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## Ionomers modulate the microenvironment in electrocatalytic CO<sub>2</sub> reduction

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The global shift toward a low-carbon society has accelerated the development of electrocatalytic CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) technology, which shows great potential in simultaneously addressing environmental pollution and energy crises. In the CO<sub>2</sub>RR system, microenvironment modulation can effectively enhance catalytic activity, product selectivity, operational stability, and energy efficiency. The introduction of ionomers into catalyst layers enables precise control of the microenvironment at the catalyst surface through their unique structural properties, significantly improving CO<sub>2</sub>RR performance. In this review, we first provide a concise overview of the key components and main influencing factors of the reaction microenvironment and the structures together with the functional mechanisms of commonly used ionomers. We then systematically discuss how various ionomers modulate the microenvironment, including their effects on CO<sub>2</sub> mass transport, stabilization and diffusion of intermediates, ion species and concentrations at the surface (affecting the pH, K<sup>+</sup> distribution and interfacial electric field), surface morphology and hydrophobicity of catalysts, and structures of interfacial water. Finally, we present a comprehensive summary that identifies current practical challenges of ionomer applications from multiple perspectives while proposing feasible solutions and outlining future research directions for this field.

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### 1. Introduction

Excessive global CO<sub>2</sub> emissions have spurred the rapid development of CO<sub>2</sub> conversion and utilization technologies. The electrocatalytic CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) has emerged as a promising technology capable of converting CO<sub>2</sub> into high-value-added products, contributing to a low-carbon environment.<sup>1–3</sup> Over the past decade, this field has evolved from prevalent catalyst designs, such as metal catalysts, dual-

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metal catalysts, single-atom catalysts, and diatomic catalysts, to comprehensive optimization of entire system components for efficient and stable operation.<sup>4–14</sup> These advancements include improvements in electrolyzers from single-chamber cells to H-cells, solid oxide cells with perovskite-based fuel electrodes, flow cells and membrane electrode assemblies (MEAs) with gas diffusion electrodes (GDEs),<sup>15–17</sup> development of ion exchange membranes (IEMs) from predominant Nafion membranes to anion exchange membranes and bipolar membranes,<sup>18,19</sup> application of ionomers progressing from a single type ionomer to various ionomer combinations,<sup>20,21</sup> and optimization of system parameters such as electrolysis temperature, pressure and water management.<sup>22–25</sup> Through systematic research and improvements of these key parameters, significant progress has been achieved in performance, including activity, selectivity, energy efficiency, and stability, paving the way for feasible industrial-scale application in the near future. The CO<sub>2</sub>RR system usually comprises a cathode, an anode, an ion exchange membrane and multiple interfaces. Chen *et al.* summarized the effect of catalyst surface/interface structures on the CO<sub>2</sub>RR process from the perspective of coordination engineering, atomic interface design, surface modification, and hetero-interface construction.<sup>26</sup> The reaction performance is significantly influenced by the microenvironment at these interfaces, making its modulation particularly crucial. Based on extensive research efforts, various approaches have been identified for modulating the microenvironment of the electrode surface: precise design at the catalyst surface through methods like defect engineering, the confinement effect and hydrophobic modification,<sup>27–29</sup> selection of the electrode substrate,<sup>30</sup> electrolyte optimizations,<sup>31</sup> and careful selection of IEMs and ionomers.<sup>18,21,32,33</sup> These modulation strategies about the microenvironment can significantly enhance CO<sub>2</sub>RR performances. Currently, comprehensive reviews have systematically summarized these modulation approaches on the microenvironment.<sup>34,35</sup>

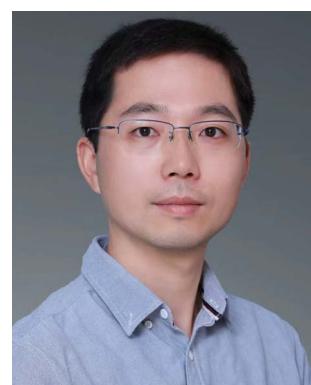


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During electrode fabrication, organic modifiers are typically introduced as binders to stabilize the catalyst.<sup>32</sup> Common binders include charged ionomers (*e.g.*, Nafion), neutral polymers (*e.g.*, polytetrafluoroethylene (PTFE) and polyamines) and organic small molecules (*e.g.*, pyridine and tetramethylammonium). Compared to neutral modifiers, the uniqueness of ionomers lies in their ability to transport ions (*e.g.*, H<sup>+</sup>, OH<sup>–</sup>, and K<sup>+</sup>) *via* their ionic functional groups, thereby modulating key properties of the catalyst surface microenvironment such as pH, interfacial electric field, and water transport.<sup>20,21,25,36</sup> Ionomers were initially extensively studied and applied in fuel cells and water electrolysis systems.<sup>37–40</sup> Subsequent research demonstrated their direct applicability to the electrocatalytic CO<sub>2</sub>RR system, where they play an indispensable role in improving the mass transport of surface species and modulating the microenvironment.<sup>41</sup> Recently, some researchers have reviewed this field. For example, Won *et al.* summarized the roles of binders (including ionomers as one type) in this system, covering their physical benefits for catalysts, chemical interactions, and developmental utilizations.<sup>32</sup> Additionally, Wang *et al.* summarized ionomer designs for the CO<sub>2</sub>RR, focusing on strategies to enhance CO<sub>2</sub> mass transport in catalyst layers, modulate local ion concentrations, and control reaction intermediate adsorption.<sup>33</sup> Nonetheless, a comprehensive and in-depth analysis of how ionomers modulate the microenvironment of catalyst surfaces in the CO<sub>2</sub>RR system remains lacking, particularly regarding which specific microenvironment is influenced by different ionomers and the underlying mechanisms. Only through a thorough understanding of ionomer-mediated microenvironment modulation can an optimal ionomer selection be achieved and reaction processes/mechanisms be fundamentally understood.

In this review, we first concisely introduce the compositions and roles of the microenvironment in the electrocatalytic CO<sub>2</sub>RR, along with commonly used ionomer structures and their mechanistic roles. Although ionomers typically exert



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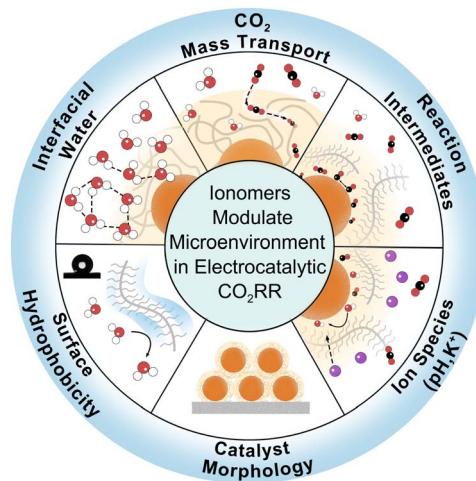


Fig. 1 Ionomers modulate the microenvironment in the electrocatalytic CO<sub>2</sub>RR.

multiple functions simultaneously in the reaction system, we find that they can be classified according to a hierarchy of primary and secondary roles, which contributes to clarifying their structure–activity relationship. So, we systematically summarize the ionomer-mediated microenvironment modulation through six key aspects: promoting CO<sub>2</sub> enrichment and mass transport, stabilizing reaction intermediates or facilitating their diffusion, modulating surface ion species and concentrations, stabilizing or adjusting catalyst morphology and state, modulating hydrophobicity of catalyst surfaces, and tuning structures of interfacial water (Fig. 1). Building on these insights, we critically discuss current challenges in ionomer applications for the CO<sub>2</sub>RR and propose original perspectives for future ionomer design and implementation strategies.

## 2. The microenvironment of the electrocatalytic CO<sub>2</sub>RR

### 2.1 Compositions and functions of the microenvironment

The performances of catalysts in the electrocatalytic CO<sub>2</sub>RR are determined not only by active sites but also by microenvironment modulation of mass transport, local kinetics, and stability for CO<sub>2</sub> and related species in a heterogeneous reaction.<sup>42,43</sup> In a strict sense, the microenvironment refers to the physicochemical properties of catalysts, while more broadly it encompasses external driving forces in local regions.<sup>44,45</sup> The microenvironment in catalysis involves multiple hierarchical levels: the molecular/atomic-level control of catalysts, involving coordination environments of the active centers and atomic/molecular interactions;<sup>46</sup> the nanoscale/microscale confinement effects, where the confined microenvironment can regulate reactant diffusion and consequently its adsorption/activation on the catalyst surfaces;<sup>47</sup> interfaces and complex surface chemistry involving mass transport, local pH, concentration gradients near active sites, and adsorption behaviours;<sup>35,48,49</sup> physical fields including light, electricity or microwaves.<sup>50</sup> In the electrocatalytic CO<sub>2</sub>RR, rational

modulation of the microenvironment of electrode surfaces, including catalyst surfaces, electrode architectures, and reactive surface species, can enhance the reaction rate and selectivity, improving the energy efficiency and establishing foundations for industrial implementation.

### 2.2 Influencing factors of the microenvironment

In the electrocatalytic CO<sub>2</sub>RR, the microenvironment primarily refers to the local environment surrounding the reaction interface, which influences both the kinetic and thermodynamic processes of the reaction.<sup>45,51</sup> Here, “local” is typically relative to “bulk”, referring to a finite, specific range or scale that differs from the overall, macroscopic, and average conditions of the bulk phase. In the CO<sub>2</sub>RR system discussed in this review, the local environment denotes the physicochemical environment at the catalyst surface, with a nanoscale dimension. This local environment primarily differs from the types and concentrations of ions and the water structure in the bulk electrolyte, as well as the bulk CO<sub>2</sub> concentration.<sup>44,45,52,53</sup> In the system, the principal factors influencing the microenvironment include: properties of catalyst surfaces,<sup>54</sup> characteristics of electrode substrates,<sup>30</sup> co-reactants,<sup>55</sup> electrolyte compositions,<sup>31,56</sup> membrane properties,<sup>57–59</sup> and reactor configurations<sup>15,17,60</sup> (Fig. 2a).

A large number of experiments demonstrate that microenvironment modulation can be systematically achieved through: (1) precise engineering of the catalyst surfaces by optimizing atomic/electronic configurations to enhance CO<sub>2</sub> adsorption and activation.<sup>27,28,61,62</sup> For instance, Guan *et al.* summarized strategies for modulating the geometric and electronic structures of the metal centers in the single-atom, diatomic, and triatomic catalysts through the design of substrates, central metal atoms, and coordination environments, thereby influencing the surface microenvironment of catalysts.<sup>61</sup> Besides, the summary by Kolding *et al.* also indicated that in a reaction, designing a tailored microenvironment, particularly by modulating the spatial environment around catalytic active sites, can effectively control the catalytic performance.<sup>62</sup> Apart from these engineering approaches, recently, numerous studies have demonstrated that ionomers can also modulate the microenvironment of catalyst surfaces. Whether the ionomer fully or partially coats the catalyst, it can promote CO<sub>2</sub> mass transport and regulate water transfer, enabling efficient reactions.<sup>20,63</sup> Additionally, ionomers can adjust the ion transport and pH at the catalyst surface and modify the hydrogen-bonded structure of interfacial water to facilitate CO<sub>2</sub> reduction.<sup>21,64</sup> Based on prior studies and our understanding, here, the microenvironment primarily emphasizes the local environment influencing the reaction, spatially encompassing the electric double layer (EDL). The key role of the microenvironment is primarily played by the Helmholtz layer closest to the catalyst surface, with a thickness of approximately 1–2 nm, which includes part of the surfacial ionomer layer. Within the local region, the OH<sup>−</sup> and K<sup>+</sup> become enriched, and the structure of interfacial water significantly differs from that of bulk water (Fig. 2b). (2) Strategic design of electrode substrates by incorporating gas diffusion layers to facilitate CO<sub>2</sub> mass transport while concurrently



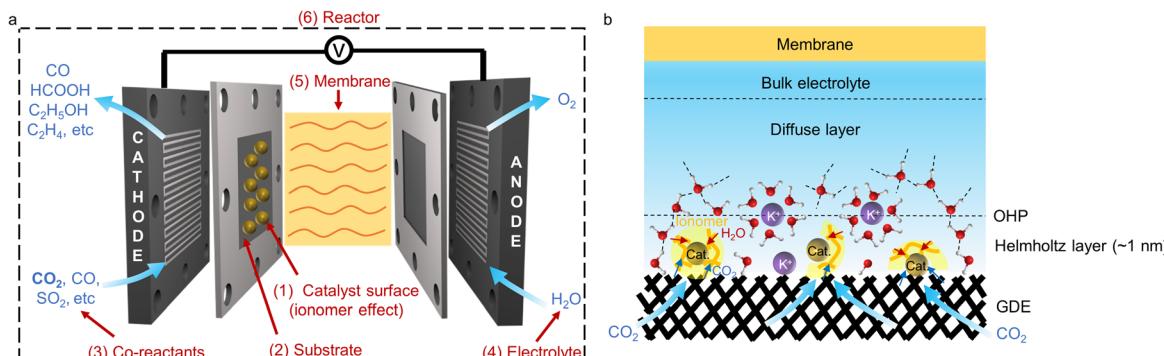


Fig. 2 (a) Influencing factors on the microenvironment in the electrocatalytic CO<sub>2</sub>RR. (b) Schematic illustration of the microenvironment at the catalyst surface modulated by ionomers. The terms Cat. and OHP represent the catalyst and Outer Helmholtz Plane, respectively.

improving the electrical conductivity and structural stability.<sup>30,65</sup> (3) Controlled introduction of co-reactants (e.g., CO introduction to selectively promote C<sub>2+</sub> product formation or coupling with N<sub>2</sub>, nitrate species, or organic compounds).<sup>55,66–68</sup> (4) Tailored modifications of electrolyte formulations through the optimization of cation concentrations or incorporation of organic cations/additives to precisely tune reaction selectivity.<sup>31,69</sup> (5) Sophisticated selection and combination of ion exchange membranes to regulate ion/water transport dynamics, establishing optimal interfacial pH conditions and specific ion concentrations at the cathode surface to modulate reaction performances.<sup>18,70–72</sup> (6) Progressive advancement of reactor architectures, evolving from simple H-cells to MEAs, solid-electrolyte devices, and forced convection configurations to enhance both the reaction rate and energy efficiency.<sup>15,17,73,74</sup> To realize the scaled-up implementation of electrocatalytic CO<sub>2</sub> reduction, these critical factors must be holistically designed and synergistically optimized to ensure highly efficient operation of the reaction.

