V.P.9 Engineering Catalytic Nanoporous Metals for Reactions Important to the Hydrogen Economy

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Objectives

The goals of this program include (a) fabrication of new nanoporous electrocatalytic metals by electrochemical dealloying, (b) development of methods to tailor the surface chemistry and composition of nanoporous metals, (c) tailoring the activity of nanoporous to optimize hydrogen oxidation and oxygen reduction, (d) integration of nanoporous metals into fuel cells as low precious metal loading catalysts.

Technical Barriers

Implementation of low precious metal fuel cells in the commercial sector will require new approaches to the materials design of catalytic materials, particularly toward the inefficient oxygen reduction reaction at the cathode. Dealloying as a chemical route to the production of ultra-high surface area conductive metals allows facile synthesis of highly active nanostructured core-shell and composite catalysts with a wide variety of compositions that may lead to large decreases in loading at fuel cell cathodes.

Abstract

The development of new catalysts for hydrogen fuel cell reactions is a critical step in the development of this technology. Factors for which there is room for improvement include improving the catalyst activity, particularly toward oxygen reduction, and the development of carbon-free catalyst layers in the membrane electrode assembly that are not prone to corrosion. A materials system that may be a potential solution for both of these problems simultaneously are nanoporous metals made by selective electrochemical dissolution of one component of a multi-component alloy (dealloying). More specifically, alloys are chosen such that as the majority alloy component is dissolved, the secondary component diffuses along the alloy/electrolyte interface, reconstructing the material into a high surface area crystal with open porosity, high surface area/volume (ligament and pore sizes 5-10 nm), and intrinsic electrical contact to all surface area. In the last year, we have focused on the formation of core/shell nanoporous NiPt (np-NiPt) and related alloys. By impregnating the matrix np-NiPt of with a protic, hydrophobic ionic liquid that absorbs oxygen from the external environment, we have created a composite catalyst that geometrically confines oxygen in the catalytic region and leads to orders-of-magnitude increases in that mass activity of the composite over nanoparticle-based catalysts.

Progress Report

Formation of nanoporous metals by dealloying that are suitable for electrocatalysis. Nanoporous metals made by dealloying require the fabrication of single-phase multi-component alloys from which the majority component is electrochemically dissolved. During dissolution, the remaining alloy components diffuse along the metal/electrolyte interface and re-form as a porous metal. The porous metal, notably, occupies the same lattice as the parent material, so porosity exists on a scale much smaller than the grain size, and grain boundaries do not play a role in its properties. The lack of grain boundaries also adds to morphological stability because sintering (for instance, of nanoparticles) is usually driven by grain boundary energy reduction. This year we have been closely studying dealloying of Ni_xPt_{1-x} ($x > 0.75$) alloys (Figure 1), for which we find a the average pore and ligament size to be nearly 2 nm. This yields specific surface areas of 44 m^2/g, essentially equal to that of nanoparticles, and a baseline requirement for fuel cell catalysis.

One important reason we have focused on the NiPt system is that we have found that the remaining porous metal composition usually sits near the $NiPt_3$ composition. This suggests that during dissolution there is accumulation of a passivating Pt layer over a porous NiPt ligament core, i.e., it is a core/shell nanoporous metal with a composition close to that of the most active catalyst for oxygen reduction known. This was a prediction based on earlier work (DOE7,8) in this program, and electrochemical assays back up this hypothesis.
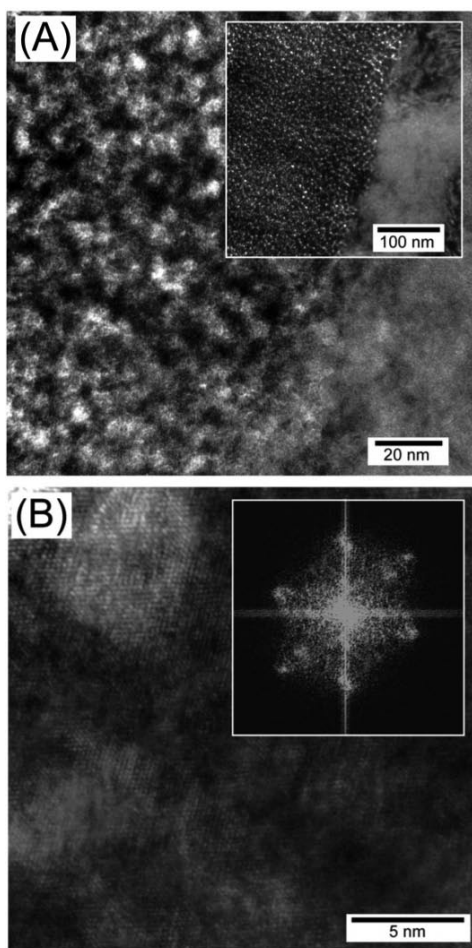
FIGURE 1. (A) TEM of a wedge slice of a NiPt foil dealloyed in 0.1 M Na_2SO_4 at 2.1 V vs. RHE with residual surface oxide reduced in dilute H_2SO_4; inset is a lower magnification view showing a sharp interface between the porous dealloyed region (left) and the undealloyed matrix (right). (B) High resolution TEM of dealloyed section with visible lattice fringes. The Fourier transform of this image in the inset confirms that np-NiPt is an extended crystalline network.

