

– SYNOPSIS –

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

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ABSTRACT

The rising urgency for effective climate change mitigation has led to the exploration of various negative emissions technologies (NETs). This study investigates recent advancements and challenges associated with electrochemical direct ocean capture (eDOC) of carbon dioxide (CO₂), a promising NET for oceanic carbon removal. The research analyzes different eDOC strategies, focusing on pH swing as the primary mechanism for ocean dissolved inorganic carbon removal, and discusses the implications of CO₂ gas extraction and carbonate mineralization. Early prototypes have relied on bipolar membrane electrodialysis (BPMED) to generate the necessary pH gradients, while recent developments have eliminated the need for membranes by relying on proton-coupled electron transfer reactions. The paper compares these different approaches and highlights the limitations of current eDOC systems, such as potential fouling, scaling issues, and high energy requirements. The techno-economic challenges, such as achieving industrially preferred current densities and reducing overall costs, are also examined. The study provides insights into the optimization of eDOC systems, suggesting that further research is needed to improve system efficiency, address design bottlenecks, and develop innovative electrochemical approaches for CO₂ removal from seawater. 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.

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FIVE RECENT KEY RESEARCH PUBLICATIONS

1. Kim, S., et al., Asymmetric chloride-mediated electrochemical process for CO₂ removal from oceanwater. *Energy & Environmental Science*, 2023, In press.
2. Digdaya, I.A., et al., A direct coupled electrochemical system for capture and conversion of CO₂ from oceanwater. *Nature Communications*, 2020. 11(1): p. 4412.
3. Yan, L., et al., An Electrochemical Hydrogen-Looping System for Low-Cost CO₂ Capture from Seawater. *ACS Energy Letters*, 2022. 7(6): p. 1947-1952.
4. Sharifian, R., et al., Oceanic carbon capture through electrochemically induced in situ carbonate mineralization using bipolar membrane. *Chemical Engineering Journal*, 2022. 438: p. 135326.
5. de Lannoy, C.-F., et al., Indirect ocean capture of atmospheric CO₂: Part I. Prototype of a negative emissions technology. *International Journal of Greenhouse Gas Control*, 2018. 70: p. 243-253.

Currently, the scientific literature lacks a review paper dedicated to the topic of electrochemical processes for oceanic carbon removal. Our comprehensive manuscript addresses this gap by being the first to critically analyze the subject, synthesizing the latest findings and advancements in the field. By providing a thorough overview and offering valuable insights and future prospects, this manuscript will serve as a valuable resource and guide for the emerging research community working on electrochemical technologies for direct ocean capture.

FIGURES

The manuscript will include 7 figures, which all are generated by the authors. The figures are either 18 cm or 9 cm wide, as recommended by the journal.

