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Bipolar membranes for intrinsically stable and scalable CO₂ electrolysis

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CO₂ electrolysis allows the sustainable production of carbon-based fuels and chemicals. However, state-of-the-art CO₂ electrolyzers employing anion exchange membranes (AEMs) suffer from (bi)carbonate crossover, causing low CO₂ utilization and limiting anode choices to those based on precious metals. Here we argue that bipolar membranes (BPMs) could become the primary option for intrinsically stable and efficient CO₂ electrolysis without the use of scarce metals. Although both reverse- and forward-bias BPMs can inhibit CO₂ crossover, forward-bias BPMs fail to solve the rare-earth metals requirement at the anode. Unfortunately, reverse-bias BPM systems presently exhibit comparatively lower Faradaic efficiencies and higher cell voltages than AEM-based systems. We argue that these performance challenges can be overcome by focusing research on optimizing the catalyst, reaction microenvironment and alkali cation availability. Furthermore, BPMs can be improved by using thinner layers and a suitable water dissociation catalyst, thus alleviating core remaining challenges in CO₂ electrolysis to bring this technology to the industrial scale.

Electrochemical CO₂ reduction (CO₂R) is a promising technology for the production of sustainable carbon-based fuels and chemicals. Having reached current densities and Faradaic efficiencies that are near commercial standards, critical parameters of interest are now stability, energy efficiency, CO₂ utilization and material availability. As a modulator of the ionic current and a separator of CO₂ conversion at the cathode and the oxygen evolution reaction (OER) at the anode, the ion exchange membrane plays a central role in the performance, material selection and stability of the configuration.

Currently, the most efficient and high-performing CO₂ electrolyzers employ anion exchange membranes (AEMs) in a membrane electrode assembly configuration (Fig. 1a). Ideally, the AEM facilitates the selective transport of hydroxide ions (OH⁻) from the cathode to the anode. However, AEM-based electrolyzers face a major challenge since a large part of the input CO₂ reacts with OH⁻ to produce (bi) carbonates, which are then transported to the anode compartment through the AEM¹.

To properly assess the industrial feasibility of AEM-based systems, we need to include the implications of CO₂ crossover on the energy and material requirements. The crossover of CO₂ in the form of (bi)

carbonates means that an alkaline environment at the anode cannot be maintained without electrolyte regeneration. At the same time, the only high-performing OER catalyst under neutral (or acidic) conditions is Ir, thus implying that AEM-based systems necessitate the use of iridium-based catalyst at the anode². However, iridium is one of the scarcest metals on Earth and its rising price is an impediment for scale-up³. Moreover, CO₂ crossover limits the (single-pass) CO₂ utilization to 50% or lower depending on the product (for CO, 50%; for C₂H₄, 25%)⁴. Given that producing a concentrated CO₂ feed requires energy (conventional CO₂ capture processes have an energy consumption between 170 and 390 kJ mol⁻¹ CO₂, depending on the source of CO₂^{5,6}) incomplete CO₂ utilization can be considered an indirect energy penalty. For example, an energy consumption of 170 kJ mol⁻¹ CO₂ would translate to a voltage of 0.88 V when recapturing CO₂ from the anode gas (assuming 100% Faradaic efficiency and CO₃²⁻ as the charge carrier). Hence, increasing the CO₂ utilization is a necessity for a scalable and efficient CO₂ electrolysis technology.

An alternative to AEMs to address these issues is the use of bipolar membranes (BPMs). BPMs consist of a cation exchange layer (CEL) and an anion exchange layer (AEL) and, depending on the

