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Hierarchically Porous Structures Prepared By Electrodeposition Onto 3D-Printed Substrates

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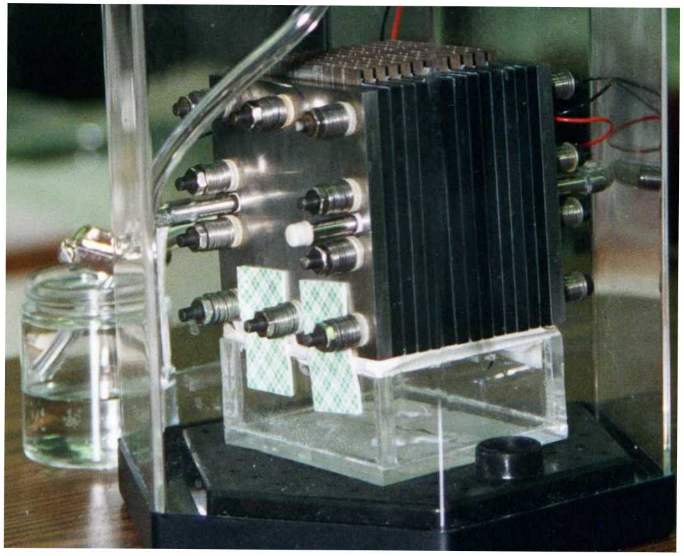
Hierarchical pores aid multiphase transport

- Technologies like batteries, fuel cells, and catalytic converters require transport between a fluid and stationary phase.
- High surface area between phases → small pores
- Rapid fluid transport → large pores
- 3D printing offers deterministic, optimal pore structures



http://www2.jpl.nasa.gov/files//images/hi-res/p48600ac.tif

Case 1: Porous electrodes for energy storage

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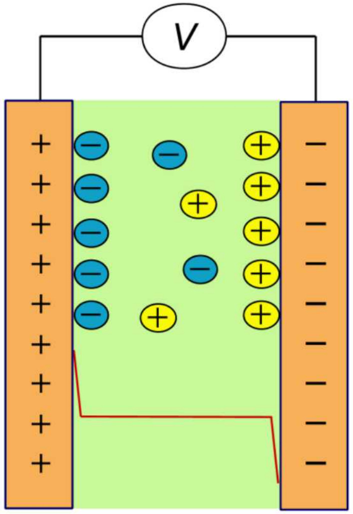
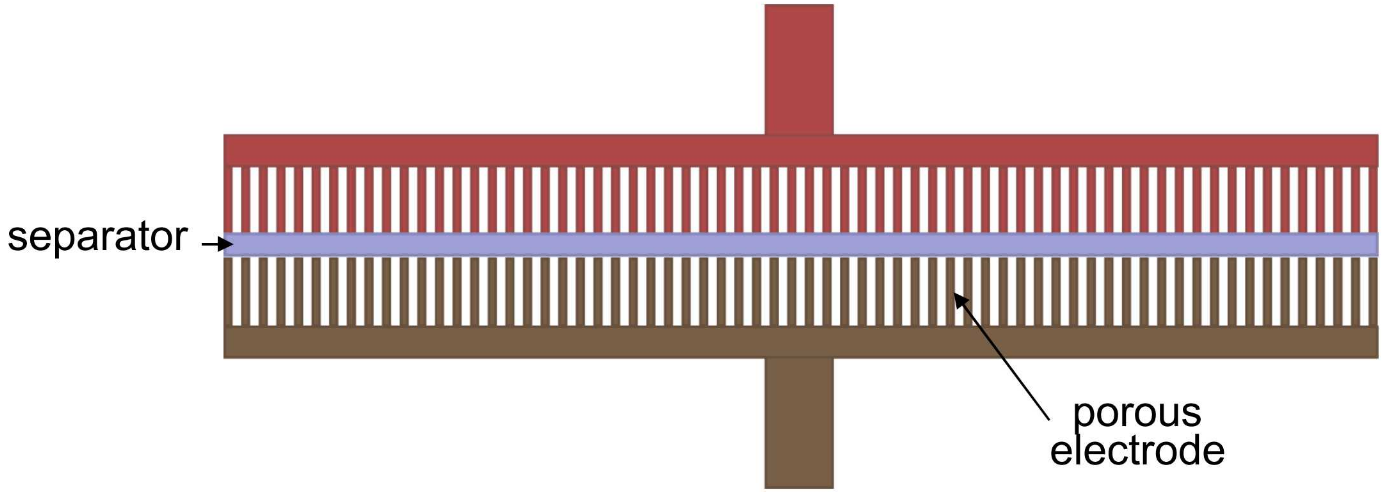
- Battery electrodes
- Electrochemical capacitors
- To charge quickly, we need device geometries that provide high interfacial surface area, and short path lengths in low-conductivity regions.