FIGURE 2. (A) surface kinetic current density of np-NiPt and np-NiPt + ionic liquid composite catalysts compared to the activity of different Pt_3Ni facets. (B) mass activity of np-NiPt and np-NiPt toward oxygen reduction as a function of porosity depth (in principle, equivalently to catalyst particle diameter) at 0.85 V and 0.9 V vs. RHE in oxygen-saturated 0.1 M $HClO_4$. The best nanoparticle-based oxygen reduction catalysts have mass activities between 0.1 and 0.7 mA/microgram.

Assessment of nanoporous NiPt toward oxygen reduction. The assessment of np-NiPt in half-cell reactions toward oxygen reduction are consistent with the core/shell hypothesis. By extrapolating the surface kinetic current of np-NiPt to a roughness factor of 1 (by examining oxygen reduction on samples with different depth of porosity), we find the kinetic current to sit in-between the values associated with single crystal low-index surfaces (Figure 2A), again, consistent with the geometric picture of the (functionally single crystal) porous metal having multiple facet orientations within the porous matrix.

Highly enhanced oxygen reduction activity in composite nanoporous NiPt/Ionic Liquid composite catalysts. Although np-NiPt is highly active toward oxygen reduction, obviously its mass activity drops off
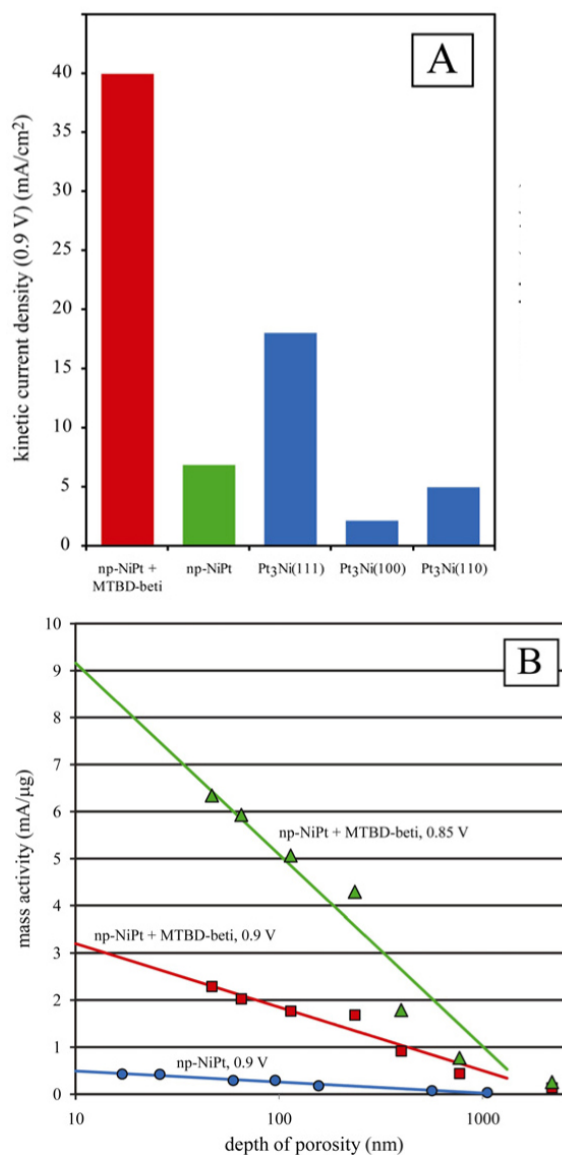
as the pore depth becomes deeper (Figure 2B). Part of this is due to the extra mass, and some of this is due to the reactants not effectively penetrating deeply into the pores. That is, the active area for oxygen reduction is actually smaller than the geometric surface area measured by hydrogen underpotential deposition; in fact, we've shown that there is a dependence of the active surface area with the overpotential (DOE1). On one hand, this is a challenge for all nanoporous metal electrodes unless they can be fabricated as

ultra-thin membranes (such as we did with Pt-plated nanoporous gold leaf, DOE4), but it has also turned into an opportunity to make a brand new kind of oxygen reduction catalyst.

