentration [114-118], (3) electrochemical capacitive absorption [119-121], and (4) electrochemically mediated amine regeneration (EMAR) [110, 122-125]. To the authors' knowledge, research on the application of electrochemical techniques to DOC, hereafter referred to as eDOC, has thus far been limited to electrochemical modulation of proton concentration methods, also known as 'pH swing'. The likely reasons for this are to avoid pollution of marine systems and practicality. By process of elimination, electrochemical generation of nucleophiles and EMAR are inapplicable for eDOC because these methods involve contacting the carbon-rich stream (in this case, seawater) with amines and other additives [124], which are foreign substances that are potentially environmentally polluting. Electrochemical capacitive absorption techniques, on one hand, function based on the electrostatic attraction of bicarbonate ions to separate the DIC from the bulk solution. This can be less efficient considering that seawater contains several other charged species at much higher concentrations than the DIC, namely chloride ions (Figure 4B). In concentrating the carbonates and bicarbonates at the diffuse layer, an additional concentration step will have to be devised, potentially making this system architecture less efficient and impractical.

On the other hand, pH swing methods rely solely on the transport of protons to or from the CO₂-rich solution to achieve separation. This is achieved in two ways. Transferring protons into seawater immediately shifts the equilibrium to generate more aqueous carbonic acid (H₂CO₃) that readily reacts with H₂O to form CO₂ [126]. Doing the reverse, i.e., increasing the pH, increases the proportion of carbonate ions in the solution until oversaturation, causing spontaneous precipitation of mineral carbonates [127]. The pH is controlled by the controlled reduction and oxidation of a proton-coupled electrochemical reaction. One such reaction could have a general form of $X + ne^- + nH^+ \rightarrow XH_n$ [117]. In this case, when the solution is in the anode chamber where proton ions are introduced to the solution, the equilibrium between the DIC species shifts to

increase the concentration of dissolved carbonic acid (H_2CO_3) that can easily evolve into CO_2 gas. Conversely, when the solution is in the cathode chamber where protons are consumed (hence, the solution pH increases), the equilibrium will shift to generate more CO_3^{2-} , which can be precipitated if sufficient metal ions are present (e.g., Mg^{2+} , Ca^{2+}).

Most of the existing experimental literature on eDOC has thus far been based on the acidification route to produce CO_2 gas. These methods are attractive for the potential downstream applications of CO_2 gas such as on-site and on-demand fuel synthesis [128] or be directly routed to existing CO_2 storage facilities. On the other side of the spectrum, CO_2 desorption methods via precipitation have been explored counting on the benefit of immediately storing the carbon permanently *in situ* without further processing. Additionally, the mineral carbonate can be utilized as a carbon-negative alternative to calcium carbonate, an important raw material used in various industrial processes.

4.1. The Scope of eDOC

The application of electrochemical methods in DOC opens up a number of opportunities for ocean-based NETs. Electrochemical methods have the capability to efficiently control pH of seawater to optimal conditions for either CO_2 gas evolution at low pH, or carbonate mineralization at high pH conditions according to the mechanisms discussed in the previous section. A key advantage of electrochemical methods lies in their inherent adaptability. Being wholly electrically driven, they afford a diverse array of design possibilities, allowing for installation and operation across a range of scales and locations in proximity to the ocean. This broad applicability eliminates the need for additional infrastructure to generate heat or store additive chemicals, requirements that are typical in more conventional processes like thermal swing CCS. Thermal swing processes employ chemicals, such as amines, to selectively bind to CO_2 to achieve separation. Furthermore, these chemicals have been found to degrade over time when exposed to high temperatures, necessitating periodic replenishment [129]. On the other hand, eDOC leverages the pH-swing based mechanism, which is inherently easier to implement on seawater, making it a more sustainable and efficient solution for direct ocean capture.

Logistically speaking, eDOC can be located onshore, offshore, and on mobile platforms as illustrated in Figure 5. In an ideal scenario, these eDOC systems are continuous systems that take seawater and renewable electricity as input, and outputs alkalized seawater and concentrated CO_2 or mineral carbonates, depending on the system design. Onshore eDOC processes are designed to operate along the coastlines, benefitting from its proximity to both the

ocean and land. This grants easier access to existing CO₂ storage facilities and a broader mix of renewable energy sources. The CO₂ generated could also be utilized as raw material for alternative fuel production and chemical manufacturing. A comprehensive review of such processes is discussed in the literature [128, 130-132]. In contrast, offshore processes are facilities erected out in the open ocean where the captured gas could be routed to facilities that permanently store CO₂ in the seafloor, such as in saline aquifers or depleted oil and gas reservoirs [133]. Examples are oil platforms that are engaged in enhanced oil recovery (EOR) processes that use CO₂ to extract otherwise unrecoverable oil while simultaneously storing the CO₂ in deep subsurface rock. In contrast to onshore facilities, offshore operations are less spatially constrained owing to the expansiveness of the ocean. These facilities can also take advantage of renewable energy generated in off-shore wind farms. Mobile eDOC systems are designed to travel across the ocean to passively accumulate CO₂ or mineralizing carbonates. The concentrated CO₂ could be discharged at receiving ports for storage or utilization. It should be noted that in the cases where the CO₂ is utilized for EOR or CO₂ utilization for fuel production, the CO₂ generated upon the combustion of these fuels extracted or produced from these processes must be recaptured for storage or re-utilization in order to maintain a closed loop (Figure 5).

However, one significant cost consideration in eDOC systems is the pumping of seawater, which contributes to overall operational expenses. To mitigate these costs, early-stage development is likely to focus on co-locating with existing facilities that already have infrastructure to intake seawater. For onshore systems, desalination plants are perfect examples, which also benefit from the removal of scale-forming carbonates [134]. The implementation of eDOC systems at the Jubail Desalination Plant in Saudi Arabia, the world's largest desalination facility with a daily capacity of 1 million m³ of seawater [135], could potentially yield an annual CO₂ capture capacity of 0.04 MtCO₂, surpassing the current global capacity of DAC systems by fourfold. In the case of offshore operations, this could involve leveraging oil platforms engaged in EOR processes, benefitting from a consistent supply of CO₂ gas. For mobile systems, eDOC can be retrofitted onto seagoing vessels that already intake seawater for cooling and other purposes.

Despite the promise of electrochemically driven systems, eDOC still lags behind conventional systems and more mature NETs in costs and scale. Thus far, there has yet to be a large-scale facility incorporated with an eDOC system comparable in capacity to more mature technologies like point source CCS and DAC. Conventional thermal processes, for instance, have achieved a high level of technological maturity, demonstrating their extensive application at the necessary large scales for CCS processes. In contrast, electrochemical operations at comparable scales are

relatively limited, posing challenges in finding technologically mature examples that can serve as reference points for scaling up the eDOC process. Compared to conventional methods, reported eDOC prototypes still require significant amounts of electricity to drive the carbon capture and current prototypes operate at lower current densities, limiting the rate of CO₂ capture. Nevertheless, over the last decade, technological growth in this field has been gaining momentum, concurring with the increasing attention on NETs. The remainder of this paper examines the progression of the bench-scale eDOC systems and future perspectives of the technologies.