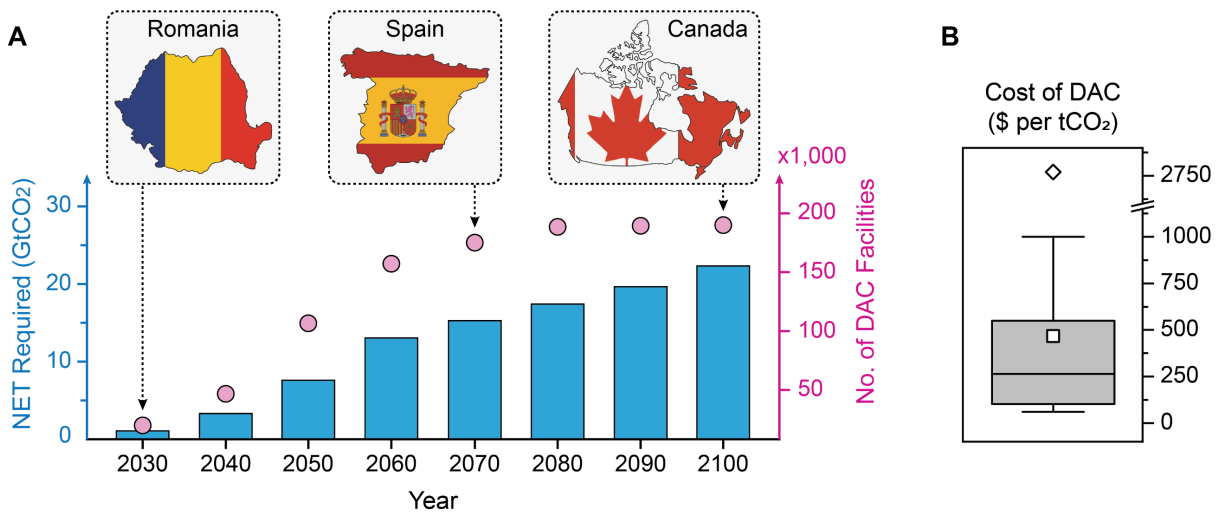


Figure 1. A Cost Analysis of Negative Emissions Technologies. (A) In order to stay on track with the 2°C warming scenario by 2100, negative emissions are necessary. Models estimate that the cumulative quantity that must be captured by 2030, 2070, and 2100 to limit warming by 2°C at a 66% likelihood are 0.7, 13.8, and 20 GtCO₂ y⁻¹, respectively. At an average cost of \$467 per tCO₂ using DAC in 2030, the cost to capture would be equivalent to the GDP of Romania in 2022. In 2070 and 2100, assuming the ideal \$100 per tCO₂, the cumulative cost would be comparable to the GDP of Spain and Canada in 2022. Assuming a 10% improvement in annual capture capacity each decade, over 100,000 facilities would have to be built by 2050 to keep us on track with the 2°C scenario plan based on UN estimates. (B) Based on values for the cost of capture using DAC per ton of CO₂ reported in the literature, 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.

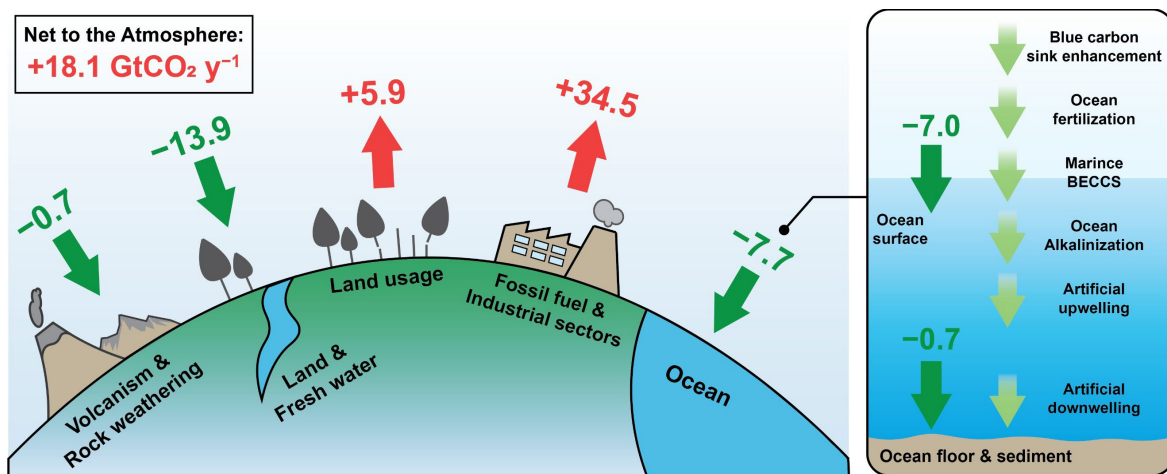


Figure 2. The Ocean Carbon Cycle. The concentration of CO₂ in the atmosphere is contributed by multiple factors. This figure shows the different sources and sinks for CO₂ in the atmosphere in GtCO₂ y⁻¹. Volcanism and rock weathering fixate around 0.7 GtCO₂ y⁻¹. The net natural influx from land including 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 7.7 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.

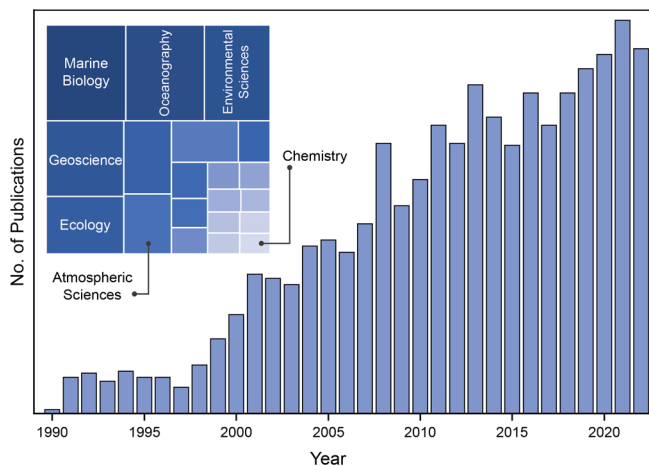


Figure 3. Trends in Ocean-based NETs Research with Ocean Alkalinization as Model. Depicted here is a sample trend in the number of publications related to ocean alkalinization since the 1990s, using data gathered from the Web of Science. While the amount of research on this topic has increased over time,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

