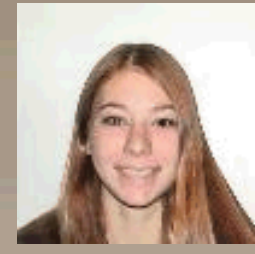
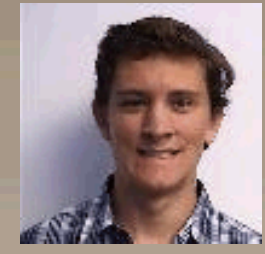


3D Printed Hierarchically Porous Metal Hydrides for Electrochemical Energy Storage

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Purpose

Nanoporous metals have the highest practical metal surface area per unit volume. However, during our prior research on planar nanoporous metal films, we encountered a fundamental challenge. When pores are too long, it takes a long time for chemical species to go in and out. Fig. 1 shows an example of high internal resistance in an electroplated nanoporous palladium film, which grew at about 1 $\mu\text{m}/\text{h}$. To overcome this, we have created hierarchical porous polymer substrates with nanopores near optimal thickness, and larger pores that allow rapid transport of ions to the interior of the electrode, and allow for much larger parts that do not face an internal resistance limit. These can serve as metal hydride batteries and capacitors that charge and discharge very quickly.

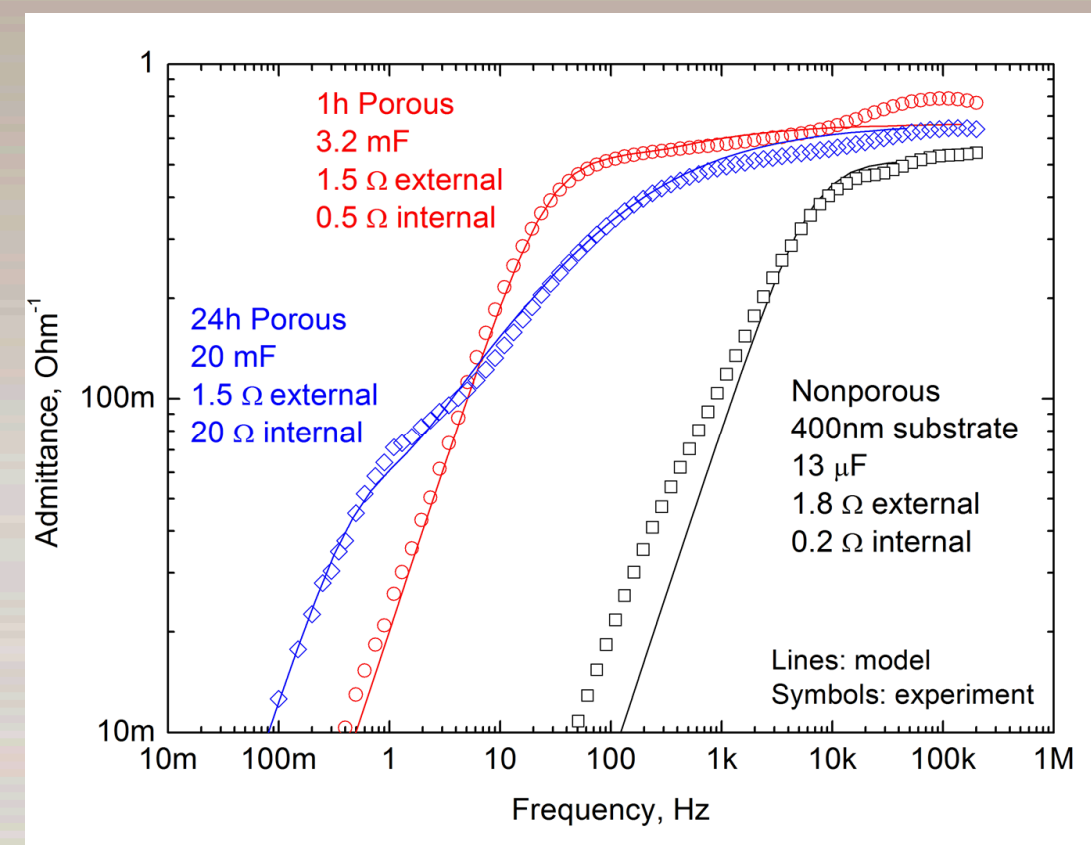


Fig. 1

Our Method

Step 1: Printing

We start by printing a hierarchical lattice in the form of a 2.8 mm tall by 2mm diameter polymer cylinder (Fig. 2) on a Nanoscribe 3D printer. The printer uses 2 photon laser polymerization method to create macroscopic parts with microscopic features.