### 3. Ionomers for the electrocatalytic CO<sub>2</sub>RR

#### 3.1 The structures of ionomers

Ionomers typically consist of a polymeric backbone and side chains containing ionic functional groups. The backbone

provides mechanical and chemical stability to the whole structure, often exhibiting high hydrophobicity due to the presence of alkyl, aryl, and fluorine-containing functional groups. The ionic side chain primarily controls properties, such as ion exchange capacity (IEC), ionic conductivity, water uptake, and swelling ratio, and is usually the most vulnerable site for degradation.<sup>19,75</sup> Currently, various materials are used to modify catalyst surfaces, including ionomers, neutral organic polymers, covalent organic frameworks (COFs) and so on. Due to their structural difference, these materials exhibit significantly different performance characteristics, requiring careful selection for research purposes. In the field of electrocatalytic CO<sub>2</sub> reduction, Nafion remains the most widely used ionomer for cathodic catalyst modification.<sup>20,57</sup> In recent years, researchers have begun exploring Nafion-like cation ionomers such as Aquivion and perfluorosulfonic acid ionomers (PFSA-L and PFSA-S) (Table 1),<sup>63,76</sup> as well as emerging anion exchange ionomers.<sup>41,77–79</sup> These materials differ in both backbone structures and ionic side chains, resulting in distinct ion transport properties. At 298 K and 1 atm in infinitely dilute water, the ionic mobility of H<sup>+</sup> is  $3.623 \times 10^{-7} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$ , while that of OH<sup>−</sup> is  $2.064 \times 10^{-7} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$ .<sup>80</sup> This explains why cation exchange ionomers typically exhibit significantly higher ionic conductivity than anion exchange ionomers. Furthermore, recent studies have shown that anion exchange ionomers generally exhibit inferior mechanical strength and chemical

Table 1 Structures and properties of typical cation exchange ionomers

Names	Structures	Ion groups	IEC (mmol g <sup>−1</sup> )	Ref.
Nafion		Sulfonate	~0.9	75
Aquivion		Sulfonate	1.0–1.3	75
PFSA-L		Sulfonate	—	63
PFSA-S		Sulfonate	—	63 and 76



Table 2 Structures and properties of typical anion exchange ionomers

Names	Structures	Ion groups	IEC (mmol g <sup>-1</sup> )	Ref.
Sustainion		Imidazolium	1.4–1.6	41 and 83
Sustainion XA-9		Imidazolium	1.6	84 and 85
1- <i>n</i> -alkylimidazolium		Imidazolium	1.57–2.34	86
Aemion		Benzimidazolium	1.4–1.7	36
Fumion		Quaternary ammonium	1.0–1.6	87
QAPEEK		Quaternary ammonium	—	77
Pention		Quaternary ammonium	1.5–2.0	88
Polynorbornene		Quaternary ammonium	—	89
c-PDDA		Quaternary ammonium	—	90
PiperION		Quaternary ammonium	2.37	78 and 91
QAPPT		Quaternary ammonium	2.55–2.65	92
<i>p</i> TPN-x		Trimethylammonium/piperidinium/pyridinium/1-methyl-imidazolium/1- <i>n</i> -hexyl-imidazolium/1-methyl-benzimidazolium	—	93
QPC-Z		<i>N</i> -Methylquinuclidinium/imidazolium/piperidinium/quaternary ammonium/quaternary phosphonium	1.8–2.3	94



stability compared to Nafion-type cation exchange ionomers.<sup>75,81,82</sup> The most common anion exchange ionomer is Sustainion,<sup>41,83</sup> including its derivatives such as Sustainion XA-9,<sup>84,85</sup> as well as imidazolium- and benzimidazolium-functionalized ionomers like 1-*n*-alkylimidazolium and Aemion.<sup>36,86</sup> Recently developed quaternary ammonium-based ionomers are more stable with higher ionic conductivity including Fumion,<sup>87</sup> quaternary ammonium poly(ether ether ketone) (QAPPEK),<sup>77</sup> Pention,<sup>88</sup> polynorbornene,<sup>89</sup> cross-linked poly(diallyldimethylammonium chloride) (c-PDDA),<sup>90</sup> poly(aryl piperidinium)-based anion exchange ionomer (PiperION),<sup>78,91</sup> quaternary ammonium poly(*N*-methyl-piperidine-*co*-*p*-terphenyl) (QAPPT),<sup>92</sup> *para*-terphenyl-trifluoroheptan-2-one-x (organic nitrogenous cations ( $R_4N^+$ )) (*p*TPN-x),<sup>93</sup> quaternary ammonium polycarbazole-anion conducting groups (QPC-Z)<sup>94</sup> and so on (Table 2). Studies have demonstrated their crucial roles in the electrocatalytic  $CO_2$ RR, such as promoting  $CO_2$  mass transport, enhancing electrode hydrophobicity, and regulating the pH at electrode surfaces.

### 3.2 Functional mechanisms of ionomers

Ionomers can transport ions through their ion-containing side chain, primarily *via* hydrated ionic domains formed when these functional groups absorb water (Fig. 3a). The mechanisms of ion transport mainly involve two pathways: vehicular transport and Grotthuss hopping.<sup>75,95,96</sup> Vehicular transport includes diffusion driven by concentration gradients and electromigration driven by potential gradients. While these two processes differ in their driving forces, both depend on the ion diffusion coefficients across the ionomer.<sup>97</sup> The ionomer structure and water content significantly influence the diffusion coefficients. Grotthuss hopping refers to forming and breaking covalent bonds from ions (*e.g.*,  $H^+$  and  $OH^-$ ) with adjacent molecules, propagating through hydrogen-bonded networks of water molecules. Both vehicular transport and hopping mechanisms require the presence of free water within ionomers,

specifically in hydrated regions where water molecules have limited interactions with the polymer backbone and side chain. However, hydration must be carefully controlled, as excessive water uptake can cause structural swelling and damage. It is noteworthy that due to the diversity of ion transport mechanisms in ionomers, they typically do not exhibit 100% ion selectivity. For example, Nafion not only transports cations like  $H^+$  and  $K^+$  but also transports anions to a small extent. Nonetheless, Nafion mainly facilitates the transport of  $H^+$ , or more precisely, it has the highest transport rate for  $H^+$  among common ions. Because of interactions of ionic charges, ionomers can relatively repel ions of the same charge type (*e.g.*, Nafion, which carries the  $-SO_3^-$  ion, repels negatively charged  $OH^-$ , while QAPPT, carrying the  $-NR_4^+$  ion, repels positively charged  $H^+$ ). By coordinating ion transport and exclusion, they can modulate the microenvironment at the reaction interface.

In addition, ionomers can also transport water and gases.<sup>75</sup> Water transport is driven by chemical potential differences across the ionomer (eqn (1)), electroosmotic drag (eqn (2)), or back-convection due to the hydrophilicity/hydrophobicity differences (eqn (3)) (Fig. 3b).<sup>98</sup> Water primarily diffuses through hydrophilic regions formed by ionic groups in the ionomer structure, while hydrophobic groups (*e.g.*, aryl or fluorine functional groups) hinder water permeation. Therefore, water transport in ionomers depends on the synergistic effect of hydrophilic and hydrophobic groups, which can be precisely designed and modulated. Ionomers facilitate gas transport (*e.g.*,  $H_2$ ,  $O_2$  and  $CO_2$ ) primarily through their three-dimensional porous channel structures and functional groups (*e.g.*, amine groups) which interact with gas molecules to enable transport (Fig. 3c). Additionally, ionomers can stabilize the morphology and state of catalysts or modulate their electronic structures through interactions between ionic groups and the catalysts, thereby exerting a modulation effect (Fig. 3d).

$$J_{\text{diff}} = \frac{\Delta\mu_{\text{LV}}}{R_w \times A} \quad (1)$$

where  $R_w$  represents the effective water permeation resistance (a function of the diffusion coefficient  $D'$  and ionomer thickness) and  $\Delta\mu_{\text{LV}}$  denotes the chemical potential difference for water transport across the ionomer.

$$J_{\text{EOD}} = \frac{j}{F} \times n_{D,\text{avg}} \quad (2)$$

$$J_{\text{HP}} = K \Delta P_{c-a} \frac{\rho}{M_{H_2O}} \quad (3)$$

where  $K$  represents the hydraulic permeability and  $\Delta P_{c-a}$  denotes the pressure difference between the cathode and the anode.

## 4. Ionomers modulate the microenvironment of the electrocatalytic $CO_2$ RR

The unique structure of ionomers and their ability to transport specific ions and water enable them to effectively modulate the

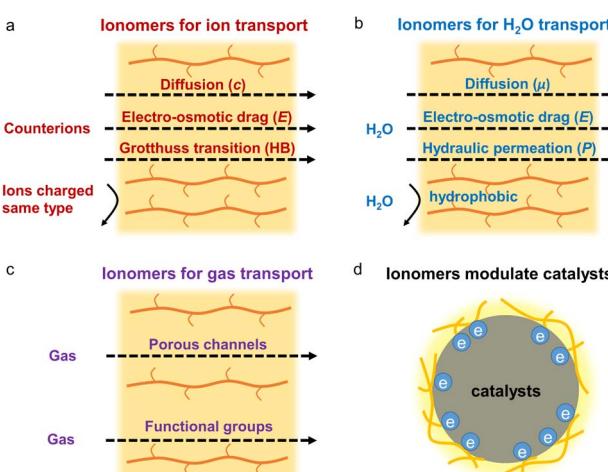


Fig. 3 Functional mechanisms of ionomers transferring (a) ions, (b)  $H_2O$ , (c) gas, and (d) modulating catalysts (where  $c$ ,  $E$ ,  $HB$ ,  $\mu$ ,  $P$ , and  $e$  represent the concentration, potential, hydrogen bond, chemical potential, pressure, and electron, respectively).



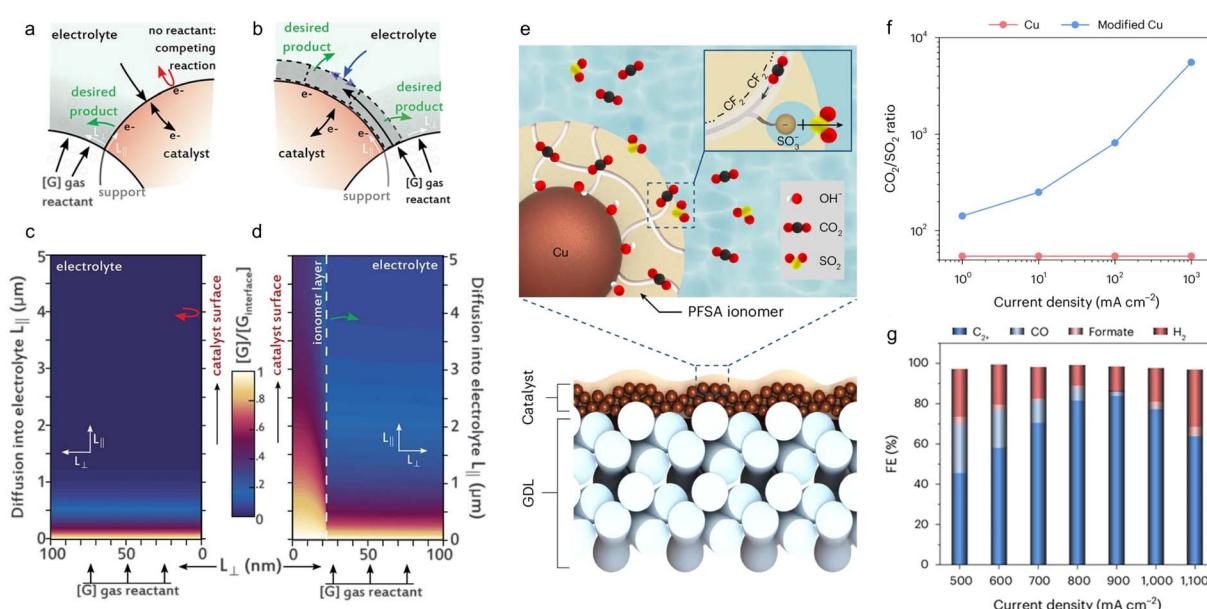
microenvironment when incorporated into catalyst surfaces. The modulations primarily occur through: enhancing  $\text{CO}_2$  mass transport, interacting with reaction intermediates, altering surface ion species and concentrations, modifying the morphology and dispersion state of catalysts, improving electrode hydrophobicity, and restructuring interfacial water networks. These effects significantly impact performances and are crucial for rational system designs, catalyst functionalities, and mechanistic understanding of the reaction processes.