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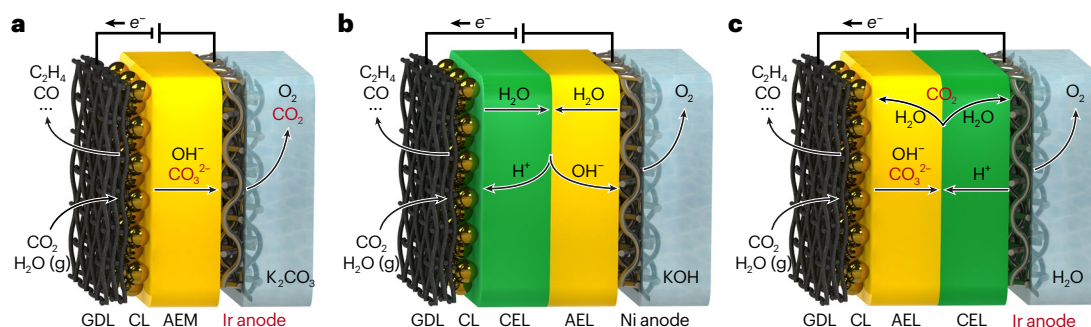


Fig. 1 | Cell configurations for electrochemical CO₂R. **a–c**, Three potential cell configurations for electrochemical CO₂R, including an AEM electrode assembly (**a**), a BPM electrode assembly in reverse-bias configuration (**b**) and a BPM electrode assembly in forward-bias configuration (**c**). All of the configurations are equipped with a GDE paired with oxygen evolution at the anode in a liquid

anolyte. The GDE consists of a gas diffusion layer (GDL) and a catalyst layer (CL). All species except for H₂O (g) in the gas channel are in the standard phase (at room temperature). Species displayed in red indicate undesired crossover or use of scarce materials.

orientation, can be used in forward- or reverse-bias configuration. In reverse-bias configuration (Fig. 1b), water dissociates into H⁺ and OH[−] at the CEL/AEL interface. The H⁺ migrates to the cathode and the OH[−] migrates to the anode, while (theoretically) no other ions can pass both layers of the BPM. Combined with proton-coupled electron transfer reactions, such as CO₂R and OER, the BPM theoretically produces or consumes H⁺ and OH[−] at the same rate as the production/consumption at the electrodes, allowing operation at a steady-state pH difference between the electrodes. This offers the benefit of a theoretically stable alkaline anolyte, which is favourable for the OER and allows the use of more Earth-abundant catalysts such as NiFeOx⁷. Moreover, the CEL rejects carbonates and the generated H⁺ recombines with carbonates to regenerate CO₂, impeding CO₂ crossover almost entirely.

However, a current bottleneck for reverse-bias BPMs is that the resulting acidic cathode environment has been associated with low Faradaic efficiencies for CO₂R products, since the competitive H₂ evolution reaction (HER) is promoted in the abundance of H⁺ (ref. 8). Fortunately, recent advances have been made in CO₂R in acidic media and the impact of cations on CO₂R is now better understood, offering strategies for suppressing the HER, providing interesting opportunities for reverse-bias BPM systems^{9–11}. Conversely, an ideal forward-bias BPM (Fig. 1c), where OH[−] from the cathode migrates through the adjacent AEL and recombines with H⁺ from the anode, enables a neutral/alkaline environment at the cathode, but fails to provide anode conditions that permit the use of Earth-abundant catalysts.

In this Perspective, we argue that BPMs have the potential to be the primary option for CO₂ electrolysis, as AEMs cannot prevent CO₂ crossover and the associated adverse energy and material implications that come with it. We assess the potential of BPMs for CO₂ electrolysis, with special attention to CO₂ utilization, energy consumption and strategies to improve product selectivity and efficiency. We conclude that for BPMs to be the new state-of-the-art option, their performance—in terms of conductance, BPM kinetics and stability—must be improved through innovation.

BPMs promote CO₂ utilization by inhibiting crossover

The CO₂ crossover in AEM-based CO₂ electrolyzers proves to be an intrinsic limitation. Typically, AEM-based systems exhibit a crossover of between 0.5 and 1.0 CO₂ per *e*[−] transferred, which corresponds to CO₃^{2−} and HCO₃[−] as the dominant charge carriers, respectively (Fig. 2a). Therefore, to achieve higher CO₂ utilization, (bi)carbonate formation/crossover must be suppressed, which can—with currently known materials—only be done by replacing AEM separators with either a BPM or a cation exchange membrane (CEM)^{12–14}.