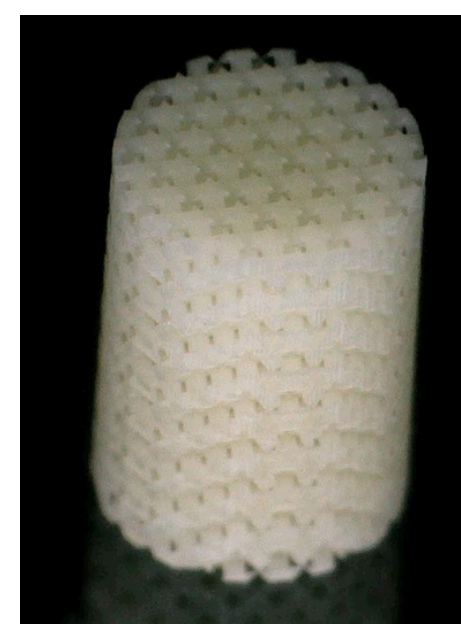


Fig. 2

Step 2: Electroless Deposition

We create Pd nanoparticles on the surface by sequential soaks in aqueous Na_2PdCl_4 and NaBH_4 , then grow more Pd using $(\text{NH}_3)_4\text{PdCl}_2$ and N_2H_4 , resulting in a conformal thin film of Pd on the polymer.

Step 3: Electrodeposition

(Fig. 3) The polymer cylinder is held in a Pd wire basket, which is coiled around the cylinder. The beaker contains a large Pd wire coil anode a Ag/AgCl reference electrode, the wire basket and polymer cylinder, and plating solution. The solution contains tetrachloropalladate, hydrochloric acid, and a block copolymer surfactant. The chemical reaction on the part (going in reverse at the anode) is: $\text{H}_2\text{PdCl}_4 + 2e^- \rightarrow \text{Pd} + 2\text{HCl} + 2\text{Cl}^-$