#### 4.1 Ionomers enhance $\text{CO}_2$ mass transport

**4.1.1  $\text{CO}_2$  transport and enrichment.** Beyond conventional roles in ion and water transport, recent studies find that unique chemical and spatial structures of ionomers can also facilitate the transport of gases such as  $\text{CO}_2$ . In 2020, Sargent's team addressed the limited  $\text{CO}_2$  mass transport in conventional H-cells by developing a hybrid catalyst design strategy. Compared to a conventional two-phase interface, the developed hybrid structure (containing the PFSA ionomer) achieves decoupled gas and electrolyte transport at its triple-phase interface (Fig. 4a and b).<sup>20</sup> The PFSA layer coating catalysts extended the gas diffusion distance from submicron to several micrometers through its hydrophobic side-chain regions. This constructed triple-phase interface significantly enhanced  $\text{CO}_2$  mass transport, achieving current densities exceeding  $1 \text{ A cm}^{-2}$  for the  $\text{CO}_2\text{RR}$ . The  $\text{CO}_2$  transport pathway begins from the cathodic gas flow channel, passing through the porous

hydrophobic carbon paper to reach the side of the carbon paper facing the ion exchange membrane. For catalysts partially coated with PFSA,  $\text{CO}_2$  can directly access the catalyst surface. While for catalysts fully coated with PFSA,  $\text{CO}_2$  can transport through the hydrophobic structural channels of PFSA to reach the reaction interface formed between the PFSA ionomer and the catalyst. Their modeling studies further introduced a 20 nm-thick interfacial channel between the catalyst and the electrolyte, where the in-plane gas diffusion coefficient ( $D$ ) differed substantially from the bulk coefficient ( $D_0$ ). Simulations revealed that the increasing  $D/D_0$  ratio promoted gas transport, extending  $\text{CO}_2$  diffusion distances to several micrometers (*versus*  $<0.5 \mu\text{m}$  without the channel), dramatically boosting the reaction current density (Fig. 4c and d).

Furthermore, Sinton *et al.* revealed that PFSA exhibited good selectivity in the transport of different gases (Fig. 4e).<sup>99</sup> This is attributed to the solubility of  $\text{SO}_2$  *via* strong dipole-dipole interactions with hydrophilic components in PFSA, coupled with its high solubility in water when PFSA absorbs electrolyte (with a solubility of  $1.47 \text{ mol L}^{-1}$  at  $20^\circ\text{C}$  and  $1.0 \text{ atm}$ , significantly higher than that of  $\text{CO}_2$ ), which slows down  $\text{SO}_2$  transport through PFSA to the catalyst surface. In contrast,  $\text{CO}_2$  interacts weakly with PFSA and has low solubility in water, allowing it to transport through the hydrophobic regions of PFSA in the gaseous form. Theoretical simulations indicated that in PFSA, the solubility of  $\text{SO}_2$  increased by  $\sim 30$  times compared to  $\text{CO}_2$ , while its diffusivity decreased to about one-fifth of that of  $\text{CO}_2$ .



**Fig. 4** Ionomers enhance  $\text{CO}_2$  mass transport. (a) The volume in which gas reactants, active sites, water, and ions coexist determines the maximum available current for gas electrolysis. Catalyst regions with limited reactant concentration promote by-product reactions. (b) When gas and electrolyte (water and ion source) transport is decoupled, the three-phase reaction interface can be extended so that all electrons participate in the desired electrochemical reaction. Modeled gas reactant availability along the catalyst surface for standard (c) and decoupled (d) gas transport in a 5 M KOH electrolyte. Reproduced with permission from ref. 20. Copyright 2020, the American Association for the Advancement of Science. (e) Schematic of a planar PFSA@Cu/PTFE heterojunction with hydrophilic and hydrophobic characteristics provided by  $-\text{SO}_3^-$  and  $-\text{CF}_2$  functionalities for interacting with  $\text{SO}_2$  and facilitating  $\text{CO}_2$  transport, respectively. (f) Modelled mass flux ratios of  $\text{CO}_2$  over  $\text{SO}_2$  on the ionomer-modified Cu and bare Cu electrodes during the co-electrolysis of  $\text{CO}_2$  and  $\text{SO}_2$ . (g) Product selectivities from the co-electrolysis of 100%  $\text{CO}_2$  and 400 ppm  $\text{SO}_2$  on PFSA@Cu/PTFE. Reproduced with permission from ref. 99. Copyright 2024, Springer Nature.

(Fig. 4f). This unique selectivity enabled  $790 \text{ mA cm}^{-2}$  partial current density for  $\text{C}_{2+}$  products with 84% selectivity when feeding  $\text{CO}_2$  gas containing 400 ppm simulated flue gas impurities by the PFSA@Cu/PTFE heterojunction (Fig. 4g). These studies demonstrate the exceptional capability of ionomers to enhance  $\text{CO}_2$  mass transport while enabling selective gas transport for broader industrial applications.

Researchers have also developed other effective ionomers to enhance  $\text{CO}_2$  adsorption and mass transport beyond PFSA. Zhuang *et al.* developed a QAPEEK ionomer, which showed a significantly higher selectivity for ethylene production in the electrocatalytic  $\text{CO}_2\text{RR}$  compared to other ionomers (*e.g.*, Sustainion, Fumasep, and PiperION) (Fig. 5a).<sup>77</sup> *In situ* infrared spectroscopy revealed a linear redshift in the asymmetric stretching vibration ( ${}^{\text{*}}\text{CO}_2$ ) band center at potentials between 0 and  $-1.1 \text{ V}$  *vs.* the reversible hydrogen electrode (RHE), indicating enhanced interaction between  ${}^{\text{*}}\text{CO}_2$  and the carbonyl oxygen atom of QAPEEK under electrochemical polarization. This interaction effectively captured  $\text{CO}_2$  and stabilized the  $\text{CO}_2$  intermediate, facilitating efficient  $\text{CO}_2\text{RR}$  (Fig. 5b and c).

Additionally, Grubbs *et al.* synthesized highly modular three-component copolymers *via* ring-opening metathesis polymerization to modify the Cu electrode, achieving 55% and 77% selectivity for ethylene and  $\text{C}_{2+}$  products, respectively (Fig. 5d).<sup>100</sup> Combined experimental and molecular dynamics (MD) simulations showed that the improved selectivity was primarily due to the ability of the ionomer to create additional  $\text{CO}_2$  diffusion pores, thereby increasing the local  $\text{CO}_2$  concentration. Xu *et al.* also developed a novel Cu@poly(ionic liquid) (Cu@PIL) composite, where the ionic liquid contained a tridentate site (one pyridine and two imidazole groups) and two

polymerizable alkenyl sites (Fig. 5e).<sup>101</sup> Experimental and theoretical studies demonstrated that isolated ion pairs in the outer PIL layer, particularly the imidazole moieties, enriched  $\text{CO}_2$  and directly increased its local concentration. Consequently, both the activity and selectivity for  $\text{C}_{2+}$  products in the  $\text{CO}_2\text{RR}$  were significantly enhanced. These studies illustrate that various ionomers can effectively enrich, adsorb, and transport  $\text{CO}_2$  to improve  $\text{CO}_2\text{RR}$  performance through their  $\text{CO}_2$ -philic functional groups, spatially ordered channels, and porous architectures.

**4.1.2 Modulating  $\text{CO}_2/\text{H}_2\text{O}$  transport ratios.** The structure of PFSAs can be tailored with variants, including long-side-chain (LSC) and short-side-chain (SSC) PFSAs beyond conventional Nafion. Adjusting the side-chain length alters ionomer properties such as ionic conductivity and hydrophobicity. For instance, Wang *et al.* developed four PFSA ionomers with varying side-chain lengths to optimize  $\text{CO}_2$  mass transport (Fig. 6a and b).<sup>63</sup> These ionomers exhibited distinct affinities for  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , enabling precise regulation of  $\text{CO}_2/\text{H}_2\text{O}$  ratios to establish separate transport channels for each component, improving the microenvironment of catalyst surfaces in MEA. Compared to SSC ionomers, LSC ionomers have higher binding energy with water while lower binding energy with  $\text{CO}_2$ , indicating enhanced  $\text{CO}_2$  transport capability and suppressed water transport (Fig. 6c). Studies further demonstrated that tuning the side-chain length and content of ionomers enhances mass transport networks in catalyst layers. According to the reaction equation, various amounts of water as reactants are required at different current densities, which is essential. This demand can be met through the hydrophilic groups of ionomers to ensure sufficient water supply. When water is abundant, increasing the  $\text{CO}_2/\text{H}_2\text{O}$  ratio at the three-phase interface enhances  $\text{CO}_2$

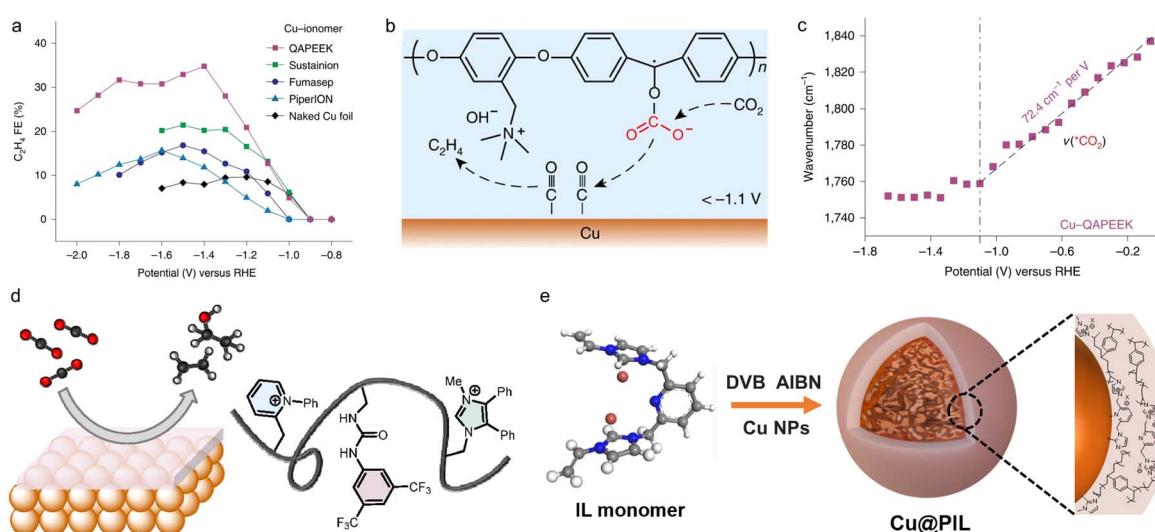


Fig. 5 Ionomers promote  $\text{CO}_2$  enrichment on the catalyst surfaces. (a) Different ionomers were tested at a Cu foil electrode with an optimized coating amount for  $\text{C}_2\text{H}_4$  production. (b) Schematic illustration of the QAPEEK promoting the  $\text{CO}_2\text{RR}$  on Cu. (c) The activated  $\text{CO}_2$  ( ${}^{\text{*}}\text{CO}_2$ ) signal on Cu-QAPEEK shifted with potential on the naked and QAPEEK-coated Cu electrode surfaces. Reproduced with permission from ref. 77. Copyright 2022, Springer Nature. (d) A tricomponent copolymer modifier on the copper surface enhances the selective electrochemical  $\text{CO}_2\text{RR}$ . Reproduced with permission from ref. 100. Copyright 2021, American Chemical Society. (e) Schematic illustration of the structure of the IL monomer and the preparation of Cu@PIL. Reproduced with permission from ref. 101. Copyright 2021, Elsevier.



coverage on the catalyst surface and promotes  $\text{CO}_2$  mass transport. However, when  $\text{CO}_2$  coverage reaches saturation, the promotional effect on  $\text{CO}_2$  reduction plateaus. Without causing electrode flooding, the amount of water can moderately regulate the catalytic microenvironment and influence the reaction. *In situ* differential electrochemical mass spectrometry (DEMS) identified optimal  $\text{CO}_2$  and  $\text{H}_2\text{O}$  transport pathways, while the attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) probed interfacial electrochemical environments, revealing  $\text{H}_2\text{O}$ -deficient and  $\text{CO}_2$ -deficient zones. It should be noted that they utilized DEMS to detect the ion currents of  $\text{H}_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{CO}$  generated during the electrocatalytic  $\text{CO}_2\text{RR}$ . Since the water consumption rates for producing these species differed, the earlier onset potential for  $\text{H}_2$  generation observed in the SSC-D72 ionomer system indirectly indicated the presence of more water channels. Conversely, the higher ion currents of  $\text{C}_2\text{H}_4$  and  $\text{CO}$  detected in the LSC-D520 ionomer system demonstrated its more developed  $\text{CO}_2$  transport channels. Furthermore, MD simulations visualized interfacial  $\text{CO}_2/\text{H}_2\text{O}$  distributions. The enhanced  $\text{CO}_2$  transport and balanced  $\text{CO}_2/\text{H}_2\text{O}$  ratio (high  $\text{CO}_2$  and low  $\text{H}_2\text{O}$  concentration) with long-side-chain ionomers achieved  $89.4 \pm 0.69\%$  faradaic efficiency for  $\text{C}_{2+}$  products with a partial current density of  $536 \pm 4.1 \text{ mA cm}^{-2}$ .

In addition, Takanabe *et al.* found that optimizing Nafion content in Cu catalyst layers significantly improved  $\text{C}_{2+}$  selectivity, attributed to Nafion's regulation for  $\text{CO}_2$  and  $\text{H}_2\text{O}$  diffusion coefficients that enhanced  $\text{CO}_2$  transport *versus* bare Cu.<sup>102</sup> Differently, Sinton *et al.* demonstrated that the SSC ionomer (Aquivion) also effectively promoted  $\text{CO}_2$  transport by elevating the  $\text{CO}_2/\text{H}_2\text{O}$  ratio compared to bare Cu (Fig. 6d and e).<sup>76</sup> The Aquivion-modified Cu catalyst delivered 66%  $\text{C}_2\text{H}_4$  selectivity

with a partial current density of  $208 \text{ mA cm}^{-2}$ , outperforming the bare Cu (Fig. 6f). These findings underscore the critical role of ionomer-mediated  $\text{CO}_2/\text{H}_2\text{O}$  ratio control in increasing the concentration of  $\text{CO}_2$  and enhancing performances.