CO₂ crossover is heavily decreased for BPM-based systems (Fig. 2a,b) due to the presence of negatively charged groups in the CEL, which inhibits CO₂ crossover through Donnan exclusion of carbonates and negatively charged CO₂R products (formate)¹⁵. We note that some crossover of co-ions can occur through uncharged membrane spaces (between charged phases)¹⁶, but this issue is minor given the typical water dissociation efficiency of >99% at 100 mA cm^{−2}, and is manageable using existing strategies against salt precipitation and electrolyte regeneration¹⁷. Additionally, reverse-bias BPMs decrease the crossover of neutral CO₂R products (for example, methanol) through the outward flux of protons, which inhibits electro-osmotic drag across the membrane, in particular at higher current densities (Fig. 2b)¹⁸.

Although CEM-based electrolyzers are able to achieve low CO₂ crossover, they are more prone to instabilities due to co-ion crossover. Furthermore, their acidic/neutral anolyte conditions require the use of scarce metals, making the BPM-based system a more suitable candidate for large-scale application^{3,13}.

BPM-based systems in either the reverse- or forward-bias configuration have been reported that achieve high single-pass CO₂ utilization values of up to 78%^{13,19}, surpassing the theoretical maximum of 50% for AEM-based systems for two-electron products¹². The typical 0.02 CO₂ lost per electron (Fig. 2b) implies a maximum of 96% CO₂ utilization, but high single-pass utilization is still expected to bring about trade-offs in selectivity and energy efficiency through the concentration overpotential caused by reactant starvation²⁰.

At the moment, the improved CO₂ utilization of reverse-bias BPM-based systems comes at the cost of lower Faradaic efficiencies and higher cell voltages (Fig. 2c,d). However, unlike the intrinsic issues of CO₂ crossover and the need for scarce metals in anode materials for AEM-based systems, in this Perspective we argue that both the selectivity and cell voltage for BPM-based systems can be further improved through innovation.

The key to low cell potentials is managing pH gradients

A large contribution to the high voltages observed in BPM and CEM electrolyzers, which is often overlooked, stems from pH gradients within the electrolyser. Assuming that an electrolyser is producing CO and O₂, the difference between the standard reduction potentials (E_{cell}^0) is 1.34 V. Because both reactions produce one H⁺ or OH[−] per electron, each pH unit causes a Nernstian shift of 59.2 mV. Theoretically, the voltage contribution of water dissociation or recombination (0.83 V) at the BPM interface is counter-balanced by the Nernstian shift in redox potential at the electrodes, which would allow all configurations to operate at the same equilibrium cell voltage (1.34 V; see E_{cell}^0 in the 'RHE scale' at the bottom of each panel in Fig. 3).