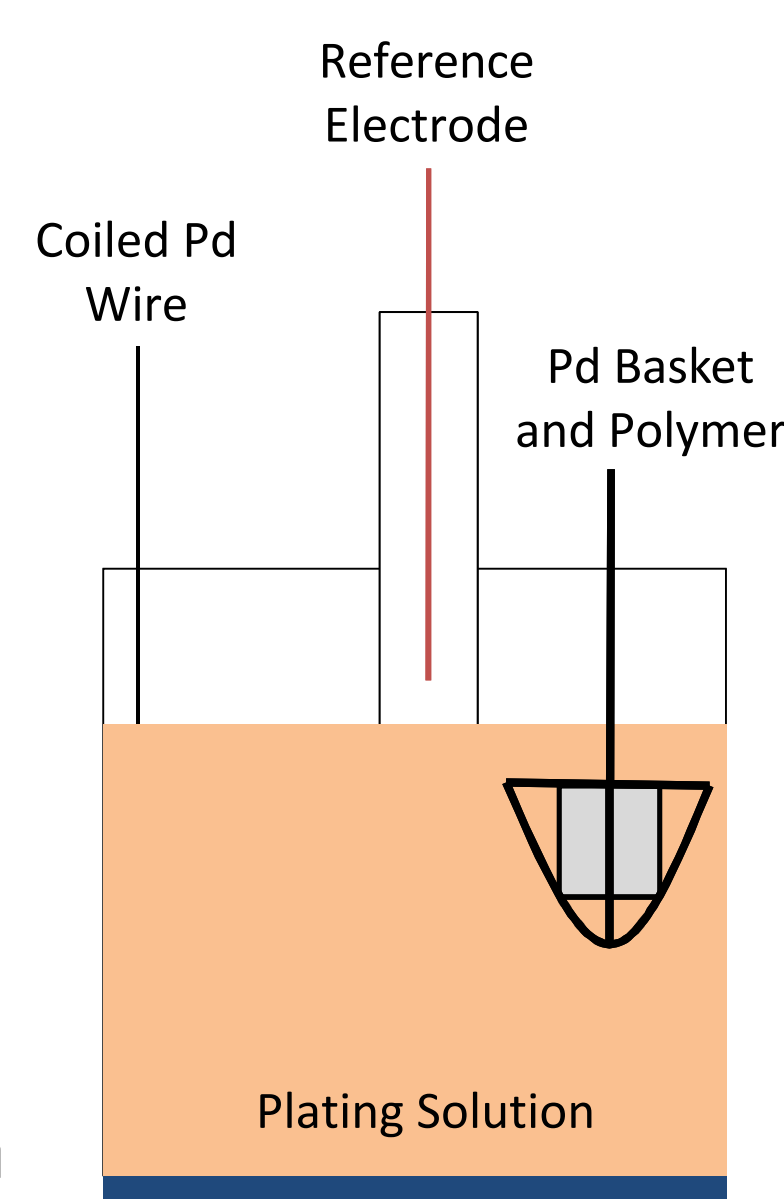


Fig. 3

Step 4: Characterization

We measure electrochemical admittance and hydriding rates in a similar electrochemical cell using dilute sulfuric acid and bubbling from a nitrogen gas line.

Results

Fig. 4 shows a part with the electroless film, showing large pores of about 100 μm and small pores of about 10 μm . Fig. 5 shows a darker part with an electrodeposited nanoporous Pd layer.

