

Unraveling the Potential of Electrochemical pH-Swing Processes for Carbon Dioxide Capture and Utilization

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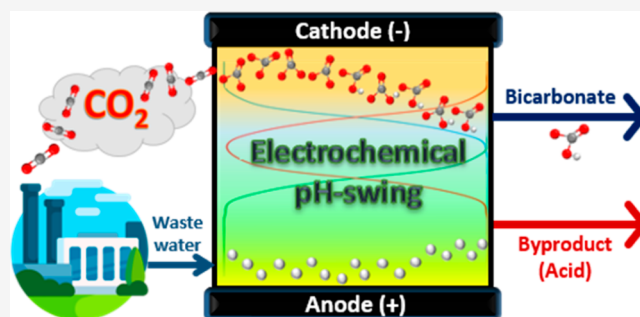


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ABSTRACT: Global warming, driven by the accumulation of anthropogenic greenhouse gases, particularly CO₂, in the atmosphere, has garnered significant attention due to its detrimental environmental impacts. To combat this critical issue, the deployment of CO₂ capture and utilization (CCU) strategies has been considered as one of the technology-based solutions, leading to extensive scientific and engineering research. Electrochemical pH-swing (EPS) processes offer a promising approach to diverse CCU pathways, such as the delivery of pure CO₂ gas, the delivery of bicarbonate (e.g., for microalgae cultivation), and the formation of carbonate minerals. In this study, we discuss several CCU pathways using EPS and provide an in-depth analysis of its mechanisms and potential applications, outlining its limitations from both thermodynamic and kinetic standpoints. The EPS process has demonstrated remarkable capabilities, achieving a CO₂ capture efficiency of over 90% and unlocking valuable opportunities for CCU applications. We also develop an initial techno-economic assessment and provide the perspectives and challenges for future development and deployment of EPS. This study sheds light on the integration of EPS with CCU, closing the carbon cycle by effectively utilizing the products generated through the process, such as carbonate minerals and bicarbonate solution. For instance, the bicarbonate product can serve as a viable feedstock for bicarbonate-based microalgae production systems, with the added benefit of reducing costs by 40–80% compared to traditional gaseous CO₂ delivery approaches. By integration of electrochemical technologies with CCU methods, this study underscores the immense potential for mitigating CO₂ emissions and advancing sustainable practices to combat global warming. This study not only addresses the urgent need for effective solutions but also paves the way for a greener and more sustainable future.



INTRODUCTION

Mitigating climate change is an existential challenge of the twenty-first century. The Intergovernmental Panel on Climate Change (IPCC) underscored a significant milestone in 2021, revealing that atmospheric CO₂ levels had surpassed the noteworthy threshold of 409.9 ppm.^{1,2} Absent effective mitigation, these levels are projected to persistently rise. The IPCC proposed to restrict the global average temperature increase to within 2 °C above preindustrial levels. A pivotal facet of this agenda hinges on industry's attainment of net zero-carbon emissions.³ Within this context, the role of CO₂ capture and utilization (CCU) is widely acknowledged as a cornerstone for success. Essential to realizing this vision is a profound understanding of the CO₂ cycle and the formulation of mitigation strategies that not only mitigate emissions but also yield revenue streams and operational efficiencies for industry. This is imperative for forging the pathways toward net zero emissions. While the challenge of mitigating CO₂ emissions

resonates globally, it is crucial to acknowledge that CO₂ serves as an indispensable feedstock across diverse sectors including industry, manufacturing, energy, and agriculture (as shown in Figure S1). Thus, the concept of CCU not only offers environmental benefits but also holds the potential for generating economic advantages while mitigating the effects of climate change.

Table 1 presents the achievable performance of various CO₂ capture technologies commonly found in the literature. One prevalent approach for postcombustion CO₂ capture involves the application of amine-based solvents through chemical

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Table 1. Achievable Performance of Various CO₂ Capture Technologies

CO ₂ source	CO ₂ concn	approach	media	duration of process	operating conditions	amount of captured CO ₂	ref
pure CO ₂	>99.99%	chemical absorption	MEA/DIPA ^a	10 min	$T = 323.15$ K; pressure = 400 kPa; $\text{pH} \geq 10$	0.77 mol-CO ₂ /mol total amine	10
flue gas	20%	chemical absorption	liquid quinones (LQ)	30 min	room temp; pressure = 10 bar	0.04 mmol-CO ₂ /mmol LQ	11
flue gas	0.06%	chemical absorption	KOH	-	pressure = 15 MPa	1 Mt-CO ₂ /year; 90 kg-CaCO ₃ /h	12
flue gas	eNRTL ^b	chemical absorption	DEEA-MAPA-H ₂ O ^c	-	$T = 313$ K; pressure = 100 kPa	0.5 mol-CO ₂ /mol total amine	13
flue gas	15%	sorption	activated carbon (AC)	27 s	$T = 303$ K; pressure = 0.15 bar	0.6 mmol-CO ₂ /g-AC	9
flue gas	20.7%	adiabatic compressed air energy storage	water	7.5 h	$T = 250$ K; pressure = 0.1 MPa	1.98 mol-CO ₂ /L	6
ambient air	500 ppm	seawater battery-carbonation	seawater	-	room temp; current density = 0.3 mA/cm ²	50 ppm-CO ₂ /h	14

^aMEA, monoethanolamine; DIPA, diisopropanolamine (MEA/DIPA/H₂O = 10/10/80). ^bSimulation model eNRTL: the electrolyte non-random two-liquid model. ^cDEEA, *N,N*-diethylethanolamine; MAPA, *N*-methyl-1,3-propanediamine.

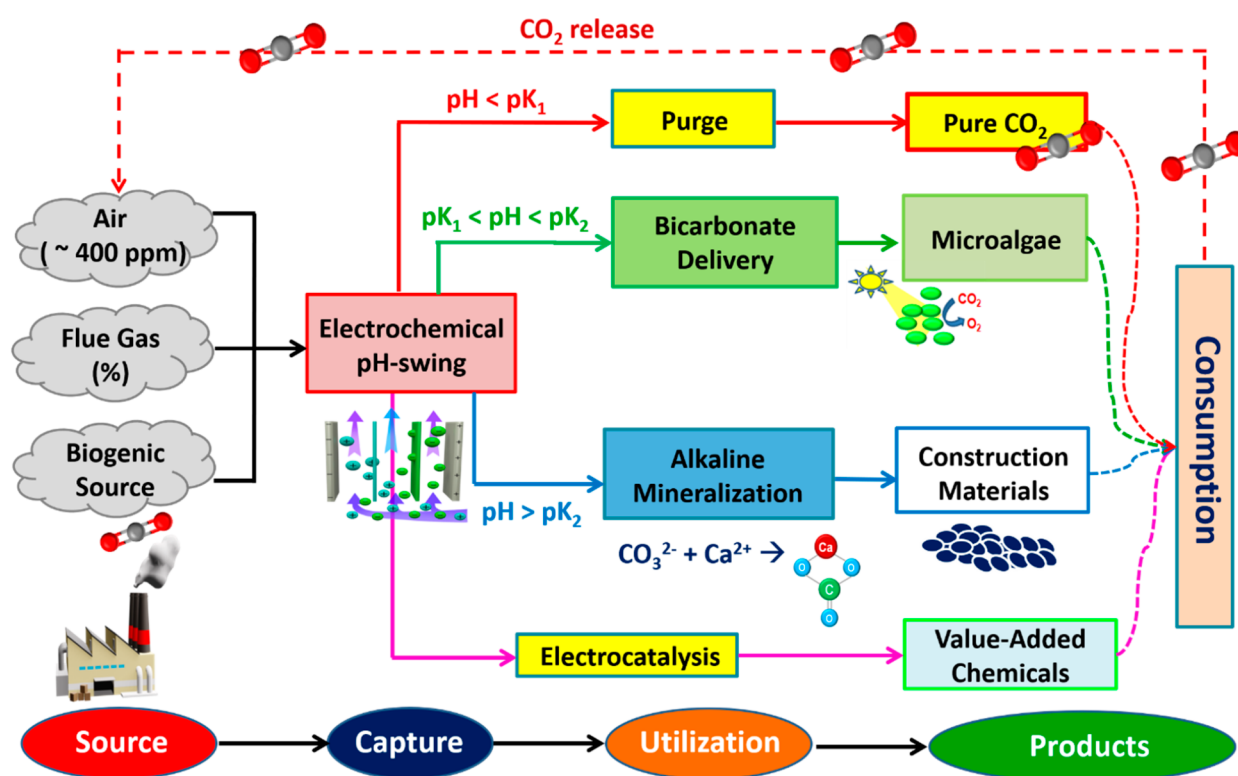


Figure 1. Application of electrochemical pH-swing (EPS) processes for CO₂ capture and utilization (CCU) toward a circular carbon economy.

absorption processes.⁴ However, it often presents challenging concerns, including issues related to volatility and toxicity. Additionally, the energy-intensive nature of the regeneration process accentuates the necessity of optimizing operational costs and minimizing environmental ramifications.⁵ In water-based CO₂ capture methods, the volume of water required for CO₂ capture under ambient pressure is notably higher due to the lower CO₂ partial pressure. In instances where water served as the adsorption fluid, thermodynamic analysis of the CO₂-rich air indicated that the mass flow of circulating water necessary for CO₂ absorption surpasses that of flue gas by over 25 times, despite the reduced CO₂ partial pressure.⁶ This investigation also unveiled that the energy consumption for CO₂ capture stood at ~ 350 kWh/t-CO₂, marking a 60–70% reduction compared to amine-based capture technologies

requiring ~ 1000 kWh/t-CO₂.⁷ Selectivity and adsorption capacity are crucial performance metrics. The underlying mechanisms hinge on factors such as (1) the molecular sieving effect, (2) thermodynamic equilibrium, and (3) kinetic effects.⁸ For adsorption processes, an increase in temperature generally resulted in a reduction in adsorption capacity, in line with the exothermic nature of the adsorption process for the current gas–solid system.⁹