#### 4.2 Ionomers stabilize intermediates or promote intermediate diffusion

The adsorption and stabilization of intermediates can steer reaction selectivity toward a specific product pathway. Ionomers can stabilize  $\text{CO}_2$  reduction intermediates or facilitate their diffusion through functional groups, enhancing performance. For instance, by stabilizing  $^*\text{CO}$  to promote C–C coupling for selective  $\text{C}_{2+}$  production, Zhuang *et al.* prepared six polyaryl ionomers (*p*TPN-X) by grafting different organic cations (TMA, Pip, Py, Meim, Hexim, and Beim) onto ionomers.<sup>93</sup> Electro-catalytic  $\text{CO}_2\text{RR}$  tests revealed that *p*TPN-Beim exhibited the highest  $\text{C}_{2+}$  selectivity. Cyclic voltammetry and *in situ* IR further demonstrated that Beim<sup>+</sup> not only facilitated  $\text{CO}_2$  conversion to  $^*\text{CO}$  but also promoted  $^*\text{CO}$  coverage and stability at the electrode surface, increasing the  $^*\text{CO}/\text{H}_2\text{O}$  ratio and being favorable for subsequent  $^*\text{CO}$  dimerization into  $\text{C}_{2+}$  products. Additionally, Beim<sup>+</sup> significantly enhanced the  $\text{CO}_{\text{LFB}}/\text{CO}_{\text{HFB}}$  ratio, meaning linearly adsorbed CO dominated over bridge-adsorbed CO, further promoting C–C coupling (Fig. 7a and b). Other researchers have explored tuning intermediate adsorption by varying the side-chain lengths of the ionomer.<sup>86</sup> They synthesized 1-*n*-alkylimidazolium ionomers with different side chain lengths (*n* = 1, 4, 10, 16) and found that longer side chains suppressed the competing hydrogen evolution reaction (HER) and methane formation. Experimental and computational studies suggested that longer side chains thermodynamically stabilized key intermediates, favoring  $\text{C}_{2+}$  production.

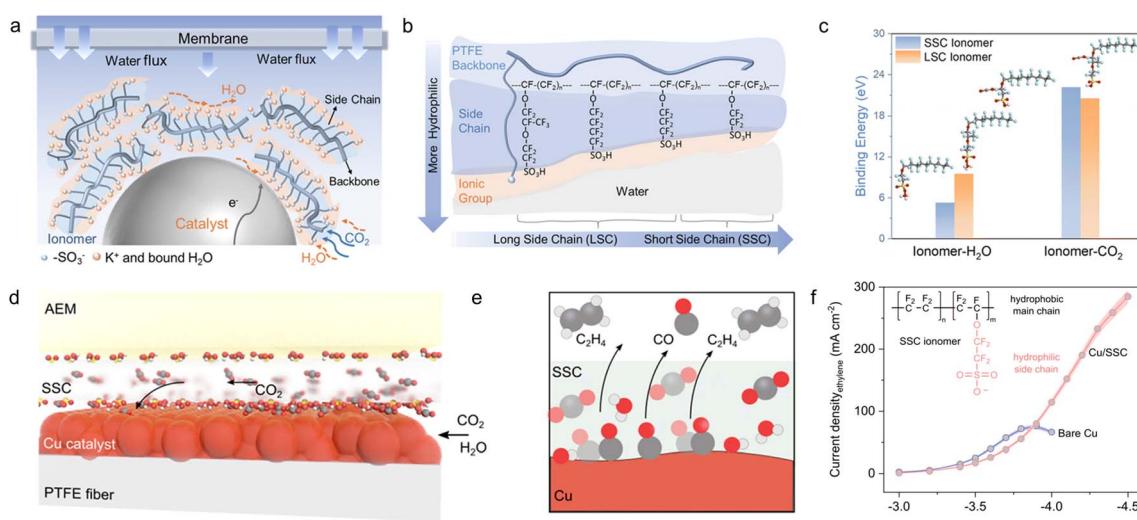


Fig. 6 Ionomers modulate  $\text{CO}_2/\text{H}_2\text{O}$  transport ratios. (a) The mass transfer diagram of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  channels at the three-phase reaction interface. (b) Chemical structure and hydrophobic properties of PFSA ionomers. (c) The density functional theory (DFT) calculation results for the binding energies of ionomer– $\text{H}_2\text{O}$  and ionomer– $\text{CO}_2$ . Reproduced with permission from ref. 63. Copyright 2025, The Royal Society of Chemistry. (d) Enrichment of  $\text{CO}_2$  species in the local reaction environment enabled by the SSC ionomer conformably surrounding the Cu surface. (e) Dominancy of the  $\text{CO}_2\text{RR}$  over the HER upon SSC ionomer modification. (f) Ethylene partial current density in a range of applied voltage for bare Cu/PTFE and SSC-modified Cu/PTFE electrodes. Reproduced with permission from ref. 76. Copyright 2020, American Chemical Society.



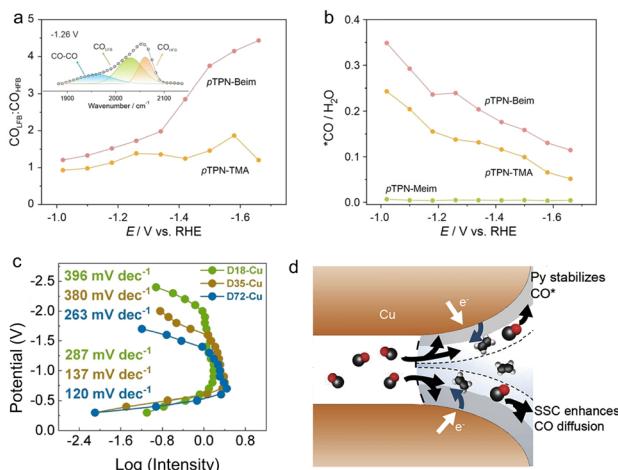


Fig. 7 Ionomers stabilize intermediates or promote intermediate diffusion. (a) Ratio of  ${}^*\text{CO}_{\text{LFB}}$  to  ${}^*\text{CO}_{\text{HFB}}$  band intensities as a function of potential (inset: peak deconvolution of ATR-SEIRAS spectra obtained on Cu/pTPN-Beim at  $-1.26 \text{ V vs. RHE}$ ). (b) Ratio of  $\nu({}^*\text{CO})$  to  $\nu(\text{H}_2\text{O})$  band intensities as a function of applied potential. Reproduced with permission from ref. 93. Copyright 2023, Wiley-VCH. (c) The analysis of the response of the  ${}^*\text{CO}$  coverage change to potential. Reproduced with permission from ref. 89. Copyright 2023, Wiley-VCH. (d) Introducing additives to improve CO diffusion and stabilize  $\text{CO}^*$  intermediates leads to enhanced  $\text{C}_2\text{H}_4$  selectivity and activity. Reproduced with permission from ref. 103. Copyright 2021, Elsevier.

In the  $\text{CO}_2\text{RR}$ , if  ${}^*\text{CO}$  forms and is consumed too quickly, its residence time at the catalyst surface will shorten, reducing  $\text{C}_{2+}$  yields. To address this problem, Wang *et al.* developed a type of quaternary ammonium-functionalized polynorbornene ionomer (D-X).<sup>89</sup> Its strong hydrophobicity induced an electrokinetic retardation effect, significantly prolonging the  ${}^*\text{CO}$  residence time on Cu. This unconventional effect was evidenced by increased Tafel slopes and reduced potential sensitivity in  ${}^*\text{CO}$  coverage (Fig. 7c). In detail, they identified linearly bound  ${}^*\text{CO}$  ( $\text{CO}_\text{L}$ ) by IR and quantified its intensity response with respect to the potential by a data processing method similar to the Tafel analysis. The obtained plots showed slopes of 287, 137, and 120  $\text{mV dec}^{-1}$  for  $\text{CO}_\text{L}$  intensity decreasing on the order of D18-Cu, D35-Cu, and D72-Cu, respectively. The descending branch of the  $\text{CO}_\text{L}$  intensity *versus* potential plot had slopes of 396, 380, and 263  $\text{mV dec}^{-1}$  for D18-Cu, D35-Cu, and D72-Cu, respectively, indicating that CO hydrogenation is kinetically more favorable at surfaces with weaker hydrophobicity (order of hydrophobicity: D18-Cu > D35-Cu > D72-Cu). The ionomer-modified Cu electrode delivered a  $\text{C}_{2+}$  partial current density of 223  $\text{mA cm}^{-2}$  with 90% selectivity, more than double that of bare Cu.

Beyond stabilization, ionomers can also enhance intermediate diffusion, playing a crucial role in the  $\text{CO}_2\text{--CO--C}_{2+}$  cascade reaction. Sinton *et al.* found that the SSC ionomer ( $\text{C}_4\text{HF}_7\text{O}_4\text{S}\cdot\text{C}_2\text{F}_4$ ) promoted the diffusion of *in situ*-generated CO across the electrode surface, boosting C-C coupling for  $\text{C}_2\text{H}_4$  and other  $\text{C}_{2+}$  products, with  $\text{C}_2\text{H}_4$  selectivity reaching 65% (Fig. 7d).<sup>103</sup> These studies demonstrate that ionomers enhance C-C coupling capability by stabilizing the key intermediate or facilitating its diffusion, thereby

improving the selectivity for  $\text{C}_{2+}$  products. They also highlight the critical role of *in situ* characterization techniques, such as IR spectroscopy, in elucidating how ionomer structures regulate the special intermediate.

### 4.3 Ionomers modulate ion species and concentrations at the catalyst surfaces

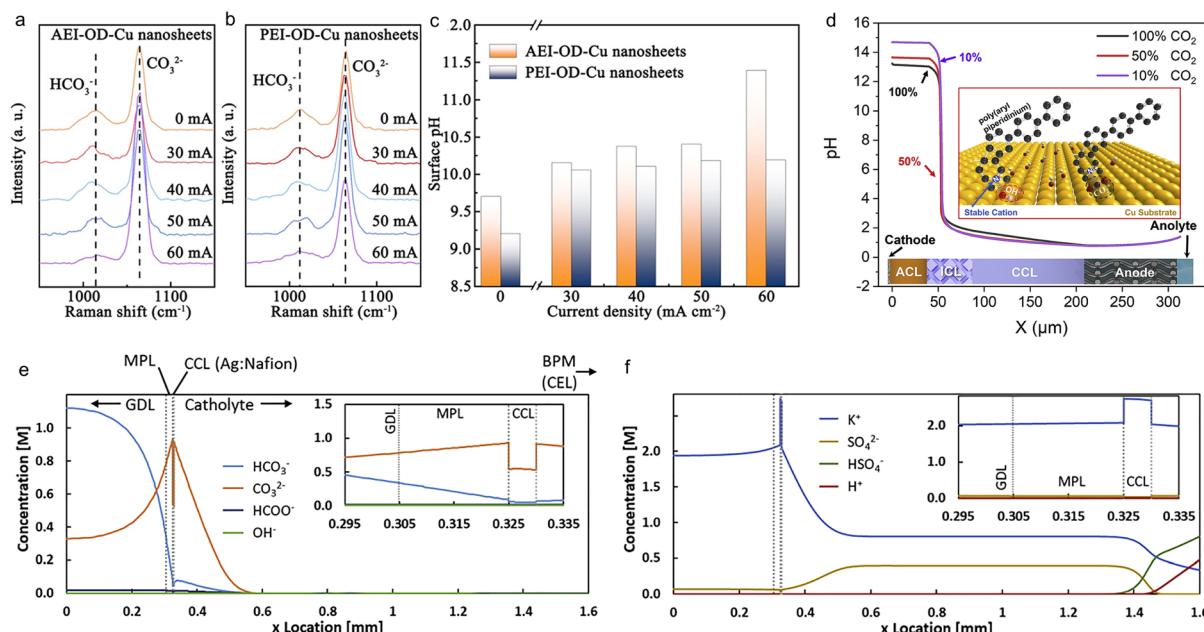
Cation exchange ionomers with anionic groups like  $\text{SO}_3^-$  and anion exchange ionomers with cationic groups like  $\text{NR}_4^+$  selectively transport cations (e.g.,  $\text{H}^+$ ) and anions (e.g.,  $\text{OH}^-$ ), respectively. This selective transport directly influences the local pH, electric field strength, and  $\text{K}^+$  concentration at the catalyst surface. They are critical factors for reaction performances. Therefore, designing and selecting an appropriate ionomer can effectively promote target product formation in the electrocatalytic  $\text{CO}_2\text{RR}$  within a specific system.

**4.3.1 Modulating pH.** Studies have demonstrated that locally alkaline environments could enhance the selectivity of the electrocatalytic  $\text{CO}_2\text{RR}$ .<sup>69</sup> Therefore, achieving high local pH through ionomer modulation is critical for improving this reaction. The type and structure of ionomers determine the species and quantity of ions transported, enabling precise modulation of reaction interfaces to influence performances. The local pH here reflects the ion species ( $\text{H}^+$  or  $\text{OH}^-$ ) closest to the catalyst surface, and the microenvironment is primarily influenced by the types and concentrations of ions within the EDL. The experimentally measured pH depends critically on the detection depth of the characterization technique. For instance, with *in situ* surface-enhanced Raman and infrared spectroscopy, the effective detection depth is  $\sim 200 \text{ nm}$  from the electrode surface, while the dominant signal contribution originates from the ionic species within several nanometers.<sup>104,105</sup> When an ionomer coats the catalyst surface, the pH mainly reflects the relevant ion concentration at the interface between them. Spatially, the measured partial ion concentration can extend into the ionomer layer.

Xie *et al.* employed an anion exchange ionomer (AEI) Pention D-18 to modulate the local pH at catalyst surfaces.<sup>88</sup> Through *in situ* Raman spectroscopy,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  signals were probed at the catalyst surface, and their ratio was used to calculate the surface pH (Fig. 8a and b). The results showed that while the pH at proton exchange ionomer (PEI)-modified Cu catalysts was stabilized at  $\sim 10$  with increasing current, AEI-modified Cu achieved a progressively higher pH (Fig. 8c), favoring  $\text{C}_{2+}$  production with 85.1% selectivity at  $800 \text{ mA cm}^{-2}$ . Theoretical calculations revealed that elevated pH reduced the energy barrier for the rate-limiting  $\text{OCCO}^*$  hydrogenation to  $\text{OCCOH}^*$ . Besides, there were other researchers tuning the interfacial microenvironment at Ag catalysts by varying alkyl chain lengths in imidazolium ionomers.<sup>106</sup> They found these ionomers could maintain alkaline conditions by restricting interfacial water/proton transport, achieving 90.1% CO selectivity. These studies demonstrate that ionomer-induced pH elevation effectively enhances  $\text{CO}_2\text{RR}$  selectivity.