The presence of nanoporosity allows a secondary phase to be impregnated into the porous matrix. We hypothesized that if this second phase were an ionic liquid (IL) that is protic (proton conducting), hydrophobic, and contained a high oxygen solubility (higher than aqueous solution), then the composite np-NiPt/IL catalyst would have higher mass activity to oxygen reduction than np-NiPt alone because oxygen that approached the composite would be chemically biased to remain near the catalytic surface until it was reduced. Two ionic liquids (MTBD-beti, MTBD-Tf2N) were found to have these characteristics, and composite catalysts could be made simply by dripping the IL onto the porous metal. Figure 3 shows representative oxygen reduction curves in O_2-saturated 0.1 M $HClO_4$, and shows that the composite catalyst shifts the oxygen reduction curve nearly 50 mV to lower overpotentials. This is a huge shift, and the mass activity of the composite catalyst (Figure 2B), while still dependent on pore depth, at 2.3 mA/microgram at 0.9 V vs. RHE, is still over 20 times more mass active than Pt nanoparticles (0.1 mA/microgram at 0.9 V). At these low overpotentials, the np-NiPt/IL composite catalyst may be the most mass active catalyst toward oxygen reduction yet discovered.
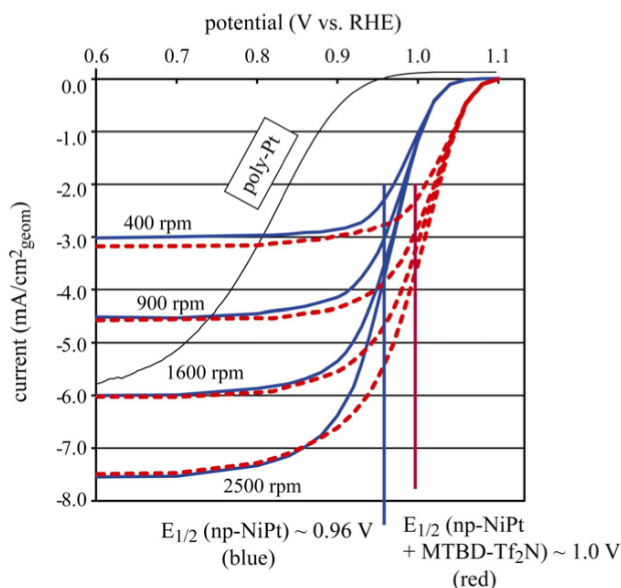
Future Directions

Integration of nanoporous metal/ionic liquid composite catalysts into fuel cells. The promising results of oxygen reduction on the np-NiPt/IL composite catalysts were found in idealized half-cell electrochemical studies. The obvious next step is to integrate such catalysts into fuel cells. We have already integrated unsupported np-NiPt ground-up powders into PEM MEAs, and shown good results (namely, identical performance to supported Pt/C down to 0.7 V). To date, to make more efficient composite catalysts, we have synthesized particles of $Ni_{80}Pt_{20}$ that are ~20 nm in diameter and tested these for oxygen reduction. We see a large increase in activity when the particles are dealloyed, and are working toward impregnation of the particles with IL.

Electrochemical and surface science investigations of the oxygen reduction reaction in nanoporous metal catalysts. So far, it is just a hypothesis that the mechanism of enhanced oxygen reduction in the composite catalyst is due to higher oxygen solubility (and the ensuing retention of oxygen near a catalytic surface). The detailed reaction kinetics of oxygen reduction in this material as a function of oxygen and proton concentration and temperature, as well as the physical characteristics of the IL (viscosity, oxygen solubility) must be examined.

Publications (including patents) acknowledging the grant or contract

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FIGURE 3. Representative potentiostatic oxygen reduction curves for np-NiPt and np-NiPt + MTBD-Tf$_2$N in O$_2$-saturated 0.1 M HClO$_4$ at differing rotation rates (roughness factor = 143 for both samples). For comparison, a potentiodynamic ORR curve (100 mV/sec) of a non-porous polycrystalline Pt disk is also shown.

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