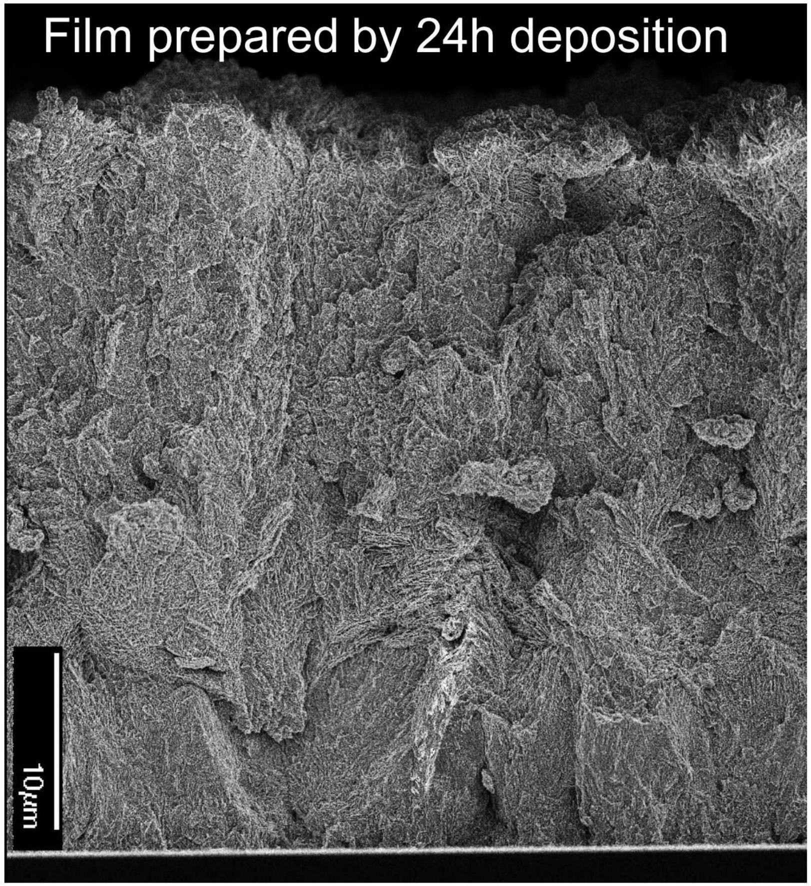


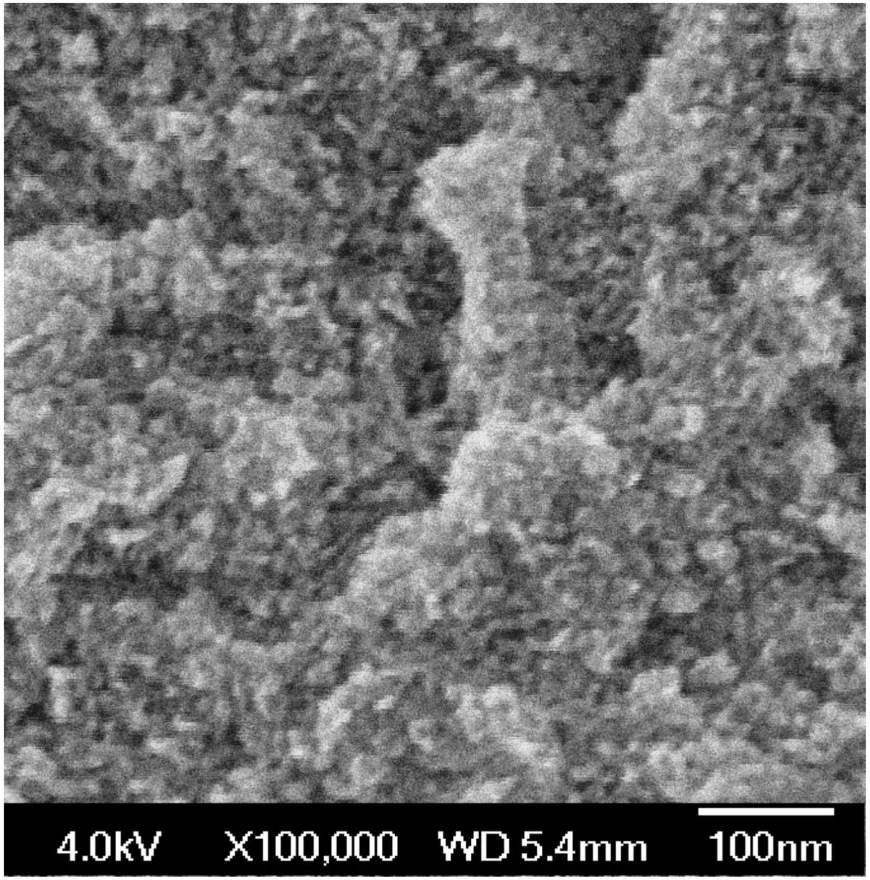


Robinson, DB. (2010). Optimization of power and energy densities in supercapacitors. Journal of Power Sources 195:3748.