To prevent salt accumulation at the cathode in the  $\text{CO}_2\text{RR}$ , recent scholars explored replacing the alkali-containing anolyte





**Fig. 8** Single ionomer modification modulates interfacial pH in the electrocatalytic  $\text{CO}_2\text{RR}$ . (a) *In situ* Raman spectra obtained from AEI-modified Cu nanosheets (AEI-OD-Cu) and (b) PEI-modified Cu nanosheets (PEI-OD-Cu). (c) pH values calculated from *in situ* Raman spectra collected at the open-circuit potential and  $60 \text{ mA cm}^{-2}$ , measured in a flow cell with KOH electrolyte. Reproduced with permission from ref. 88. Copyright 2022, American Chemical Society. (d) COMSOL simulation showed the pH distribution at different dissolved  $\text{CO}_2$  contents (100% is the ambient  $\text{CO}_2$  solubility limit). Reproduced with permission from ref. 78. Copyright 2022, Elsevier. COMSOL-simulated 1D cross-sections of solution species concentrations at  $500 \text{ mA cm}^{-2}$  using  $0.4 \text{ M K}_2\text{SO}_4$  ( $\text{pH} = 7$ ) as the electrolyte with Ag/Nafion electrodes: (e) Concentrations of  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCOO}^-$ , and  $\text{OH}^-$ . (f) Concentrations of  $\text{K}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{HSO}_4^-$ , and  $\text{H}^+$  (insets show magnified views within the catalyst layer). Reproduced with permission from ref. 107. Copyright 2022, Elsevier.

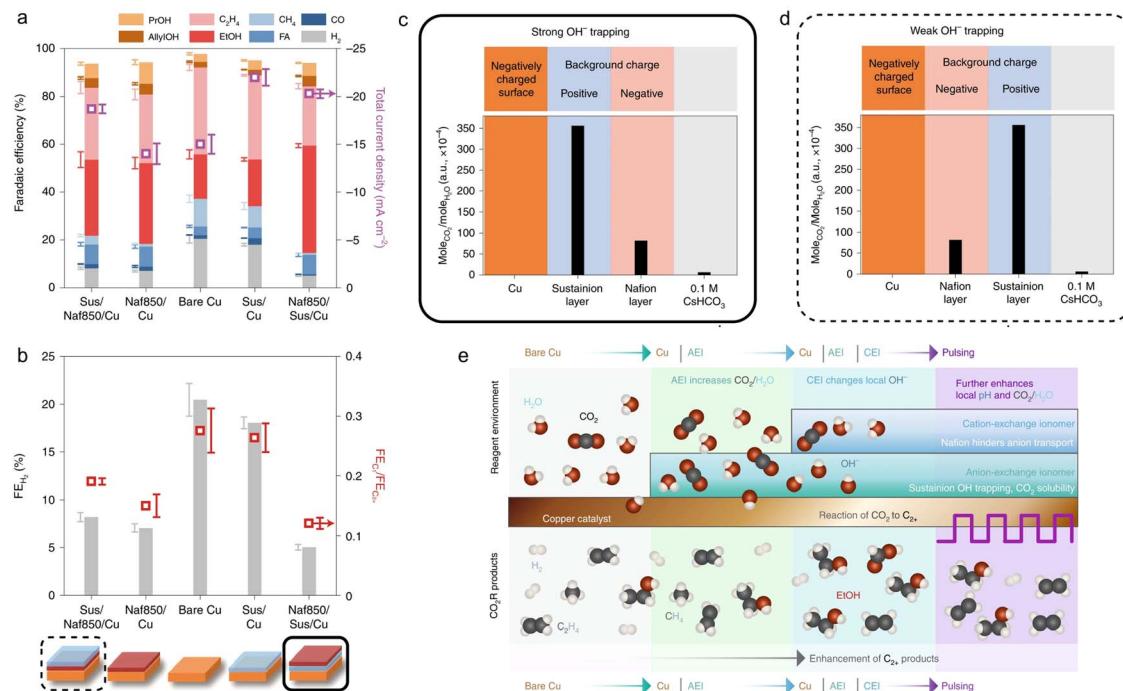
with pure water or pure acid solution. However, this often causes severe pH drop due to missing alkali cations. Sinton *et al.* addressed this by modifying Cu with an anion exchange ionomer PiperION, maintaining  $>80\%$  selectivity at  $40\text{--}240 \text{ mA cm}^{-2}$  while hypothesizing an alkaline cathode surface.<sup>78</sup> COMSOL simulations confirmed a high local pH near the cathode surface regardless of  $\text{CO}_2$  concentrations (100%, 50%, or 10%) (Fig. 8d), showing that cationic groups of PiperION could effectively confine  $\text{OH}^-$  while blocking  $\text{H}^+$  migration, mimicking alkali cation effects. Additionally, through 2D multi-physics modeling, 1D species distributions at the surface of ionomer-containing catalyst layers were revealed.<sup>107</sup> Simulations indicated the  $\text{SO}_3^-$  group of Nafion induced Donnan exclusion of  $\text{CO}_3^{2-}/\text{HCO}_3^-$ , sustaining high  $\text{CO}_3^{2-}$  concentrations after  $\text{HCO}_3^-$  conversion to elevate the pH (Fig. 8e). The cathode surface exhibited markedly increased  $\text{K}^+$  and reduced  $\text{H}^+$  concentrations (Fig. 8f), demonstrating how ionomers optimized  $\text{CO}_2\text{RR}$  selectivity *via* controlling the pH. Evidently, significant advances in *operando* characterization techniques and simulations have enabled precise interfacial pH modulation through ionomers.

Interestingly, Bell *et al.* made the first attempt to use bilayer ionomers to modulate the microenvironment at the electrode surface, including the pH and  $\text{CO}_2/\text{H}_2\text{O}$  ratios.<sup>21</sup> They ingeniously designed comparisons of catalytic performance and surface pH among bare Cu surfaces, Nafion-modified Cu surfaces, Sustainion-modified Cu surfaces, Nafion (inner layer)/

Sustainion (outer layer)-modified Cu surfaces, and Nafion (outer layer)/Sustainion (inner layer)-modified Cu surfaces (Fig. 9a and b). The study found the two ionomers played distinct roles: Sustainion increases  $\text{CO}_2$  solubility, while Nafion enhanced the local pH by trapping  $\text{OH}^-$  and blocking  $\text{HCO}_3^-$  from entering the reaction interface. This led to an optimal configuration, Naf850/Sus/Cu, where the Sustainion inner layer near the Cu surface increased the  $\text{CO}_2$  concentration, while the Nafion outer layer trapped *in situ*-generated  $\text{OH}^-$  from the catalyst and blocked  $\text{HCO}_3^-$  to elevate the interfacial pH (Fig. 9c), synergistically achieving the highest  $\text{CO}_2\text{RR}$  selectivity (90%  $\text{C}_2+$  products, only 4% HER). In contrast, the Sus/Naf850/Cu configuration significantly reduced the  $\text{CO}_2/\text{H}_2\text{O}$  ratio at the catalyst surface and exhibited poor  $\text{OH}^-$  trapping, leading to a notable pH decrease and exacerbated the HER (Fig. 9d). Fig. 9e clearly demonstrates that AEI can increase the  $\text{CO}_2/\text{H}_2\text{O}$  ratio (*i.e.*,  $\text{CO}_2$  concentration), while the combination of AEI (inner layer)/cation exchange ionomer (CEI outer layer) further elevates local pH, thereby synergistically enhancing  $\text{C}_2+$  product selectivity. This study about the sophisticated combination of CEI and AEI provides invaluable guidance for the synergistic use of different ionomers.

Besides, Ngene *et al.* conducted similar studies on bilayer ionomer-modified electrodes and drew consistent conclusions: Sustainion monolayer modification aggravated the HER.<sup>108</sup> Nafion, whether as a monolayer or as an outer layer over Sustainion, promoted  $\text{C}_2+$  product formation. There were





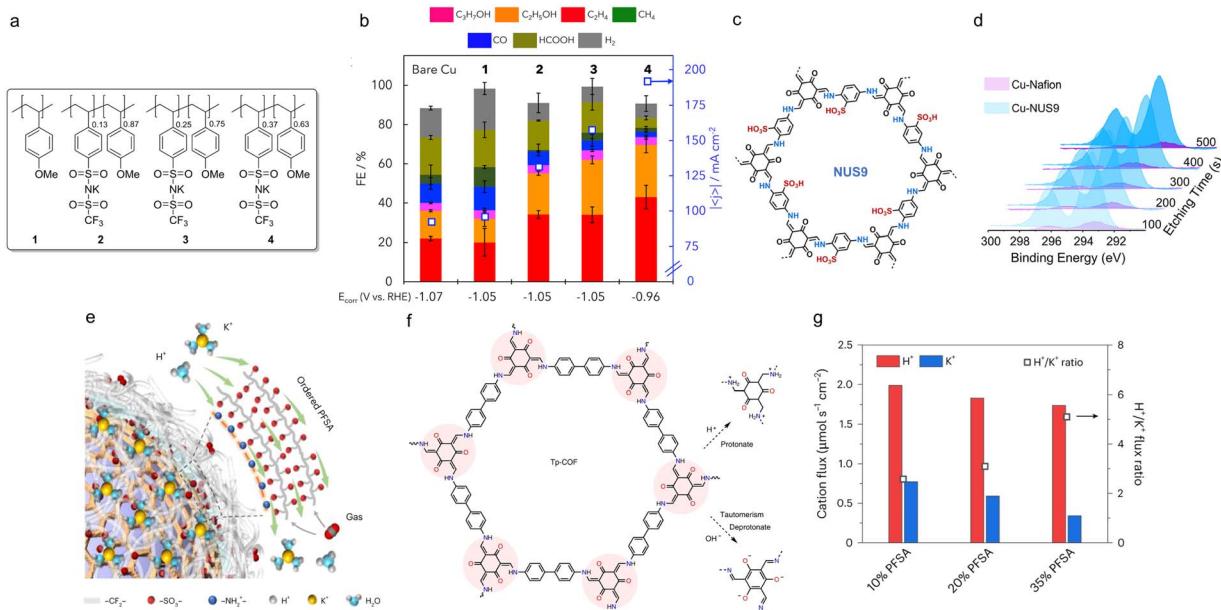
**Fig. 9** Bilayer ionomers modulate the interfacial pH in the electrocatalytic CO<sub>2</sub>RR. (a) CO<sub>2</sub>RR performance of stacked-ionomer-modified Cu in 0.1 M CsHCO<sub>3</sub> electrolyte at -1.15 V vs. RHE. (b) Product distribution trends for stacked-ionomer-modified Cu catalysts. Schematic illustrations of Naf850/Sus/Cu (c) and Sus/Naf850/Cu (d) configurations, showing CO<sub>2</sub>/H<sub>2</sub>O ratios and space-charge distributions. (e) Mechanism of the ionomer-enhanced CO<sub>2</sub>RR: an AEI layer on Cu increases the CO<sub>2</sub>/H<sub>2</sub>O ratio, while a subsequent CEI outer layer creates a bilayer microenvironment that modulates the local OH<sup>-</sup> concentration. Reproduced with permission from ref. 21. Copyright 2021, Springer Nature.

additional findings, including Nafion mitigated salt deposition and agglomeration of the Cu catalyst, while Sustainion shifted product selectivity from ethylene to ethanol to some extent. These results demonstrate that the ordered combination of cationic and anionic ionomer layers simultaneously improves CO<sub>2</sub> adsorption on the catalyst surface and elevates the interfacial pH, which is very important for enhancing reaction selectivity.

**4.3.2 Enrichment of alkali metal cations.** Recent studies have shown that alkali metal cations play crucial roles in the electrocatalytic CO<sub>2</sub>RR, such as increasing pH at catalyst surfaces, stabilizing intermediates, and modulating interfacial electric fields.<sup>84,109-114</sup> Among them, Koper *et al.* made significant contributions. Through rigorous experiments, characterization studies, and DFT calculations, they demonstrated that the CO<sub>2</sub>RR did not occur on Cu, Au, or Ag electrodes in the absence of metal cations in solution. The dominant role of alkali metal cations is to stabilize the CO<sub>2</sub> intermediate through short-range electrostatic interactions after partial desolvation.<sup>114</sup> Their work proved that positively charged species in the electrolyte were the main factor stabilizing key reaction intermediates. Clearly, surface enrichment of alkali metal cations like K<sup>+</sup> is essential for reaction performances without causing salt precipitation. To enrich K<sup>+</sup> on the catalyst surface, Agapie *et al.* synthesized a series of polystyrene-based ionomers (Fig. 10a).<sup>115</sup> By adjusting the ratio of different blocks in the ionomers, they effectively modulated the K<sup>+</sup> content. When these ionomers were used to modify Cu electrodes, they

regulated the local K<sup>+</sup> concentration at the electrode surface. Studies showed that the partial current density of C<sub>2+</sub> products increased with higher K<sup>+</sup> content in the ionomers (Fig. 10b). However, when K<sup>+</sup> was substituted by organic cations like Me<sub>4</sub>N<sup>+</sup>, the selectivity dropped to the level of bare Cu, highlighting the critical role of K<sup>+</sup> in enhancing the product selectivity of CO<sub>2</sub> reduction. Further MD simulations revealed that CO<sub>2</sub> diffusivity increased with the higher K<sup>+</sup> concentration, indicating that these ionomers effectively promoted CO<sub>2</sub> mass transport.