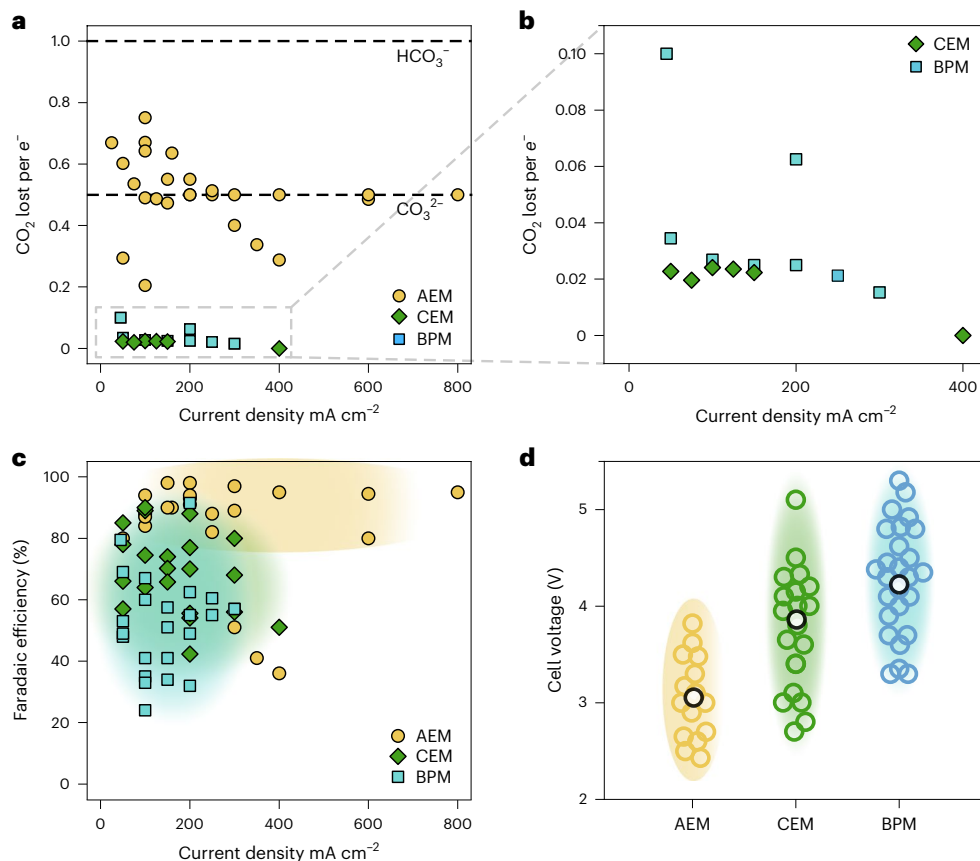


Fig. 2 | Comparison of performance parameters for AEM-, BPM- and CEM-based CO₂ electrolyzers. a, b, Relative CO₂ crossover per charge transferred. The data points represent values from several studies, whereas the lines represent the theoretical values when CO₃²⁻ or HCO₃⁻ are the main charge carriers. This assumes one OH⁻ per reaction electron (valid for most CO₂R reactions and HERs) and no H₂CO₃ crossover. The results shown in **b** are a magnification of the section

outlined by a dashed box in **a**. **c**, Faradaic efficiency for carbon-based products. **d**, Cell voltages for the different membrane systems at current densities between 50 and 300 mA cm⁻². The values shown by a white circle outlined in black show the average cell voltage of all of the data points. See Source Data Fig. 2 for underlying data and specific accompanying refs. [2,9,10,12–14,31,34,38,39,49–60](#).

In practice, however, pH gradients and buffering effects will change the local pH and therefore the observed difference in redox potentials and cell potentials. Accurately determining the pH in the cathode reaction environment remains a challenge for zero-gap configurations. Whereas the catholyte pH is largely controlled by the generated OH⁻ and carbonate equilibrium constant, the anolyte pH depends on [K⁺] and the partial pressure of CO₂ in the mixed anode gas. For the sake of this discussion, we assume a cathode pH of 10.5 (close to the carbonate acid dissociation constant (pK_a)) and an anolyte pH of 8.1 (equilibrium at 1 MK⁺ and 0.5 bar partial pressure CO₂)^{9,21}. Hence, the pH gradient over the AEM increases the cell voltage by at least 0.14 V ((10.5 – 8.1) × 0.0592 = 0.14; Fig. 3a).

In a reverse-bias BPM electrolyser, a large pH gradient is observed between the CEL and the catalyst layer, since the BPM interface produces H⁺ whereas the produced OH⁻ and carbonate pin the pH to ~10.5 (Fig. 3b). This gradient does not allow the complete balancing of the water dissociation voltage of 0.83 V. At a cathode pH of 10.5, only 0.21 V is compensated. Operating a cathode at acidic pH would be extremely beneficial for this configuration, since removing the internal pH gradient would lower the overall cell potential by 0.62 V. Additionally, the BPM requires an overpotential for water dissociation and increased ohmic resistance can be caused by the formation of bubbles at the CEL interface²².

For an electrolyser with a forward-bias BPM (Fig. 3c), the buffering effects occur both in the catalyst layer and at the BPM interface. The Nernstian pH shift added by the alkalinity in the cathode region in this scenario is 0.56 V. The forward-bias BPM electrode assembly

configuration could potentially recover this energy at the BPM junction, but recent work²³ shows that the main recombined species is H₂CO₃ instead of water, lowering the maximum regained voltage to 0.38 V (derived from 0.0592pK_a(H₂CO₃)).

