

V.G.3 Control of Reactivity in Nanoporous Metal/Ionic Liquid Composite Catalysts

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Program Scope

In this program, we have been exploring a new concept in nanostructured heterogeneous catalysis design: the use of a nanoporous metal, either alone or impregnated with an ionic liquid (IL) to form a composite catalyst [3,4]. The idea behind this concept is to tailor the chemical environment within and near the pores of a metallic electrocatalyst in order to enhance the aggregate composite activity and selectivity. Most recent electrocatalyst design focuses upon lowering the activation barrier for a particular synthesis reaction. While we also try to minimize this quantity, one should also recognize that significant catalytic enhancements can be made by biasing the reaction to completion via control of the environment in which the reaction occurs. Specific ideas we are exploring in this program include (a) bias of mass transport of reactants to the surface and products away from it and (b) corralling of reactants and products to spatially separate them and reduce side reactions.

Fiscal Year (FY) 2016 Highlights

A more specific aim of this program is to develop electrocatalysts for the electroreduction of small molecules such as oxygen, carbon dioxide, or ultimately nitrogen. The oxygen reduction reaction (ORR), for its relevance to the fuel cathode reaction, has been a first choice of study. In recent studies, by ourselves and others [1,2], it was found that impregnating dealloyed nanoporous nickel-platinum (np-NiPt) with hydrophobic and oxophilic ionic liquids increases the aggregate activity of the electrocatalyst. Multiple mechanisms are potentially operative here, in particular, (a) higher oxygen solubility near the catalyst surface adds a diffusive driving force to draw oxygen in from the aqueous environment, (b) hydrophobicity expels products from the catalyst surface, and (c) IL properties such

as proticity or viscosity are affecting reaction conditions. Figure 1 shows results of oxygen reduction activity over np-NiPt for a survey of ionic liquids exhibiting a range of properties, each of which to some extent improves the ORR activity by shifting the half-wave to higher potentials. This study concluded that the primary determinants of ORR improvement are simultaneous high oxygen solubility and high hydrophobicity [3].

An ancillary goal of this study was to see if aprotic ionic liquids in the nanoporous metal could stymie proton

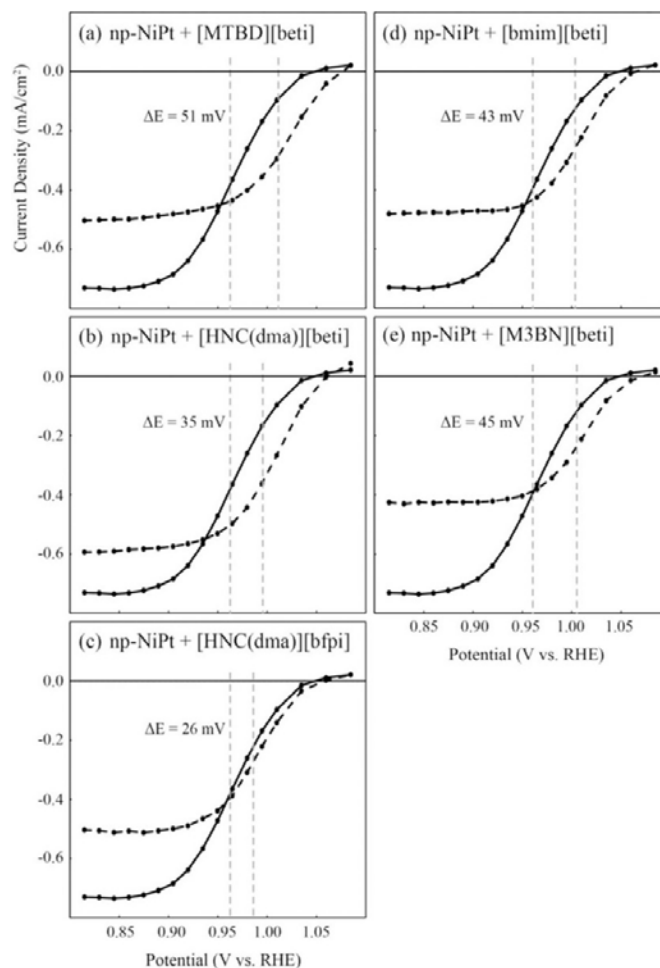


FIGURE 1. Potentiostatic ORR current density versus potential for np-NiPt (solid line) filled with a variety of different ionic liquids (a) np-NiPt+[MTBD][beti] (high oxygen solubility), (b) np-NiPt+[HNC(dma)][beti] (high proton conductivity and low viscosity), (c) np-NiPt+[HNC(dma)][bfpi] (relatively high hydrophobicity), (d) np-NiPt+[bmim][beti] (aprotic and high viscosity), and (e) np-NiPt+[M3BN][beti] (aprotic and low viscosity) [3]

