PÔSTER - RESUMO - MATERIAIS E BIOMATERIAIS

HYDROGEL-ENABLED BIOINSPIRED ELECTROCATALYTIC SYSTEMS FOR SMALL MOLECULE CONVERSION

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Metalloporphyrins and enzyme-based hybrid materials have emerged as promising platforms for sustainable electrochemical energy conversion, bridging biological and synthetic catalysis. Inspired by enzymatic microenvironments and natural CO2-concentrating mechanisms, we developed two hydrogel-assisted bioinspired systems targeting the hydrogen evolution reaction (HER), oxygen

reduction reaction (ORR), and CO2 electroreduction (CO2RR). In this work, we aim to develop hydrogel-assisted bioinspired electrocatalytic platforms combining metalloporphyrins and enzyme-derived nanostructures to enable sustainable electrochemical conversion of H2, O2, and CO2. In the first strategy, the hydroxocobalamin acetate (CoP), a biomimetic molecular catalyst structurally analogous to heme active sites, was immobilized within an agarose/glutaraldehyde hydrogel matrix 1 . The hydrogel provides a hydrated and diffusion-controlled microenvironment, enabling electrochemical evaluation under quiescent conditions that emulate low-convection biological systems. The CoP-hydrogel system exhibited clear pH-dependent bifunctionality. Under acidic conditions (pH 5, N2 atmosphere), enhanced HER activity was observed, reaching approximately -1.2 mA cm-² at -1.5 V (vs. Ag/AgCl), attributed to high proton availability and efficient charge transport within the matrix. Under alkaline conditions (pH 9) and O2 saturation, the same system displayed ORR activity, with current densities approaching -0.5 mA cm?² at -0.8 V. The catalytic onset potentials were consistent across replicates, and extended polarization experiments indicated stable operation with minimal catalyst leaching. These results demonstrate that hydrogel-confined CoP operates as a pH-switchable electrocatalyst, with local proton activity and oxygen availability modulating redox response. In a second strategy, inspired by carboxysomal CO2-concentrating mechanisms, hybrid copper phosphate-carbonic anhydrase nanoflowers (CA-HNF) were synthesized via self-assembly and immobilized on electrode surfaces using the same hydrogel matrix layer as an adhesive interface. In this configuration, the hydrogel functions primarily to maintain the biomimetic architecture at the electrode surface. Electrochemical characterization in CO2-saturated Tris-HCl buffer (pH 8.0) revealed that CA incorporation significantly enhanced the CO2 concentration process at the interface. The optimized CA-HNF005 system achieved a current density of -9.34 ± 0.12 mA cm-² at -1.7 V (vs. Ag/AgCl), representing an approximately 50% increase compared to the nanoflower control (-6.19 ± 0.16 mA cm-?²). Spatially resolved micro-FTIR measurements confirmed localized conversion of HCO3? to CO2 at the catalyst interface, evidenced by the characteristic O=C=O stretching band (~2350 cm?¹). Product analysis by HPLC demonstrated reduction of CO2 to formate. Additionally, online electrochemical mass spectrometry showed that CA shifts the onset potential of the competing HER from -1.0 V to -1.2 V. Together, these results highlight hydrogel-assisted immobilization strategies as effective routes for constructing bioinspired hybrid materials for sustainable electrochemical conversion of H2, O2, and CO2. By

combining molecular catalysts or enzyme-based nanostructures with hydrated polymer interfaces, the systems emulate biological organization while maintaining synthetic tunability, contributing to the development of hybrid materials for sustainable electronic and energy-related applications.

Reference

1 Albuquerque, Fhysmélia F., et al. "Biomimetic Cobalt Complex Stabilized by Hydrogel on High-Edge-Density Graphite for ORR and HER in Quiescent Solutions." Langmuir 41.34 (2025): 22738-22748.

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Palavras-chave: metalloporphyrins; biomimetic catalyst; enzyme-based hybrid materials.