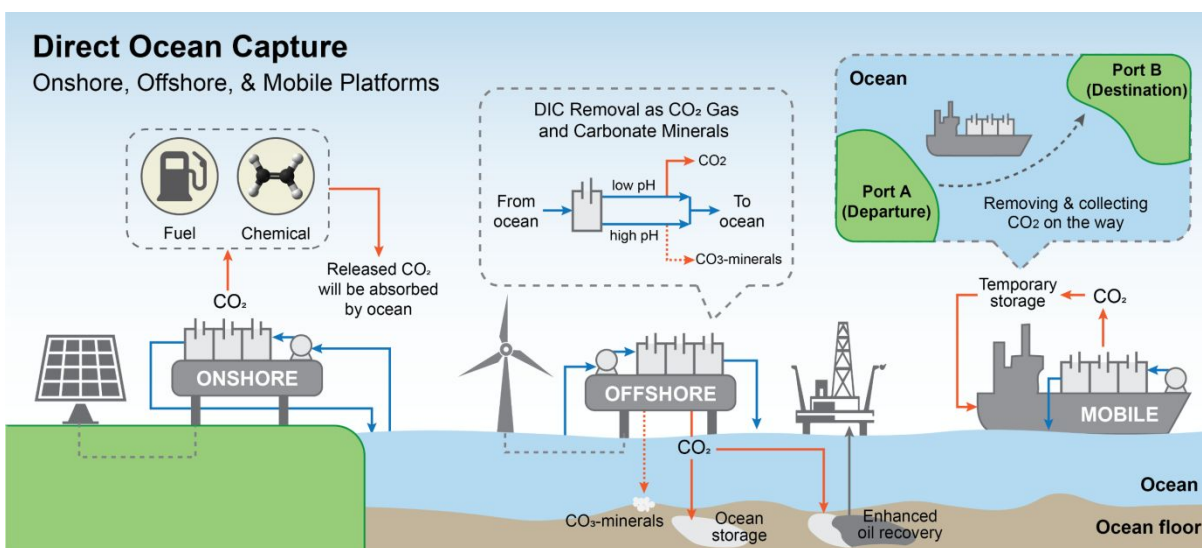


Figure 5. Direct Ocean Capture Domains. Illustrated here are the three domains to which eDOC can be applied. On-shore deployment could involve co-location with facilities that take in seawater as input, such as desalination plants and power plants. The CO₂ generated could also be potentially utilized as raw material for alternative fuel production and chemical manufacturing. Off-shore deployments involve co-location with off-shore platforms such as oil rigs and off-shore energy farms. The captured gas could also be routed to facilities that permanently store CO₂ in the subseafloor, such as in saline aquifers or depleted oil and gas reservoirs. Lastly, mobile deployment involves the installation of eDOC systems to seagoing vessels that can passively reduce marine DIC and deposit them at destination ports. Generally, these processes will involve the intake of seawater into an electrochemical process that removes DIC as CO₂ or mineral carbonates by strategically changing its pH.

4.2. Recent Advances in eDOC

As discussed in the previous section, CO₂ can be separated from aquatic systems by controlling the pH of the system to shift the equilibrium of the carbonates in the solution, yielding either CO₂ gas or carbonate minerals. Over the years, a number of electrochemical systems have been designed with this principle in mind that specifically uses seawater as feed for the purpose

of achieving DIC removal. This section endeavors to summarize the current literature on eDOC since 2010 grouped according to the general approach mentioned.

DIC Removal by CO₂ Gas Separation

The earliest published research work on CO₂ extraction primarily from seawater for the purpose of negative emissions utilized bipolar membrane electro dialysis (BPMED) systems as a means to generate protons to simultaneously acidify and basify two seawater streams (Figure 6A) [66]. Bipolar membranes (BPMs) are bilayers of cation and anion-exchange membranes that generate H⁺ and OH⁻ ions out of each respective membrane layer upon the application of a sufficient voltage [136]. Several studies have demonstrated their use in eDOC applications. The current study was an advancement from a previous system designed by the same group for CCS and DAC applications wherein gaseous CO₂ absorbed by an alkaline solvent as CO₃²⁻ and HCO₃⁻ [137]. To regenerate the solvent, the CO₂-rich stream was fed into a BMPED system consisting of alternating stacks of anion exchange membranes (AEM) and BPMs to separate the inorganic carbon anions through the AEMs upon the application of an electrical current. This approach was deemed impractical for DOC applications due to the excess quantity of Cl⁻ ions in seawater in comparison to anionic DIC. Hence in the more recent study, the BPMED system was redesigned such that H⁺ ions generated by the BPMs were transported into the CO₂-rich stream (in this case, seawater) instead to directly decrease its pH to achieve separation [66]. By acidifying the seawater, the carbonate equilibrium would shift such that the dominant form would be aqueous H₂CO₃ which readily decomposes to CO₂ gas and water. The CO₂ was stripped from the acidified seawater by passing it through a commercial membrane contactor system that consists of microporous hollow fiber membranes that selectively allow CO₂ to pass through by applying a vacuum inside the hollow fibers. The study demonstrated that the voltage requirement (proportional to the energy consumption rate at constant current density) was dependent on the final seawater pH and influent seawater flow rate. A minimum energy consumption rate of 1,528 kWh tCO₂⁻¹ at 3.1 liters per minute (lpm) of feed was achieved by adjusting the final pH to 5 at a CO₂ extraction efficiency of 59%. Further increasing the influent flow rate to 6 lpm at an end pH of 3.7 improved the extraction efficiency to 68%, which resulted in an 18% increase in energy consumption. However, the reported energy consumption rate reported solely includes the energetics of the electrochemical cell and does not account for energy requirements for pumping.

In a later publication, the same research group sought to estimate the overall cost of the system if scaled up accounting for pumping costs, and assessed which operating parameters are the most cost-sensitive using a techno-economic model [107]. The group created a prototype of

the seawater acidification system using BPMED to gather data to feed into the model. The efficiency of the prototype acid process was identical to the results from the earlier study. The estimation assumes co-location with an existing facility that takes seawater as input, such as a desalination plant to cut pre-treatment costs and minimize pumping costs. At an assumed extraction capacity of $20 \text{ kmol CO}_2 \text{ h}^{-1}$ based on the loading capacity of a medium-sized desalination plant, and a current density of $1,000 \text{ A m}^{-2}$, the overall energy consumption rate was estimated to be $3,131 \text{ kWh tCO}_2^{-1}$. Their analysis found that the BPMED system accounted for 80% of the overall energy consumption of the system. The high energy requirement contribution of the BPMED is likely due to the relatively high minimum voltage requirement of electrochemical water splitting. The researchers added that from their previous study, they found that between 25 and 30% of the total energy was consumed at the electrodes.

