

Materials Science

Special Topic: Key Materials for Carbon Neutrality

Towards energy-efficient (bi)carbonate electrolysis: Innovation and challenges

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Electrochemical CO₂ reduction reaction (CO₂RR) stands out as a promising approach for converting greenhouse gases into valuable chemicals and fuels, contributing to the closure of the artificial carbon loop. However, most current CO₂RR electrolyzers necessitate purified CO₂ feed gases and fail to directly convert atmospheric CO₂ or flue gases (the primary sources of CO₂ emission). In order to utilize the latter, CO₂RR electrolyzers work in conjunction with CO₂ capture and purification units, which typically rely on thermal swings to release concentrated CO₂, thereby imposing significant energy costs [1]. It is well known that atmospheric CO₂ or flue gases can be absorbed by alkaline hydroxide solutions to form aqueous (bi) carbonates. A simple change in pH conditions can reverse this reaction, allowing for the capture and subsequent release of CO₂. Building on this concept, direct (bi)carbonate electrolysis emerges as an energy-efficient CO₂RR process by enabling local CO₂ regeneration from the (bi)carbonate solution *via* pH swing and further electroreduction within the electrolyzer, bypassing the need for energy-intensive purification or pressurization steps [2]. In addition, it effectively alleviates the flooding issue and improves CO₂ utilization compared to traditional gas-fed CO₂RR [3]. Such a technology allows for the direct conversion of CO₂ captured from point sources or the atmosphere into valuable chemicals and fuels, making it a compelling option for sustainable and cost-effective carbon management.

The (bi)carbonate electrolysis process relies on locally generated CO₂, which originates from the acid/base reaction between (bi)carbonate ions and a continuous supply of protons. These protons typically derive from water dissociation inside a bipolar membrane (BPM) or from an acidic anolyte through a cation exchange membrane (CEM). They then diffuse to the cathode and react with HCO₃[−] to form gaseous CO₂, which is subsequently reduced into products (*e.g.*, CO, CH₄, HCOOH, C₂H₄) at the gas diffusion electrode (GDE) surface. Given the diversity of involved species and the complexity of the reaction process, balanced mass transfer of local species (*i.e.* H⁺ and HCO₃[−]) is crucial to maintaining a high local CO₂ concentration and

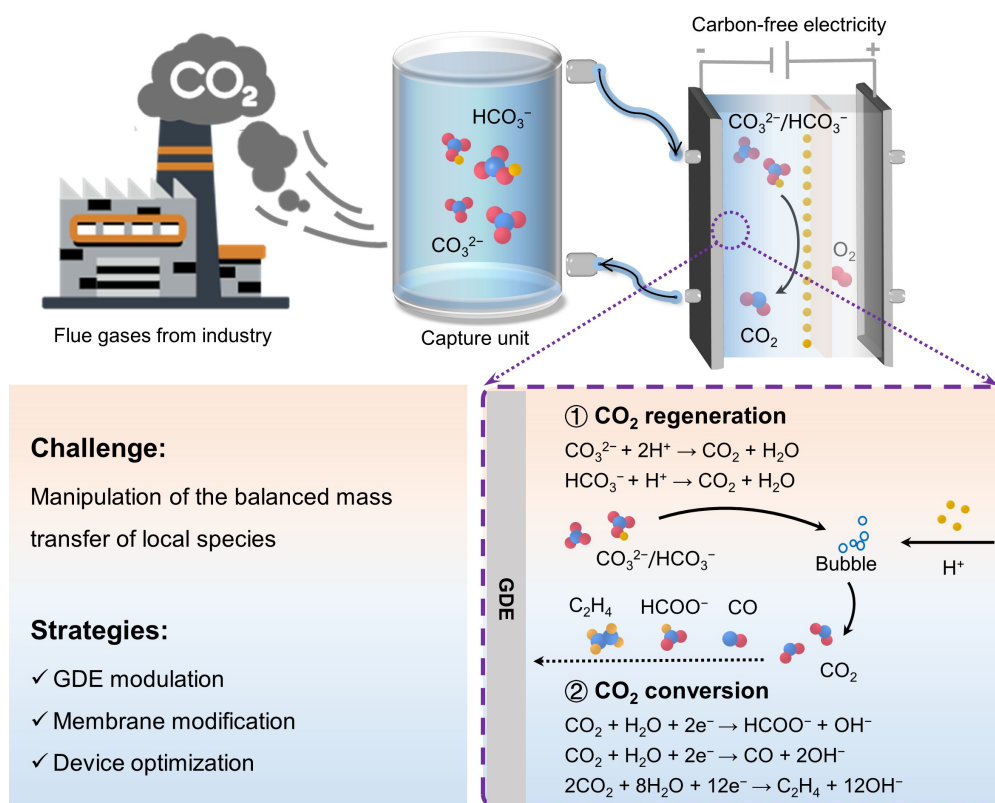


Figure 1 Schematic showing the concept of (bi)carbonate electrolysis, where the blue, pink and yellow balls represent C, O and H atoms, respectively.