Traditional CO₂ capture systems have employed variations in temperature and pressure, relying on chemisorption/physiosorption mechanisms that influence the chemical redox state of CO₂. Conversely, the electrochemical pH-swing (EPS) approach capitalizes on the distinct pK_a states of CO₂ in an aqueous context, encompassing forms like bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻). Renowned for their

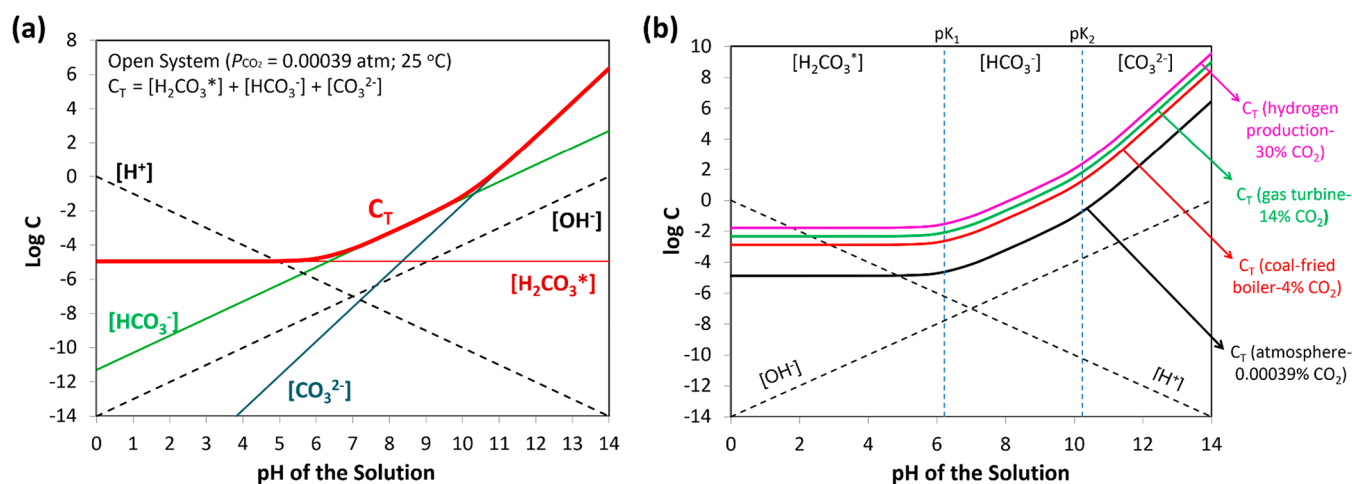


Figure 2. (a) Logarithmic concentration diagram for carbonate species in an open system ($P_{\text{CO}_2} = 10^{-3.5} = 0.00039$ atm, at 25 °C). (b) Logarithmic concentration of total inorganic carbon (C_T) in an open system produced under different scenarios of CO_2 sources such as flue gas comparing with CO_2 in the air at 25 °C. Data on flue gas were referred from ref 25.

environmentally conscious attributes, electrochemical technologies hold the promise of carbon neutrality when coupled with renewable or nuclear energy sources. As shown in Figure 1, EPS processes offer a range of production pathways. These pathways include the delivery of pure CO_2 gas, the delivery of bicarbonate (e.g., for microalgae cultivation), and the formation of carbonate minerals. Within the realm of EPS techniques, dynamic manipulation of pH facilitates the conversion of dilute CO_2 gas into dissolved CO_2 (carbonic acid) or bicarbonate. For instance, in the pure CO_2 gas delivery system, dilute CO_2 is captured within an aqueous hydroxide solution (or carbonate solution) at a high pH ($>pK_2$). Subsequently, pure CO_2 is released by acidifying the solution (at $\text{pH} < pK_1$), and the sorbent is regenerated through alkalization.

Similarly, EPS processes hold the potential to efficiently capture CO_2 and provide a solution with a high concentration of bicarbonate, which is essential for microalgae cultivation—a widely adopted biological CCU approach. However, conventional methods for microalgae cultivation exhibit limited efficiency in utilizing CO_2 , leading to increased operational costs. The conventional CO_2 sparging system used in microalgae cultivation is a significant energy consumer with substantial capital requirements.^{15,16} In contrast, the EPS system offers the capability to provide dissolved bicarbonate, thereby reducing the capital and energy expenses associated with a traditional sparging system.¹⁷ Utilizing a bicarbonate-based feeding system for CO_2 has also demonstrated lower CO_2 losses to the environment compared to the use of gaseous CO_2 .¹⁸ As highlighted by Chi and co-workers,¹⁹ the pH level within the bioreactor plays a crucial role in shaping algal growth dynamics. In the context of extended outdoor microalgae cultivation, the continuous supply of flue gas containing 3–6% CO_2 can lead to a decrease in pH, resulting in significant buffering costs within the microalgae production process. This highlights the seamless compatibility of the EPS approach with bicarbonate-based algae cultivation—an emerging pathway that not only effectively reduces biomass cultivation costs but also optimizes carbon utilization efficiency, in addition to facilitating pH adjustment and buffering processes.

EPS also demonstrates the capacity to capture CO_2 using seawater and converting it into carbonate precipitates, such as calcium or magnesium carbonate, through *ex-situ* mineral carbonation.^{20,21} This attribute also positions EPS as a promising technology for mitigating CO_2 emissions through direct air capture, involving the utilization of seawater to capture atmospheric CO_2 in the form of carbonate minerals. Sarifian et al.²² conducted a study evaluating the feasibility of bipolar membrane electrodialysis (BMED) for oceanic carbon capture via *in situ* alkaline mineralization. However, technical hurdles arise due to scaling issues at alkaline pH levels exceeding 9. It is important to note that scaling issues can lead to membrane fouling, affecting not only the longevity of the membrane but also its surface area. This, in turn, contributes to other operational constraints such as voltage loss and increased energy consumption for pumping.²³

While the EPS process appears to be straightforward with only two pH regimes required, there is still significant room for optimization. Design enhancements are necessary to improve both the efficiency of CO_2 capture and concentration as well as the release and discharge processes. Currently, there is limited research focused on exploring the potential applications of EPS processes for CCU, such as CO_2 concentration, purification, or delivery of bicarbonate in a soluble form. In this study, we present a CCU pathway using EPS and provide an in-depth analysis of its mechanisms and potential applications, outlining its limitations from both thermodynamic and kinetic standpoints. We also develop an initial techno-economic assessment, and provide the perspectives and challenges for future development and deployment of EPS. This study sheds light on the integration of EPS with CCU, contributing to the objective of closing the carbon cycle.

■ ELECTROCHEMICAL PH-SWING: PRINCIPLE AND THEORY

Carbon Chemistry and Its Thermodynamic Limits.

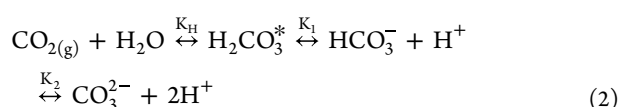
According to Henry's law (eq 1), CO_2 can be naturally dissolved in water, including seawater, due to the gas–water equilibrium.²⁴ When the CO_2 concentration increases, the solubility of CO_2 in water (i.e., CO_2 capture capacity) increases because of the correlation between the solubility of CO_2 and gas partial pressure. In addition, as the temperature

Table 2. Comparison of Approaches Using pH-Swing Concepts to Capture CO₂

electrochemical method using the pH-swing concept	advantages	technical challenges	pH range (acid–base)	current efficiency (%)	energy consumption (kJ/mol-CO ₂)	ref
electrodialysis (ED)	· simple construction	· high voltage (~2 V) required for ΔpH = 14 · high-concentration polarization losses	0–14	60–95	290–1,267,200	27–29
bipolar membrane electrodialysis (BMED)	· ambient temperature operation · minimum voltage of 0.829 V is required for ΔpH = 14.	· high salt ion leakage · high energy consumption · low faradaic efficiency · membrane fouling at high pH · not suitable for higher temperatures > 60 °C and long-term operation · slow kinetics of the carbonate precipitation	3–9	50–95	100–640	26,30–32
hybrid system (EDI + BMED)	· good stability after repetitive cycles of adsorption–desorption. · reducing the concentration polarization losses. · possibility of recovery/removal of heavy metals and organic acids	· possible in basic pH · inexpensive ion-exchange resin required · possibility of resin fouling	neutral pH	60–80	2775–6940	33–36
redox-active carriers	· possible to obtain a pure CO ₂ stream from a gas mixture (e.g., air) · self-sufficient H ⁺ provided through redox-active carriers	· catalysts are required to improve electron transfer. · difficult to simultaneously control acid and base pH in a practical process. · suitable solvent is required	-	60–90	55–106	37,38

risers, the gas solubility decreases, necessitating additional circulating water for effective CO₂ capture. This leads to increased power consumption for water pumping.⁶ The CO₂ equilibrium state differs in open and closed systems, contingent on exposure to air or confinement within the cell. As illustrated in eq 2, the proportions of species at equilibrium within a closed system reveal that the interaction between gaseous CO₂ and water generates both aqueous CO₂ (CO_{2(aq)}) and carbonic acid (H₂CO₃). In water chemistry, [H₂CO₃*] is equivalent to the combined concentration of CO_{2(aq)} and [H₂CO₃]. The carbonic acid then transforms into bicarbonate (HCO₃⁻) and eventually carbonate ions (CO₃²⁻) as the pH increases. Therefore, the concentration of total inorganic carbon (C_T) in water can be calculated by eq 3.

$$[\text{H}_2\text{CO}_3^*] = K_{\text{H}} \times P_{\text{CO}_2} \quad (1)$$



$$C_{\text{T}} = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (3)$$

where K_{H} is the Henry's constant of CO₂ in pure water (e.g., 10^{-1.47} M/atm at 25 °C), P_{CO_2} is the partial pressure of CO₂ (e.g., $P_{\text{CO}_2} = 10^{-p\text{CO}_2} = 0.00039$ atm in the atmosphere), and K_1 and K_2 are the first dissociation constant (10^{-6.35}) and the second dissociation constant (10^{-10.33}) of H₂CO₃, respectively.

