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Hydrogel-Immobilized Cobalt Porphyrin for HER and ORR in Bioinspired Microenvironments

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Metalloporphyrins such as cobalt(II) porphyrin (CoP) have garnered significant interest as biomimetic electrocatalysts, owing to their structural analogy with the active sites of heme-containing enzymes, offering a molecular platform to bridge biological and synthetic catalysis. This work explores the electrocatalytic behavior of CoP immobilized within an agarose/glutaraldehyde hydrogel matrix, evaluated as a bifunctional catalyst for the hydrogen evolution reaction (HER) and the oxygen reduction reaction (ORR) under distinct pH conditions and atmospheric environments (N_2 and O_2). Electrochemical measurements were conducted under quiescent conditions to emulate the low-convection microenvironments typical of natural enzymatic systems, where diffusion is the dominant mode of mass transport. This configuration enables a more physiologically relevant assessment of catalytic behavior and mimics bioelectrocatalytic confinement. At pH 5, under N_2, the CoP-hydrogel system demonstrated enhanced cathodic current densities for HER, reaching ca. -1.2 mA cm^{-2} at -1.5 V (vs. Ag/AgCl), attributed to high proton availability and efficient charge transport through the hydrogel matrix. The catalytic onset potential for HER was clearly defined and consistent across replicates, suggesting a robust electrocatalytic interface between the redox center and the polymeric host. Under alkaline conditions (pH 9), the same system revealed significant activity toward ORR, particularly in O_2-saturated environments, with current densities approaching -0.5 mA cm^{-2} at -0.8 V (vs. Ag/AgCl). This pH-dependent bifunctionality underscores the role of local proton activity and oxygen solubility in modulating redox kinetics, and aligns with known mechanistic shifts between inner-sphere proton-coupled electron transfer (PCET) and outer-sphere pathways in metalloporphyrin catalysis[1]. The hydrogel scaffold not only stabilizes the molecular catalyst but also preserves its accessibility to electrolyte and gaseous substrates, offering an electrochemically addressable and diffusion-controlled architecture[2]. The system exhibited stable operation during extended polarization, pointing to minimal catalyst leaching or deactivation, thus reinforcing the potential of hydrogels as bioinspired immobilization platforms for molecular electrocatalysts[3]. Overall, this study demonstrates that hydrogel-confined CoP functions as a pH-switchable electrocatalyst, displaying selective and enhanced activity for HER and ORR depending on environmental conditions. These findings reinforce the viability of polymeric confinement strategies for designing hybrid systems that emulate enzymatic selectivity while retaining synthetic tunability.

References:

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