Moreover, researchers have recently discovered that COFs, owing to their porous structures, can be specifically designed to enrich both CO<sub>2</sub> and K<sup>+</sup>. The COF is a type of material distinct from an ionomer, because the COF is a long-range ordered, porous crystalline material formed by strong covalent bonds linking structural units, while the ionomer is a long-range disordered amorphous/semi-crystalline material containing polymer chains with ionic groups. However, through functional designs, some COFs can exhibit ionomer-like characteristics, such as introducing ionic groups into COFs to enable ion transport like ionomers, thereby becoming ionic polymers. For instance, Wang *et al.* developed a two-dimensional sulfonated COF nanosheet (COF-NS) ionomer (NUS9) (Fig. 10c).<sup>116</sup> When used to modify a Cu catalyst, it increased methane selectivity in the electrocatalytic CO<sub>2</sub>RR over 60% under both acidic (pH = 2) and alkaline (pH = 14) conditions. Through XPS depth profiling analysis and K<sup>+</sup> retention experiments, they confirmed that the pore walls of NUS9 contained high-density sulfonic and



**Fig. 10** Ionomers promote  $\text{K}^+$  enrichment at surfaces in the electrocatalytic  $\text{CO}_2\text{RR}$ . (a) Structures of a series of synthesized ionomers. (b) Catalytic performances of Cu/PTFE modified with ionomers 1–4 in 1 M  $\text{KHCO}_3$  electrolyte. Reproduced with permission from ref. 115. Copyright 2024, Elsevier. (c) Chemical structure of NUS-9. (d) X-ray photoelectron spectroscopy (XPS) depth profiles of K in Cu-Nafion and Cu-NUS9 electrodes after  $\text{CO}_2$  reduction. Reproduced with permission from ref. 116. Copyright 2024, American Chemical Society. (e) Schematic of functionalized COF particles modulating the ionomer structure and local ion/gas transport. (f) Structure of amphoteric Tp-COF and its sensitivity to the surrounding acidity. (g) Apparent cation fluxes across different COF:PFSA composite layers and the corresponding  $\text{H}^+/\text{K}^+$  flux ratios at 200  $\text{mA cm}^{-2}$ . Reproduced with permission from ref. 117. Copyright 2023, Springer Nature.

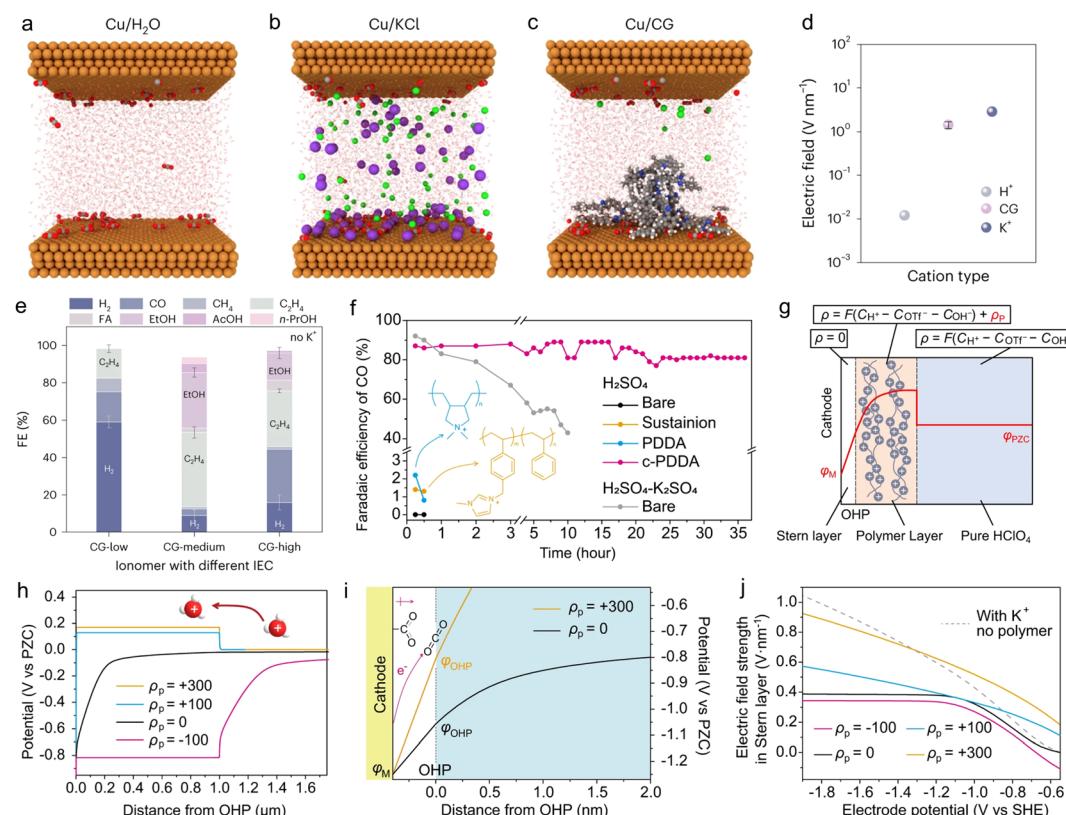
carbonyl groups that enriched  $\text{K}^+$  (Fig. 10d). Here,  $\text{K}^+$  retention experiments were conducted under applied potential throughout the test, and results closely reflected surface-adsorbed  $\text{K}^+$  in the EDL. In contrast, XPS depth profiling analysis was performed after cleaning the catalyst surface, detecting  $\text{K}^+$  strongly interacting with the NUS9. Comparing the catalytic performances of Nafion-modified and NUS9-modified Cu in electrolytes with varying  $\text{K}^+$  concentrations, they found that reducing the  $\text{K}^+$  concentration decreased the extent of  ${}^*\text{CO}$  conversion to multi-electron reduction products at Nafion-modified Cu, while NUS9-modified Cu showed minimal changes. This indicated that NUS9 could maintain a high local  $\text{K}^+$  concentration even at low bulk cation levels. Similarly, Sargent *et al.* combined another COF with the PFSA ionomer to create a heterogeneous catalyst coating (Fig. 10e).<sup>117</sup> The study revealed that Tp-COF, containing imine and carbonyl groups, modulated PFSA dispersion and molecular configuration of PFSA, creating uniformly distributed cationic and hydrophilic–hydrophobic nanochannels. This formed an efficient proton flux-limiting overlayer (Fig. 10f). The COF further enriched cations on the catalyst surface (Fig. 10g), improving the reaction microenvironment. As a result, 75%  $\text{C}_{2+}$  product selectivity at 200  $\text{mA cm}^{-2}$  was achieved for the electrocatalytic  $\text{CO}_2\text{RR}$  even under strongly acidic conditions. These findings collectively demonstrate that it is an efficient way to enrich  $\text{K}^+$  through ionomers in enhancing  $\text{CO}_2\text{RR}$  performances.

#### 4.3.3 Modulating the intensity of the interfacial electric field.

In an acidic electrolyte, alkali metal cations can modify

interfacial electric fields, buffer local pH and regulate interfacial water networks to promote the electrocatalytic  $\text{CO}_2\text{RR}$ .<sup>52,53,118</sup> However, the accumulation of alkali metal cations ultimately leads to salt deposition on cathodic catalyst surfaces and electrode failure. Therefore, researchers have sought to use ionomers as substitutes for alkali metal cations to modulate the interfacial electric field. Sinton *et al.* employed a modified Poisson–Boltzmann model in COMSOL to predict the interfacial electric fields generated by  $\text{K}^+$  and immobilized cationic groups (CGs) (Fig. 11a–c).<sup>36</sup> In the Gouy–Chapman–Stern (GCS) model, the ionomer was assumed to be uniformly distributed at the catalyst surface, which may lead to some deviations from actual conditions. Nonetheless, calculations based on the GCS model could still provide some valid predictions and guidance. In the model, the OHP was defined by the plane formed by cations carried by ionomer layers closest to the catalyst surface. MD simulations revealed that CGs could generate an interfacial electric field of the same order of magnitude as  $\text{K}^+$ , with the OHP on the Cu surface coated with CGs being  $\sim 6.4 \text{ \AA}$  (Fig. 11d). Simulations showed that the electric field induced by  $\text{K}^+$  and CGs could stabilize negatively charged  $\text{CO}_2$ , promoting  $\text{CO}_2$  adsorption and activation. In contrast, the effect of  $\text{H}^+$  on the electric field was negligible compared to  $\text{K}^+$  and CGs. On the Cu surface, CG modification resulted in the lowest water density across different potentials, indicating the  $\text{H}_3\text{O}^+$ -blocking effect while simultaneously enhancing the local  $\text{CO}_2$  concentration under an applied potential. Based on these simulations, they modified Cu catalysts with the moderate concentration of the





**Fig. 11** Ionomers modulate the interfacial electric field in the electrocatalytic CO<sub>2</sub>RR. MD-simulated atomic configurations of (a) Cu/H<sub>2</sub>O, (b) Cu/KCl, and (c) Cu/CG systems at the end of NVE simulations ( $\Delta U = 2.5$  V). (d) Comparison of electric fields generated by H<sup>+</sup>, K<sup>+</sup>, and CG in the OHP. (e) Catalytic selectivity of Cu modified with CG-low, CG-medium, and CG-high in 0.2 M H<sub>2</sub>SO<sub>4</sub> at 100 mA cm<sup>-2</sup>. Reproduced with permission from ref. 36. Copyright 2023, Springer Nature. (f) FE for CO production on different ionomer-modified Ag catalysts at 200 mA cm<sup>-2</sup> (electrolyte: 0.1 M H<sub>2</sub>SO<sub>4</sub>; bare Ag nanoparticle system used 0.4 M K<sub>2</sub>SO<sub>4</sub> as an additive). (g) Simulation model:  $\rho$  denotes the total charge density;  $\rho_p$  represents the charge density carried by the ionomer layer. (h) Potential profiles on Ag electrodes covered by ionomer layers with different  $\rho_p$  values (unit: C cm<sup>-3</sup>) in 10 mM HOTf at -1.8 V vs. SHE. (i) Potential profiles on Ag electrodes coated with  $\rho_p = 300$  C cm<sup>-3</sup> and  $\rho_p = 0$  ionomer layers. (j)  $E_{\text{Stern}}$  versus electrode potential. Solid curves: Ag electrodes with different  $\rho_p$  ionomer layers (unit: C cm<sup>-3</sup>) in 10 mM HOTf. Gray dashed curve: the bare Ag electrode in 10 mM HOTf + 40 mM KOTf. Reproduced with permission from ref. 90. Copyright 2023, Springer Nature.

cationic ionomer (Aemion<sup>+</sup>), achieving 80% C<sub>2+</sub> product selectivity at 100 mA cm<sup>-2</sup> under acidic conditions (Fig. 11e).

Gu *et al.* conducted a more in-depth study on ionomer-mediated interfacial field modulation.<sup>90</sup> Previous research showed that bicarbonate formation at the cathode surface was unavoidable even in an acidic electrolyte. However, the system requires cation enrichment in the OHP to alter the electric double-layer field distribution, thereby suppressing H<sup>+</sup> migration through shielding of the cathode field. Additionally, cations stabilize polar intermediates in CO<sub>2</sub> reduction by enhancing the electric field of the Stern layer. Theoretically, cationic ionomers can replace alkali metal cations. Gu *et al.* compared various polyelectrolytes and found that PDDA had the highest cationic density (6.19 mmol g<sup>-1</sup>), approximately three times that of Sustainion XA-9 (2.06 mmol g<sup>-1</sup>).<sup>90</sup> When used in the acidic CO<sub>2</sub>RR, PDDA performed poorly due to its high solubility in the electrolyte. However, cross-linked PDDA (c-PDDA) delivered near 90% CO selectivity at 200 mA cm<sup>-2</sup> with stable operation exceeding 35 hours (Fig. 11f). Subsequent GMPNP simulations showed that ionomers significantly altered the charge density distribution in the OHP (Fig. 11g). The

simulated potential distribution revealed that the positively charged ionomer layer shielded H<sup>+</sup> migration from the bulk electrolyte to the cathode, with the shielding efficiency increasing with the ionomer charge density (Fig. 11h). Ionomers also affected the field strength of Stern layer ( $E_{\text{Stern}}$ ). Adsorbed CO<sub>2</sub> (\*CO<sub>2</sub>) possesses a solution-oriented dipole moment, which can be stabilized by  $E_{\text{Stern}}$  (Fig. 11i). Thus, regardless of the mechanisms of CO<sub>2</sub> reduction, enhancing the  $E_{\text{Stern}}$  accelerated the reaction. Simulations indicated that ionomers with +300C cm<sup>-3</sup> charge density produced a higher  $E_{\text{Stern}}$ , demonstrating that cationic ionomer layers promoted CO<sub>2</sub> reduction at electrode surfaces. Comparisons of  $E_{\text{Stern}}$  on Ag electrodes coated with different ionomers showed that neutral or anion ionomers could not continuously accelerate CO<sub>2</sub> reduction with increasing overpotential, as  $E_{\text{Stern}}$  plateaued after initial enhancement. In contrast, cationic ionomers enabled  $E_{\text{Stern}}$  to increase steadily with more negative potential, with the +300C cm<sup>-3</sup> ionomer matching the promotional effect of K<sup>+</sup> (Fig. 11j). It is clear that the enhanced interfacial electric field induced by ionomers improved the performance of the electrocatalytic CO<sub>2</sub>RR. It is noteworthy that compared to K<sup>+</sup> (0.04 mol L<sup>-1</sup>) in