The pH plays a crucial role in governing the distribution of inorganic carbon species, thereby influencing the extent of the CO₂ captured in both open and closed systems. In a closed system, C_T remains unaltered, despite variations in the pH of the water. However, within an open system, an ongoing interchange prevails between CO₂ gas and water, resulting in a consistent concentration of [H₂CO₃*] regardless of pH. By capitalizing on the pH-dependent thermodynamic equilibrium, we could harness the pH-swing process for the capture of CO₂ in an open system. As shown in Figure 2a, an increase in pH

leads to the conversion of CO_{2(g)} into CO_{2(aq)}, with the solubilized form transitioning into bicarbonate and/or carbonate. In other words, the open system could effectively operate as a continuous capture mechanism under appropriate conditions of temperature and gas partial pressure. Figure 2b shows a logarithmic concentration diagram illustrating various inorganic carbon species across different CO₂ feed concentrations. This visual representation underscores a direct correlation among the source concentration, pH, and carbonate concentration. Notably, at pH levels below 6, the predominant form within C_T is dissolved CO_{2(aq)}, whereas at pH levels exceeding 10, the primary component of C_T is carbonate. In the intermediate pH range, C_T primarily comprises bicarbonate ions.

Process Configurations and Applications. EPS for CO₂ capture has been demonstrated through various electrochemical techniques, such as electrolysis (ED), bipolar membrane electrodialysis (BMED), redox-active carriers, and hybrid processes combining two or more methods, as presented in Table 2. These advancements in EPS have also found application in diverse resource recovery systems. For instance, ED has been studied in multiple configurations for aqueous CO₂ capture and release, spanning applications like ocean capture and the concentration of KHCO₃ from K₂CO₃ capture sorbents, thereby enhancing vacuum regeneration efficiency.²⁶ The utilization of bipolar membranes, commonly termed BMED, also offers alternative routes. Water molecules experience a substantial electric field and, sometimes with the assistance of a water dissociation catalyst, undergo water splitting into OH⁻ and H⁺ on the surface of a bipolar membrane. Consequently, OH⁻ migrates toward the anode, while H⁺ moves toward the cathode. This electrochemistry principle establishes and maintains a pH difference between the two compartments within a BMED system.

In this context, we present several illustrative instances of applying EPS principles to CO₂ capture. Figure 3a shows the work of Yan and co-workers,³⁹ where an electrochemical hydrogen-looping process directly captured 91% of CO₂ at an

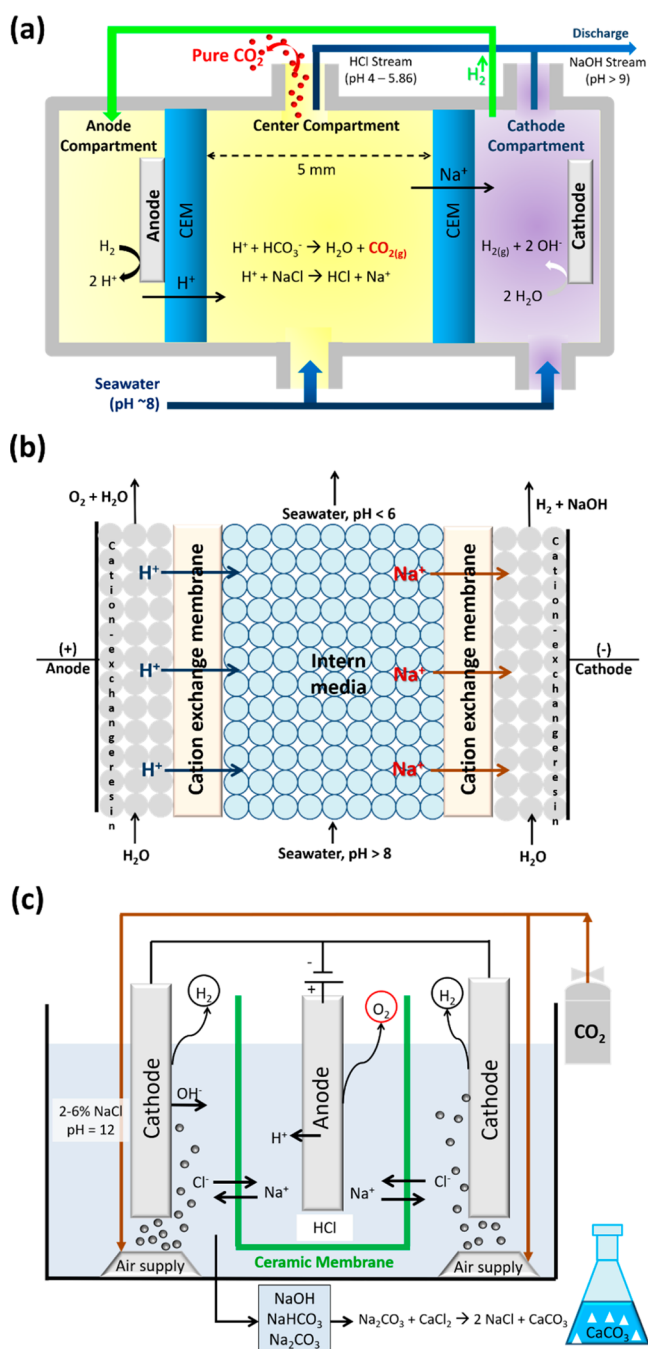


Figure 3. Schematic of (a) electrochemical hydrogen-looping cell for removing CO₂ from seawater. Figure reproduced with permission from ref 39. Copyright 2022, American Chemical Society. (b) CO₂ capture and H₂ production via seawater acidification and water electrolysis. Figure reproduced with permission from ref 35. Copyright 2014, American Chemical Society. (c) CO₂ fixation by membrane-separated NaCl electrolysis. Reproduced with permission from ref 40. Copyright 2015, MDPI.

electric energy consumption of 660 kWh/ton-CO₂. This involved the simultaneous generation of protons and OH⁻ from seawater, inducing a pH shift from 8 to 4. Similarly, Willauer and co-workers³⁵ employed water electrolysis coupled with a cation exchange membrane to produce H₂ and acidify seawater. The acidified seawater was then used to recover CO₂ through ion-exchange resin-packed chambers. During operation, the pH levels of the influent and effluent seawater were

shifted from above 8 to below 6, as depicted in Figure 3b. In the work by Park and co-workers (see Figure 3c),⁴⁰ CO₂ fixation was achieved through the electrolysis of NaCl in seawater using a ceramic membrane. This led to the formation of CaCO₃, with a NaOH absorbent solution produced under room temperature and pressure. This solution captured CO₂ gas and produced a NaHCO₃ solution along with calcium carbonate (CaCO₃) precipitates. It is worth noting that the operational temperature and pressure are pivotal factors influencing the CO₂ absorption efficiency and the associated energy consumption of the process. Notably, the formation of CaCO₃ as the ultimate product for CO₂ storage or utilization obviates the need for a subsequent CO₂ desorption step, resulting in lower process energy consumption when compared to conventional CO₂ absorption–desorption processes.

■ ELECTROCHEMICAL PH-SWING FOR CO₂ MINERALIZATION

Utilizing EPS principles to optimize alkaline mineralization for CO₂ capture shows great promise. In this section, we present an overview of the enhanced performance and energy consumption aspects of EPS in CO₂ mineralization. Furthermore, we delve into the challenges posed by the process from both thermodynamic and kinetic perspectives.

Performance and Process Energy Consumption. In Table 3, we summarize the operational parameters and performance across various systems that adopt EPS mechanisms for the capture of CO₂ through mineralization. In general, EPS effectively facilitates CO₂ mineralization in seawater by generating carbonate minerals at pH levels exceeding 8. Sharifian and co-workers²² also observed a remarkable 97% C_T extraction using a stacked BMED-CEM configuration with 10 cell pairs, achieved by elevating the pH to above 9.6. The corresponding energy consumption, at 318 ± 29 kJ per mol of CaCO₃, proves to be significantly lower than previously recorded figures for alkaline mineralization, which ranged from 640 to 2880 kJ per mol of CaCO₃.^{32,41} Apart from seawater, another abundant source of Ca²⁺ and Mg²⁺ is hard water, with concentrations differing based on factors such as industrial effluent. For mineral carbonation process, the separation of Ca²⁺ and Mg²⁺ ions allows for the acquisition of commercially viable pure products contingent on pH adjustment for precipitation.⁴² In a study by Xie and co-workers,⁴³ ED was used to recover Ca²⁺ and Mg²⁺ ions through mineralization, with HCl regeneration occurring at the anode region.