Nanoporous Palladium Electrodes

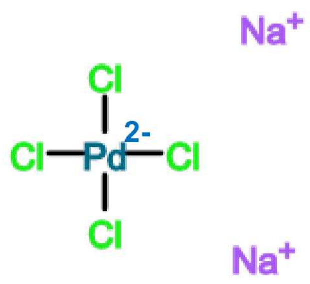
- Films prepared by electrodeposition with block copolymer pore template
- Disordered 10-20nm pores

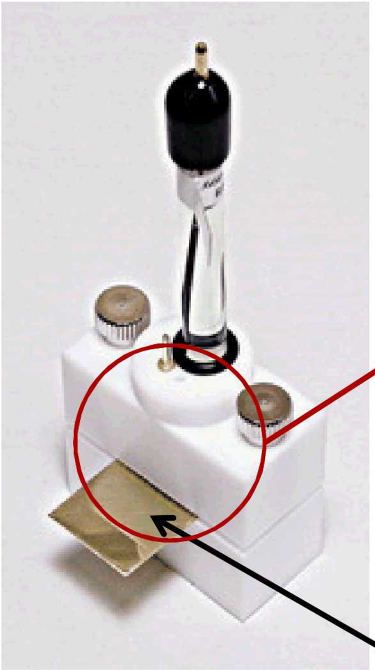


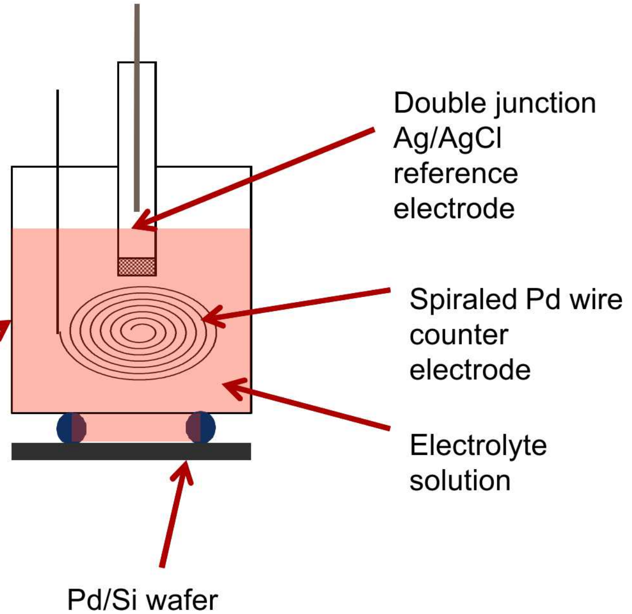


Electrodeposition of Nanoporous Palladium

$$PdCl_4^{2-} + 2e^- \rightleftarrows Pd + Cl_4^-$$







Pluronic F127 micelle former
EO_{101} PO_{56} EO_{101}
where $EO_2PO_2EO_2$ is :