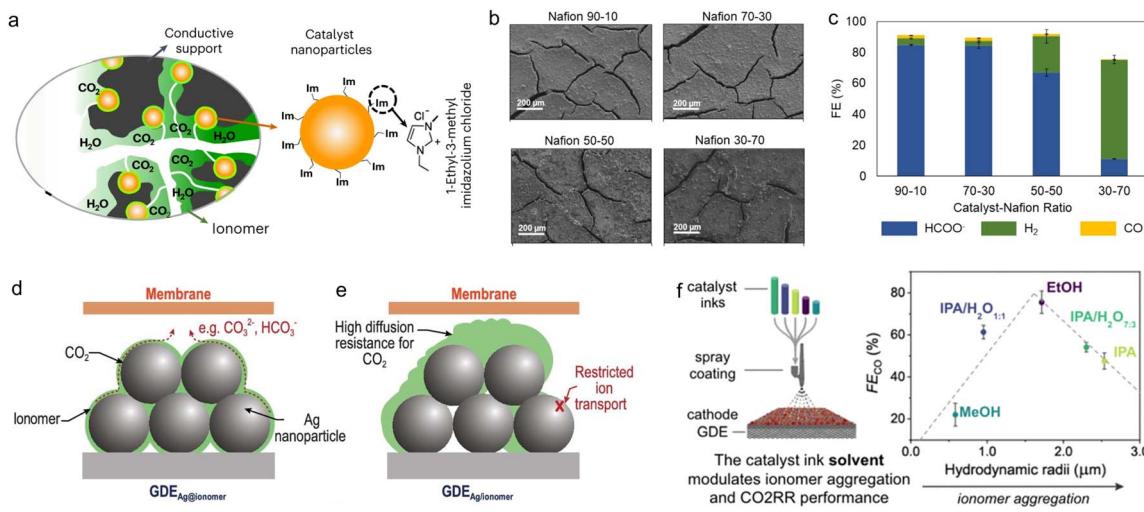


Fig. 12 Ionomers stabilize or modulate catalyst surfaces. (a) Schematic of the catalyst microenvironment composed of Mo<sub>3</sub>P nanoparticles covered by an Im layer coated with an anion exchange ionomer and deposited on a conductive carbon support. Reproduced with permission from ref. 85. Copyright 2023, Springer Nature. (b) Scanning electron microscopy images and water contact angle measurements of GDEs prepared with varying catalyst:Nafion ratios. (c) Product selectivity at different catalyst–Nafion ratios. Reproduced with permission from ref. 121. Copyright 2025, American Chemical Society. Schematic of GDE fabrication *via* (d) Ag@ionomer and (e) Ag/ionomer. Reproduced with permission from ref. 122. Copyright 2024, Oxford University Press. (f) Correlation between dispersion solvents, ionomer aggregation, and CO FE. Reproduced with permission from ref. 123. Copyright 2021, American Chemical Society.

the study, the cation density of the ionomer PDDA is relatively low. Moreover, since cations from PDDA are fixed to the polymer chains, their mobility is often restricted, which may result in an electric field generated by PDDA being significantly weaker than that generated by K<sup>+</sup>. However, simulations showed comparable interfacial electric fields by them, likely due to the behaviour differences in how these cations form the EDL. Nonetheless, many ionomers can achieve catalytic performances in pure acid or pure water similar to those in the system containing certain concentrations of alkali metal cations.<sup>64,77,90,92,93,119</sup> Besides, in the same way, the interfacial electric field can be modulated by the QAPPT ionomer.<sup>120</sup> In acidic MEA, addition of QAPPT shielded the cathode field, inhibiting H<sup>+</sup> and K<sup>+</sup> cross-membrane diffusion. This improved CO selectivity, achieving 95.6% FE at 100 mA cm<sup>-2</sup>.

#### 4.4 Ionomers stabilize or modulate catalyst morphology and state

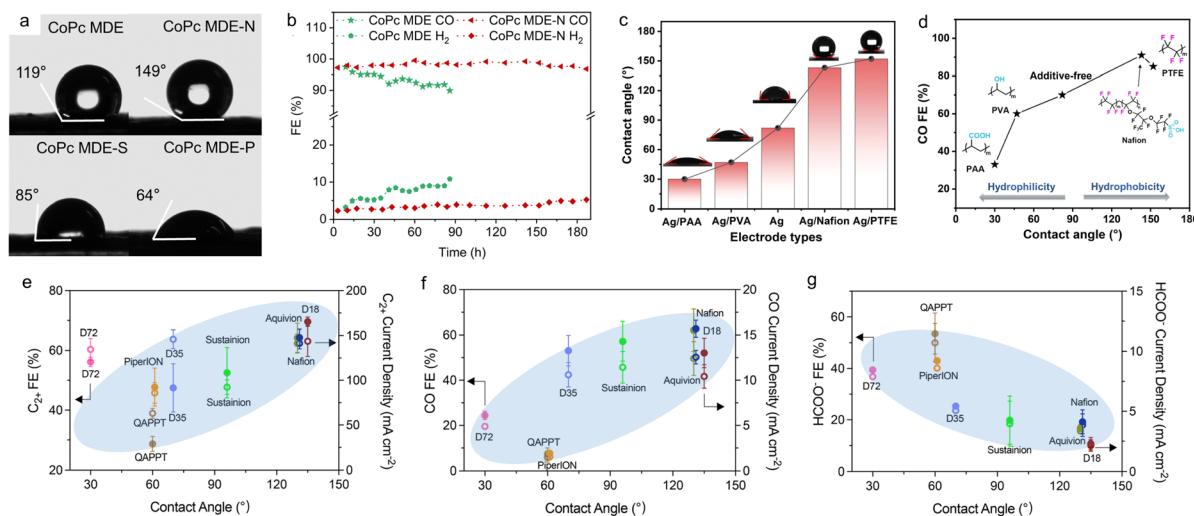
The stability of catalyst surfaces is crucial for the steady operation of the electrocatalytic CO<sub>2</sub>RR. When ionomers are introduced onto catalyst surfaces, their high stability often prevents catalyst deactivation. For instance, Asadi *et al.* found that the ionomer Sustainion XA-9 stabilized imidazole (Im)-functionalized Mo<sub>3</sub>P nanoparticles, enabling stable operation at nearly 400 mA cm<sup>-2</sup> for 100 h while maintaining ~90% propane selectivity (Fig. 12a).<sup>85</sup> Post-analysis revealed that Sustainion XA-9 primarily preserved the structural integrity of the organic Im modifiers, preventing their decomposition. Beyond stabilizing catalyst surfaces, ionomers can also directly influence catalyst dispersion. For instance, researchers prepared four different electrodes by adjusting the catalyst-to-Nafion ratio and observing that Nafion significantly altered catalyst dispersion, modifying surface morphology

(Fig. 12b).<sup>121</sup> Their results indicated that the Nafion content should not exceed 30%, because a higher proportion would exacerbate the HER (Fig. 12c). Similarly, Sustainion was found to suppress the HER regardless of loading amounts. However, exceeding 30% Sustainion would block CO<sub>2</sub> transport, ultimately reducing the product selectivity.

Furthermore, researchers innovatively proposed a pre-confinement ionomer (PiperION) during catalyst synthesis, ensuring uniform outer-layer encapsulation.<sup>122</sup> Compared to simple mixing (Ag/ionomer), the pre-confinement method yielded Ag@ionomer with more homogeneous distribution, enhancing CO<sub>2</sub> mass transport (Fig. 12d and e). Furthermore, Berlinguette *et al.* discovered that ink solvents influenced the ionomer dispersion, affecting the microstructure of the catalyst layers on GDE and performance.<sup>123</sup> Using methanol, ethanol, isopropanol, and isopropanol/water mixtures, they found ethanol promoted moderate ionomer aggregation, achieving the highest catalytic performance (Fig. 12f). There was another study that examined spray-coating techniques for ionomer application.<sup>124</sup> Results showed that Nafion content critically impacted the dispersion uniformity of catalysts on GDEs, with the automated spraying outperforming manual methods, highlighting the importance of an optimized deposition process. Collectively, these findings demonstrate that rational selection of ionomer types, loading amounts, and adding methods will influence catalyst stability and surface morphology and state, ultimately regulating reaction performances.

#### 4.5 Ionomers modulate the hydrophobicity of catalyst surfaces

In the electrocatalytic CO<sub>2</sub>RR, water directly contacts the catalyst surface as a reactant, often leading to surface flooding



**Fig. 13** Ionomers modify the hydrophobicity of electrodes and catalyst surfaces. (a) Water contact angles of CoPc-MDE systems. (b) Stability tests of the CoPc-MDE electrode at  $100 \text{ mA cm}^{-2}$ . Reproduced with permission from ref. 91. Copyright 2024, The Royal Society of Chemistry. (c) Contact angles of the bare Ag electrode versus the polymer/ionomer-modified Ag electrode. (d) Correlation between the CO faradaic efficiency and the contact angle at  $200 \text{ mA cm}^{-2}$ . Reproduced with permission from ref. 125. Copyright 2025, Elsevier. Selectivity correlations with contact angles for: (e)  $\text{C}_2^+$  products at  $-4.3 \text{ V} \pm 0.1 \text{ V}$ , (f) CO at  $-3 \text{ V} \pm 0.2 \text{ V}$ , and (g) formate at  $-3 \text{ V} \pm 0.2 \text{ V}$  at the Cu electrode coated with different ionomers. Light blue shadings are used to represent the correlation trend. Reproduced with permission from ref. 126. Copyright 2024, The Royal Society of Chemistry.

under high current density or prolonged operation. This makes maintaining the hydrophobicity of the catalyst surface critically important. In high-efficiency flow cells and MEA, the triple-phase interface is essential for reaction selectivity. If the electrode hydrophobicity is destroyed, leading to flooding, the reaction irreversibly shifts toward the competing HER. Thus, significant efforts have been made to design and improve the hydrophobicity of electrode surfaces. Ionomers, containing the hydrophobic backbone or functional group, can effectively prevent electrode flooding. For example, Gao *et al.* used three ionomers (Nafion, Sustainion, and PiperION) to modify Ag nanoparticles and molecularly dispersed cobalt phthalocyanine (CoPc MDE).<sup>91</sup> They found these ionomers had minimal impact on the hydrophobicity of the Ag electrode but significantly affected CoPc MDE (Fig. 13a). Nafion notably enhanced the hydrophobicity of CoPc MDE, enabling stable operation for 180 h at  $100 \text{ mA cm}^{-2}$  (Fig. 13b). In contrast, aryl-containing ionomers (Sustainion and PiperION) increased the electrode hydrophilicity through the non-covalent interaction, accelerating the HER. This highlights the need to carefully consider ionomer hydrophobicity and compatibility with catalysts before reactions. It is worth mentioning that carbon paper also plays critical roles in modulating electrode hydrophobicity besides the ionomers. The rational design of carbon paper (*e.g.*, increasing PTFE content) enhances the hydrophobicity of the electrode surface.<sup>30</sup> Together, they maintain the entire electrode hydrophobicity. The hydrophobic nature of the electrode facilitates CO<sub>2</sub> mass transport to the three-phase reaction interface while preventing surface flooding.

Moreover, Gong *et al.* modified Ag electrodes with Nafion and other polymers (polyacrylic acid (PAA), polyvinyl alcohol (PVA), and PTFE), observing that their modification could

change the contact angle of catalyst surfaces (Fig. 13c). PAA and PVA reduced the hydrophobicity of catalyst surfaces, while Nafion and PTFE enhanced hydrophobicity. Further experimental results demonstrated that hydrophobicity strongly correlated with CO selectivity specifically, increasing with enhanced hydrophobicity of catalyst surfaces (Fig. 13d).<sup>125</sup> They attributed the hydrophobic enhancement of Nafion to its fluorine-rich backbone. Similarly, Wang *et al.* investigated multiple ionomers (Aquivion, Sustainion, PiperION, QAPPT, and Nafion) and found selectivities of  $\text{C}_2^+$  and CO positively correlated with hydrophobicity, while formate selectivity decreased (Fig. 13e–g).<sup>126</sup> However, Pention-class ionomers (*e.g.*, D18, D35 and D72) slightly deviated from this trend. This is because their ionic side chains can alter the double-layer structure, affecting  $\text{C}_2^+$  selectivity and activity. Bulkier side chains with a lower hydration number form a looser double layer, promoting C–C coupling despite the poorer hydrophobicity. Thus, surface hydrophobicity significantly influences the reaction selectivity, but it is not the sole determinant, and other factors also need to be considered.