Chen and co-workers⁴⁴ introduced an integration of BMED and a crystallization chamber to simultaneously capture CO₂ and extract nesquehonite (MgCO₃·3H₂O) from seawater at pH levels below 11. However, it is worth noting that the presence of OH⁻ in the alkali chamber led to membrane fouling due to the low solubility of Mg(OH)₂. Therefore, the prevention of membrane fouling becomes paramount to minimize energy consumption during both MgCO₃·3H₂O production (1.67 kWh·kg⁻¹) and CO₂ capture (1.22 kWh·kg⁻¹). This objective is achieved through meticulous control of parameters, such as the CO₂ flow rate, temperature, and applied current density.

Thermodynamic or Kinetic Limits. CO₂ mineralization using seawater demonstrates a remarkable potential to remove all C_T in seawater since the concentrations of Ca²⁺ and Mg²⁺ are respectively 4 and 25 times higher than that of C_T. In an open system, maintaining a constant CO₂ concentration, the

Table 3. Comprehensive Studies of Aqueous CO₂ Capture and Final Products for Storage via EPS^a

approach	source of feedwater	operating condition ^b	pH range	CO ₂ capture efficiency	capacity(g/L)	energy consumption	ref
E-CEM	seawater	CC = 30 mA·cm ⁻² in 40 min	2.0–8.0	92% CO ₂	-	42 kWh·m ⁻³ H ₂	35
BMED (BPM-CEM)	synthetic seawater	CC = 40 mA·cm ⁻² in 120 min	4.5–10.0	97% DIC	0.1 kg CO ₂ /m ³ -seawater (0.28 kg-CaCO ₃ /m ³ -seawater)	318 ± 29 kJ·mol ⁻¹ CaCO ₃ (0.88 kWh·kg ⁻¹ CaCO ₃)	22
BMED-AEM	seawater	CC = 0.4 mA·cm ⁻² per lpm ⁻¹	4.0–8.5	59% CO ₂	-	242 kJ·mol ⁻¹ CO ₂	26
BMED-CO ₂ R	seawater	CC = 3.3 mA·cm ⁻²	4.7–8.5	71% CO ₂	-	0.98 kWh·kg ⁻¹ CO ₂	45
BMED	seawater	CC = 2.2 mA·cm ⁻²	9–10	0.77 kg MgCO ₃ ·3H ₂ O/kg CO ₂	2 kg-CO ₂ /ton-seawater	1.67 kWh·kg ⁻¹ MgCO ₃ ·3H ₂ O	44
ED (AEM)	hard water	Cell potential = 0.84 V at 100 mA	pH = 10.4–12.3 (Mg ²⁺) pH = 12.5 (Ca ²⁺)	2.56 tons MgCO ₃ /tons CO ₂ ; 2.27 tons CaCO ₃ /tons CO ₂	0.9–3.8 kg CO ₂ /m ³ -seawater	1.22 kWh·kg ⁻¹ CO ₂	43
ED (CEM-AEM)	high salinity wastewater	Cell voltage = 0–7 V in 12 h	3.9–12.0	0.05 mM·cm ⁻² ·h ⁻¹ of HCl and NaHCO ₃	-	-	46
PCET	saline water	CC = 20 mA·cm ⁻² in 40 min	4.0–13.4	100% CO ₂	-	121–237 kJ·mol ⁻¹ CO ₂	47
EHL	seawater	CC = 2 mA·cm ⁻² ; Cell voltage = 0.48 V	4–8	91% CO ₂	9.0 kg-CO ₂ /m ³ -seawater	0.66 kWh·kg ⁻¹ CO ₂	39

^aNote: BMED, bipolar membrane electrodialysis; E-CEM, a three-chambered electrolytic cation exchange module; EHL, electrochemical hydrogen-looping; PCET, proton-coupled electron transfer; CO₂R, a vapor-fed CO₂ reduction cell. ^bCC = constant current.

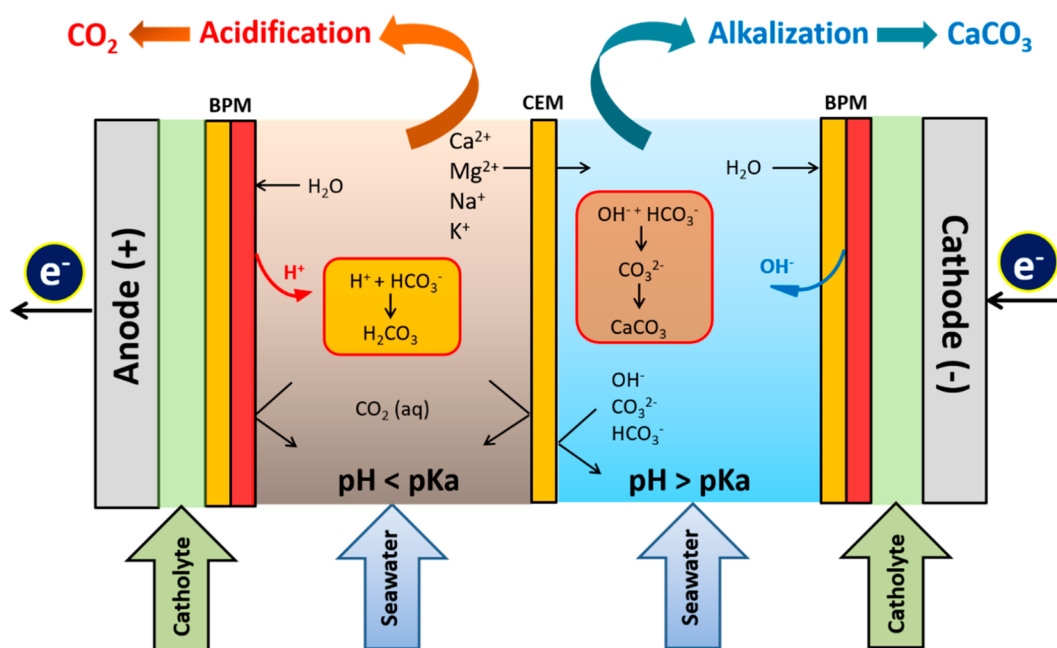


Figure 4. Conceptual design of electrochemical pH-swing in a stacked BPM-CEM-BPM cell for CO₂ capture from seawater incorporated with mineralization. Left-hand side: acidification route for release of CO₂ from seawater. Right-hand side: alkalization route for CO₂ mineralization.

pH range of 9.3–9.6 favors mineralization. Conversely, within a closed system where C_T remains constant, the CO₂ concentration diminishes as the pH varies. The efficacy of CO₂ mineralization through the EPS process is critically dependent on its kinetic constraints. These constraints encompass a range of factors impacting the reaction rate and carbon mineralization efficiency. Primarily, alterations in the pH exert a significant influence on the rate of species hydration in the solution. By control of the pH range, the hydration rates can be enhanced, thus expediting mineralization reactions. The initial rates of hydration for CO₂ and HCO₃⁻ are $2.9 \times 10^{-2} \text{ s}^{-1}$ and $2.0 \times 10^{-4} \text{ s}^{-1}$, respectively, as their reactions follow pseudo-first-order kinetics.⁴⁸ When considering the CO₂/

HCO₃⁻ system and its second-order reaction mechanism, these rates can be enhanced significantly to approximately $6.0 \times 10^3 \text{ M}^{-1} \cdot \text{s}^{-1}$ and $4.1 \times 10^4 \text{ M}^{-1} \cdot \text{s}^{-1}$ under both basic and acidic conditions.^{33,49} Additionally, reaction kinetics directly affect the pace of pH transitions and the overall CO₂ removal efficiency. To optimize operational conditions and counteract pH-swing kinetics, specific adaptations are essential. These encompass the requirement for (1) a broader pH-swing range ($\text{pH} < \text{p}K_{a1}$ and $\text{p}K_{a2} < \text{pH}$), as shown in Figure 4, and (2) the application of catalysts such as carbonic anhydrase enzyme⁵⁰ or formate dehydrogenase⁵¹ to improve kinetics and overall reactions. Effective pH swings should be reversible, transition-

ing from high pH capture to low-pH release to prevent operational pH drifts that reduce CO₂ capacity.

Furthermore, the kinetics of carbonate precipitation reactions needs to be considered. The formation of carbonate minerals such as calcium and magnesium carbonates is a pivotal step in CO₂ mineralization. While mineralization can be enhanced through seeded crystallizers, there is a risk of membrane contamination in stacked-ED cells, subsequently impeding carbonate precipitation kinetics. In Figure 5, we

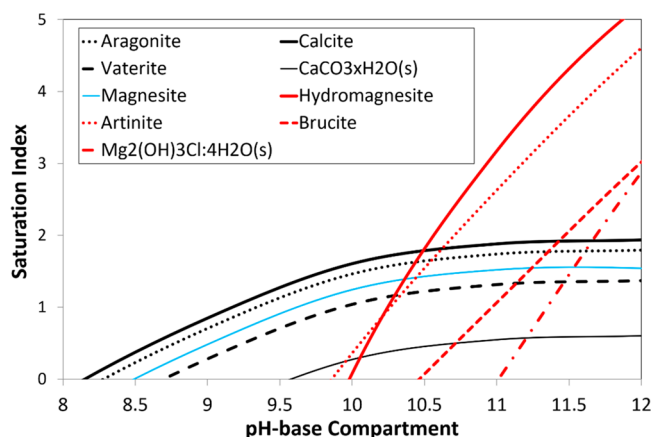


Figure 5. Saturation index (SI) of all thermodynamically possible minerals in seawater with different base-pH values determined by Visual MINTEQ 3.1 at 25 °C (Data of minerals used to calculate SI can be found in Table S1).

provide the pH threshold for calcium and magnesium carbonate precipitation using the saturation index (see eq S1). Mg²⁺ completely precipitates at a pH of 10, while Ca²⁺ begins to precipitate at a pH > 12. This implies that between pH 10 and 12, Mg²⁺ ions fully precipitate, potentially causing early membrane fouling in the electro dialysis process, while calcium ions remain in solution. The rate of carbonate mineral precipitation directly impacts carbon removal efficiency within the electrochemical pH-swing process, necessitating a comprehensive understanding and enhancement of precipitation kinetics.