Further development of BPMED systems for eDOC via acidification improved upon the previous design that utilized water as both the electron donor and acceptor at the electrodes *via* oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), respectively [138]. Instead, the BPMED system used a reversible redox-couple reaction that has a lower theoretical reaction potential than OER and HER. The system design consisted of two inner chambers wherein synthetic seawater flowed through that are separated by a BPM, and two electrode chambers on each adjacent side separated by CEMs (Figure 6B). The reversible redox reaction between potassium ferrocyanide ($\text{K}_3\text{Fe}(\text{CN})_6$) and ferricyanide ($\text{K}_4\text{Fe}(\text{CN})_6$) facilitated the transport of electrons at each electrode (i.e., $\text{Fe}(\text{CN})_6^{3-} + \text{e}^- \rightarrow \text{Fe}(\text{CN})_6^{4-}$). During operation, H^+ ions produced by the BPMED accumulated in one of the seawater chambers and Na^+ ions migrate to the cathode chamber through the CEM dividing the two chambers. Meanwhile, OH^- from the BPMED and K^+ from the anode chamber accumulated in the opposite seawater chamber. Overall, the total operating voltage was minimized by utilizing ferro/ferricyanide redox-couple reaction instead of conventional HER and OER which required a higher thermodynamic voltage window. Additionally, the researchers computationally determined the optimum current density at the operating flow rate that minimized energy consumption and maximized the CO_2 removal rate. The system was reported to achieve 71% capture efficiency at an energy consumption rate of $980 \text{ kWh tCO}_2^{-1}$ at a current density of 33 A m^{-2} . The researchers, however, pointed out that in order to effectively restore the alkalinity of the effluent seawater stream (by increasing the pH to 10.6) before discharging back into the ocean, the concentrations of Mg^{2+} and Ca^{2+} present in excess will have to be reduced. This is due to the favorable formation of magnesium and calcium hydroxide precipitates upon the addition of OH^- , as indicated earlier by our developed model (Figure 4). The use of ferro/ferricyanide raises some concerns regarding the potential pollution of

the ocean upon the eventual discharge of the re-alkalinized stream. The study scope did not include the monitoring of residual ferricyanide and ferrocyanide in the effluent streams.

Conventionally, systems that utilize ion exchange (IX) membranes have been associated with higher capital and maintenance costs relative to their membrane-less counterparts [139, 140]. Since the end goal of this technological race is to reduce the overall cost of NETs, minimizing the use of membranes is desirable. The first tested design that eliminated the use of a BPM system achieved pH swing by generating protons from the electrocatalytic oxidation of hydrogen gas [141]. The system sought to reduce operating and capital costs by utilizing a working redox couple at the electrodes with a low theoretical voltage, and inexpensive electrode materials in addition to avoiding the use of BPMs. The working principle of the system was that H₂O in seawater is split to generate H₂ gas at the cathode, which would subsequently be transferred and utilized as the electron donor at the anode ($E^\circ = 0$ V) resulting in a theoretical cell voltage of 0.48 V. This system, which the authors called electrochemical hydrogen-looping (EHL), consisted of three chambers separated by two CEMs, with the outer chambers being the cathode and anode (Figure 6C). On one end is the cathode chamber where seawater is continuously pumped and water is split *via* HER to generate H₂ gas that would be used in the anode chamber. The protons generated from the hydrogen oxidation reaction migrate to the central chamber through a CEM where seawater is continuously pumped. Sodium ions from the middle chamber migrate through the CEM into the anode chamber to restore charge neutrality, thus closing the loop.

Using a platinum-on-carbon (Pt/C) catalyst coated on a carbon paper electrode, the study was reported to achieve a 91% CO₂ capture efficiency at an energy consumption rate of 660 kWh tCO₂⁻¹ and a current density of 80 A m⁻². The authors, however, noted that unwanted accumulation of ions crossed in the Pt catalyst at the anode could gradually degrade its efficiency. Additionally, the high pH conditions created by the generation of OH⁻ at the cathode from the HER allows for the precipitation of unwanted magnesium and calcium hydroxides that could gradually degrade the electrode performance. Furthermore, the system still relied on ion-selective membranes that could degrade over time and increase the cost. The presence of hydrogen gas as an important component to the functioning of the system could pose potential issues in the scale-up of this system. In particular, hydrogen gas is widely known to be a highly flammable gas and is prone to easily leak due to its small molecular size and lower density [142]. These concerns will need to be addressed in future studies.

One of the most recent developments in eDOC technology that sought to completely eliminate the use of membranes by utilizing active electrodes that undergo proton-coupled electron transfer

reactions (PCET) [114]. In this recent work, pH swing was achieved via reversible Faradaic reactions of one of the working electrodes that cyclically intercalate and de-intercalate protons from the seawater. This intercalating electrode system, henceforth referred to as intercalating electrodes system (IES), consisted of a two-step process involving two connected chambers with asymmetric electrochemical cells that used bismuth and silver electrodes (Figure 6D). In the intake chamber, the bismuth anode was oxidized in the presence of chloride and water to form bismuth oxychloride (BiOCl), generating two moles of H⁺ per mole of Bi (i.e., $\text{Bi} + \text{Cl}^- + \text{H}_2\text{O} \rightarrow \text{BiOCl} + 2\text{H}^+ + 3\text{e}^-$), resulting in a decreased pH. The overall charge was then balanced by the simultaneous reduction of the silver chloride (AgCl) cathode to silver metal (Ag) which generated chloride ions as a result (i.e., $\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$). Upon separation of the CO₂ gas from the acidified seawater, the decarbonated stream was sent to a secondary chamber which is the reacted version of the first chamber, i.e., the electrodes are BiOCl and Ag but with the polarity of the cell reversed. This step was necessary to restore the pH of the decarbonized seawater before discharging back to the ocean and, at the same time, regenerate the electrodes of this chamber to form Bi and AgCl in order for it to be used as the next intake chamber during the succeeding cycle. The operation of this system, therefore, required the switching of the intake flow of seawater between the two chambers and reversing the polarities of the electrodes at each cycle.

The researchers tested their prototype system for 10 cycles and reported no appreciable decrease in performance after each cycle. At a constant current density of 10 A m⁻², their system, on average, was able to remove 87% of the DIC at 92% relative Faradic efficiency (defined as the ratio between the observed and maximum charge utilization efficiency) and an energy consumption rate of 770 kWh tCO₂⁻¹. The researchers, however, report that the system suffers from Mg(OH)₂ scaling on the electrode surface due to the local high pH at the electrode in the second regeneration step. Additionally, silver was detected in the effluent streams indicating that deterioration of the electrode occurred. Although the system evaded the need for any membranes, this deterioration of the silver electrode is a point of concern, especially considering the cost of such materials. In the interest of avoiding metal pollution in the ocean, it is important that the electrodes used for these applications must be exceptionally stable.

DIC Removal by Carbonate Mineralization

On the opposite spectrum of the pH swing methods is carbonate mineralization, which is achieved by increasing the pH of the seawater in order to oversaturate carbonate salts, and eventually decreasing DIC. In all of the methods developed thus far involving acidification, CO₂

gas removal has been achieved by passing the acidified seawater through membrane contactors. These are devices that facilitate gas-liquid separation by controlling the pressure between the two sides of a microporous membrane in order to selectively allow the target gases to pass through. However, one techno-economic analysis on BPMED-based systems for eDOC applications established that the cost contribution of membrane contactors to the capital expenses was considered significant [134]. Additionally, the transport and storage of CO₂ gas can be challenging, and further processing is necessary if it is to be used as a raw material for downstream processes. Therefore, DIC as mineral carbonates has been considered an attractive alternative.