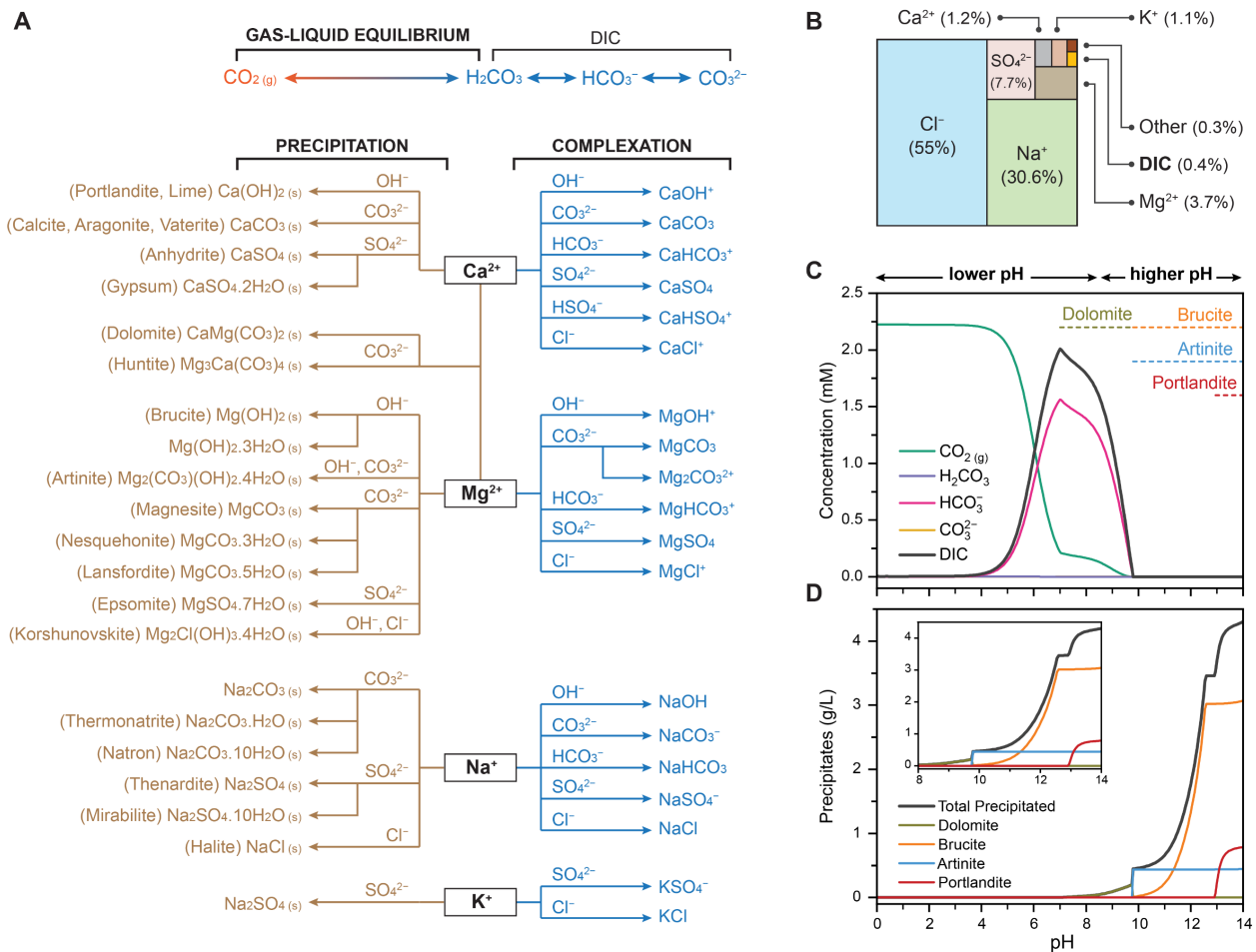


Figure 4. Complete Thermodynamic Analysis of DIC Speciation and Removal. For an aqueous solution reflecting typical ocean water concentrations, a rigorous thermodynamic framework based on speciation analysis was developed. (A) The thermodynamic model was developed to predict the speciation of DIC in 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 CO_2 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 ($\text{CaMg}(\text{CO}_3)_2$) precipitation dominates until pH 9.7, beyond which precipitation is dominated by artinite ($\text{Mg}_2(\text{CO}_3)(\text{OH})_2$) and brucite ($\text{Mg}(\text{OH})_2$).