300nm Pd on Si wafer
10nm Ti adhesion layer
Surface area: $0.4 cm^2$

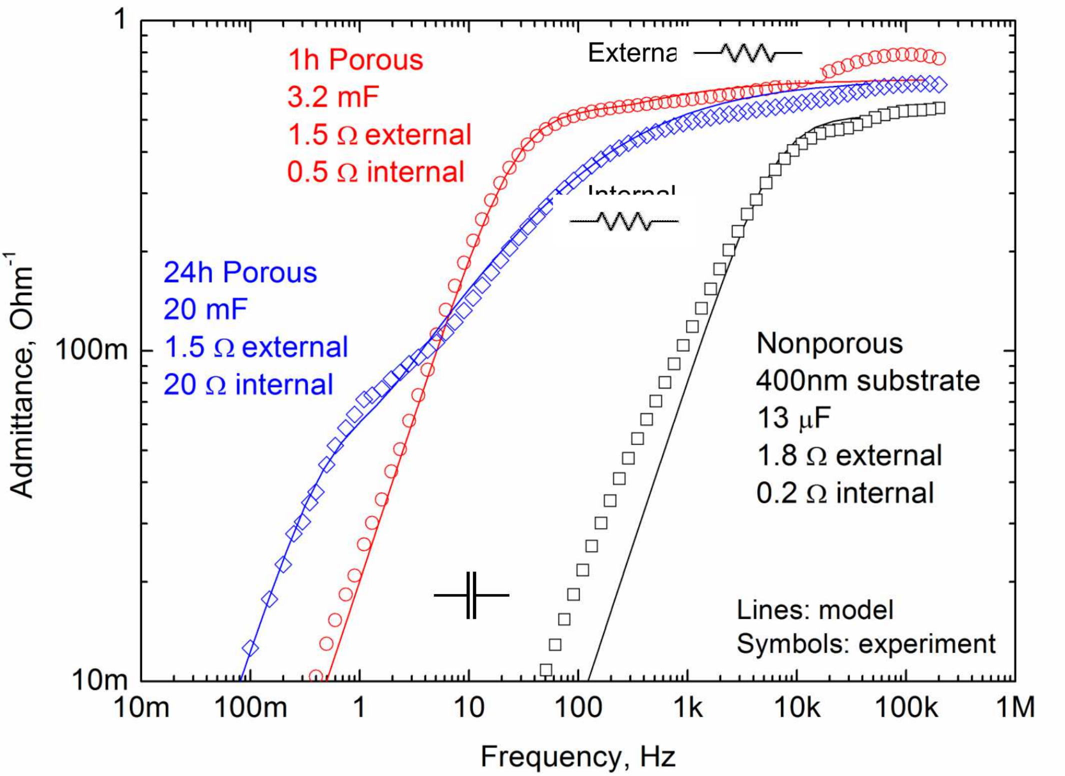
electrolyte solution:
200µl 0.25M Na_2PdCl_4
200µl 1M HCl
200µl 10% F127

Apply -1 to -2.5 mA/cm^2 for 1-24 hours
Working electrode is about 0.2 V
Counterelectrode is about 0.8 V

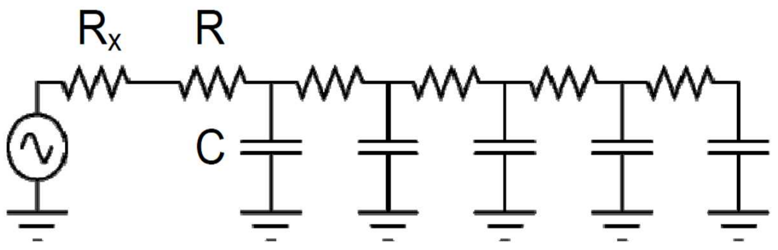
Extends Wang et al., Chem Mater. 24 1591 (2012)

Electrochemical admittance

- Measures reversible electrostatic adsorption of aqueous ions to surface without chemical reactions
- Provides a measure of surface area, charging rate