The first attempt at this method was done in parallel to an acidification system described earlier [107]. In the study, this approach was proposed as an alternative operation of the same system that involved swinging the pH of the seawater in the other direction, i.e., 'base process', to precipitate the DIC as mineral carbonates. This process followed the same concept as the 'acid process' but instead adds OH⁻ generated from the BPMED system into a seawater stream. The increase in pH causes the equilibrium to shift towards the dominance of CO₃²⁻ ions (as shown in Eqn. 1). Under the same assumptions, the energy consumption rate of the base process required to extract 20 kmol CO₂ h⁻¹ was estimated to be at 4,152 kWh tCO₂⁻¹. The study reported that the base process required more energy per CO₂ removed compared to the acid process because it required a higher molar quantity of OH⁻ to remove the same quantity of CO₂. This means that more energy was needed by the electro dialysis system to generate the required quantity of OH⁻ to reach the ideal pH for precipitating CaCO₃ (at pH 9.6). This is significant considering that the BPMED system accounted for 80% of the overall energy consumption of the system. The researchers, however, pointed out that although operating costs for the base process are expected to be higher, it benefits from not requiring a secondary downstream process, such as a membrane contactor, to effectively remove the carbon.

The most recent research work so far that uses a base process utilized a BPMED system consisting of stacks of CEM-BPM units to generate OH⁻ in the channel between the two membrane layers to increase the pH of the seawater stream flowing through it (Figure 6E) [127]. Prior to this research, methods of mineralizing DIC from seawater involved precipitating CaCO₃ externally to the BPMED system. This meant that higher pH gradients across the BPMED were needed, which require higher voltage. The novelty in their system was that precipitation was induced *in situ* that necessitated a milder pH gradient, just enough to reach the optimum seawater pH to precipitate CaCO₃ (9.6 – 9.8) which required only 0.32 V, which is much lower compared to 0.83 V for pH gradient of 14 [143]. Subsequently, instead of mixing the acidified and CO₂-depleted

alkalinized streams for neutralization, the study proposed direct discharge of the alkalinized stream to contribute to counteracting ocean acidification, while the acidified stream will be used for other industrial purposes. It reported a capture efficiency of 60% at an energy consumption rate of 2,008 kWh tCO₂⁻¹ at 50 A m⁻². However, there are concerns regarding Mg²⁺ and Ca²⁺ carbonate scaling in the more alkaline compartments. As such, the same research group recently explored fouling management strategies that can be applied to remedy this [144]. The study investigated different strategies to minimize fouling in BPMED systems employed to mineralize DIC in seawater. These measures involved testing different membrane configurations and exploring fouling removal methods. The study showed that cell voltage and pressure drop due to fouling increased with cell residence time and current density. Lower scaling tendency at lower residence times (higher flow velocities through the channels) was said to have been likely due to greater shear forces that mechanically removed the fouling particles that built up on the membranes. Higher current densities cause greater pH gradients (i.e., higher pH in the precipitation chamber) thereby increasing the precipitation of hydroxide minerals. In terms of configuration, it was observed that an AEM-BPM configuration resulted in the least pressure drop and voltage increase across the BPMED system caused by fouling compared to a CEM-BPM configuration. This was due to the higher flux of Ca²⁺ and Mg²⁺ through the CEMs creating regions of high saturation indices of carbonate and hydroxide minerals at the membrane surface. Among the fouling removal methods tested, such as sparging with air and CO₂, cleaning using dissolved CO₂ and acid, flow rate increase, and the application of back-pressure, the study concluded that acid washing was the best strategy.

Carbonate precipitation as a pathway for eDOC is a complex and currently poorly understood phenomenon that demands extensive theoretical and experimental study and validation. The intricacies of the interactions between different chemical species, especially in an electrochemical environment, have yet to be fully unraveled. A meticulous examination of the thermodynamics, focusing on the precipitation of magnesium and calcium as influenced by pH, uncovers a delicate variability in the forms of precipitation. Figure 4 illustrates that artinite and dolomite could be the preferred forms of carbonate precipitation in the presence of magnesium. However, the complexities of the system likely extend beyond this initial observation. For example, a preferential formation of artinite may result in a quicker depletion of magnesium, subsequently shifting the equilibrium toward calcium-magnesium salts. This change could have cascading effects that profoundly alter both the system's chemistry and dynamics. Additionally, concentration and pH gradients across the device, particularly near the electrode, may be more extreme than in the bulk, potentially influencing the precipitation substantially. Understanding these complex

dynamics requires a holistic, multi-dimensional approach encompassing modeling, simulation, and experimental validation on both thermodynamics and kinetics ends. These insights might then form the foundation for strategic guidelines to refine the design and function of eDOC systems, optimizing them to enhance carbon removal efficiency.

