V.D.15 Nanoporous Metal Membranes with Monolayer-Thick Precious Metal Catalyst Skins

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Objectives

Nanoporous metal membranes formed by dealloying provide an ultra-high surface area, conductive, and thin foil substrate on which one may build designer multilayer and multicomponent catalysts with monolayer-level control of composition. Primarily, we are working with Pt-plated nanoporous gold leaf, and are developing strategies for fabrication of these nanocomposites and testing them in functional PEM fuel cell environments. By rationally correlating the performance of these materials with their microstructural characteristics, we will assess the effect of composite stresses, surface morphology and surface composition on catalytic activity, and identify the next generation of high performance cathode and anode catalysts.

Technical Barriers

Core-shell nanoporous metal membranes promise advances in methods of synthesis of ultra-low loading precious metal catalysts that simultaneously exhibit high performance and stability. They provide a framework in which all catalyst is intrinsically in good electrical contact with the external circuit, optimizing catalyst utilization. The versatility of nanoporous gold membranes in particular to surface chemical modification allows for rapid assessment of new catalysts, not just metals, but also bio-inspired organic catalysts.

Abstract

The goals of this program are to explore the use of thin nanoporous metal membranes as catalyst supports in proton exchange membrane fuel cells. The structure of the catalyst layer in our study is an ultra-thin (~100 nm) mesoporous membrane with pore size ca. 15 nm on which has been deposited an epitaxial catalytic layer (or layers), with thickness control of order one monolayer.

The motivations to explore this route to catalyst manufacture include ultra-low platinum loading (<0.05 mg Pt/cm^2), increasing the thermal stability of the catalyst layer by taking advantage of substrate/catalyst elastic interactions, exploring the nature of Pt/substrate catalytic activity as it pertains to carbon monoxide poisoning, and develop new catalysts for use in PEM fuel cells. Our research initially concentrated on characterization of a model system, Pt-plated Nanoporous Gold (Pt-NPG) in H_2/O_2 fed fuel cells, with which we are able now to make stable PEM MEAs that exhibit specific powers of 4.5 kW/g-Pt, with Pt loadings of only 0.03 mg/cm^2 on both anode and cathode (gold substrate loading is 0.1 mg/cm^2). Having shown that the Pt-NPG system is a viable, if not exceptional, catalyst, our research has branched into (a) detailed investigations of the strained epitaxial growth mode of Pt on nanoporous gold, (b) development of new chemistries to coat NPG with multilayers catalysts (e.g., Au/Ni/Pt) in an effort to develop new catalysts for oxygen reduction, (c) investigation of our discovery that nanoporous gold by itself exhibits non-trivial activity as a catalyst for oxygen reduction, and (d) development of new ternary Pt-Ag-Au alloys that can be dealloyed to create new stable catalytic materials with ~2 nm pore sizes.

Progress Report and Future Directions

Characterization of the model Pt-NPG system: In order to set a baseline for fuel cell activity utilizing Pt-NPG catalytic membranes, we have set up a fuel-cell testing station and developed robust Pt-NPG membrane electrode assemblies (MEAs). Pt-NPG is formed by electroless reduction of Pt on nanoporous gold membranes themselves formed by dealloying of silver/gold precursor membranes. The material formed is a highly porous form of gold with pore sizes tunable from 5-30 nm which is encrusted, inside and out, with a epitaxial “skin” of Pt controllable to monolayer thickness. We have found that the growth of Pt follows the Stranski-Krastanov mode in which one first observes a monolayer-thick wetting layer followed by the formation of epitaxial islands at greater thicknesses.

We have developed methods to attach Pt-NPG membranes to Nafion® membranes, and manufactured a fuel-cell testing station to characterize the performance of the material. The apparatus and testing conditions are close to optimized, and we have achieved a stable and reproducible baseline. The material works well, and we can reproducibly and stably generate 5 kW/g Pt [DOE1]. In studies of the current/voltage characteristics of cells made with Pt-NPG we have confirmed the structure/property hypothesis that the performance varies with coverage of platinum in a way related to the microstructure: with increasing (but low) Pt coverage, there is an increase in the active surface area due to the formation of Pt islands on the substrate, roughening it.