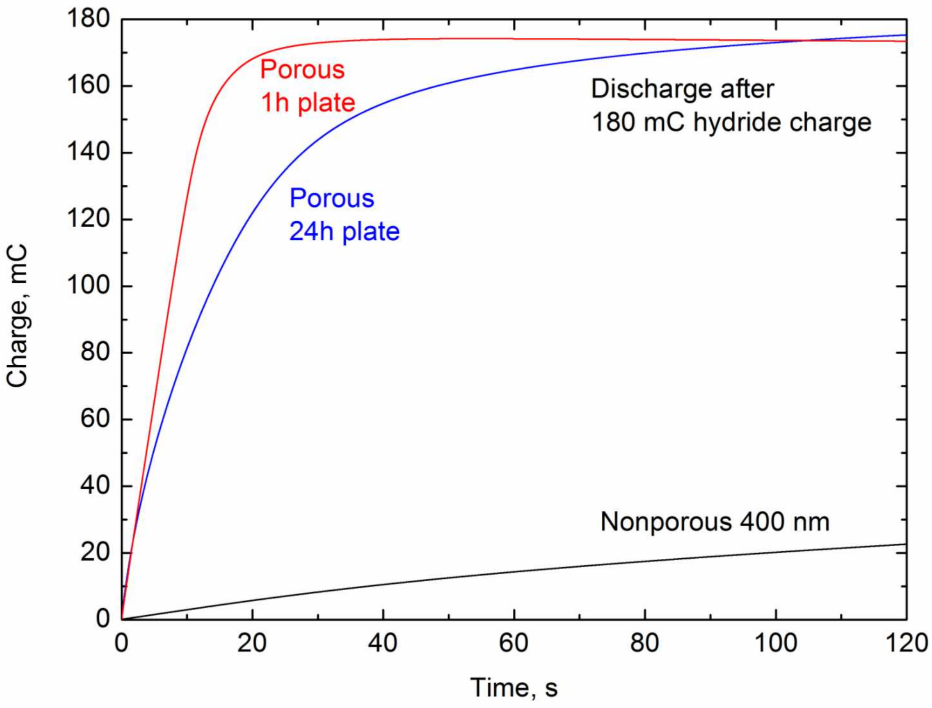


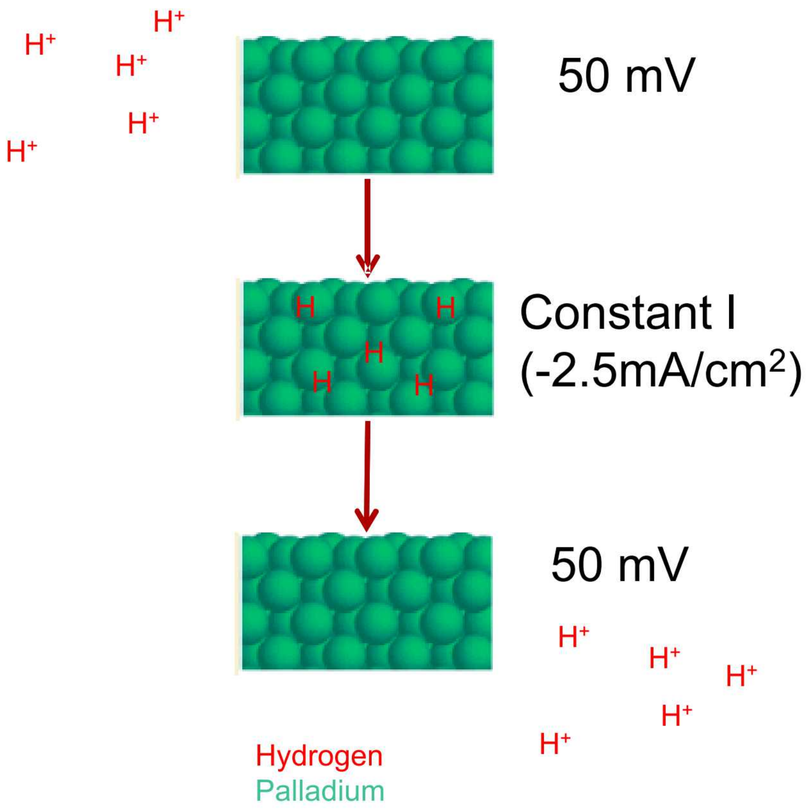
R_x – resistance external to pore
R – resistance internal to pore
C – pore capacitance



Electrochemical hydriding rates

- Apply negative current for fixed time: $Pd + H^+ + e^- \longrightarrow PdH$
- Then step to positive potential, observe reverse reaction