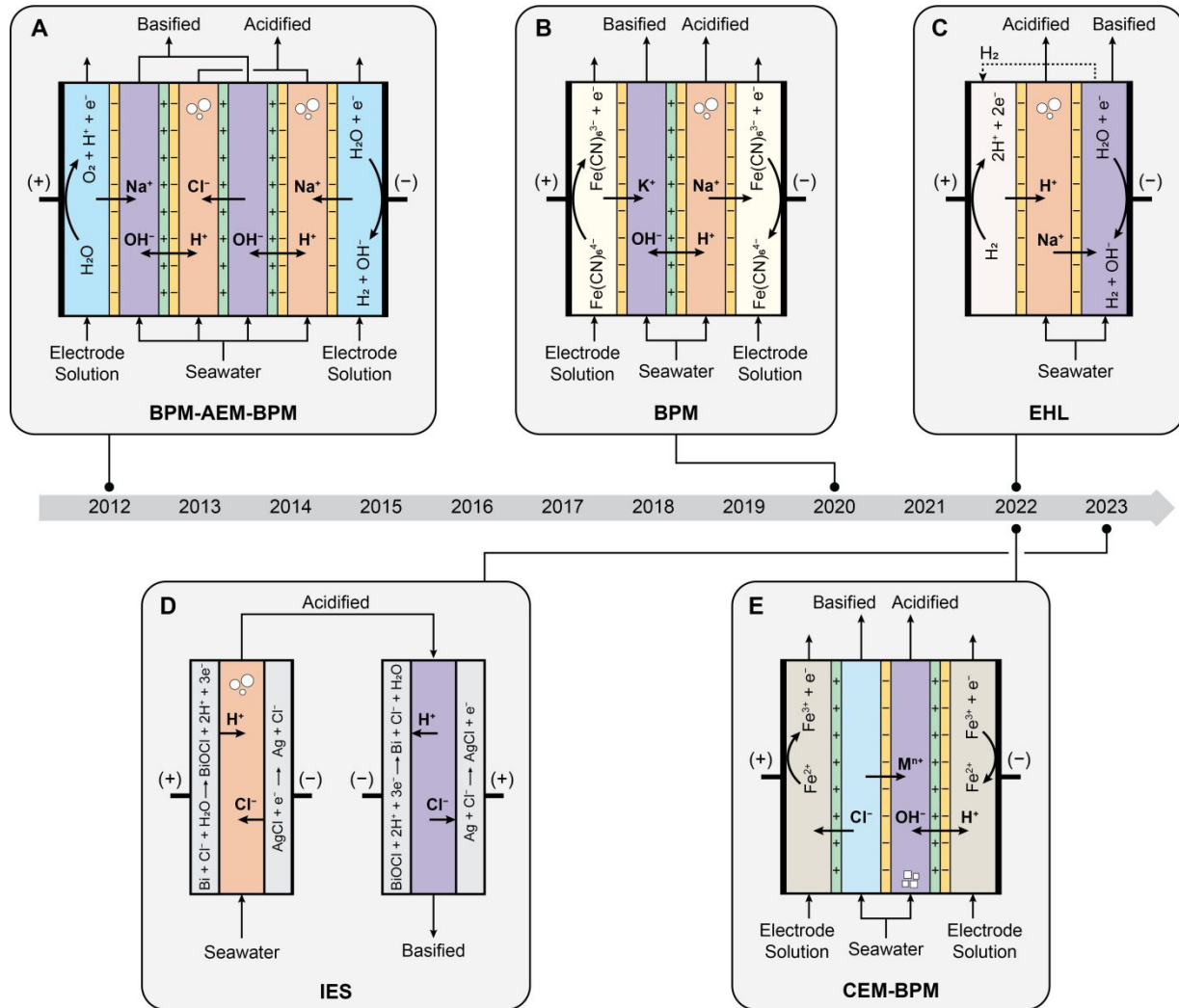


Figure 6. Evolution of eDOC Designs. Shown here is the timeline of the technological development of eDOCs reported in the current literature with each represented as simplified schematics. The first four (A-D) were designed to separate the DIC as CO₂ gas (acid process) while the last one (E) generates mineral carbonates (base process). (A) This is the earliest design published in 2012 that utilized BPMED systems to create acidified and basified chambers through which in the seawater was pumped. The unit cells were configured as BPM-AEM-BPM. (B) The next design published in 2020 employed a simple BPMED system consisting of a single stackable BPM unit between two CEMs. One of the novelties of this design was that the electrode solution contained ferro/ferricyanide which was done to reduce the

voltage contribution at the electrodes. (C) This system published in 2022 was the first design that did not feature a BPM but consisted of three chambers separated by two CEMs. The defining feature of this design is that hydrogen gas is generated at the cathode, which is then sent to the anode to be oxidized. This was done to reduce the voltage contribution at the electrodes. The system was named 'electrochemical hydrogen looping' or EHL by the authors. (D) This design was the first membraneless system introduced in 2023 which featured two sets of asymmetrical electrochemical cells in which the electrodes are active. The second cell is reverse version of the first cell (E) In 2022, a carbonate mineralization system was developed involving a cell with stackable units of CEM-BPM. One of the innovations of this system was that the electrolyte solution contained $\text{Fe}^{2+}/\text{Fe}^{3+}$ which was done to reduce the voltage contribution at the electrodes.

The scientific literature on eDOC has thus far focused predominantly on seawater acidification methods. However, interest in CO_2 mineralization approaches has been gaining attention as seen in the proposals for novel seawater alkalization technologies that have been put forward in the last few years. Actual experimental data using bench-scale prototypes of these models have yet to be put forward. One group acknowledged the benefits of eliminating the use of membranes and designed a flow-through membraneless electrolytic reactor using mesh electrodes configured as a rotary drum filter to precipitate carbonate minerals [145]. In their conceptual system, water is reduced at the mesh electrode surface to generate OH^- to oversaturate mineral carbonates in the solution. The precipitates are continuously separated by the action of the rotary drum filter when the crystal size exceeds the mesh pore size. The authors estimated that the energy consumption rate could fall anywhere between 800 and 1,200 kWh tCO_2^{-1} based on the efficiency of commercial electrolyzers and utilization of the H_2 gas byproduct for energy.

In another proposal, a combination of microbial and electrochemical CO_2 mineralization processes using BPMED [146] was conceptualized. The method aims to utilize autotrophic marine microorganisms to take advantage of two of their strategically beneficial attributes. One is their natural ability to feed on CO_2 as part of their metabolic processes. The second is their tendency to excrete anionic metabolites that create a local alkaline environment around the cell. To maximize their growth rates, the authors propose to cultivate or bioengineer acid-tolerant microalgae that can thrive in acidic environments where dissolved CO_2 is more abundant. This has in fact been achieved in a few studies [147, 148]. Acidified seawater generated by a BPMED system will be used to cultivate the acid-tolerant microalgae, which are then sent to a tank containing the generated alkali seawater to seed the CO_2 mineralization. However, scaling of photobioreactors relying on the growth of microalgae will be a significant challenge. To illustrate, the paper assumes that the rate of CaCO_3 precipitation will be half that of the productivity rate of the microalgae. To construct a $1\text{-MtCO}_2 \text{ y}^{-1}$ plant at the reported productivity rate of the proposed

cyanobacteria strain, the photobioreactor would need to be 47 million m³ in size based on a productivity of 0.263 g biomass L⁻¹ day⁻¹ [149].

The increasing interest in eDOC as a viable approach for achieving negative emissions has permeated not only academic research but also the commercial landscape. Prominent startups, such as Captura, SeaO2, Ebb Carbon, Equatic, and sHYp, have made significant strides in progressing the large-scale application of electrochemical methods for DOC [150-154]. These companies, some of which were started by the researchers that developed the prototypes described, employ electrochemical pH swing methods to facilitate either carbon dioxide gas evolution or carbonate mineralization. On the other hand, ventures like Phykos, Vesta, TROFX, Running Tide, and Seafields adopt innovative ocean-based interventions for carbon sequestration [155-159]. These advancements encompass various stages, ranging from the installation of pilot facilities and securing investments to planned deployments of systems capable of annually removing hundreds of tons of carbon dioxide. Some of these startups have ambitious goals to remove millions of metric tons of carbon competitively within the next decade, aligning with the increasing demand for NETs.

However, while significant progress has been made in eDOC technology and various startups are actively working toward commercialization, notable challenges still need to be addressed. Expensive and fouling-prone IX membranes present a significant challenge, as these can impact system efficiency and drive-up costs. The manufacturing process of high-selectivity, and high mechanical and chemical stability membranes remains to be complex and expensive. Consequently, these factors drive up the overall costs of majority of the current eDOC systems demonstrated, affecting their competitiveness with other NETs. On top of their cost, IX membranes are prone to fouling, which can severely impede the membrane's functionality. Fouling can occur due to a variety of factors, including contaminants in seawater or reaction byproducts. As fouling progresses, it forms a barrier to the electrochemical circuit, thereby decreasing the overall efficiency of the system. Moreover, cleaning or replacing fouled membranes incurs additional maintenance costs and results in system downtime, both of which negatively impact the operational viability and cost-effectiveness of membrane-based eDOC systems.

The requirements for high-cost electrode materials and the limitations imposed by low current densities presents an added complex barrier to effective carbon sequestration. The use of precious metals such as platinum, the most common electrode material in eDOC systems presented thus far, poses challenges that extend beyond mere costs. Although indispensable due

to their high catalytic efficiency, the global supply of these metals is finite and already in demand for various industrial applications, such as automotive catalysts and medical devices. Scaling up eDOC systems to capture significant quantities of CO₂ would necessitate enormous amounts of these rare metals. This raises critical questions about the sustainability of relying on such scarce resources for a technology intended for widespread use. Simultaneously, the bottleneck of low current densities adds further complexity. In the context of electrochemical systems, current density is a fundamental parameter that directly influences the efficiency, scalability, and overall viability of the technology.

The current density ranges that have been tested in the eDOC prototypes developed so far are still relatively low, ranging between 8 to 80 A m⁻². This is lower than the "industrially preferred" range for electrolytic systems, which is over 100 A m⁻², as discussed previously. At the highest current density achieved among the current eDOC prototypes [141], it would require 700 tons of platinum to build a plant that could capture 1 MtCO₂ per year, equivalent to almost four times the world supply in 2022 [160]. Additionally, the total size of the electrodes would be equivalent to the land area five times that of Central Park in New York City. Assuming 100% efficiency, the required seawater intake will have to be 25 million m³ per day, which is about 25 times the capacity of the current largest desalination plant in the world [135] and roughly equivalent to cooling water intake of the world's third largest operational nuclear power plant [161]. Table 1 summarizes the required electrode area, quantity and energy if each eDOC prototype is scaled up to 1 MtCO₂ y⁻¹ at their current performance.