By addressing and comprehending the kinetic boundaries associated with the EPS process, researchers and engineers can devise strategic approaches to optimize and elevate the efficacy of CO₂ mineralization using seawater, thus, advancing CCU technologies.

■ ELECTROCHEMICAL PH-SWING FOR BICARBONATE DELIVERY

Microalgae cultivation systems offer a promising technology for tackling CO₂ emissions and extreme climate change. Various economically significant algal species have been systematically reviewed for their biomass productivity across different CO₂ concentrations.⁵² Notably, microalgae have exhibited the capacity to generate one kilogram of biomass by utilizing ~1.83 kg of CO₂. Within the framework of biological CCU, *Chlorella* species and *Spirulina platensis* have exhibited mean CO₂ fixation efficiencies of 46% and 39%, respectively, when subject to an input CO₂ concentration of 10%.⁵³ Similarly, *Scenedesmus obliquus* attained a peak biomass yield of 2.3 kg per m³ when exposed to a 15% CO₂ concentration.⁵⁴ Despite the heightened responsiveness of

certain algae species to elevated CO₂ concentrations, further investigations are imperative to optimize CO₂ levels, ensuring maximal biomass productivity.^{16,52} A technical hurdle arises in the form of an artificial CO₂ supply for microalgae growth, predominantly facilitated by concentrated CO₂ gas. This practice is associated with diminished utilization efficiency and elevated production costs. To overcome this issue, a viable solution involves employing a high concentration of bicarbonate as a carbon source through EPS. This approach obviates the necessity for energy-intensive artificial CO₂ provisioning, concurrently addressing transient CO₂ storage predicaments. In this section, we discuss the application of EPS for bicarbonate delivery in a microalgae cultivation system.

Configuration for Microalgae Production. Although CO₂ can be directly consumed by microalgae, the mass transfer is limited with low productivity of < 3 g·m⁻²·day⁻¹.^{55,56} Bicarbonate, which dominates the pH range of 6–10, has emerged as an alternative substitute carbon source for microalgae cultivation. This can be accomplished within a pH-tuned, integrated system for both CO₂ capture and a microalgae production system. As shown in Figure 6a, atmospheric CO₂ can be efficiently harnessed through a bicarbonate pool, such as soda lakes.⁵⁷ Microalgae growth thrives at elevated bicarbonate concentrations, effectively converting carbon into the biomass. Given the disparity between the 12-h availability of light and the 24-h occurrence of CO₂ transfer into water, the carbon-concentrating mechanism during nighttime operates by accumulating CO₂ as a bicarbonate pool, ensuring a proficient CO₂ supply during light hours. Yet, despite its advantages, the efficiency of bicarbonate regeneration faces limitations due to the suboptimal CO₂ volumetric mass transfer and the modest concentration of CO₂ transferred from the air.¹⁵ In the pursuit of efficient microalgae production, photobioreactors (PBR) are designed to stimulate photosynthesis and enhance the CO₂ capture efficiency. These PBRs harmonize the objectives of achieving enduringly elevated biomass productivity while carefully managing the expenses and energy outlay associated with light provisioning. When operating under the optimal conditions, as shown in Figure 6b, PBRs equipped with a bicarbonate delivery system hold the potential to notably mitigate the overall production costs.

In the context of practical deployment, electro dialysis (ED)-based EPS processes exhibit linear scalability. This scalability allows for designing the capacity size to accommodate service cycles effectively.⁵⁸ As a result, it becomes feasible to conduct preventative maintenance on a unit while maintaining a peak production capacity. Moreover, the stack of cells required for ED-based EPS does not need to be overly large to achieve economic viability. One notable advantage is that an identical design and system of ED-based EPS can be seamlessly adapted to various capacity requirements up to the limits of the power supply. This obviates the necessity for a redesign when expanding or contracting the system.

Carbon Utilization Efficiency. Carbon utilization efficiency (CUE, see eq 4)⁵⁶ serves as a crucial metric for assessing the effectiveness of microalgae cultivation systems for CCU. This indicator represents the proportion of carbon captured and utilized by microalgae in relation to the total input carbon. In the context of a conventional CO₂-based system, the total input carbon corresponds to the quantity of carbon introduced in the form of CO₂ during the operational processes. Meanwhile, the measurement of fixed carbon within

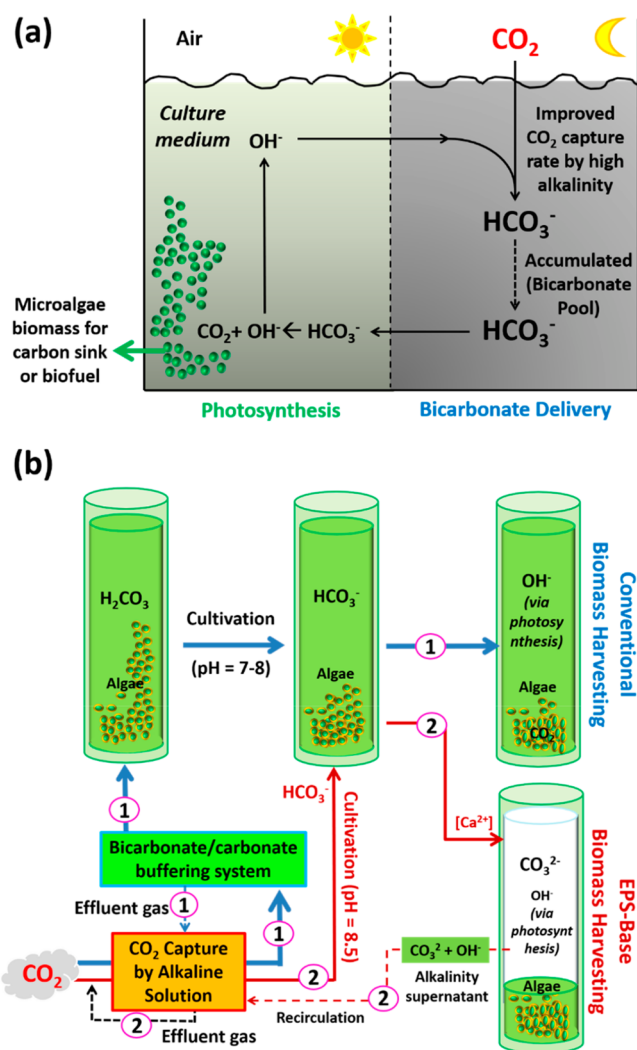


Figure 6. (a) Mechanism of the bicarbonate pool's role in the efficient capture of CO_2 from the air and rapid carbon supply for photosynthesis. Image reproduced with permission from ref 57. Copyright 2020, Elsevier. (b) Demonstration of bicarbonate-based integrated carbon capture and algae production systems with ① a system with a conventional bicarbonate/carbonate buffer system, or ② a closed-loop bicarbonate-carbonate recirculation using EPS for microalgal cultivation, harvesting, and CO_2 capture.

microalgae encompasses the carbon content found within the final biomass of microalgae, and this value is then multiplied by the weight obtained after ash-free drying.

$$\text{CUE}(\%) = \frac{\text{mass of carbon fixed in microalgae}}{\text{mass of total input carbon}} \times 100 \quad (4)$$

Table 4 presents the performance of integrated bicarbonate-based CO_2 capture and utilization for microalgae cultivation. The reported findings on microalgae cultivation in the literature^{16,55} revealed that bicarbonate-based cultures exhibited significantly higher CUE than CO_2 -based cultures. This disparity effectively highlights the pivotal role played by substrate accessibility in this context. In the cultivation of microalgal species with a preference for high salinity, such as those found in seawater, the concentration of carbonate species at a pH of 8.1 and a temperature of 25 °C notably favors the adoption of a bicarbonate-based cultivation system over a

CO_2 -based one. This is attributed to the fact that seawater conditions provide relatively low concentrations of CO_2 (10 $\mu\text{mol}/\text{kg}$), juxtaposed against significantly higher levels of HCO_3^- at 1,818 $\mu\text{mol}/\text{kg}$.⁵⁹ However, it is important to note that the heightened salinity inherent to seawater environments could hinder the solubility of CO_2 , thus leading to a reduced CO_2 fixation efficiency and an escalated rate of outgassing. To overcome this challenge, the strategic employment of alkalihalophilic strains becomes imperative. These strains are adept at thriving in high-pH, high-bicarbonate conditions, thereby enabling the attainment of elevated biomass productivity and concentration—two pivotal factors for real-world applicability.

