Influence and interfacial kinetics of Binary Protic Ionic Liquid ElectrolyteMixtures on Intermediate-Temperature Polymer Electrolyte Membrane Fuel Cells

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Operation of polymer electrolyte membrane fuel cells (PEMFCs) at elevated temperatures above 100 °C has attracted increasing attention. Compared to conventional low-temperature and high-temperature fuel cell technologies, there are advantages due to due to an accelerated electrode kinetics, improved tolerance toward fuel impurities, and a simplified thermal and water management [1]. However, suitable electrolytes for operation above 100 °C at low-humidity or anhydrous conditions are still lacking, motivating increasing interest in ionic liquids as promising candidates, due to their high thermal stability and tunable transport properties. Nevertheless, the coupling between proton transport, oxygen transport, interfacial charge transfer, and local ionic environment during the oxygen reduction reaction (ORR) remains insufficiently understood[2]

Herein, a binary protic ionic liquid electrolyte mixture system composed of acidic [DESPA][TfO] and neutral [Dema][TfO] is systematically investigated to elucidate how the local ionic environment governs the interplay between electrochemical kinetics and mass-transport processes during ORR. Linear sweep voltammetry combined with temperature-dependent Tafel analysis reveals that increasing [DESPA][TfO] content substantially lowers the charge-transfer barrier and accelerates proton-coupled electron-transfer kinetics (PCET). However, electrochemical impedance spectroscopy demonstrates that enhanced interfacial kinetics do not necessarily correlate with improved ionic transport, indicating a decoupling between bulk conductivity and ORR activity. Chronoamperometric analysis further shows that oxygen diffusion coefficient, oxygen concentration, and overall oxygen transport capability exhibit pronounced composition-dependent behavior, with mixed ionic liquid systems exhibiting significantly enhanced oxygen transport compared with the neat electrolytes. Notably, this work demonstrates that ORR activity in protic ionic liquid electrolytes cannot be interpreted solely by charge-transfer kinetics or ionic conductivity, but instead arises from the coupled contributions of electron transfer, oxygen diffusion, oxygen solubility, ionic transport, and solvent structural dynamics. The present study provides a mechanistic framework for rationally designing ionic liquid electrolytes for operation at elevated temperatures.

[1] Greaves, T. L.; Drummond, C. J. Protic ionic liquids: Properties and applications. Chem. Rev. 2008, 108, 206−237.
[2] H. Hou, H.M. Schutz, J. Giffin, K. Wippermann, X. Gao, A. Mariani, S. Passerini, C. Korte, Acidic Ionic Liquids Enabling Intermediate Temperature Operation Fuel Cells, ACS Appl Mater Interfaces, 13 (2021) 8370-8382.