We used a stamping method make MEAs using Pt-NPG. The primary technical hurdle to overcome was, if we attached the membrane to dry Nafion®, then when we tested such an MEA it swelled breaking apart the conductive membrane and degrading. This problem will be ubiquitous for any catalyst layer placed on dry Nafion®, e.g., sputter deposited platinum. Our solution was a variation of stamping in which we first dried the catalyst membrane on an non-adhesive oxide disk (mica), and then stamped the disks onto humidified, pre-swelled Nafion®. Now, when the membranes dried, the catalyst layers simply buckle, but they remain robust and conductive when integrated into a cell. Incidentally, measurement of the wavelength of the buckling instability of nanoporous gold is an effective way to find its Young's modulus, and we have performed a systematic study of this quantity with pore size, discovering an anomalous increase in the modulus for materials with pore sizes less than 10 nm (DOE2).

Figure 1 shows how the electrochemically active surface area correlates to the growth of Pt on NPG. Initially, a wetting layer forms, followed by the development of an island morphology; during growth, there is an increase in active area, but once the morphology is locked in the layer simply thickens with no further increase in area. This yields an "optimum" loading of about 0.03 mg Pt/cm^2, which gives the most specific power.

To characterize in detail the growth the Pt on nanoporous gold, we have been using our ultra-high vacuum chamber to deposit Pt on planar gold and have found that the growth mode in this case seems to be in the planar, or, Frank-van der Merwe, growth mode with a critical thickness less than 1 nm. This is in contrast to the islanding growth mode on NPG we see in the solution based deposition method we use to make MEA catalysts. The reasons for this seem to be two-fold; first, Pt on NPG is akin to the concept of growing thin films on nanoscale terraces, which allow different elastic relaxation modes than misfit dislocation injection, and second, Pt on gold is influenced by surface roughness introduced when gold is immersed in highly acidic environments, which create highly mobile step edges that in turn lead to surface roughness.

As an ancillary product of this effort, we have developed a new method to create large, single crystals of Au(111) via surface-energy driven abnormal grain growth, a metallurgical phenomena seen in highly plastically deformed rolled foils in which defect free (111) grains grow much faster than any other orientation, driven by the strain energy built up during deformation. We have examined for the first time the surface structure of such recrystallized grains, and found them to be of extremely high quality, yielding atomic resolution with minimal effort. We believe that this substrate sample preparation method will be of significant interest to the catalyst community generally.

Development of new chemistries to coat NPG with multilayers catalysts. A number of predictions have been made as to the activity of surface alloys, or surface multilayers, toward the oxygen reduction reaction (ORR). For instance, a recent article predicts that $Pt_3Ni(111)$ is particularly effective [1], while first principles calculations and single-crystal experiments predict that Pt/Pd(111) should also be a good material for ORR [2]. NPG is essentially (111) microfaceted, and thus development of new ways to control the surface composition is a logical strategy to make and test some of these new materials.

The particular issue with NPG is that one must coat all interior pores, and not just the geometric surface. We have been using controlled electrochemical deposition to avoid skinning over the outer surface, as well as underpotential deposition (e.g., of Cu) followed by galvanic replacement (e.g., by Pt) to exploring the viability of making NPG coated with Cu, Ag, Ni and