TECHNO-ECONOMIC ASSESSMENT

Performance Indicators Involved in the Large-Scale EPS Process. A techno-economic analysis of EPS for CCU processes should be considered to evaluate the viability of the proof-of-concept system. The scale and energy requirements inherent to the pH-swing process, as they pertain to CO_2 capture, mineralization, and microalgae cultivation, will significantly impact the initial capital cost. In this study, we provide a preliminary estimate for the total cost of capturing CO_2 and the value added to produce carbonate minerals and bicarbonate liquids with the EPS process (as shown in Figure 7). The choice of the membrane plays a pivotal role in determining the overarching expenses associated with the EPS process. The cost of cation-exchange membrane (CEM) is approximately a third of the cost of bipolar membrane (BPM). A direct comparison of cost assessments considering both the operation and maintenance reveals a substantial disparity between the CEM utilized for CO_2 capture and the BPM.⁴⁵

The energy cost of EPS for CO_2 capture within an ocean water system boasting a pH of 4 can be calculated using eq 5:

$$\text{energy cost} = \frac{C_e \times V \times I}{\frac{1}{n \times F} \times 3600 \times M_p} \quad (5)$$

where C_e is the cost of electricity (USD/kWh), assumed as 0.117 for businesses and 0.092 for households in Taiwan,⁶⁴ V is the applied voltage (V); I is the applied current (A); n is the number of participating electrons in EPS; F is the Faraday constant (96,485 $\text{A}\cdot\text{s}\cdot\text{mol}^{-1}$); M_p is the molar mass of final product, such as CaCO_3 (molar mass of 0.1 $\text{kg}\cdot\text{mol}^{-1}$).

When considering CO_2 mineralization, it is important to account for the value of products, such as carbonate minerals. Instead of relying solely on the quantification of CO_2 capture (measured in kilograms), the calculation methodology integrates the weight of extracted carbonate minerals (measured in moles of CO_2 per mole of carbonate minerals). Table 5 presents the indicators pertinent to the assessment of potential large-scale carbonate mineralization alongside the bicarbonate–microalgae system. This compilation of indicators is instrumental in gauging the holistic energy consumption associated with these processes. Within this table, the spotlight is on calcite (CaCO_3) as the primary precipitant. Its selection is rooted in its heightened thermodynamic stability, setting it apart from alternative minerals. In the realm of bicarbonate-based microalgae cultivation, microalgae act as intermediaries in generating valuable products, such as biofuels,⁶⁵ biofertilizers,⁶⁶ food, and supplements,⁶⁷ or feed ingredients.⁶⁸ Despite the diverse range of products attainable through microalgae cultivation, the cost of the bicarbonate–microalgae system

Table 4. Performance of Integrated Bicarbonate-Based CO₂ Capture and Utilization for Microalgae Cultivation

strains	carbon source	[HCO ₃ ⁻] (mol·L ⁻¹)	pH	cultivation time (d)	biomass concentration (g·L ⁻¹)	volume of productivity (g·L ⁻¹ ·d ⁻¹)	specific growth rate (d ⁻¹)	harvesting efficiency (%)	products	ref
<i>Haematococcus pluvialis</i>	Flue gas (3–6% CO ₂) in KOH	-	7.5	62	4	-	-	-	Astaxanthin ^a	18
<i>Spirulina platensis</i>	NaHCO ₃ + CO ₂ (air)	0.3	10.0–12.5	70	3.45 ± 0.08	1.0	0.48 ± 0.02	-	protein, PHA	57
<i>Euhalotheca ZM001</i>	NaHCO ₃	1.0	10.5	8	4.79	1.21	0.69	-	protein	60
<i>Neochloris oleoabundans</i>	NaHCO ₃	0.3	8.5	180	1.64 ± 0.03	0.40 ± 0.01	1.70 ± 0.03	97.7 ± 0.2	lipid	61
<i>Chlorella sorokiniana</i> str. SLA-04	Glucose +5% CO ₂	-	8.2–10.0	35	2.25	0.74 ± 0.02	-	-	lipid	15
<i>Chlorella sorokiniana</i> str. SLA-04	CO ₂ (air) ^b	>0.02	>10.0	120	-	38.5 ± 2.3 ^c (July) 18.0 ± 1.8 ^c (October) 15.2 ± 1.0 ^c	-	-	Lipid	16
Cyanobacterial consortium	CO ₂ (air)	0.3–0.5	10.4–11.2	20	-	-	-	-	-	62
<i>Synechococcus</i> sp. PCC 7002	NaHCO ₃ + 5% CO ₂	0.09	9.5	6	6	1.1	-	-	carbohydrate	63

^aKeto-carotenoid astaxanthin has high antioxidant activity and is a useful material for a nutrient supplement, pharmaceuticals, animal feedstock, and cosmetics. ^bCO₂ in the atmosphere was mixed by paddlewheels into high pH and high alkalinity media for microalgae cultivation in a raceway pond. ^cThe unit of g·m⁻²·day⁻¹ was reported. Abbreviations: PHA (polyhydroxyalanoale).

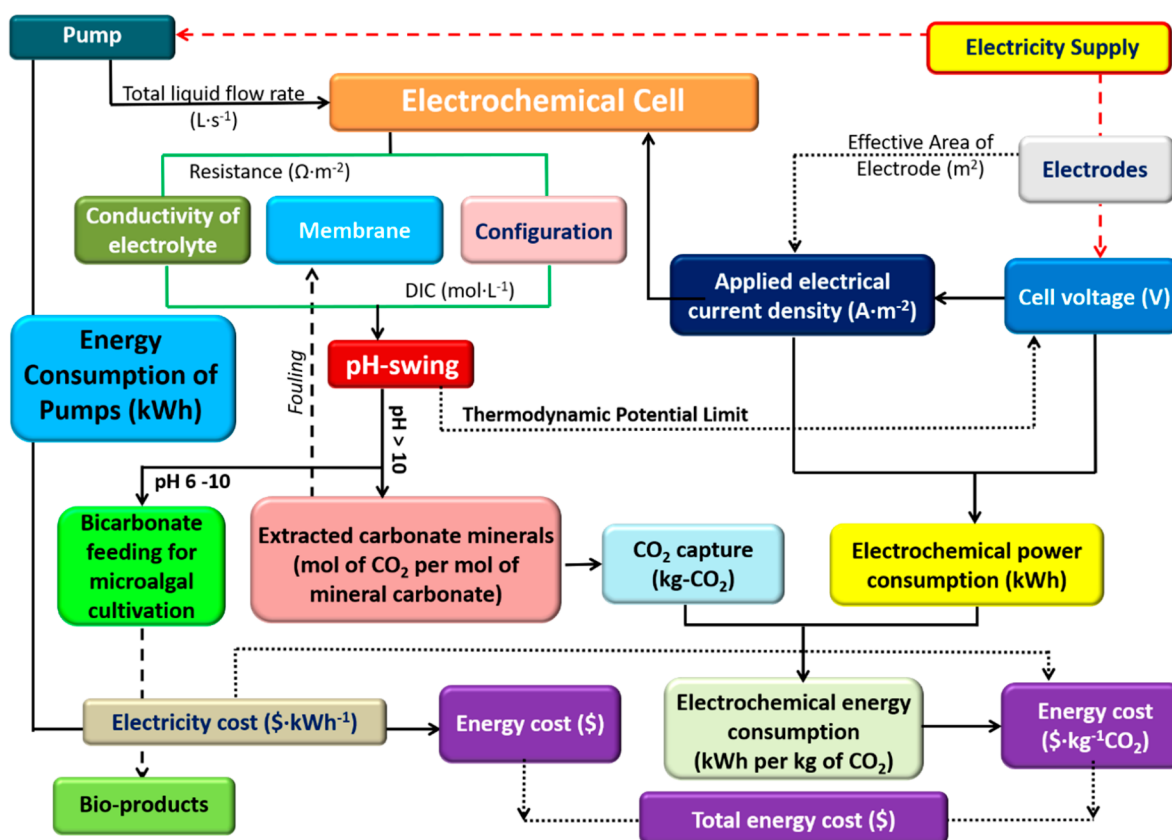


Figure 7. Flowchart of details used to calculate the total energy consumption for EPS.

emerges as a critical determinant for the practical feasibility and market viability of the final products.

To evaluate the possible economic benefits from investment in the system, cost-benefit analysis (CBA) is applied to compare the economic feasibility of implementing different projects and supporting decision-making works through the calculation of net profit (NP):⁶⁹

$$NP = \sum B_i - \sum C_i \quad (6)$$

where B_i is the value of the benefit item i , and C_i is the value of the cost item i . If the result is $NP > 0$, the project is feasibly applicable. Otherwise, if the result is $NP < 0$, the project is not suitable in economic terms.

Table 5. Indicators of Large-Scale CO₂ Capture, Storage, and Utilization through the EPS Process

indicators	symbol	unit	equation
daily energy consumption of EPS	E_{EPS}	kWh per m ³ per day	total daily cost of ED = $E_{\text{EPS}} \times W_{\text{feed}} \times C_e$
daily volume of seawater or feed	W_{feed}	m ³ per day	
cost of electricity	C_e	USD per kWh	
concentration of captured CO ₂	$[\text{CO}_2]$	mM	dissolved organic carbon (DIC): $[\text{DIC}] = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{CO}_2]$ (mM)
concentration of removed C _T	$[\text{C}_T]$	mM	
concentration of removed bicarbonate	$[\text{HCO}_3^-]$	mM	
concentration of removed carbonate	$[\text{CO}_3^{2-}]$	mM	
extracted carbonate minerals	-	kg CO ₂ per kg carbonate mineral	
C _T removal ratio (%)	R_{CT}	%	$R_{\text{CT}} (\%) = (\text{DIC}_i \cdot [\text{DIC}_e]) / [\text{DIC}_i] \times 100$
daily amount of carbonate minerals	m_{CaCO_3}	kg·m ⁻³ ·day ⁻¹	
daily amount of seeded calcium	m_{seed}	g·m ⁻³ ·day ⁻¹	
energy cost based on CaCO ₃ production	E_{CaCO_3}	USD·kg CaCO ₃ ⁻¹	
energy cost based on bicarbonate liquid	E_{biomass}	USD·L (bicarbonate) ⁻¹	
bipolar membrane voltage to create pH-swing	V_{BPM}	V	$V_{\text{BPM}} = 0.059 \times [(\text{base-pH}) - (\text{acid-pH})]$
flow rate of influent	q	m ³ ·s ⁻¹	
membrane active area (bipolar membrane)	A	m ²	
residence time	t_r	s	
thickness of cell compartment	d	m	
BPM-limiting current density	i_{lim}	A·m ⁻²	
required current density	i	A·cm ⁻²	$i = [([\text{OH}^-]_{\text{produced}}] \times F \times q) / (A)] + i_{\text{lim}}$
energy consumption based on produced CaCO ₃	E_{cons}	kJ·molCaCO ₃ ⁻¹	$E_{\text{cons}} = (i \times A \times V) / (q \times n_{\text{CaCO}_3})$
Total energy cost ^a	$\sum E$	USD	Total energy cost = $E_{\text{CaCO}_3} + E_{\text{biomass}}$

^aIt is assumed that the foreign exchange rate of 1 USD (United States Dollars) is equal to 30 NTD (according to the Bank of Taiwan).