Why forward bias fails to solve CO₂ electrolysis challenges

The forward-bias BPM electrode assembly configuration (Fig. 1c) has the advantages of maintaining an alkaline environment at the cathode (which ensures a high Faradaic efficiency) and decreasing CO₂ loss without a very high energy penalty. However, in addition to the incomplete recovery of the Nernstian pH shift due to carbonate formation, this configuration has additional challenges. In the forward-bias configuration, the formation of water and gaseous CO₂ at the interface of the BPM causes blistering and delamination in commercial BPMs at current densities above 20 mA cm⁻², thus rendering them ineffective in practice. Additionally, as shown in recent works^{23,24}, (bi)carbonate ions and weak acids can induce large neutralization overpotentials and the inefficient transport of the produced CO₂ leads to low limiting current densities.

Effective removal of CO₂ generated at the BPM interface is this essential and future research should address this issue with smart membrane design strategies such as the use of a hybrid liquid–membrane interface or an AEL with a porous or micro-channelled structure^{25–27}, including successful operation for 200 h¹⁹. Alternatively, designing BPMs with high selectivity for OH⁻ ions over co-ions (such as carbonate, formate or acetate) could mitigate ionic blockades and elevate limiting current densities to industrially relevant rates (>100 mA cm⁻²).

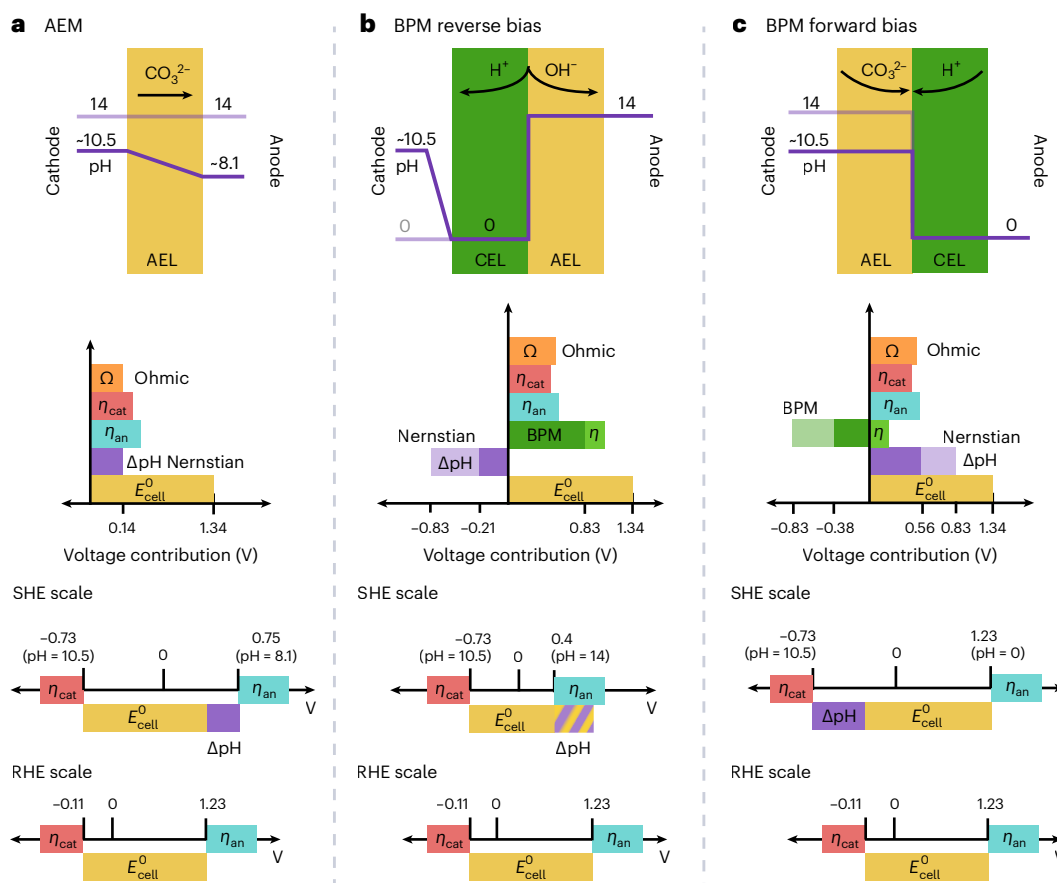


Fig. 3 | Simplified membrane electrode assembly configurations and the voltage contributions of the different components. **a–c**, Membrane electrode assembly configurations and voltage contributions for the AEM electrode assembly system (**a**), reverse-bias BPM electrode assembly (**b**) and forward-bias BPM electrode assembly (**c**). Top, pH profiles for ideal case (light purple lines) and realistic conditions (dark purple lines). Middle, η_{an} and η_{cat} represent the overpotentials of the anode and cathode, respectively, Ω represents the ohmic resistance contribution, E_{cell}^0 is the difference between the equilibrium redox potentials of the two reactions, ΔpH Nernstian represents the Nernstian pH shift

and BPM is the voltage associated with the water dissociation or recombination reaction at the BPM interface. Contributions for E_{cell}^0 , ΔpH Nernstian and BPM were calculated (see main text), whereas Ω , η_{an} and η_{cat} are indicative. The light shaded Nernstian and BPM contributions correspond to the ideal pH profile, whereas the saturated shaded contributions correspond to the realistic pH profile. The voltage contributions of the reactions on the individual electrodes are also displayed on the scales of standard hydrogen electrode (SHE) and reversible hydrogen electrode (RHE) to highlight the effect of pH on the equilibrium redox potentials.