Table 1. Comparative Analysis of Different eDOC Prototypes. This table provides a comparison of the eDOC prototypes discussed if they were to be scaled to 1 MtCO₂ per year capacity plants at their current performance.

Prototype	Energy Requirement ^a (MWh)	Electrode Area ^b (km ²)	Rarest Element used in the Electrode		
			Element	Amount Required (ton)	Percent of Global Supply (%)
BPM-AEM-BPM	1528	112.2	Iridium (Ir)	2,008	27,502 ^c
BPM	980	42.1	Platinum (Pt)	59	31 ^d

CEM-BPM	2008	27.8	Platinum (Pt)	39	20 ^d
EHL	660	17.4	Platinum (Pt)	695	366 ^d
IES	770	139.1	Bismuth (Bi)	215,849	1,079 ^e

^a As a reference, the average annual energy consumption of a household in the US is 10.6 MWh based on 2020 data [162].

^b As a reference, the size of Central Park in New York City is 3.41 km² [163].

^c Based on 2018 data [164]

^d Based on 2022 data [165]

^e Based on 2022 data [166]

There are several factors that are limiting the current density of existing eDOC systems. One example is demonstrated in the IES wherein the formation of Mg(OH)₂ at the electrode surface was suspected due to the high local pH generated at the surface of the electrodes. The researchers observed that by lowering the current density, the local pH decreased resulting in an increase in performance. Similar observations were also made by Sharifian et al. [127, 144] on membranes. At higher current densities, scaling has been observed to accelerate due to the high local OH⁻ concentration generated. Although lowering the current density was seen as an effective solution, developing systems that can operate at higher current densities are desired in the long run. Their proposed strategy of acid washing was proven to be successful at effectively eliminating the foulant, it might be disruptive to the continuous operation of the system and can add to operational costs. As such, other measures to avoid such phenomena will need to be devised. This includes the development of better electrode materials and optimizing flow conditions and cell geometry, to name a few.

As in any technology, energy consumption is a significant concern in the research and development. Impressively, the EHL and IES prototypes have achieved impressively low energy consumption values of 660 and 770 kWh tCO₂⁻¹, respectively. However, these values represent the energy consumed specifically for CO₂ capture and do not include pumping costs. When considering the energy consumption of pumping based on typical seawater pumping costs (approximately 8% of the energy consumption of the electrochemical process) [167], the total operational energy consumption would range between 715 and 834 kWh tCO₂⁻¹, which is comparable to DAC systems. Lagging the energy race is the base process utilizing a BPMED

system. The EHL and IES were able to surpass the energy consumption performance of BPMED systems by avoiding the use of BPMs. One of the limitations of systems that utilize BPM is the relatively high voltage required to achieve water dissociation even at milder pH gradients ($V_{\text{BPM}} \geq 0.6$) for currently available units [99]. Additionally, BPMs have been observed to contribute significantly to overall ohmic losses, especially at higher current densities [168]. However, it is important to note that the energy consumption data reported does not account for downstream energy consumption during the transport, storage, and processing of CO_2 or mineral carbonate products.

As a benchmark, the performances of the eDOC prototypes were compared to one of the currently most discussed NET, which is DAC. While not classified as a NET, conventional CCS technology from point sources was additionally considered as a benchmark for comparison considering that it is widely recognized as a highly mature and well-understood technology that has been deployed commercially on a large scale. Figure 7 summarizes the ranges of energy consumption and current density tested for each eDOC prototype published in the literature relative to the ranges typical in commercial DAC and conventional point-source carbon capture systems. Although DAC is one the most widely discussed and researched NET, with several plants in operation and more underway, its energy requirement is still considered high, ranging from 972 to 2,750 kWh tCO_2^{-1} for solid and liquid solvent-based systems, respectively [28, 32]. For conventional CCS, the regeneration energy consumption of amine scrubbing technology range between 320 and 1,500 kWh tCO_2^{-1} [169]. The averages of the energy consumption values of DAC and point-source CCS were taken as benchmarks to compare the emerging eDOC technologies as shown in the green rectangle in Figure 7. The benchmark rectangle is completed by the industrially preferred current density range of 100 to 1,000 A m^{-2} for electrolytic systems [170, 171]. A higher current density would allow for more efficient energy use and higher production rates, which would increase efficiency and reduce the overall cost per unit of captured substances. It would also reduce the size and cost of equipment needed since smaller electrodes and reactors can be used for the same production volume.

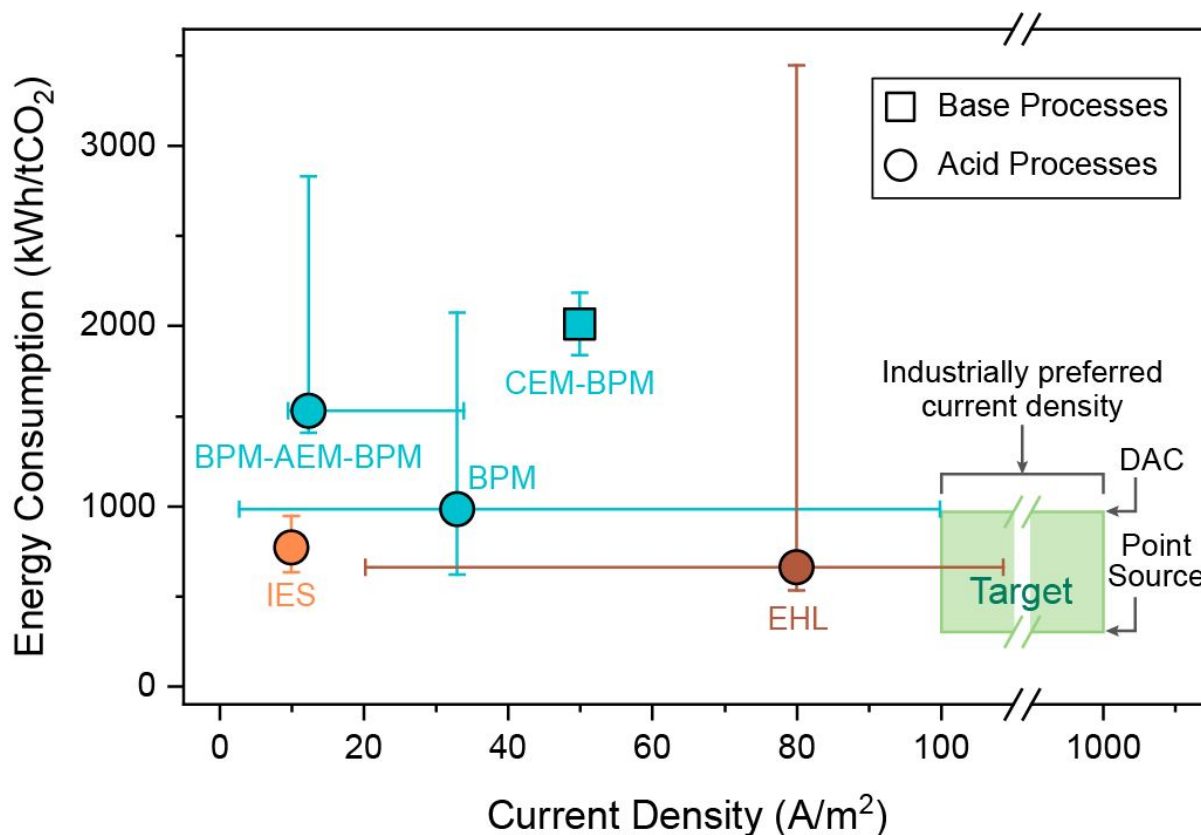


Figure 7. Energy and Current Density Performance of eDOC Prototypes. Progression of the energy consumption and current density performance ranges of the eDOC technologies developed within the last decade. The systems that extract CO₂ (acid process) are represented by circles, while those that generate mineral carbonates (base process) are in squares. The blue color represents systems that utilize BPMs; red represents BPM-less systems; and orange represents membraneless systems. The set baseline for energy consumption is that of commercially deployed DAC and point-source CCS (the optimistic scenarios), while current density is based on the industrially preferred range for electrolytic systems as defined by the green rectangle.