An extensively utilized indicator in cost-benefit analysis (CBA) is the benefit-cost ratio (BCR).⁷⁰ This ratio takes into account the financial gains generated by a project in relation to the expenses incurred in its execution. The calculation of the BCR is as follows:

$$\text{BCR} = \frac{R'_t}{C'_t} \quad (7)$$

where R'_t is the revenue gained in the tenth year, C'_t is the cost investment in the tenth year, and t is the expected operation period. Likewise, a higher BCR equal to or exceeding one signifies a greater economic viability for the invested project.

Cost Estimation of CO₂ Mineralization. As presented in Table 5, the outcomes pertaining to the energy consumption of the pH-swing process for CO₂ capture display considerable variability dependent upon the specific operational conditions. For instance, to delve further into the BCR analysis, a single cell of EPS using BPM is put forth as a foundation, aligning with prior research. This approach is in line with the proposed concept within this analysis.²² In light of this framework, the thermodynamic electrical energy consumption for the production of CaCO₃ is determined to be 35 kJ·mol⁻¹ or equivalently, 0.097 kWh·kg-CaCO₃⁻¹. Therefore, the energy cost based on CaCO₃ production amounts to approximately 8.7–10.0 USD per kilogram of CaCO₃. It is notable that the market price of CaCO₃ globally falls within the range of 0.13–0.33 USD-per kilogram of CaCO₃.⁷¹ Aspects such as personnel and electrical device costs will not be factored into this calculation; only the energy cost pertinent to CaCO₃ production will be considered. According to eq 7, the resulting BCR in this specific context is projected to be 0.03. This value suggests that solely producing carbonate mineralization falls short of meeting the prerequisites to render the EPS process

economically viable. Given this analysis, it is strongly recommended that additional products should be integrated into the process. An exemplary addition is the cultivation of microalgae based on bicarbonate feeding, aimed at generating valuable bioproducts and concurrently contributing to water purification. This strategic diversification is advocated to meet the burgeoning societal demand for sustainable water-energy interactions as well as to address the imperative of combatting climate change through CCU approaches.

In the broader context, the practical applications of precipitated mineral carbonates are intricately tied to their purity and a diverse array of physicochemical attributes. According to a study conducted by Kamkeng and co-workers,⁷² the current global usage of CO₂ for direct purposes, such as enhanced oil recovery and the food and beverage industry, stands at 42.4 million tonnes per year (MT/yr). The demand for CO₂ in these domains remains steady, largely due to consistent industrial valorization. However, it is the indirect utilization of CO₂ (about 232 MT/yr) that truly stands out, outpacing direct applications (42 MT/yr) by nearly 6-fold.⁷² This category encompasses significant uses such as urea production (132 MT/yr), inorganic carbonate production (70 MT/yr), and methanol production (10 MT/yr) and also includes production of formaldehyde and dimethyl ether (5 MT/yr each), among other smaller-volume markets. In this context, the potential conversion of CO₂ into carbonate minerals emerges as a promising avenue. Such a conversion could substantially elevate the value of CO₂ and act as a catalyst for a heightened investment in CCU processes. This trajectory holds considerable promise, positioning the EPS process as an attractive avenue for CO₂ mineralization and subsequent deployment.

Cost Estimation of Bicarbonate-Based Microalgae Cultivation. By exploring bicarbonate as an alternative carbon

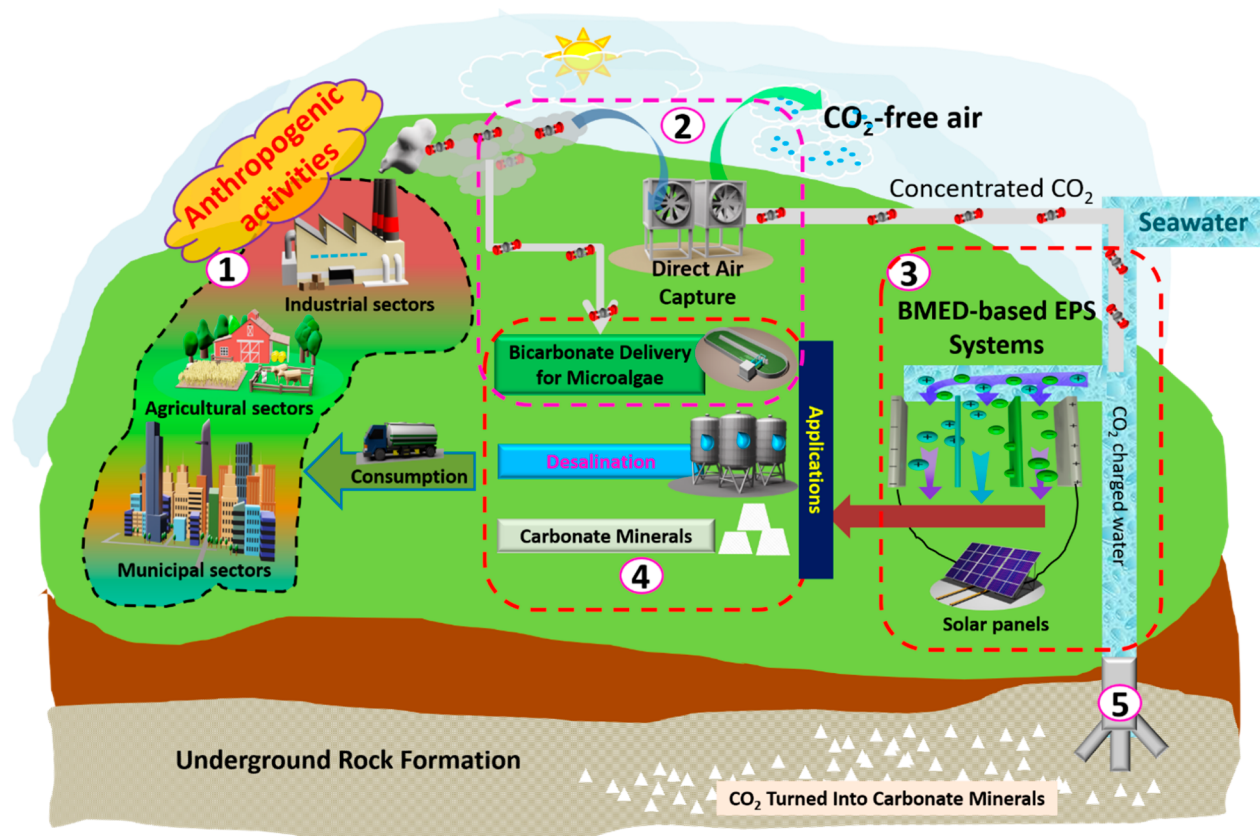


Figure 8. Integration of electrochemical pH-swing processes with simultaneous CO₂ capture, desalination, bicarbonate delivery, and production of mineral precipitates.

source, we address a range of challenges. This strategic shift leads to reductions in costs and energy requirements associated with carbonate regeneration, as well as the transportation and storage of gaseous CO₂.¹⁷ A key setback in the past has been the limited CUE and productivity, primarily due to suboptimal CO₂ mass transfer at neutral pH, hampering the progress of large-scale microalgae cultivation. However, the adoption of bicarbonate-based cultures offers a solution to this predicament by boosting CUE and streamlining the cultivation process. Pioneering research by Kim and colleagues^{56,73} showcases the potential of this approach. They demonstrated that the specific growth rate of *Dunaliella sp.*, a halophilic green algae, experienced enhancement when it was supplied with 5 g/L NaHCO₃, produced via electrochemical CO₂ mineralization. The system relying on NaHCO₃ as a feed exhibited a markedly higher CUE (91.4%) in comparison to systems supplied with pure CO₂ (3.6%). This improvement can be attributed to the elevated water solubility of NaHCO₃ (9.21 wt %), leading to significantly improved operational dynamics.

In another scenario involving the pH-swing process, where a pH variation from 3 to 8 is employed to generate liquid bicarbonate, the voltage required for a bipolar membrane to effectuate the pH swing stands at 0.177 V. Notably, this voltage is notably lower compared to the pH-swing of five necessary for CaCO₃ production as per a prior study ($V_{\text{BPM}} = 0.326$ V).²² Assuming other parameters remain consistent with that study, including current density and membrane surface flow rate, the energy consumption for bicarbonate production would be lower, quantified in kJ/mol of HCO₃⁻.