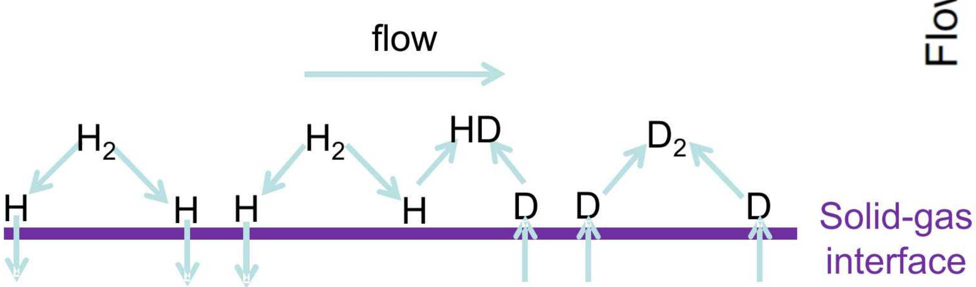


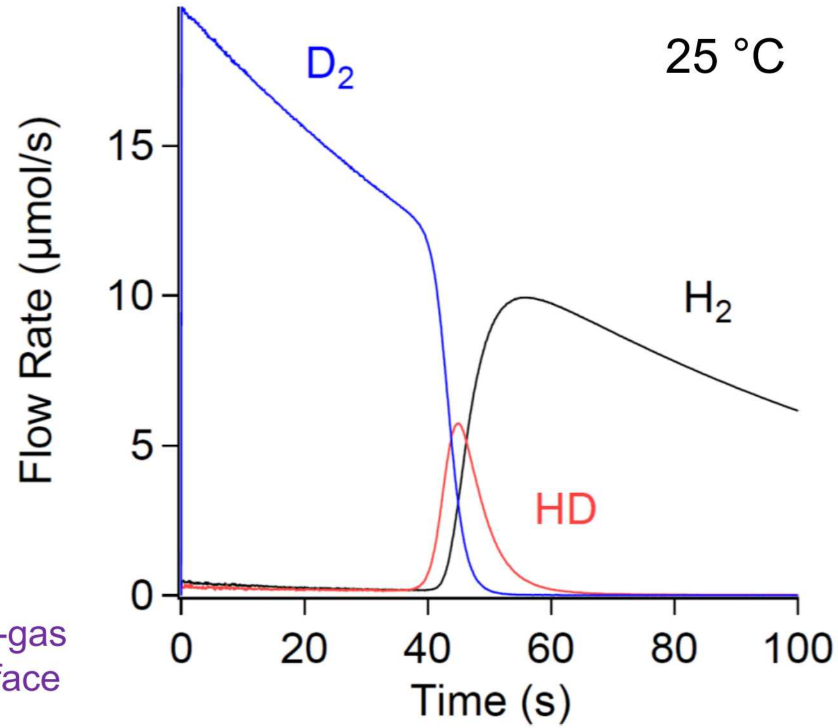


- Porous films dehydride more quickly
- 1 hour has faster dehydriding due to lower pore resistance

Case 2: Isotope exchange gas chromatography

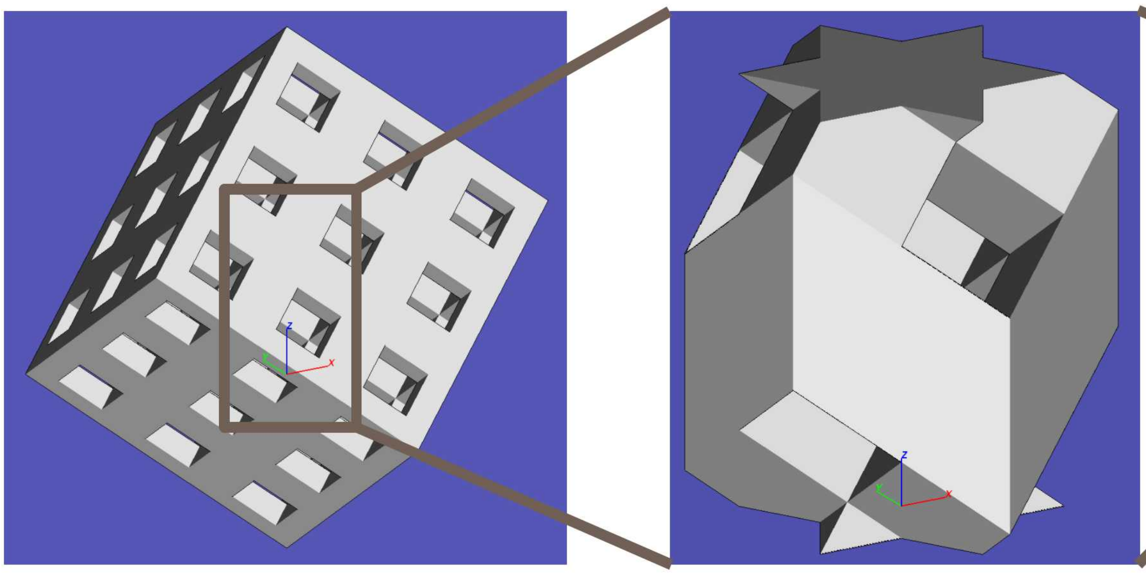
- Second-order kinetics: sharp, steady-state composition boundary
- $H_2 + PdD_{0.6} \rightarrow D_2 + PdH_{0.6}$
- Elute with H_2 (protium), measure D_2 eluate with mass spectrometer
- HD peak width indicates broadening mechanisms
  - Reaction kinetics
  - Gas-phase axial, radial diffusion
  - Solid-phase diffusion (no bulk reaction)
- 2 mm diameter, 20 mm long column
- 190 mg Pd powder, 50 psi drop