transport to the electrocatalyst surface. If this were possible, then reduction of other small molecules from an essentially aqueous solution could occur even at highly reducing potentials, in particular at potentials at which hydrogen evolution occurs, below 0.0 V vs. reference hydrogen electrode (RHE). This remains a viable new strategy for CO₂ or N₂ reduction, but requires design and synthesis of ionic liquids with essentially no water solubility. In our above-mentioned survey, we found that even “very hydrophobic” ionic liquids had water solubilities of order 1 M.

However, the result also suggested a second strategy to stymie hydrogen evolution via control of reaction kinetics in aqueous solution. Our hypothesis was that if the oxygen flux to the surface can be maintained higher than a proton flux to the surface, then adsorbed oxygen will block hydrogen evolution. Such a scenario is easily satisfied without an IL in O₂-saturated electrolytes above ~ pH 3, because O₂ solubility is of order 1 mM. Figure 2 shows a key result, that at pH 4,

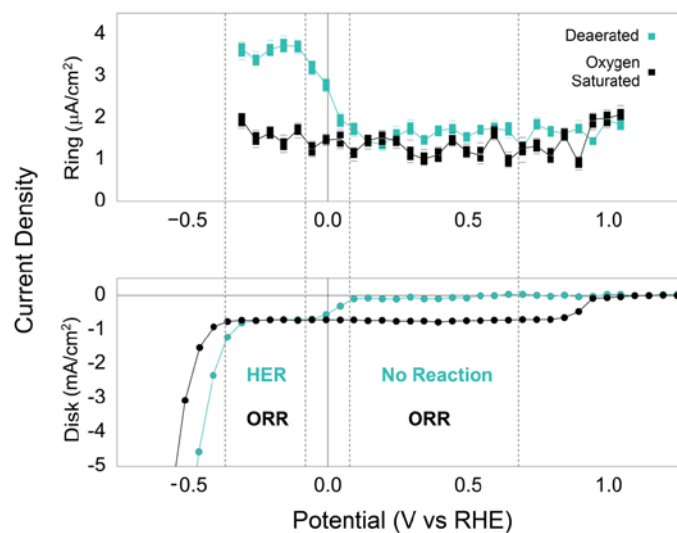


FIGURE 2. Potentiostatic rotating ring disk electrode measurements of current density vs. potential at pH 4 in oxygen-saturated vs. deaerated solutions. Here, both hydrogen evolution reaction (HER) and ORR is expected to occur under proton diffusion limited conditions. Hydrogen evolved in deaerated solutions below 0.0 V vs. RHE is detected via hydrogen oxidation at the ring. In oxygen-saturated solutions, HER is suppressed in favor of oxygen reduction, due to a combination of a higher flux of oxygen to the electrode than protons, and a pH gradient within the pores [4].

oxygen evolution under proton-diffusion limited conditions in a rotating disk electrode setup can be maintained to potentials nearly 400 mV below 0.0 V vs. RHE, to potentials negative enough to reduce water directly. Most interestingly, this effect is only possible using a nanoporous electrode which is transiently conditioned to introduce a pH gradient within the porosity itself. Having established a viable reaction scenario in which hydrogen evolution is kinetically suppressed, we are exploring this strategy for CO₂ reduction, and will be extending this strategy to non-aqueous electrolytes to reach extreme reducing potentials without reducing water.

References

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3. E. Benn, H. Uvegi, J. Erlebacher, “Characterization of Nanoporous Metal-Ionic Liquid Composites for the Electrochemical Oxygen Reduction Reaction,” *J. Electrochem. Soc.*, 162 (2015), H759-H766.
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