According to findings by Zhu,¹⁷ considering CUE values within the 50–90% range, the cost of bicarbonate for

producing one kg of algal biomass would range from 0.778 to 1.4 USD per kilogram. This stands in contrast to a CO₂ price range of 1.47–7.33 USD per kilogram.¹⁷ To illustrate this further, we examine the case of *Spirulina platensis* cultivation. With a feeding rate of 8.4 mg/L of NaHCO₃ and a CUE of 104 ± 3%, the cost of bicarbonate for one kilogram of biomass equates to 0.214 USD per kilogram.⁷⁴ However, when considering the assessment of BCR for final products derived from microalgae, the calculations become more intricate. This complexity arises due to several factors, such as NaHCO₃ preparation methodologies, system configurations, microalgae species, biomass productivity, and the energy expenses linked with system operation.

■ CHALLENGES AND OPPORTUNITIES

The practical utilization of mineralized carbonates within industries hinges upon a multitude of factors. These include properties such as purity, polymorphism, shape, size, distribution, color, brightness, and density, among others. Carbon mineralization products, most notably CaCO₃, bring forth distinct advantages due to their ease of transportation, storage, and versatility across a spectrum of sectors including coatings, paints, paper production, and construction materials. As we cast our gaze toward the future trajectory of CCU, the imperative lies in implementing integrated strategies that establish robust connections between the pivotal production and consumption sectors. This encompasses not only industrial domains but also extends to the agricultural and municipal sectors. A compelling blueprint for this journey is outlined in the form of a closed-carbon cycle, initiating from

CO₂ emission points linked to anthropogenic activities. This cycle unfolds into a series of cascading stages, culminating in the creation of final products. Figure 8 visually maps out this closed-carbon cycle, wherein each stage corresponds to specific areas of activity. This visualization underscores the comprehensive and all-encompassing approach mandated for the successful and efficient execution of CCU strategies.

As shown in Figure 8, the CO₂ emissions originating from industrial, agricultural, and municipal sectors (①) undergo capture via appropriate technologies (②). An illustrative example is the pilot-scale Carbfix project in Iceland, wherein CO₂ was directly captured from emission sources, such as geothermal power plants.⁷⁵ This captured CO₂ was then employed to generate the CO₂-saturated water. This water, rich in cations, facilitated in situ carbonate mineralization within basalt formations.⁷⁶ Although not directly comparable to the proposed EPS process, the concept of underground carbon storage in the form of carbonate minerals (⑤) remains a viable strategy for mitigating GHG concentrations.

In the integrated EPS approach, CO₂-saturated seawater is channeled into advanced electrochemical technologies (③), such as the integrated BMED system. The EPS process inherently demands substantial water input due to the evaporation and electrolysis processes triggered by the high vapor pressure of water. This becomes particularly relevant during drought periods. However, operating at ambient temperatures could significantly curb water loss through evaporation. The long-term operational efficacy of the process faces challenges from the formation of corrosive mixtures, leading to performance decline and maintenance complexities. Considering these aspects, an intermediate stage, such as desalination or water reclamation from wastewater, emerges as a potential solution to mitigate water loss and enhance the efficiency of the process. Despite its merits, the water-based pH-swing process for CO₂ capture does produce corrosive mixtures and membrane fouling, affecting the long-term performance. Approaches such as air and CO₂ gas sparging, dissolved CO_{2(aq)} cleaning, backpressure, flow rate adjustment, and acid-washing have been introduced to address these issues, with a combination of acid-washing and back pressure proving to be effective in eliminating inorganic fouling. A study conducted by Sharifian et al.⁷⁷ indicated that a combination of acid-wash and back pressure was effective in eliminating inorganic fouling, restoring both the cell voltage and pressure drop to their initial values.

To minimize energy consumption costs and GHG emissions (③), the incorporation of renewable energy sources such as solar or wind energy is envisioned, depending on the geographical location. However, it is worth noting that the CCU process invariably requires substantial renewable energy input, which can pose implementation challenges.⁷⁸ Region (④) represents the possible products derived from the EPS process in the context of region (③), including bicarbonate feeding for algae cultivation, water reclamation, and carbonate minerals. The final products from this region (④) are subsequently harvested (e.g., water, biofuels, and carbonate minerals) and supplied back to the initial emission region (①), thus creating a closed carbon cycle. Moreover, the bicarbonate feeding-based algal production system holds promise as an alternative for carbon capture in high pH and high alkalinity environments, complementing direct air capture methods.

CONCLUSION

Carbon capture and utilization (CCU) has garnered significant attention as a potent method to combat rising atmospheric CO₂ levels. This approach holds the dual potential of mitigating the CO₂ concentration while simultaneously transforming it into valuable commodities such as carbonate minerals and bicarbonate for algal cultivation. Amidst the ongoing exploration of pH-swing processes, BMED systems have emerged as prominent contenders. These systems adeptly generate both acid and base pH conditions through the process of water splitting. However, it is notable that this method demands a higher applied current than the membrane's limiting current, leading to escalated energy requirements. In the pH range spanning from 6 to 10, bicarbonate becomes the dominant chemical species. This prevalence opens avenues for integration with bicarbonate-based processes, such as microalgae production. In fact, harnessing bicarbonate within an EPS system demonstrates enhanced energy efficiency and economic viability compared with the direct supply of CO₂ gas. This enhancement is particularly significant, considering the challenges posed by low mass transfer in the direct CO₂ gas supply approach. As we chart a course for the future, it is imperative to steer research efforts toward crafting a closed carbon cycle characterized by high energetic efficiency and economic feasibility. This trajectory holds the potential to lay the foundation for robust CCU strategies, ultimately achieving a net carbon-zero outcome.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.3c02183>.

Summary of CO₂ utilization in various production fields; ion composition of the synthetic seawater used to calculate saturation index (SI) by Visual MINTEQ 3.1; The equation of SI (PDF)

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Author Contributions

S.Y.P. and S.W.S. supervised the preparation of this manuscript. T.N.D.C. and Y.J.L. conceived the topic. Y.I.L. collected references and wrote the manuscript. S.N. participated in some contents and figures. T.N.D.C., S.Y.P., and S.W.S. revised and finalized the manuscript. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

Biographies



Thanh Ngoc-Dan Cao embarked on her academic journey at Ho Chi Minh University of Technology in Vietnam, culminating in the successful completion of her bachelor's degree in Environmental Engineering. Continuing her pursuit at the Sirindhorn International Institute of Technology in Thailand, she specialized in environmental technology and science throughout her master's program. Transitioning seamlessly, she joined the faculty of environmental and natural resources as a research assistant, collaborating with esteemed professors and inquisitive students on diverse projects related to water and wastewater treatment and management. In 2016, she earned admission to the Ph.D. program under the sponsorship of the Ministry of Education at National Taiwan University of Technology, Taiwan. Her current research primarily revolves around water and wastewater treatment, carbon capture, and the conversion of bioenergy using microbial fuel cells, solidifying her career in the realm of environmental academia.



Seth W Snyder is a Directorate Fellow in Energy and Environment S&T, Idaho National Laboratory (USA). He leads programs and strategy across clean energy with a focus on hydrogen, decarbonization, electrification, manufacturing, and water. He received his Ph.D. in Biophysics from the University of Virginia. His work with federal staff and the other National Laboratories has significantly raised the priority of the Energy-Water Nexus in the U.S. Department of Energy. He has been recognized with three R&D100 Awards and a Federal Laboratory Consortium Award for Excellence in Technology Transfer. He has published research with more than 6000 citations and received 20 patents. Seth has adjunct faculty positions at Northwestern University's McCormick School of Engineering and Arizona State University's Ira Fulton School of Engineering.



Yu-I Lin is currently a Ph.D. candidate of the Department of Bioenvironmental Systems Engineering at National Taiwan University. Her Ph.D. research focuses on the development of green technologies and environment issues. Specifically, she is working on developing an advanced separation process based on electrochemistry or ecofriendly materials for wastewater reuse and nutrient recovery. She holds a patent related to a water technology of treating discharge containing salts and acids. She is also devoted to several research projects investigating the impact of climate change on water quality. Her work has been recognized with the Student Paper Award at the Agricultural Engineers Society conference and Environmental Engineering conference in Taiwan. Additionally, she was honored with the "2021 Living Lab Awards" in Taiwan.

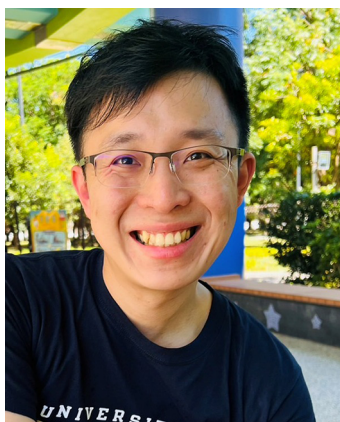


Yupo J Lin is a Group Leader of Chemical and Biological Technologies, Argonne National Laboratory (USA). He has extensive research and development experience in applied electrochemical technologies using innovative materials and processes. His group addresses the technical and economic challenges of chemical and biochemical processing by developing novel membrane separations technologies. The multidisciplinary team has conducted several pilot-

scale technology demonstrations in the oil, gas, chemical, and biorefinery industries, targeting issues of aqueous corrosion, chemical and biochemical/biofuel production, and produced water purification. Recently, his group has been engaged in developing enabled separation technologies to realize the emerging fields of industrial decarbonization, circular economics of waste to energy, and CO utilization. He holds 24 U.S. patents and 3 international patents related to manufacture and applications of electrochemical technologies and membrane separations.



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■ ABBREVIATIONS

BMED = bipolar membrane electro dialysis
 CCU = carbon capture and utilization
 CCUS = carbon capture, utilization, and storage
 CEM = cation exchange membrane
 CT = total inorganic carbon concentration
 CUE = carbon utilization efficiency
 ED = electro dialysis
 EDI = electrodeionization
 EHL = electrochemical hydrogen-looping
 EPS = electrochemically generated pH-swing
 SI = saturation index

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