avoiding undesirable side reactions. Specifically, insufficient H^+ concentration dissatisfies the need for regenerating an adequate local CO_2 concentration, hindering the subsequent CO_2RR process; excess H^+ can facilitate sufficient CO_2 release by reacting with HCO_3^- , but may lead to H^+ buildup near the cathode, triggering the competing hydrogen evolution reaction (HER). Additionally, OH^- generated during the electrolysis also has an impact on the cathode microenvironment. While it promotes the C–C coupling process and enhances CO_2RR selectivity, it also consumes released CO_2 reactants and hinders their mass transfer. Therefore, the effective manipulation of the mass transfer of local species is key to realizing the full potential of (bi)carbonate electrolysis. Strategies such as GDE modulation, membrane modification and optimization of overall operation parameters are crucial to ensuring efficient $\text{H}^+/\text{HCO}_3^-$ balance to increase local CO_2 regeneration, prevent CO_2 consumption and enhance CO_2RR performance (Figure 1).

GDEs for (bi)carbonate electrolysis should be tailored to enhance local CO_2 generation at the catalyst surface and improve CO_2 utilization efficiency. Unlike GDEs used for gaseous CO_2 electrolysis, the electrodes for (bi)carbonate electrolysis should be hydrophilic [4,5]. Efficient (bi)carbonate electrolysis requires the effective transport of aqueous (bi)carbonate solutions from the flow field to the catalyst/membrane interface, which contrasts to the hydrophobic nature of gas-fed CO_2 electrolyzer electrodes. Experiments have demonstrated that removing PTFE treatment or the microporous layer from gas-phase GDE benefits (bi) carbonate electrolysis [5]. These treatments or constituents inhibit the transport of solvated HCO_3^- ions through the GDE, reducing the amount of locally generated CO_2 . Additionally, the porous structure of the

GDE enhances the permeability of (bi)carbonate solutions [4,6]. Increasing the porosity and decreasing the thickness of the catalyst layer contributes to better CO₂RR performances by shortening the diffusion distance for (bi)carbonates transported from the flow plate through the catalyst layer to the H⁺ source from BPM/CEM. This faster (bi)carbonate mass transport results in more local CO₂ formation. Worth noting is that catalyst design remains the key to GDE tailoring. Knowledge accumulated from gas-fed CO₂RR can be transplanted here, and is not the focus of our discussion in this short perspective.

Membranes are critical for (bi)carbonate electrolysis due to their essential roles in supplying protons, with BPM and CEM being the most commonly used types. Water dissociation in the BPM provides the necessary H⁺ for generating electrochemically active CO₂. However, BPM-based electrolyzers still incur considerable energy losses due to the slow water dissociation at the anion exchange layer/cation exchange layer (AEL/CEL) interface and the required voltage penalty of >0.83 V [7]. In this regard, a water dissociation catalyst, *e. g.* anatase TiO₂, can be used to reduce this voltage [8]. On the other hand, CEM can be leveraged to transport protons from the anodic electrolyte, enabling a lower full-cell voltage compared to a BPM system [3,9]. Nevertheless, acidic anode conditions often necessitate expensive precious metals like Ir and Ru as OER catalysts, resulting in higher costs. It is important to note that whether using BPM or CEM, (bi)carbonate electrolysis requires the careful management of protons to impede the competing HER. This management could be achieved by modulating the distance between the catalyst and the membrane interface, for example, by adding a hydrophilic layer to form a pH gradient along this distance. It effectively prevents the direct transport of H⁺ to the cathode, and regulates the local H⁺ concentration [3], thereby mitigating HER and promoting the effective conversion of locally generated CO₂ into the target products.

Beyond GDEs and membranes, optimizing experimental parameters and innovative flow designs to improve CO₂ mass transfer dynamics are crucial. For instance, elevated bicarbonate solution flow rates can promote the HCO₃[−] mass transfer and rapidly carry off CO₂RR products to refresh the electrocatalyst surface [10]. Additionally, the flow direction of the (bi)carbonate electrolyte can be optimized to first pass through the acidic membrane, then move to the alkaline electrocatalyst surface, and finally flow out of the electrolyzers. This sequence ensures a sufficient HCO₃[−] supply directly to the membrane surface, where it combines with H⁺ to enhance CO₂ mass transfer [9].

Collectively, while (bi)carbonate electrolysis offers a promising approach for CO₂ capture and conversion, achieving energy-efficient and scalable systems requires concerted efforts in material science, membrane technology, and device engineering. By addressing these challenges and leveraging innovative strategies, we can advance toward a sustainable future where CO₂ is effectively utilized as a valuable resource rather than a detrimental greenhouse gas.

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Conflict of interest

The authors declare no conflict of interest.

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