Although blistering and delamination can be overcome by engineering techniques, the forward-bias case suffers from decreased voltage gain due to carbonic acid recombination, unfavourable pH conditions in the anode and the necessity for scarce anode materials, which are difficult to overcome.

Controlling the BPM microenvironment to promote CO_2R

Until recently, the reverse-bias BPM-based membrane electrode assembly showed low Faradaic efficiency due to the acidic microenvironment favouring the HER. However, recent studies have demonstrated that manipulating cation concentrations, ionomer properties and system configuration promotes CO_2R relative to the HER. The presence of alkali cations with small hydrated radii, such as Cs^+ and K^+ , was demonstrated to promote CO_2R even in strong acid¹⁰. Unlike the HER, which involves proton-coupled electron transfer, the rate-limiting step for CO_2R is the adsorption of CO_2 onto the catalyst by cation-coupled electron transfer (the formation of cation-stabilized CO_2 adsorbate, $cat^+ \cdot CO_2^-$)²⁸. Therefore, the cation concentration near the catalyst has an important role in determining CO_2R kinetics²⁹. Moreover, since cation-coupled CO_2R is a hydroxide-generating reaction instead of a proton-consuming reaction, it can neutralize incoming protons and thereby suppress the HER from proton reduction¹¹. In this way, water reduction is not

suppressed, but this reaction happens at more negative potentials. The challenge is controlling the reaction microenvironment (including pH and alkali cations).

We highlight five strategies for controlling the reaction microenvironment to achieve high Faradaic efficiency in reverse-bias configuration. First, introducing a thin alkali cation-rich catholyte layer (Fig. 4a) provides the necessary cations in the vicinity of the catalyst particles, whereas the H^+ ions provided by the BPM react with OH^- so that carbonate production is minimized. Xie et al.¹³ added a 65 μm thin catholyte layer with 0.5 M K_2SO_4 and achieved a Faradaic efficiency for CO_2R products of ~80% at 300 mA cm^{-2} .

Similar to the previous strategy, pre-conditioning the BPM with K^+ or Cs^+ ions (Fig. 4b) would ensure the presence of alkali cations in the vicinity of the catalyst, promoting CO_2R . Xiao et al.³⁰ successfully exchanged the H^+ in a Nafion membrane with Na^+ or K^+ ions, which led to a Faradaic efficiency of CO (FE_{CO}) of 91.5% in the initial stage of CO_2 electrolysis. The salt deposition problems that occur for the CEM case after 1 h may be resolved when applying this strategy to a BPM, as the supply of new cations is blocked by the AEL.