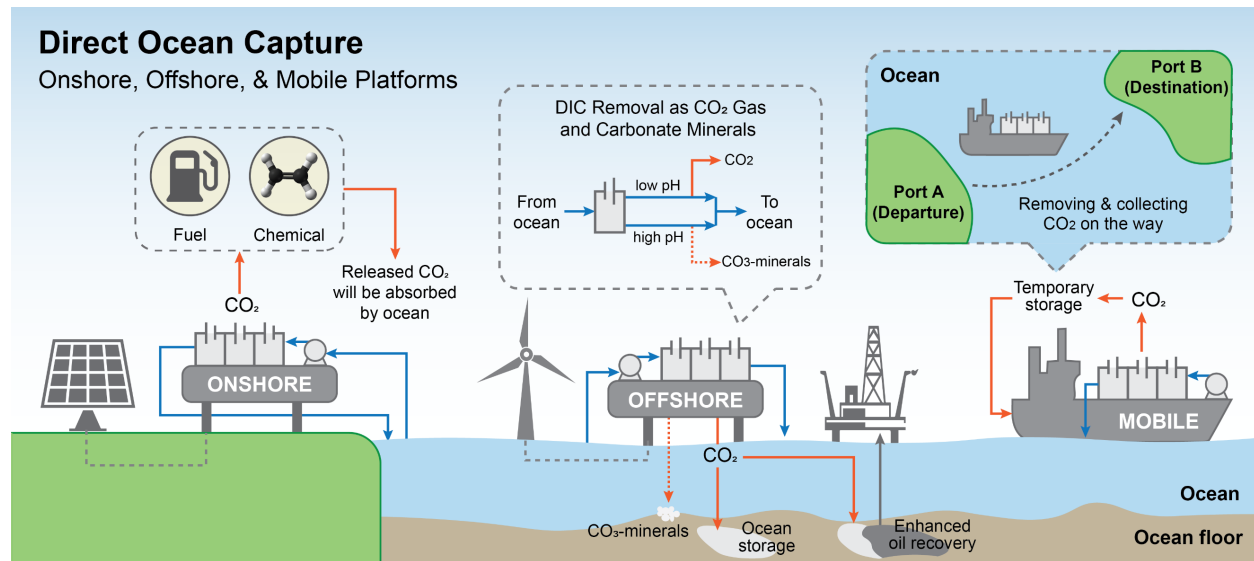


Figure 5. Direct Ocean Capture Domains. Illustrated here are the three domains to which eDOC can be applied. On-shore deployment could involve co-location with facilities that take in seawater as input, such as desalination plants and power plants. The CO₂ generated could also be potentially utilized 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.