Thus far, the prototype utilizing the EHL method shows the most promise in terms of energy consumption and current density. However, the presence of hydrogen gas in the system could potentially pose challenges on larger scales. For instance, hydrogen gas is widely known to be highly flammable and leakage is a commonly encountered issue considering its small molecular size and density [142]. These concerns will need to be addressed in future larger-scale prototypes. A close contender which emerged very recently is the IES. Although both prototypes each have their drawbacks, membraneless designs have the potential to significantly reduce the cost and improve overall operability. Considering the observed tendency of fouling in BPMED systems, membraneless systems could be the natural direction forward in eDOC. Although the membraneless system performed competitively in terms of energy consumption, it lags behind in

current density due to scaling and electrode lifetime concerns. As discussed previously, high current densities are generally desired for scale-up and thus should be addressed in future improvements.

5. Future Design Considerations

Based on the trajectory observed in the literature, pH swing is the way forward as the primary mechanism in ocean DIC removal for eDOC. The choice of product (i.e., CO₂ gas, carbonate mineral) also significantly impacts the design of the system, particularly the product collection method, which in turn, can substantially affect overall costs. In the case of CO₂ gas extraction, these methods necessitate downstream membrane contactors to strip the CO₂ gas from the acidified seawater which can be costly. In one of the studies discussed earlier, membrane contactors were estimated to account for about 60% of the total equipment cost [138]. Subsequent compression and transport of the recovered CO₂ can also contribute to the overall costs. In carbonate mineralization, the main challenge is to design a system in that precipitation can be effectively controlled in a way that does not negatively affect the functioning of the system (i.e., scale formation on key components).

Thus far, the majority of the experimental eDOC prototypes have predominantly involved the use of BPMs that necessitate the use of multiple membranes to achieve pH swing. These systems become costly, especially when dealing with streams with high multivalent ions such as Mg²⁺ and Ca²⁺. In almost every case, membrane fouling has been reported to be a potential challenge to these systems, often recommending additional pretreatment of the influent seawater (e.g., removal of Ca²⁺ and Mg²⁺), which would be impractical. To put it into perspective, the energy cost associated with pretreatment using reverse osmosis would amount to 1,909 kWh tCO₂⁻¹ [167]. This cost is approximately 50% to 290% of the energy cost of the eDOC systems. According to more recent research, a highly effective way to minimize fouling in BPMED systems is to avoid the use of CEMs near high-pH channels [144]. This is because CEMs create local high concentrations of Ca²⁺ and Mg²⁺ on the surface which promote fouling.

One other potential concern is biological fouling in membrane-utilizing systems. In the literature available so far on eDOC systems, biological fouling has not been significantly considered. It has been established previously that co-location with facilities that have seawater pumping and pre-treatment infrastructure already in place significantly reduces overall costs [134]. Desalination plants, for instance, have dedicated filtration pretreatment processes that utilize

filters with pore sizes ranging between 10 and 0.1 μm to protect their reverse osmosis systems from foulants such as microorganisms [172, 173]. One of the studies discussed previously utilized real seawater in their experiments which were pre-treated the seawater using a 10 μm filter. However, eDOC systems that operate as stand-alone facilities are not implausible. If such systems will involve membranes, one of the biggest challenges would likely be seawater pre-treatment.

The emergence of membraneless systems offers a pathway that could significantly minimize concerns with fouling. For this reason, these systems are expected to emerge motivated by the need to reduce overall system costs. The utilization of PCET reactions to achieve pH swing holds promise for the development of membraneless systems, which is likely to gain increasing attention in the next few years. However, not all PCETs are ideal for eDOC applications. In conventional CCS from point sources, quinone is the most researched family of compounds used for this purpose [116, 174]. However, these methods involve the quinones being mixed in the CO_2 -rich aqueous stream (i.e., it must be presented in the aqueous phase), and hence, are out of the question in DOC applications due to toxicity concerns [175]. While it may seem obvious, it is an important aspect to bear in mind to ensure that these systems have minimal impact on the marine environment.

Alternative PCET reactions that involve environmentally benign substances have been previously demonstrated to achieve pH swing but for CCS applications. The first of such demonstrations utilized manganese oxide (MnO_2) to reversibly react with H^+ in solution upon reduction (intercalation), and then release the proton upon oxidation (de-intercalation) [117, 176]. In the prototype electrochemical cell, the cathode was unreacted MnO_2 , while the anode was MnO_2 fully intercalated with H^+ creating a surface layer of MnOOH . This paved the way for systems that no longer rely on BPMs to achieve a pH gradient. The most recently published prototype thus far built upon this principle to develop the a membraneless eDOC system using BiOCl [114]. Although the prototype showed great promise in terms of energy consumption, its capacity for higher current densities still needs to be progressed.

A major bottleneck in further advancing eDOC systems is the low operating current density. Hence, to achieve commercial readiness, developing a system that can operate at the industrially preferred ranges must be achieved (i.e., current densities ranging from 100 to 1,000 A m^{-2}). In the tested systems so far, optimum current densities were constrained to less than 100 A m^{-2} as described earlier. There are two general benefits for this: (1) higher current densities would result in more efficient energy use, and (2) operating high current densities allow for less electrode area,

hence a more compact system. To achieve this, a number of design bottlenecks will have to be addressed. For instance, measures to avoid extreme pH at the electrode surface at higher current densities will need to be adapted. This is to minimize the tendency of undesired carbonate mineralization at the electrode surface. Theoretically speaking, the current density is a function of the exchange current density and the mass transfer of the redox active species between the electrode surface and bulk solution, by virtue of the Butler-Volmer equation. The exchange current density is a measure of a material's efficiency at transferring electrons, which can be seen as a function of the surface properties of the electrode, such as electrical conductivity, topology, surface area, and degree of catalytic activity [177]. Therefore, the choice of electrode materials and optimizing structural properties can be an approach to achieve higher operating current density. Additionally, optimizing the mass transfer limitations could also be an approach. Depending on the design architecture, this could be achieved by optimizing cell geometry or improving flow conditions.

