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Catalytic Peculiarity of Electrode/ Polyelectrolyte Interfaces Toward CO₂ Reduction

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A prominent feature of modern electrochemical technologies, such as fuel cells, water electrolysis, and CO₂ electrolysis, is to employ polyelectrolytes instead of liquid electrolytes. This shift not only mitigates risks like corrosion and leaks associated with liquid electrolytes, but also facilitates the construction of zero-gap membrane electrode assembly (MEA) devices. In the MEA setups, the anode and cathode are tightly pressed against a micron-thick polyelectrolyte membrane, which can significantly reduce internal resistance and enhance energy conversion efficiency. Electrocatalysis forms the scientific bedrock underpinning these electrochemical technologies. Currently, electrocatalysis studies are primarily conducted in traditional liquid electrolytes. However, disparities between electrolyte types induce that insights from fundamental research may not directly apply to practical MEA devices. Therefore, there is a pressing need to investigate the structural and catalytic properties of the electrode/polyelectrolyte interface directly. Yet, the zero-gap configuration of MEA devices restricts the use of conventional research methods like three-electrode testing and *in-situ* spectroscopies, hindering exploration of catalytic behaviors and reaction details at the electrode/polyelectrolyte interface. Despite efforts in the literature^[1,2], investigating electrocatalytic behavior and mechanisms at the pure electrode/polyelectrolyte interface remains challenging.

To address these issues, Zhuang's group proposed a versatile approach for studying electrode/polyelectrolyte interfacial catalysis^[3](*J. Am. Chem. Soc.* 2024, 146, 17377). Their method involves using a working electrode coated with a thin layer of anion-exchange membrane together with a liquid electrolyte containing large-sized organic cations (Fig. 1(a)). This setup allows gas reactants like CO₂ to diffuse through the polyelectrolyte ad-layer while preventing liquid electrolyte crossover, enabling both regular three-electrode testing and attenuated total reflectance surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) measurements. To validate their approach, they examined Au-catalyzed

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CO₂ reduction as a model reaction, mainly for two reasons: firstly, this reaction is relatively simple and typically produces only CO and a byproduct H₂^[4], making it suitable for mechanistic studies; secondly, there is ongoing controversy regarding whether CO₂ reduction can occur in polyelectrolytes only with grafted organic cations, as alkali metal cations in liquid electrolytes have often been considered essential promoters in CO₂ reduction^[5,6]. It was found that while CO₂ reduction at the electrode/liquid electrolyte interface (blank Au) with only organic cations is challenging, it is surprisingly active at the electrode/polyelectrolyte interface (Au/QAPPT) in the absence of any alkali metal cations. *In-situ* ATR-SEIRAS revealed that this unique catalytic performance arises from distinct structural characteristics. The polyelectrolyte-grafted organic cations made it difficult to form a tight double-layer structure seen at conventional electrode/liquid electrolyte interfaces. This aided in preserving an undisturbed hydrogen bond network within the interfacial water under cathodic potentials, thereby facilitating CO₂ hydrogenation/deoxygenation processes and boosting CO product selectivity (Fig. 1(b)).

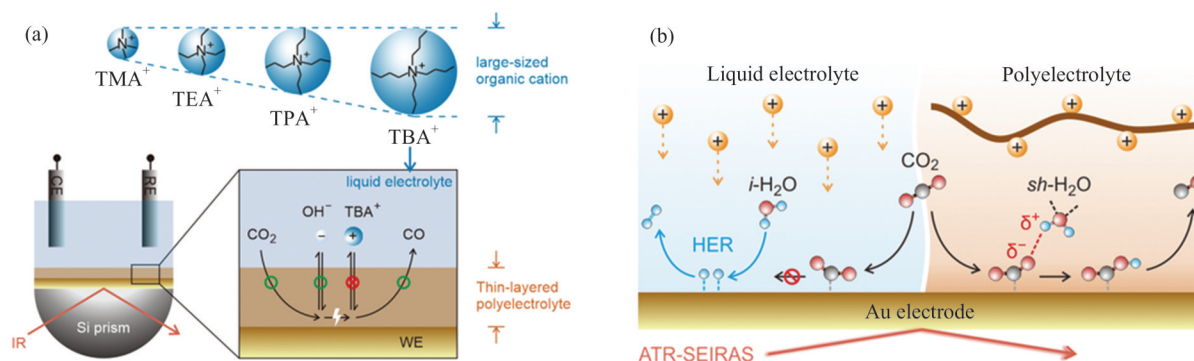


Fig. 1 (a) Methodology for *in-situ* spectroelectrochemical study of electrode/polyelectrolyte interfacial catalysis toward CO₂ reduction, (b) Scheme of the different reaction pathways at the electrode/liquid electrolyte interface (blank Au) and the electrolyte/polyelectrolyte interface (Au/QAPPT)^[3]

In conclusion, Prof. Zhuang's group put forward a novel, universally applicable method for investigating electrode/polyelectrolyte interfacial catalysis. These findings shed light on the different structural and catalytic characteristics at the electrode/polyelectrolyte interface when compared to conventional electrode/liquid electrolyte interfaces, providing essential insights to propel the development of polyelectrolyte-based electrochemical technologies.

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