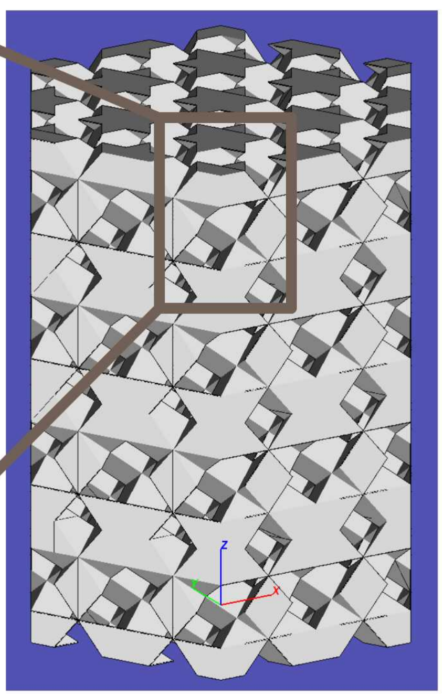




3D-printed porous structure

- Space diagonal-oriented cube-edge lattice
  - Simple flow paths, all at same angle vs. flow direction
  - Near their resolution limit, 3D printers are best at making simple lattices
- 5 to 50% solid fraction
- Tile hexagonal prism unit cell, crop to part shape





M. Salloum, D. B. Robinson. AIChE J. 64 1874-1884
10.1002/aic.16108

Autodesk Ember 3D printer

- Projects blue-light images into photopolymer resin in tray through silicone-coated window
- First layer glues itself to metal base plate on z stage
- Stage moves up, tray sloshes resin, repeat 100-1000x
- Image is 912x1140 array of 50 µm pixels
- Resin contains photoinitiator, absorber, mono- and oligo-acrylate monomers
- $7k instrument, $100/L resin
- Mostly open source polymers, software, and hardware
- Window adhesion limits lattice geometries

Autodesk Ember

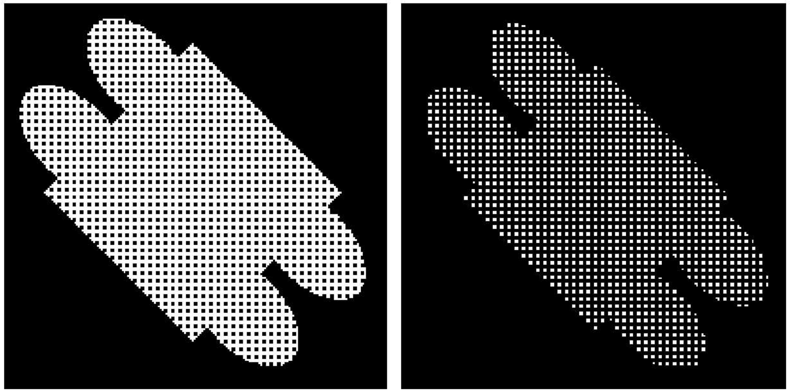
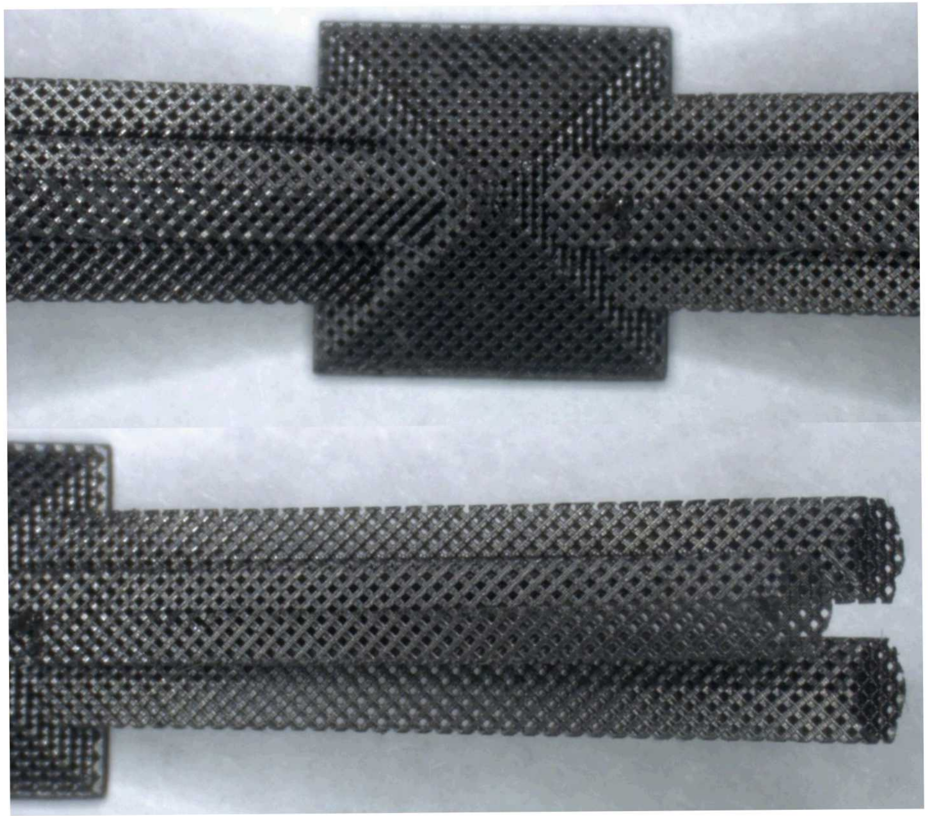


