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Nanoporous Metal Films Formed with Aqueous Organic Templates

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Purpose

Nanoporous metals have the highest practical metal surface area per unit volume. They are of potential value for surface-catalyzed chemical reactions; supercapacitors; metal hydride batteries; and chemical separations based on electrical potential-dependent adsorption, such as capacitive deionization. We have developed methods to grow thick films of nanoporous palladium by electrodeposition. The ability of palladium to reversibly store hydrogen is of value for small-scale metal hydride batteries, as well as hydrogen gas or pH sensors. We aim to show that nanoporosity in such thick films can yield rapid capacitive charging, and rapid electrochemical absorption and release of hydrogen.

Prior Research

Electrodeposition of nanoporous metals was first demonstrated by a group at Southampton: Science 278 838 (1997). They used paste-like concentrated soap solutions to define pores. Later, Yamauchi et al. found that thin films of nanoporous platinum can be much more conveniently defined by 1-10% aqueous solutions of block copolymers or small-molecule-surfactants: Chem. Mater. 24 1591 (2012). We have modified their approach to yield thick films of nanoporous palladium.

Our Method

We use a 400nm Pd sputtered film on Si with 10nm Ti as an adhesion layer as our substrate. (Fig.1) The wafer is sealed to a Teflon chamber with an o-ring. The chamber contains a large Pd wire coil anode, and a Ag/AgCl reference electrode. A constant current of about 1-2 mA/cm^2 is applied for several hours.

The solution contains Pd^{2+}, hydrochloric acid, and a block copolymer surfactant. The chemical reaction at the mesh (going in reverse at the anode) is:

$$H_2PdCl_4 + 2e^- \rightarrow Pd + 2HCl + 2Cl^-$$

Deposition of thick films requires monitoring and optimization of conditions at both electrodes.

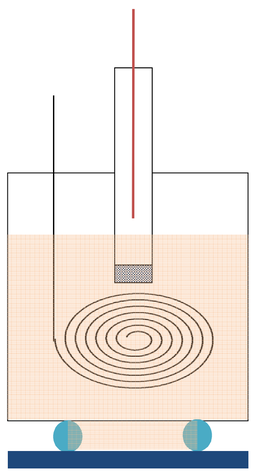

Fig.1

Results

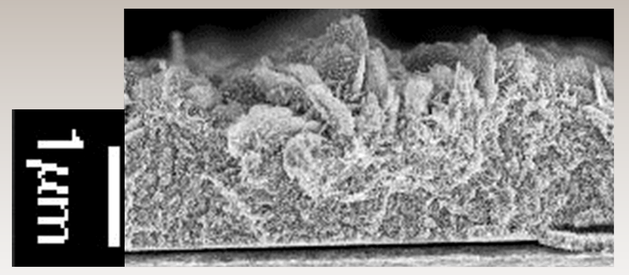

Fig.2

Cross section of films grown for 1 hour (Fig. 2) or 24 hours (Fig. 4). Films grow at about 1 um per hour. Pore diameters are 10-20 nm. The porosity is quite uniform throughout the samples.

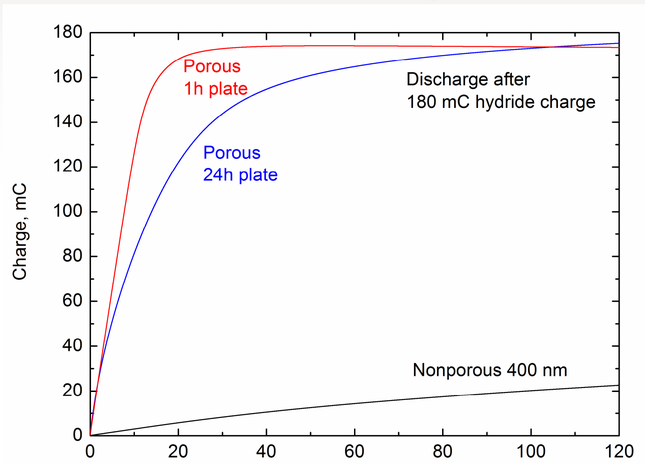

Fig. 3

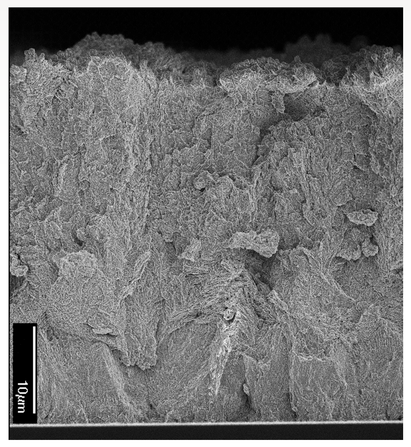

Fig. 4

Porous films desorb hydrogen much more quickly than nonporous films (Fig. 3) but there is apparently an optimal film thickness.

Electrochemical admittance (Fig. 5) measures reversible electrostatic adsorption of aqueous ions to surface without chemical reactions.

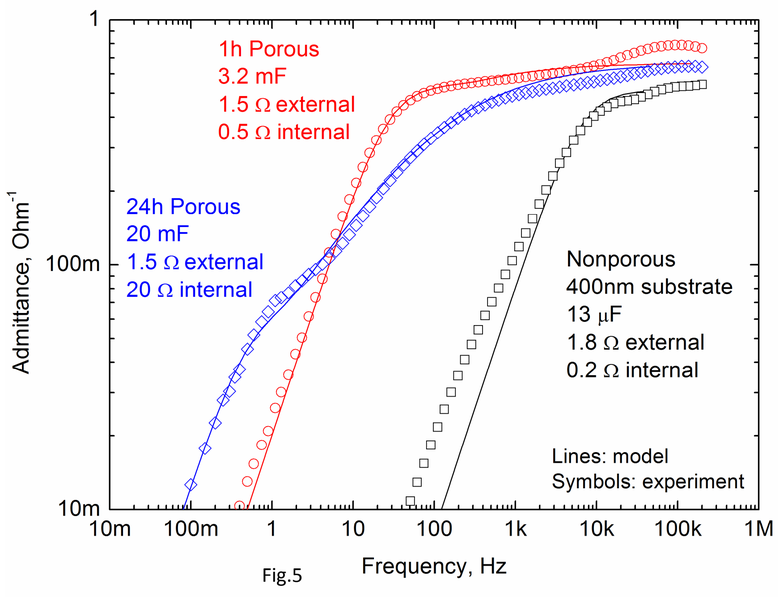

Fig.5

Admittance provides a measure of surface area, which is proportional to capacitance, and charging rate, which is related to internal resistance. Porous films have much higher surface area than nonporous films. Thicker films store more charge, but also charge and discharge more slowly.

Conclusions and Outlook

We can create thick films of nanoporous palladium that conform to a conducting substrate. Porous films have increased capacitance and faster dehydriding rates vs. nonporous films. The dehydriding of the 1hr samples is faster than the 24hr samples, suggesting that transport can be slow through long, narrow pores, and an optimal thickness exists where both the rate and capacity of hydrogen or capacitive charging are high.

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