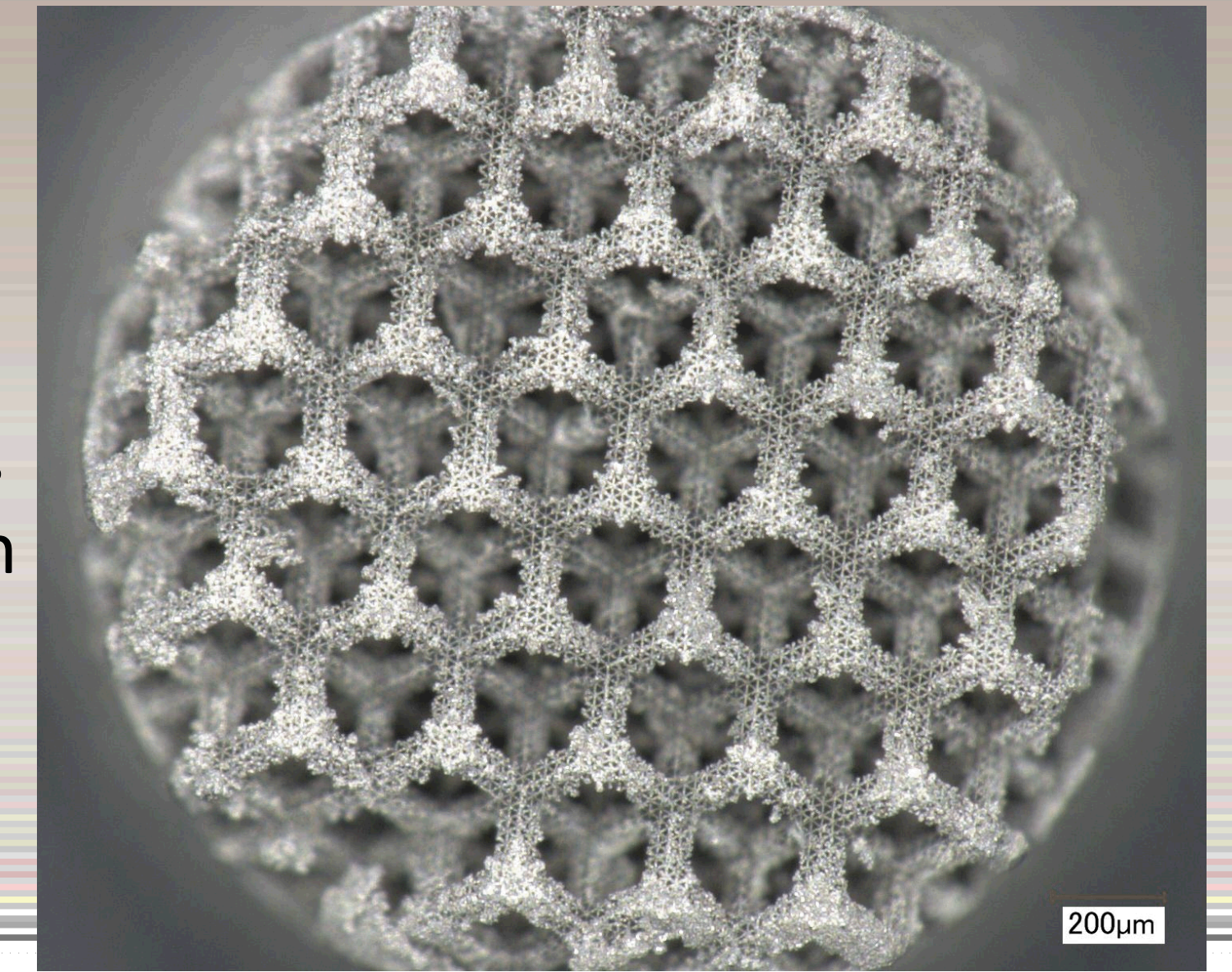


Fig. 4

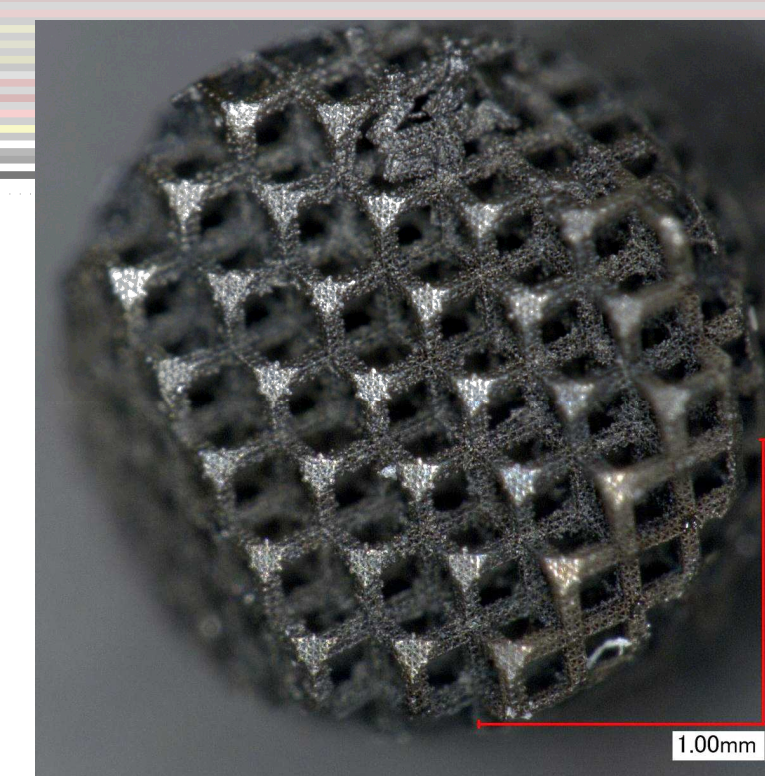


Fig. 5

(Fig. 6) Admittance experiments measure the current resulting from a small voltage oscillation. They allow deduction of surface area, which is proportional to capacitance, and charging rate, which is related to internal resistance. Nanoporous Pd coated cylinders have much higher surface area than those without this layer, but they do not show significant limitation due to internal resistance.