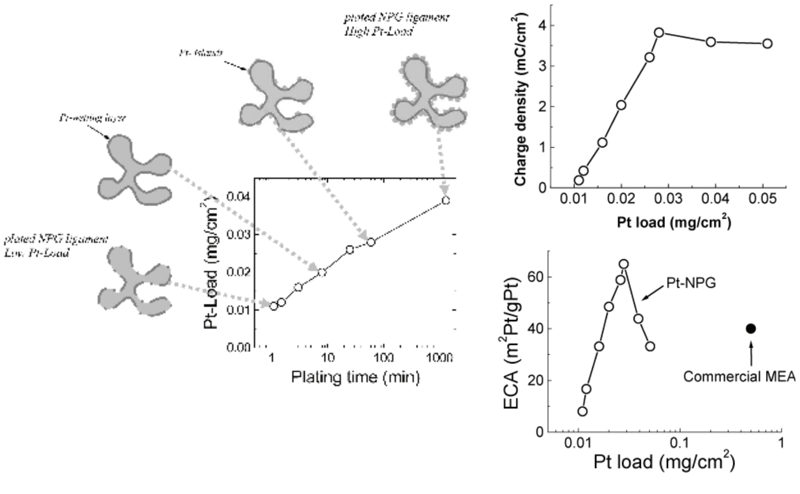

FIGURE 1. Electrochemically active surface area (ECA) of Pt-NPG correlated to load and microstructure.

Co. The next step will be to galvanically replace some or all of this coating with Pd or Pt, and also to examine porphyrin-based organic catalysts.

ORR activity of nanoporous gold by itself. We have been surprised by an observation that nanoporous gold by itself is active to oxygen reduction. We are investigating this as a function of NPG pore size, correlating the performance to the surface area and structure of the NPG membranes.

Ternary Pt-Ag-Au for new stable catalytic materials with ~2 nm pore sizes. NPG is very versatile, but in highly acidic aqueous environments tends to coarsen. Such coarsening is stabilized by the presence of a Pt overlayer, but it would be more useful to start with a stabilized structure with even smaller initial pore size (2-5 nm vs. 10-15 nm for regular NPG). To achieve this goal, we have been exploring dealloying of single phase Pt-Ag-Au alloys, and have found that a 6 at. % Pt (34/60 at. % remainder Au/Ag) alloy does precisely this. Figure 2 shows a micrograph of this new material, and its very small pores. We are working to make this alloy into leaf form, so that we can make thin membranes. We expect thermal and chemical stability, and the final material should also be surface enriched in Pt, as well as low loading (0.01 mg Pt/cm^2). Incidentally, the addition of small quantities of impurities to alloys has long been known to stymie dealloying (e.g., 1% As in brass); our experiments here will allow us to examine this important corrosion phenomenon in a more controlled context.

References

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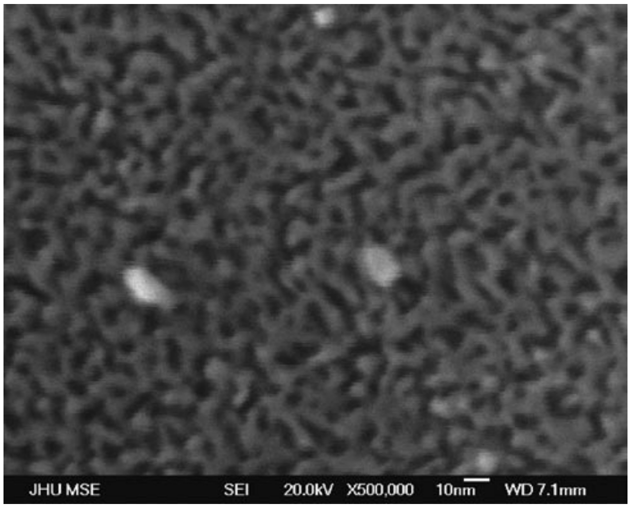

FIGURE 2. SEM micrograph of dealloyed $Pt_6Au_{33}Ag_{61}$ that was "coarsened" in nitric acid for 24 hours in order to make the porosity grow to an observable level (here, ~5 nm pores). This material has an initial pore size ~2-3 nm.

Publications (Including Patents) Acknowledging the Grant or Contract

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