The third strategy involves employing catalysts that are CO_2R active in acidic media (Fig. 4c). From a theoretical standpoint, a strongly acidic cathodic environment resembles the ideal electrode potentials (Fig. 3b) and warrants high ionic conductivity. Immobilized molecular

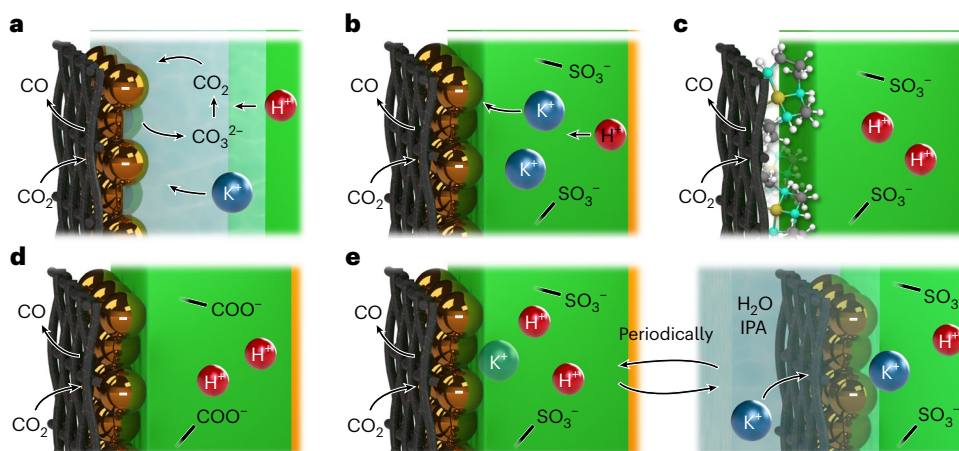


Fig. 4 | Strategies to alleviate BPM–catalyst interaction. **a–e**, Strategies for the alleviation of BPM–catalyst interaction include adding a catholyte layer (**a**), loading the CEL with K^+ (**b**), employing CO_2R selective molecular catalysts for acidic media (**c**), using CELs with weakly acidic groups (**d**) or periodically injecting K^+ from the back of the GDE with water and isopropanol (IPA) (**e**).

catalysts have the potential to catalyse CO_2R under such acidic conditions. For example, Siritanaratkul et al.³¹ used $[Ni(1,4,8,11\text{-tetraazacyclotetradecane})]^{2+}$ to achieve 40% higher FE_{CO} compared with an Ag catalyst in a zero-gap reverse-bias configuration. Also, co-depositing Lewis acids, which are proven for local pH tuning in seawater electrolysis³², is inspiring in modification of the local environment in CO_2R .

The fourth strategy leverages weak acids to decrease the acidity in the reaction microenvironment (Fig. 4d). Weak acidic groups decrease the membrane charge at low pH and thus the H^+ concentration. Using alternating poly(acrylic acid) and poly(allylamine hydrochloride) as weakly acidic groups in the CEL demonstrated an increased FE_{CO} (40%)³³. When further optimizing this strategy, it must be considered that the near-neutral pH will shift the cathode potential (Fig. 3b). Theoretically, the water dissociation could occur at <0.83 V if the H^+ concentration in the CEL is <1 M, but it seems unlikely to fully compensate for the cathode potential shift (for example, pH 4 would imply $[H^+] = 0.1$ mM, which would cause transport limitations in the CEL).

The final strategy is the periodic injection of cations from the back of the gas diffusion electrode (GDE; Fig. 4e). This strategy has not been applied to BPM-based electrolyzers, but Endrödi et al.³⁴ supplied Cs^+ ions (isopropanol/water with 1 M $CsOH$) every 12 h and achieved stable operation in an AEM electrode assembly electrolyzer ($\sim 90\%$ FE_{CO} for over 200 h).

The first strategy is the most simple and has proven efficacy at small scales¹³. However, introducing a catholyte layer can pose engineering challenges during scale-up related to GDE breakthrough or flooding and the formation of CO_2 gas bubbles near the BPM^{13,35}. The second and fourth strategy can also be applied on the ionomers often used in the catalyst layer to modify the reaction microenvironment. Strategies that ensure the presence of cations (first, second and fifth) could be largely affected by water evaporation at the GDE, causing the cations to be removed as aerosols in the product stream and compromising the electrolyser stability. To minimize cation loss, the humidity of the CO_2 gas stream, the process temperature and cation crossover (required at small rates to replenish cations) are key parameters to optimize.