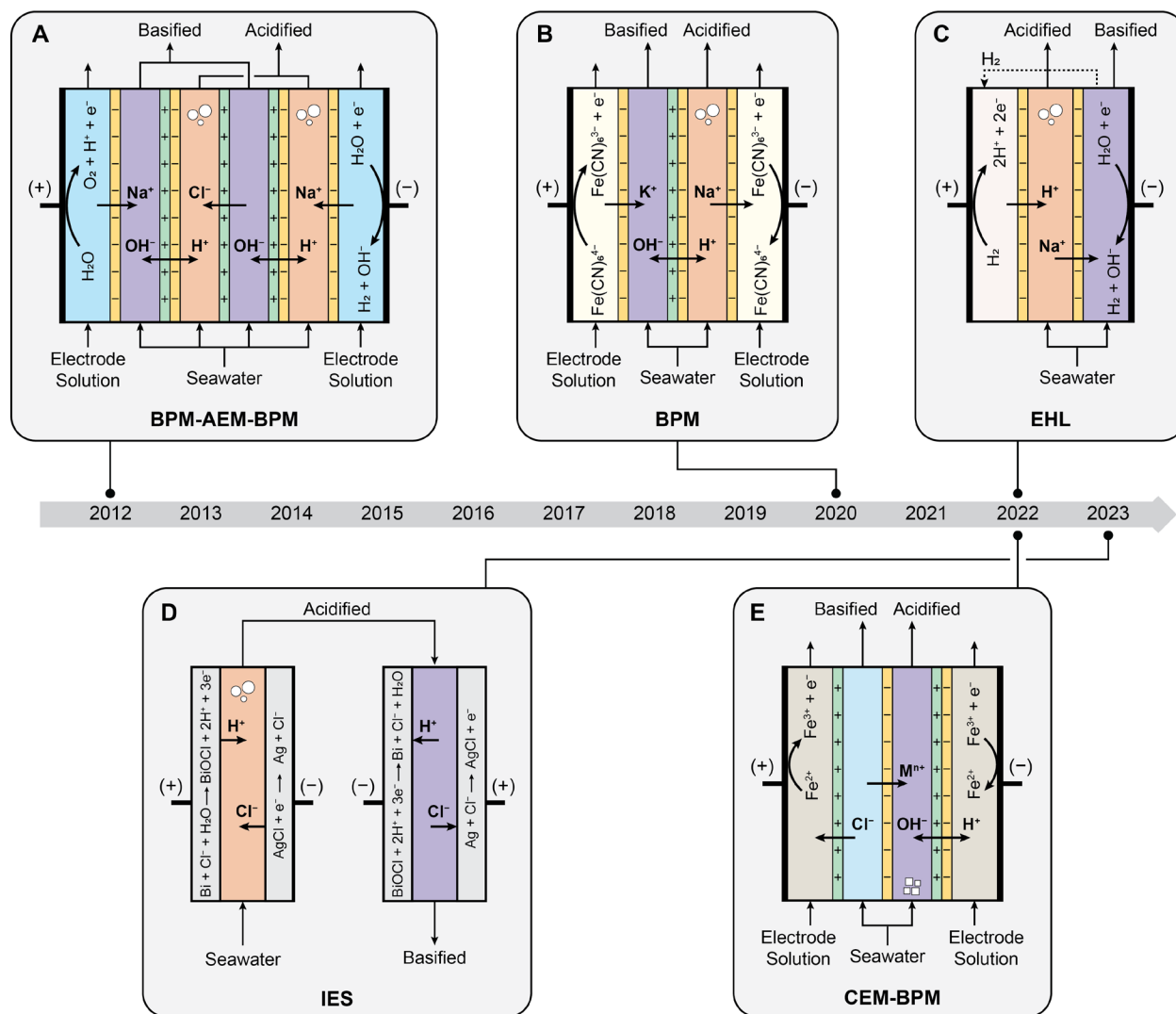


Figure 6. Evolution of eDOC Designs. Shown here is the timeline of the technological development of eDOCs reported in the current literature with each represented as simplified schematics. The first four (A-D) were designed to separate the DIC as CO₂ gas (acid process) while the last one (E) generates 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 Fe²⁺/Fe³⁺ which was done to reduce the voltage contribution at the electrodes.

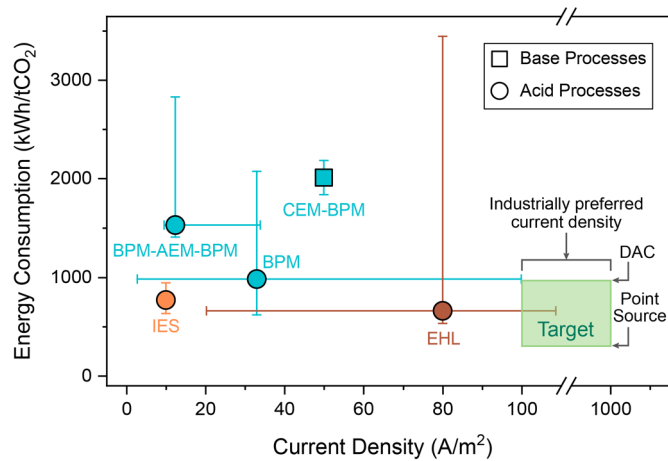


Figure 7. Energy and Current Density Performance of eDOC Prototypes. Progression of the energy consumption and current density performance ranges of the eDOC technologies developed within the last decade. The systems that extract CO₂ (acid process) are represented by circles, while those that generate 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.