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3D Printing of Hierarchical Lattices for Electrochemical Energy Storage

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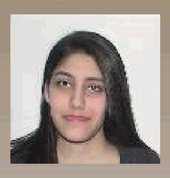





Purpose

Nanoporous structures are designed to have optimized arrangements of surface area per unit volume. However, prior research indicates that in thick planar nanoporous electrodes, the pores are too long, and they transport chemical species too slowly. For example, in the plot in Fig. 1, showing films plated at about 1 µm/h, there is high internal resistance in the thickest film, but not the film plated for 1 h. Our goal is to overcome this limit by creating millimeter-scale structures with hierarchical porosity, including nanopores with near-optimal thickness, and larger pores that allow ion transport throughout the parts.

With the capability to charge and discharge quickly, hierarchically porous electrodes could be useful in electrochemical capacitors or metal hydride batteries.

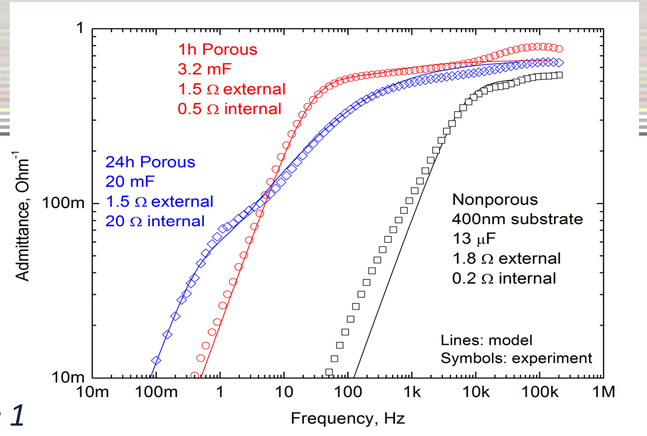
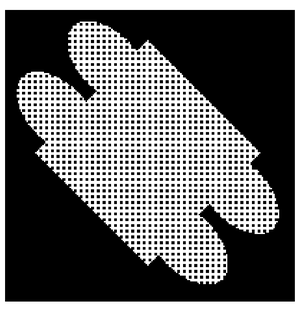
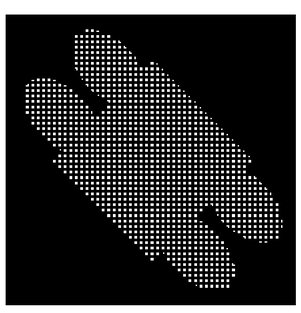


Figure 1

Technology and Design





We use an Autodesk Ember 3D printer, which can make cm^3-scale parts with 50 µm resolution in about 1 hour. We use software to create 3D models and slice them into cross-sectional layers. A layer is projected as blue (405 nm) light through a silicone-coated window in a tray filled with resin consisting of a photoinitiator, acrylate monomers, and an absorbing dye. The resin solidifies in the regions exposed to light. The first layer glues itself onto a metal plate. After each exposure, the plate moves up, and the tray moves sideways to agitate the resin. The cycle repeats hundreds of times. The part is then scraped from the plate and soaked in isopropanol to remove uncured resin.

Figure 2. What the printer sees: slices 76 and 85 of 633.