The third strategy, which involves using catalysts active in acidic media, has the added promise of decreasing the cell potential by mitigating the pH gradient between the CEL and catalyst layer. However, such catalysts are in an early stage of development and face challenges such as deactivation by CO and degradation³¹. Nevertheless, we would urge the electrocatalysis field to focus more efforts in this direction, since a stable CO_2R catalyst that operates in acidic media would solve both main challenges associated with reverse-bias BPM operation.

Outlook

Parameters known to optimize BPMs are conductivity, water dissociation kinetics, water permeability, lifetime and counter-ion selectivity³⁶. Ion exchange membranes often exhibit a trade-off between conductivity and selectivity. Specifically for BPM-based CO_2 electrolysis, the conductivity and water dissociation kinetics of commercial BPMs should mainly be improved.

To improve conductivity and water permeability, the most straightforward method is to decrease the membrane thickness. Highly conductive polymers with sufficient mechanical stability for an ultrathin (<30 μm), self-standing layer already exist for the individual polymers (for example, the perfluorinated, sulfonic acid-based Nafion for CEMs and quaternary ammonium-based polymers (such as Orion and PiperION) for AEMs). Compatible chemistries with similar swelling degrees must be found for a stable BPM with a long lifetime. Additionally, since water can be most easily supplied from the anolyte, and some AEMs (such as PiperION) have a low water permeability³⁷, an asymmetric BPM with a thin AEL is a logical design strategy. Although decreasing the thickness will increase co-ion crossover, we argue that a minor amount of cation crossover from the anolyte could actually be beneficial for the performance of the system³⁸, or it could be tuned by using larger cations. Moreover, crossover of (bi)carbonates will probably be irrelevant at high current densities (>1 A) due to the electro-osmotic drag in the opposite direction³⁹.

Simultaneously increasing both the conductivity and the selectivity of ion exchange membranes is a widely known challenge, but it is a progressing field. Kitto and Kamcev⁴⁰ are working on increasing the charge density by placing the charged functional groups in the polymeric backbone itself, to remove trade-off of cross-linking versus functionality. Other promising methods to increase the conductivity include the alignment of the polymeric chains in order to optimize ionic pathway; for example, by conducting the polymerization under an electric field⁴¹.

Solutions for enhanced water dissociation kinetics include three-dimensional (3D) interfaces and water dissociation catalysts blended between the layers. A 3D interface can be created by, for example, electrospinning the two ionomers simultaneously, which increases the contact area and improves the adhesion between the layers^{42,43}. A catalyst blended in the interfacial layer enhances the kinetics of water dissociation and has been shown to largely decrease the ohmic resistance of BPMs⁴⁴. Understanding of the catalysis mechanism with respect to the application can contribute to the design of these interfacial catalyst layers^{33,45,46}, as the catalyst criteria could differ for water dissociation, water recombination and carbonate recombination.

The use of graphene oxide and thin layers has demonstrated stable low overpotentials (<250 mV at 1 A cm²), and strongly asymmetric BPMs have even reached 9 A cm² (refs. 47,48), surpassing the 600 mA cm² limiting current of existing commercial BPMs.

In summary, we argue that avoiding CO₂ crossover and ensuring favourable anode conditions are crucial steps towards the scale-up of CO₂ electrolysis. Reverse-bias BPMs provide these conditions for a stable and scalable process, but improvements are needed in the cathode interaction and water dissociation efficiency. We have shown that the Faradaic efficiency can be improved when the acidic CO₂R catalyst interfaces and proton mobility are controlled: five strategies are available for that. When also implementing thickness optimization, 3D interfaces with new water dissociation catalysts and available conductive polymers, the reverse-bias BPM system has high potential as the primary choice of separator for stable and scalable CO₂ electrolysis.

Data availability

Source data are provided with this paper.

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Additional information

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