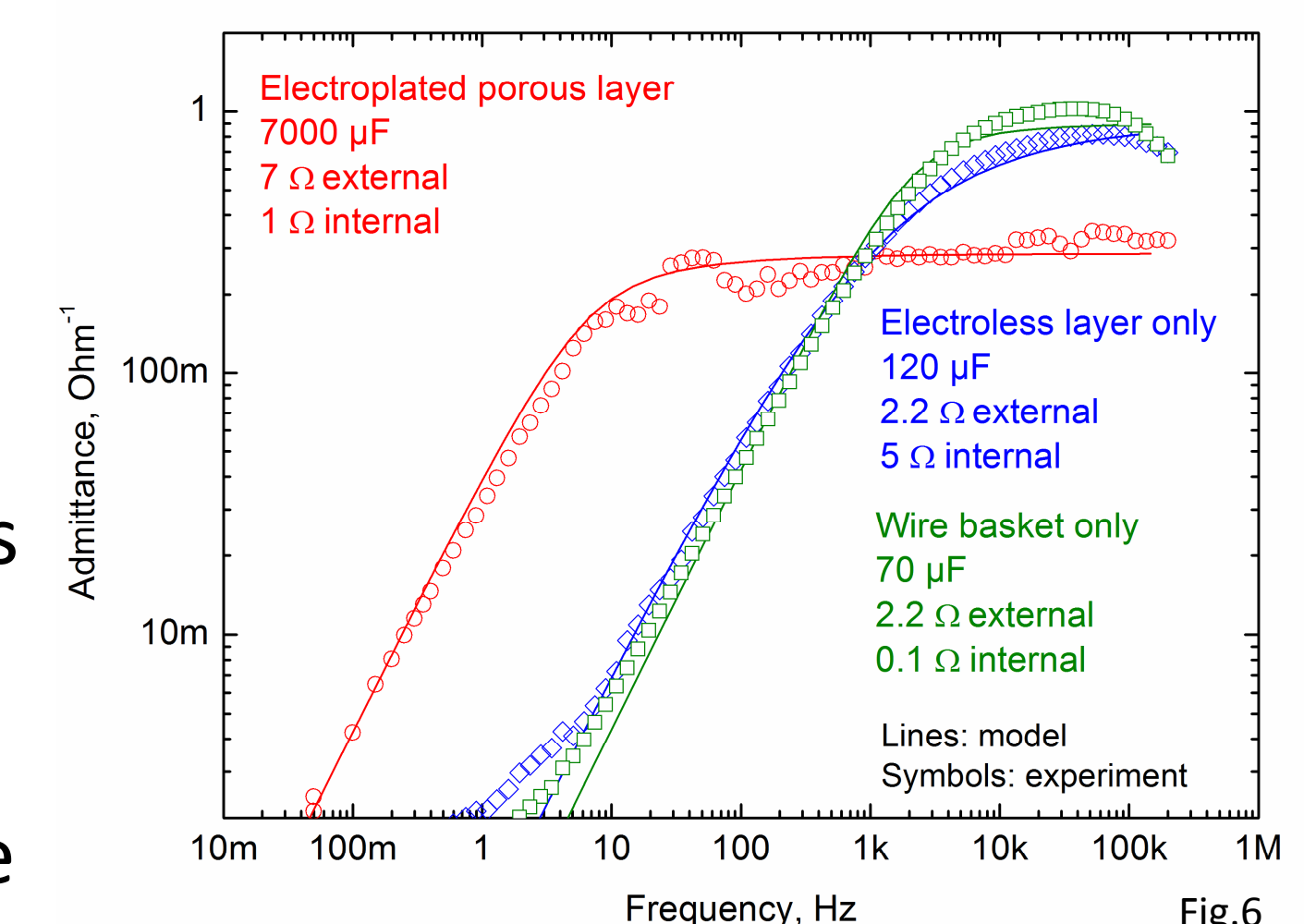


Fig. 6

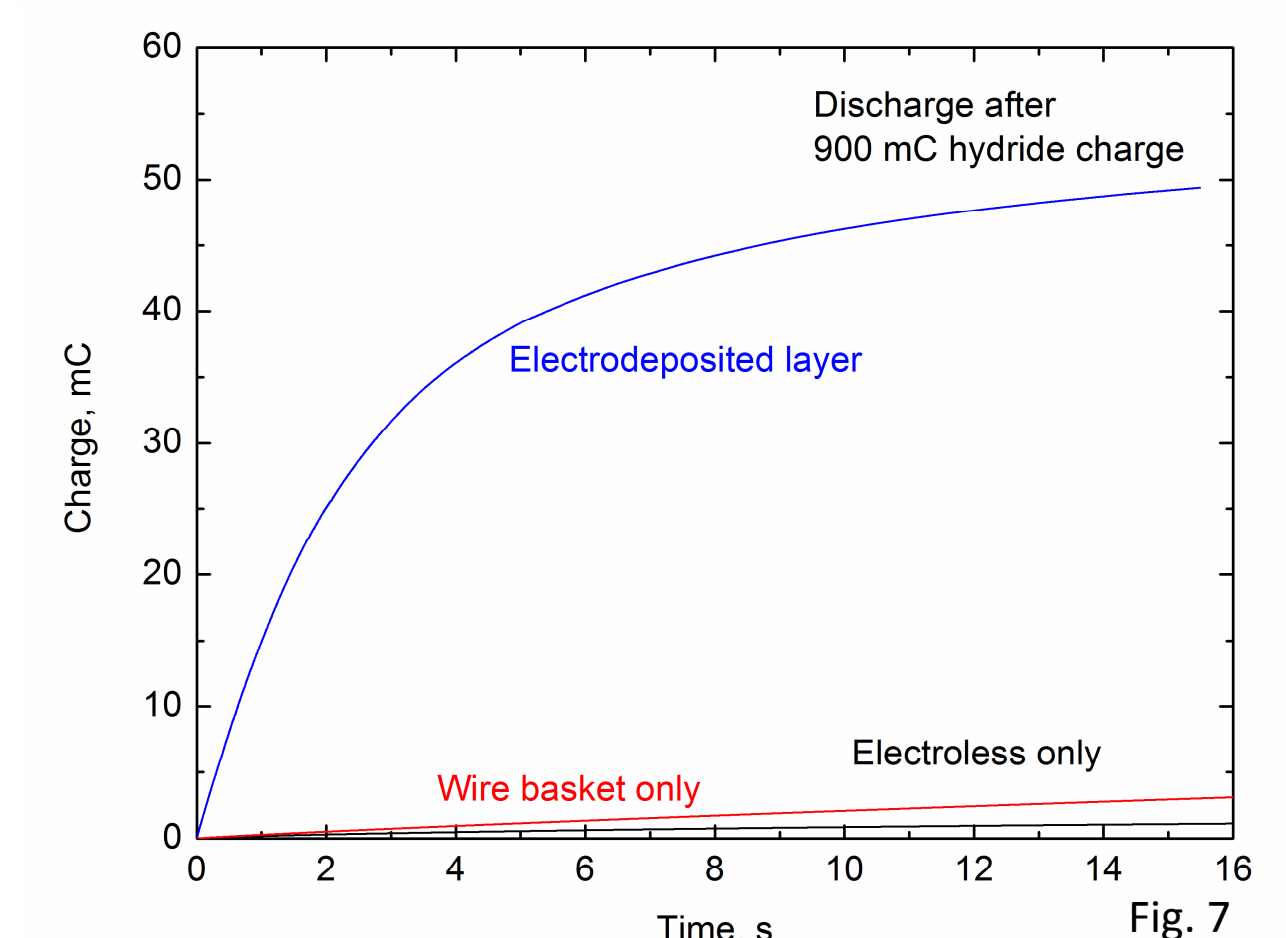


Fig. 7

A negative current applied for a fixed time causes the reaction $\text{H}^+ + e^- \rightarrow \text{PdH}_x$ at the electrode. Stepping to a positive potential then causes the reverse reaction to occur rapidly. Fig. 7 shows the discharge rate of parts with and without the electrodeposited nanoporous layer. The nanoporous layer shows much more charge released on the 10 s timescale, although there is a low charge yield overall. Dissolved O_2 decomposes PdH_x , and our N_2 bubbling method appears to not work as well for this part and cell geometry as it did for our planar films.

Conclusions

We can create thick films of nanoporous palladium that conform to a hierarchical lattice substrate. Hierarchical pores allow us to make electrodes with macroscopic thickness that do not show the internal resistance limit observed in our planar films with thickness $> 10 \mu\text{m}$. The nanoporous layer improves the ability of the parts to electrochemically absorb and discharge hydrogen.