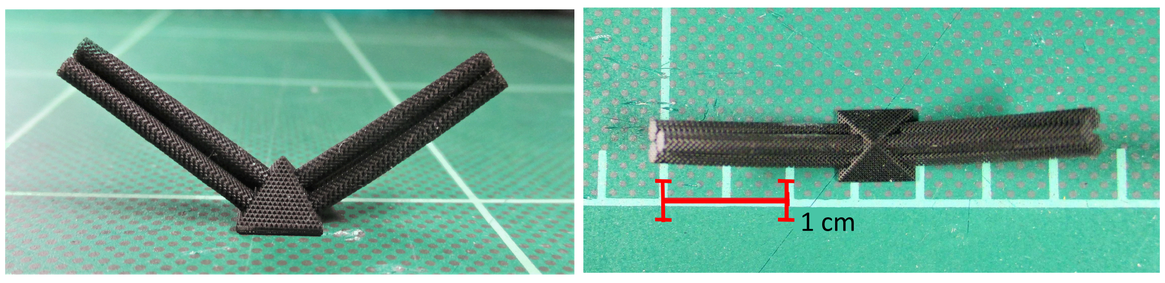


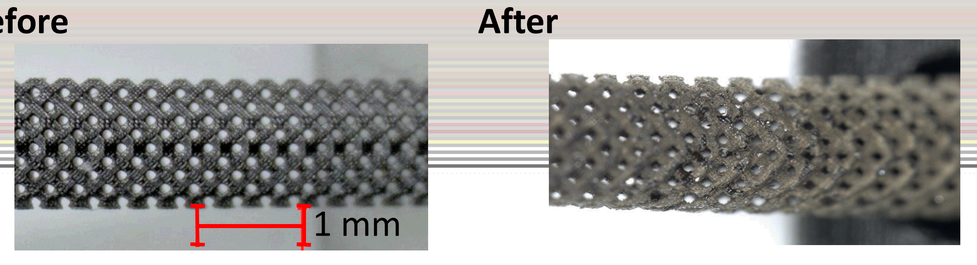
Figure 3. What is printed: Pyramid base is 7.5 mm; Cylinders are 2 mm diameter, 20 mm long

We are printing cylindrical lattice structures with a 3D network of 150 µm pores, which are the smallest pores that we can make reliably on this printer. The printer makes voxels that are 50 µm cubes. We make pores in the vertical and two perpendicular horizontal directions by printing alternating layers of grid and post patterns of these voxels (Figure 2). The patterns fill a volume that defines the part. The cylinders are oriented at about 35.3 degrees so that all paths through the pores have the same angle versus the cylinder axis. The cylinders can be sliced from the pyramidal base that holds them at this angle. After metal coating, a 50 µm wire can be threaded through the lattice for electrochemical studies.

Results and Discussion

In order to create hierarchal porosity, palladium is electrolessly deposited onto the parts (Fig. 4). Subsequently, the parts are electrodeposited with nanoporous palladium. Electrochemical characterization of the part then allows us to observe that the addition of a porous layer of palladium permits a larger charge storage capacity, as depicted in Fig. 5.

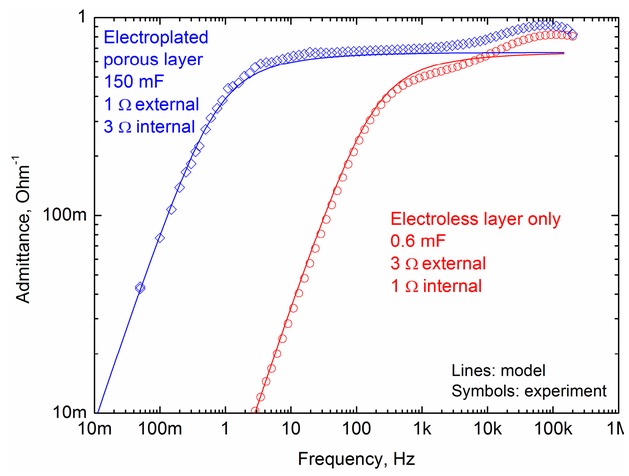
Figure 4



Before: 3D-printed cylinder without nanoporous Pd, showing large pores of about 150 µm.
After: 150 µm cylinder with an electrodeposited nanoporous Pd layer.

To measure electrochemical admittance, current is measured in response to a small voltage oscillation. The results are compared to a circuit model to determine the capacitance, which is proportional to the surface area of the structure, the internal resistance of the pores, and the external solution resistance. Fig. 5 shows that the nanoporous layer significantly increases the capacitance, but in this geometry, the increase in internal resistance is not significant.

Figure 5



Conclusions

We have fabricated hierarchically porous cylindrical lattice structures of metal-coated polymers. The structures can be used as electrodes for electrochemical energy storage. The nanopores result in high electrochemical surface area. 150 µm larger pores allow the nanoporous layer to be µm-scale while the overall part thickness is a few millimeters. As a result, the electrodes show an internal pore resistance that is not much more than the external resistance, so the electrodes can charge and discharge quickly. Fabrication of the parts is enabled by new and rapidly advancing 3D printing technology, which may allow for finer pore sizes and faster printing in the near future.

Figure 6. Ember 3D printer Ember.autodesk.com

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