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Electrodeposition and Stacking to form 3D Hierarchically Porous Structures

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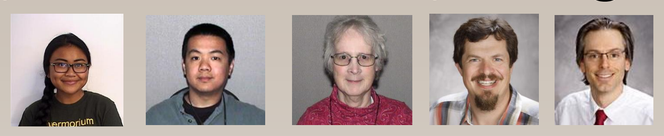


Purpose

Rapid transport between fluid and solid phases can yield high power density in electrochemical energy storage systems, and efficient chemical separations in chromatography. Transport is often slower in the solid phase, and in long, narrow channels of the fluid phase, but multiscale pore geometries can allow faster transport. We have fabricated hierarchically porous metal hydride electrodes with overall dimensions in the centimeter range. Convection channels are tens of micrometers wide, and diffusion channels are on the 10 nm scale.

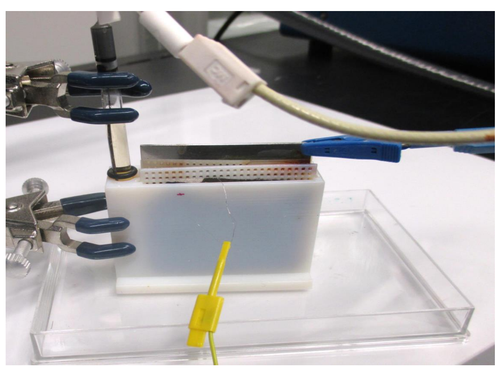
Prior Research

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 nanopores can be much more conveniently defined by 1-10% aqueous solutions of block copolymers or small-molecule-surfactants: Chem. Mater. 24 1591 (2012)

Our Method

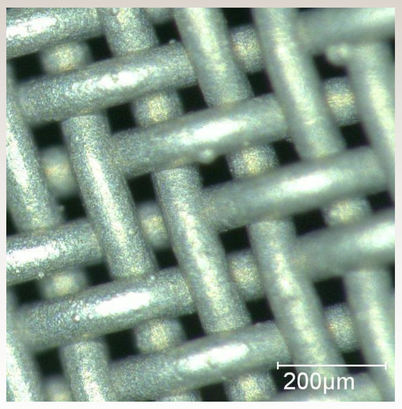
We use a 3D-printed electrochemical cell to make the best use of the plating solution. A silver mesh is held between two Pd anode plates and two 3D-printed spacer plates. There is a chamber for a reference electrode, and space for a stir bar at the bottom.

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

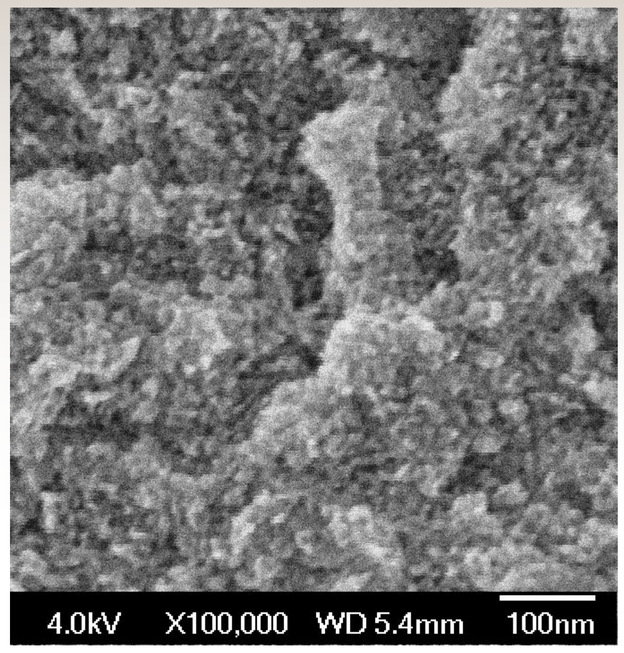


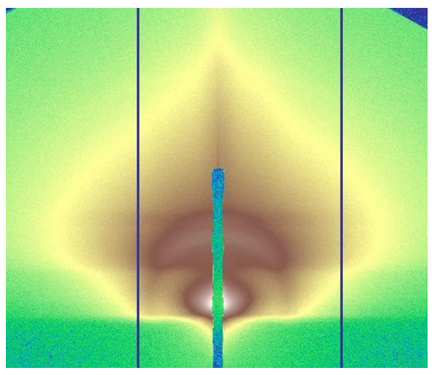
$$H_2PdCl_4 + 2e^- \rightarrow Pd + 2HCl + 2Cl^-$$

Results



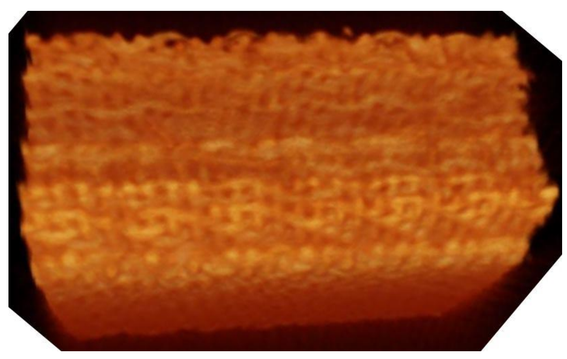
The product has mesh-defined pores of about 50 µm. Before plating, wires are 50 µm and pores are 80 µm.





Scanning electron microscopy of a cross section of a mesh coating shows 10 nm-scale pores (above). Arcs in the small-angle X-ray scattering pattern (left) provide further evidence of nanoscale porosity throughout a wafer sample.

To make a 3D porous structure, we have stacked mesh pieces into a 3D-printed frame. An X-ray image of the stack is at right.



Thick nanoporous layers require careful optimization of reaction conditions to balance the rates of film growth and block copolymer adsorption, and to ensure that both the anode and mesh reactions proceed efficiently enough to maintain a steady-state solution composition.

Conclusions and Outlook

We have synthesized hierarchically porous palladium structures with architecture defined on scales ranging from centimeters to nanometers. We have begun efforts to measure rates of hydrogen uptake and release, both as an electrochemical and as a gas-phase reaction. We will compare the rates against samples that lack porosity on a specific length scale to determine whether improved transport rates can be realized.

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