While higher current densities offer the potential for improved efficiency and economic viability, it is crucial to acknowledge the associated challenges and implement appropriate mitigation measures. A key aspect is the careful engineering design of the system, ensuring it can handle increased current densities and maintain proper distribution and flow of the redox active reactants and products. Strategies such as optimizing cell geometry and improving flow conditions are valuable for enhancing mass transfer and preventing undesirable concentration gradients, which can restrict current density. Material selection is another critical consideration when targeting higher current densities. Surface properties like electrical conductivity, topology, surface area, and catalytic activity impact the exchange current density [178, 179]. Moreover, higher current densities exacerbate the challenge of electrode fouling [180]. Unwanted deposits that accumulate on the electrode surface can reduce system efficiency and stability, hence, strategies to mitigate the fouling will have to be employed.

Undoubtedly, the significant consumption of expensive metals such as platinum and the high flow rates necessary for CO₂ capture present considerable challenges for the practical and economic feasibility of large-scale eDOC systems. These concerns drive the need to explore less expensive, environmentally benign, and more abundantly available electrode materials. The work with MnO₂ and BiOCl illustrates the potential for developing alternative electrode materials that maintain efficiency, stability over long operating periods, and low cost. The development of proton or hydroxide-intercalating electrode materials such as MnO₂ or the developed BiOCl electrodes showcases how concerted research efforts can address these challenges, aligning with the overarching goals of reducing costs and minimizing environmental impact.

As with any other emerging technologies, the high capital and operating costs need to be reduced to a point that it becomes economically viable enough to compete with current commercially available options. In the case of NETs, the benchmark is set by DAC and BECCS, which are currently considered the most mature NETs. Currently, the cost of BECCS and DAC reported in the literature range from \$15 to \$400, and \$60 to \$2,770 per tCO₂, respectively [30, 31, 33]. Based on the techno-economic analysis done by Eisaman et al. [134], it is estimated that the most-likely cost of the eDOC acid process is approximately \$717 tCO₂⁻¹, assuming a removal rate of 20 kmol CO₂ h⁻¹ and co-location with a desalination plant. The cost for the eDOC base process is estimated to be approximately \$603 tCO₂⁻¹ under similar conditions, which is higher than the acid process due to the higher concentrations of OH⁻ needed to initiate precipitation. However, when considered for a stand-alone plant, the cost is significantly higher at up to \$2,355 tCO₂⁻¹ and \$1,349 tCO₂⁻¹ for the acid and base process, respectively. The cost savings primarily stem from reduced pumping requirements, the avoidance of pretreatment expenses, and a reduction in additional piping needs. The cost difference between the acid and base process is attributed to the expenses associated with membrane contactors. This will be an important consideration in determining the product route, i.e., CO₂ gas or mineral carbonates.

A vital consideration in improving eDOC technology is minimizing the total cell operating voltage to reduce energy consumption and optimizing cell design and components to cut capital costs. Previous research has demonstrated that establishing a theoretical framework or model of the operating electrochemical cell is an indispensable tool in understanding the overall thermodynamics, particularly the contributions to the total operating voltage [138, 181]. For instance, the total practical cell voltage of systems that employ BPMs and IX membranes can be expressed as:

$$V_{cell, practical} = \frac{RT}{F}(pH_{base} - pH_{acid}) + V_{BPM loss} + V_{IX} + V_{seawater} + V_{electrolyte} + V_{electrode} \quad (3)$$

where $pH_{base/acid}$ is the pH at the base or acid compartment, $V_{BPM loss}$ is the voltage loss across the BPM, V_{IX} is the voltage loss across the IX membranes, $V_{seawater}$ is the voltage losses across the seawater, $V_{electrolyte}$ is the voltage loss across the electrolyte solution in the electrode chamber, and $V_{electrode}$ is the voltage loss at the electrodes. This theoretical foundation has helped investigators to diagnose inefficiencies and identify key parameters that can be optimized, such as electrolyte quality, electrode material, and redox couple reaction. As such, defining these parameters should be one of the first steps in modeling and designing eDOC systems.

The future design considerations for eDOC technologies must carefully address four essential challenges to enhance both efficacy and economic viability. Firstly, in addition to the challenges

of handling higher current densities, there is a pressing need to tackle the expensive and fouling-prone nature of ion exchange membranes, which constitute both a significant cost and operational hindrance. Innovative approaches that can reduce the costs and minimize fouling would create a significant positive impact. Secondly, the use of high-cost electrode materials like platinum must be reevaluated. Cost-effective alternatives that don't compromise performance would encourage more scalable applications. Thirdly, addressing the low current densities in eDOC systems is vital, focusing on optimizing efficiency and making large-scale operations feasible. Finally, the various concerns related to energy consumption must be addressed comprehensively. The design should aim for minimizing energy consumption, not only in the CO₂ capture process but also considering auxiliary operational aspects like pumping.

Finding the right balance between higher current densities and system stability is pivotal for the success of electrochemical systems. By addressing these challenges through meticulous engineering design, careful material selection, and effective fouling mitigation strategies, the full potential of electrochemical-based DOC can be realized.

6. Conclusions

Harnessing the vast potential of eDOC technology is a challenging yet crucial task in broadening our NET arsenal against climate change. eDOC technology has proven itself to be a promising contender, especially given its ability to tap into the ocean's natural capacity to absorb CO₂ from the atmosphere. Electrochemical processes also benefit from the capability to be operated and powered solely by electricity, unlike conventional processes that require large quantities of heat. This gives it a distinct potential for straightforward integration into existing infrastructures for rapid deployment at variable scales. However, despite these promising aspects, eDOC technology still faces hurdles on the path to large-scale implementation. These include further reducing overall capture cost, reducing the amount of energy and materials it needs, and figuring out how to make it work more practically on a larger scale.

The current literature suggests that pH swing is the most effective method to achieve DOC. As the field of eDOC technology advances, researchers must address several key design bottlenecks to enable commercial readiness. An important consideration is the choice of product (i.e., CO₂ gas or mineral carbonates) since this can play a crucial role in determining the overall system design and cost. The earliest prototypes have relied on BPMED systems to generate the necessary pH gradients for DIC removal. Membrane-based systems have demonstrated promising results in terms of energy consumption and current density but suffer from fouling and

scaling issues. Recent research has focused on the development of membraneless systems, such as those employing electrochemically mediated PCET reactions, to reduce fouling concerns and overall system complexity. Another important criterion for scalability is operability at higher current densities, specifically in the industrially preferred range of 100 to 1,000 A m⁻². Future research in eDOC technology should prioritize the development of environmentally benign and efficient pH swing mechanisms, the advancement of electrode materials and cell designs to achieve higher current densities, and the exploration of alternative product routes to optimize system costs. Additionally, a comprehensive understanding of the thermodynamics and kinetics of eDOC systems is crucial for optimizing system performance, which can be achieved through the development of theoretical frameworks and electrochemical models.

As the urgency of addressing the global CO₂ emissions problem increases, continued research and development in the field of eDOC technology are essential to overcome the current challenges and unlock their full potential. Further research and development are needed to optimize eDOC systems and overcome the current challenges they face. The urgent need to address the global CO₂ emissions problem underscores the important role that eDOC technology can play in achieving carbon neutrality.

Author Contributions

Conceptualization: P. A., A. R., M. A., A. H., M. R.; Investigation: P. A., A. R., M. A., A. H., M. R.; Methodology: P. A., A. R., M. R.; Software: A. R.; Supervision: M. R.; Validation: P. A., A. R., M. A., A. H., M. R.; Visualization: P. A., M. R.; Writing – original draft: P. A.; Writing – review & editing: P. A., A. R., M. A., A. H., M. R.

Conflict of Interest

The authors have no conflicts of interest to declare.

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