#### 4.6 Ionomers modulate structures of interfacial water

The unique structure of ionomers enables some of them to alter interfacial water structures when coated on catalyst surfaces and exposed to electrolytes, thereby modulating the catalytic activity. Interfacial water refers to the transitional water layer between bulk water and another phase, whose properties are significantly altered by interfacial interactions (typically, beyond the first monolayer of water molecules, the subsequent 1–2 molecular layers also exhibit interfacial effects).<sup>127</sup> It possesses unique structural, dynamic, and thermodynamic

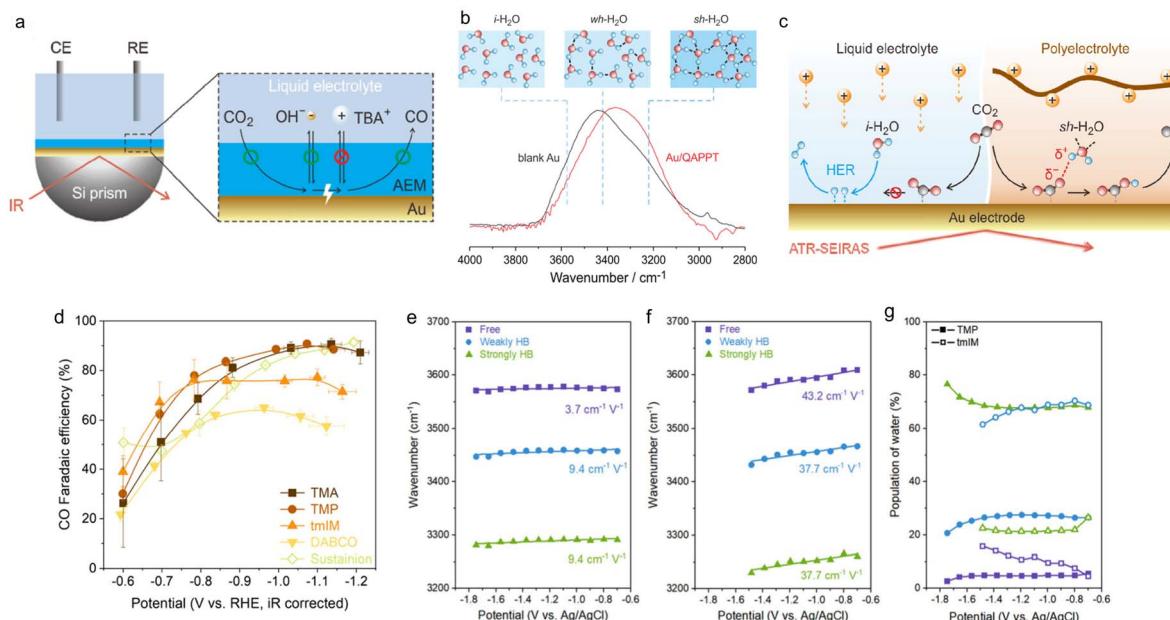


Fig. 14 Ionomers modulate structures of interfacial water at cathodes in the electrocatalytic  $\text{CO}_2\text{RR}$ . (a) Schematic of *in situ* IR and interfacial configuration for the QAPPT-coated Au electrode. (b) The  $\nu(\text{O}-\text{H})$  bands (normalized) recorded at  $-1.45\text{ V}$  under a  $\text{CO}_2$  atmosphere at the interface of blank Au and Au/QAPPT. (c) Mechanism of ionomers altering structures of interfacial water to shift  $\text{CO}_2\text{RR}/\text{HER}$  selectivity. Reproduced with permission from ref. 64. Copyright 2024, American Chemical Society. (d) CO selectivity on various QPC-based anion exchange ionomer-modified Ag electrodes. *In situ* IR characterization of interfacial water in  $\text{CO}_2$ -saturated 0.1 M KCl: wavenumber shifts of water stretching vibrations versus potential for (e) TMP-modified and (f) tmIM-modified Ag. (g) Potential-dependent proportions of water structures at TMP/tmIM–Ag interfaces. Reproduced with permission from ref. 94. Copyright 2025, American Chemical Society.

properties. Compared to bulk water, interfacial water exhibits partially broken, distorted, or reconfigured hydrogen-bonded networks, with increased or decreased ordering, and highly oriented molecular alignment. When an ionomer is introduced onto the catalyst surface, interfacial water specifically refers to the water at the catalyst–electrolyte and catalyst–ionomer interfaces (spanning about 2–3 water molecular layers), which may partially extend into the ionomer layer (as shown in Fig. 2b).

Zhuang *et al.* recently coated an Au electrode with the QAPPT ionomer and investigated its effect on catalytic activity and structures of interfacial water through combined electrochemical tests and *in situ* IR (Fig. 14a).<sup>64</sup> Experimental results demonstrated that the QAPPT-modified Au electrode significantly enhanced CO selectivity in the electrocatalytic  $\text{CO}_2\text{RR}$  compared to the bare Au (from  $<15\%$  increasing to  $48\%$ ). To elucidate the role of QAPPT, they characterized interfacial species *via* *in situ* IR, where the QAPPT film was deposited on the Au catalyst. The acquired  $\nu(\text{O}-\text{H})$  band of water was deconvoluted into three components, corresponding to the three structures of interfacial water: the isolated water ( $i\text{-H}_2\text{O}$ ), the weakly hydrogen-bonded water ( $wh\text{-H}_2\text{O}$ ), and the strongly hydrogen-bonded water ( $sh\text{-H}_2\text{O}$ ). Results revealed that QAPPT strengthened the hydrogen-bonded network of interfacial water, notably increasing the proportion of  $sh\text{-H}_2\text{O}$  (Fig. 14b). Correlating with other species changes, they proposed that  $sh\text{-H}_2\text{O}$  facilitates  $^*\text{COO}$  hydrogenation to  $^*\text{COOH}$ , promoting selective CO formation (Fig. 14c). Similarly, Won *et al.* explored

different ionomers to tailor the interfacial microenvironment, particularly water structures.<sup>94</sup> They synthesized six QPC-based anion exchange ionomers with varied ionic groups.  $\text{CO}_2\text{RR}$  tests showed that the selection of ionic groups dramatically altered CO selectivity, with TMP (trimethyl phosphonium) and tmIM (tetramethylimidazole) groups yielding the better and worse performances, respectively (Fig. 14d). *In situ* IR analysis revealed that the QPC-TMP ionomer induced the restructuring of interfacial water, reducing the Stark tuning slope (from  $3.7\text{--}9.4\text{ cm}^{-1}\text{ V}^{-1}$  of QPC-tmIM to  $37.7\text{--}43.2\text{ cm}^{-1}\text{ V}^{-1}$  of QPC-TMP) (Fig. 14e and f), while increasing the content of strongly hydrogen-bonded water (from  $\sim 20\%$  of QPC-tmIM to  $70\%$  of QPC-TMP), which suppressed the HER and favored  $\text{CO}_2$  reduction (Fig. 14g). These studies confirm that ionomers can fine-tune the reaction microenvironment by engineering structures of interfacial water, and strongly hydrogen-bonded water favors the selective formation of CO in their testing systems.

## 5. Summary and outlook

Substantial research efforts have demonstrated that ionomers play a crucial role in the electrocatalytic  $\text{CO}_2\text{RR}$  by precisely modulating the interfacial microenvironment to enable efficient and stable operation. Table 3 summarizes typical ionomers reported in the reaction, including their performances and specific modulation roles. Based on systematic analysis, ionomers modulate the microenvironment primarily through the following ways: (1) ionomers enhance  $\text{CO}_2$  mass transport at



Table 3 Performances of the electrocatalytic CO<sub>2</sub>RR and the corresponding modulation roles with typical ionomers

Ionomers	Performances	Modulation roles	Ref.
PFSA (Nafion)	$j = 1.32 \text{ A cm}^{-2}$ ; FE <sub>C<sub>2</sub>H<sub>4</sub></sub> = 91.7%	Promote CO <sub>2</sub> transport	20
QAPEEK	$j = 1 \text{ A cm}^{-2}$ ; FE <sub>C<sub>2</sub>H<sub>4</sub></sub> = 42%	Promote CO <sub>2</sub> enrichment	77
LSC-PFSA	$j = 0.6 \text{ A cm}^{-2}$ ; FE <sub>C<sub>2</sub>H<sub>4</sub></sub> = 89.4%	Modulate CO <sub>2</sub> /H <sub>2</sub> O transport ratios	63
$\rho$ PTN-Beim	$j = 1 \text{ A cm}^{-2}$ ; FE <sub>C<sub>2</sub>H<sub>4</sub></sub> = 33.1%	Stabilize intermediates *CO	93
Pention D-18	$j = 0.8 \text{ A cm}^{-2}$ ; FE <sub>C<sub>2</sub>H<sub>4</sub></sub> = 85.1%	Modulate the pH	88
Naf850/Sus/Cu	$j = 0.02 \text{ A cm}^{-2}$ ; FE <sub>C<sub>2</sub>H<sub>4</sub></sub> = 90%	Modulate the pH and enrich CO <sub>2</sub>	21
Polystyrene-based ionomer	$j = 0.274 \text{ A cm}^{-2}$ ; FE <sub>C<sub>2</sub>H<sub>4</sub></sub> = 82%	Enrich K <sup>+</sup>	115
Tp-COF	$j = 0.2 \text{ A cm}^{-2}$ ; FE <sub>C<sub>2</sub>H<sub>4</sub></sub> = 75%	Enrich K <sup>+</sup>	117
Aemion <sup>+</sup>	$j = 0.1 \text{ A cm}^{-2}$ ; FE <sub>C<sub>2</sub>H<sub>4</sub></sub> = 80%	Enhance the interfacial electric field	36
c-PDDA	$j = 0.2 \text{ A cm}^{-2}$ ; FE <sub>CO</sub> = 90%	Enhance the interfacial electric field	90
Sustainion XA-9	$j = 0.4 \text{ A cm}^{-2}$ ; FE <sub>propane</sub> = 90%	Stabilize the catalyst	85
Nafion	$j = 0.1 \text{ A cm}^{-2}$ ; FE <sub>CO</sub> = 99%	Enhance hydrophobicity	91
QAPPT	$j = 0.006 \text{ A cm}^{-2}$ ; FE <sub>CO</sub> = 48%	Modulate interfacial H <sub>2</sub> O	64

catalyst surfaces and enable selective transport based on molecular polarity of gases. Functional groups (*e.g.*, carbonyl, amine, *etc.*) in ionomers elevate the CO<sub>2</sub> concentration, promoting its enrichment at catalyst surfaces. By designing ionomer structures with segregated CO<sub>2</sub>/H<sub>2</sub>O transport channels, the CO<sub>2</sub>/H<sub>2</sub>O ratio at catalyst surfaces can be precisely regulated, simultaneously accelerating CO<sub>2</sub> diffusion and preventing electrode flooding. (2) Designing ionomer structures enables selective adsorption and stabilization of specific reaction intermediates (*e.g.*, linearly adsorbed \*CO) and facilitates intermediate diffusion. (3) Ionomers regulate the interfacial pH through selective ion transport and repulsion effects. Multi-physics transport simulations can reveal ion concentrations and transport behaviour within ionomers. A rational combination of multilayer ionomers can increase the surface pH and promote CO<sub>2</sub> mass transport. Well-designed ionomers or their functional groups (*e.g.*, sulfonate and carbonyl groups) can enrich K<sup>+</sup>, thereby improving reaction selectivity. Cationic ionomers can mimic alkali metal cations by generating an interfacial electric field to stabilize adsorbed \*CO<sub>2</sub> or reduction intermediates. (4) The binding effect of ionomers can be used to stabilize the catalyst surface and prevent its reconstruction. The amount of ionomer added significantly affects catalyst dispersion and performance. The mixing method of ionomers with catalysts, as well as the solvents used in the prepared ink solution, greatly influence their performances. (5) Different ionomers usually exhibit varying hydrophilicity/hydrophobicity, and their modification to different catalysts gives rise to distinct effects. Therefore, selective pairing is required during ionomer applications to maximize the hydrophobicity of catalyst surfaces. (6) Ionomers can regulate the structure of interfacial water by forming hydrogen bonds with H<sub>2</sub>O, promoting CO<sub>2</sub> reduction.

While significant progress has been made in ionomer research, several challenges remain: (1) many ionomers have poor solubility in common solvents (*e.g.*, ethanol, isopropanol), which significantly limits their applicability. Additionally, due to solvent effects, certain solvents like dimethyl sulfoxide may impact reaction selectivity, and thus careful considerations for ionomer solubility are required. (2) Ionomers face some

problems in applications, including their swelling during prolonged operation and structural instability under localized high alkalinity and a strong electric field. (3) Constructing an ordered hydrophilic/hydrophobic channel and a well-aligned CO<sub>2</sub>/H<sub>2</sub>O transport pathway in ionomers remains highly challenging. (4) When using multilayer ionomers, potential challenges include crosslinking between them and dynamic changes at their interface during reactions. (5) While ionomers can enrich K<sup>+</sup>, this capability may concurrently induce issues about salt accumulation. (6) Real-time monitoring of ionomer states under operating conditions, directly elucidating their functional mechanisms, and developing techniques to visualize ion/water transport within ionomers are under development. Facing these challenges, we propose the following recommendations and future research directions based on our understanding: (1) develop diverse ionomer–catalyst mixing methods and coating techniques to achieve faster CO<sub>2</sub> mass transport. (2) Drawing inspiration from Guiver's work,<sup>128</sup> explore magnetic field-assisted fabrication of the ordered ionomer structure to create aligned ion/water transport channels. (3) Design ionomers with inert protective groups to prevent degradation of ionic functional groups. (4) Develop K<sup>+</sup>-self-sufficient ionomers to inhibit the binding between K<sup>+</sup> and CO<sub>3</sub><sup>2-</sup> and salt accumulation. (5) Investigate alkali-metal-free CO<sub>2</sub> electroreduction systems using pure water or acidic electrolyte with ionomers, identifying and resolving underlying scientific challenges. (6) Advance multiscale *operando* characterization techniques to study ionomer behaviour and dynamic changes during reactions.

Regarding the rational selection of ionomers in different systems (acidic, alkaline, and neutral), from the perspective of their ion transport properties (including H<sup>+</sup>, K<sup>+</sup>, OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, and HCO<sub>3</sub><sup>-</sup>), Nafion is more suitable for neutral and alkaline systems, because when used in an acidic system it transports H<sup>+</sup> to the catalyst surface, exacerbating the HER. Cationic ionomers, on the other hand, carry cations that can partially block H<sup>+</sup> transport, making them applicable in acidic systems to maintain a high pH at the catalyst surface. When used in alkaline or neutral systems, cationic ionomers can facilitate the transport of CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>, alleviating salt accumulation, which is also beneficial. However, cationic ionomers often



exhibit poor solubility in common alcohol–water solvents, making their effective application challenging. Additionally, many cationic ionomers lack sufficient hydrophobicity, which will easily lead to electrode flooding. In low-concentration or pure water/acid systems, ionomers with higher ionic conductivity need to be selected to enhance ion transport. To be applicable under various reaction conditions, ionomers possessing a combination of properties, including high hydrophobicity, high ion conductivity, selective suppression of  $H^+$  transport, good dispersion with catalysts, ability to enrich  $CO_2$ , and stabilization of reaction intermediates, are optimized. We firmly believe that through persistent research and explorations, ionomers will ultimately fulfill their pivotal role in precisely modulating the microenvironment of electrocatalytic  $CO_2$  reduction, enabling highly efficient and stable system operation, making tangible contributions toward achieving the goal of carbon neutrality.

## Author contributions

S. R. and S. X. conceived the topic and structure of the review. S. R. wrote the original draft of the manuscript. All authors reviewed and revised the original draft.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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