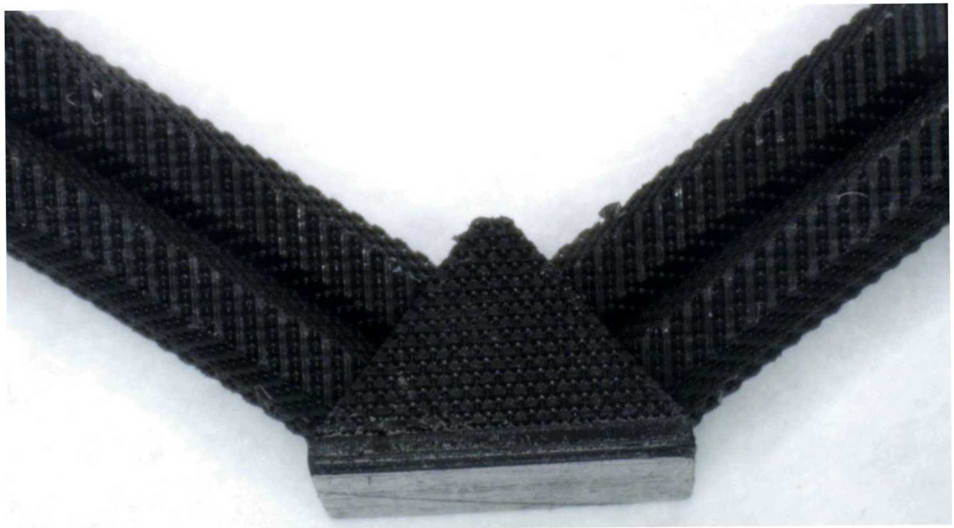
Image slice examples

Ember lattice

- This Ember part has 150 µm pores. The part is grown at an angle so that the cube-edge lattice is aligned with the growth direction, allowing full use of the printer's resolution.

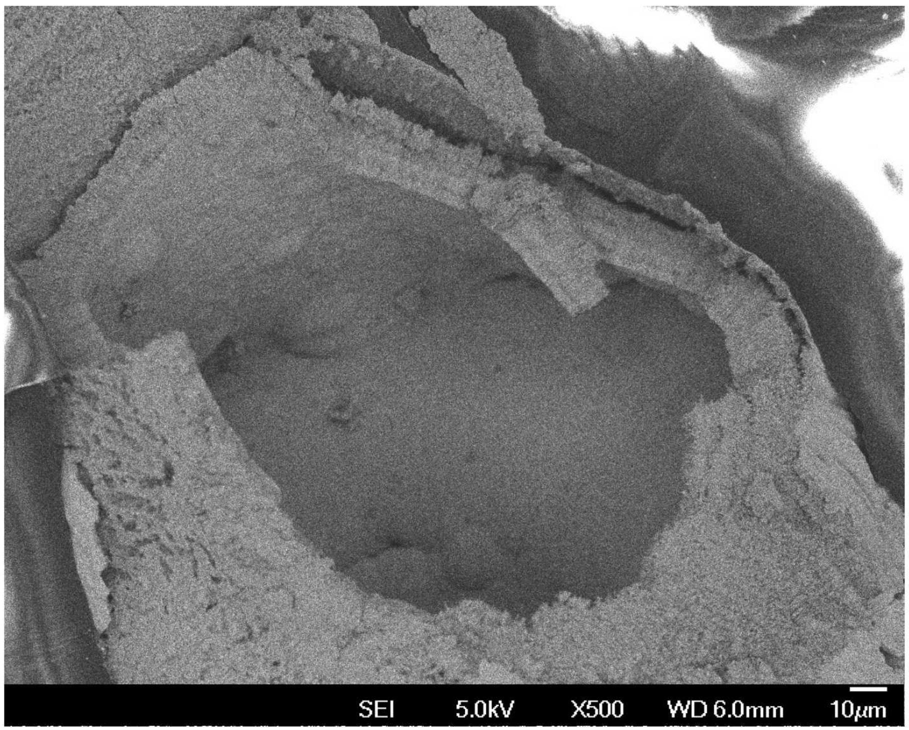


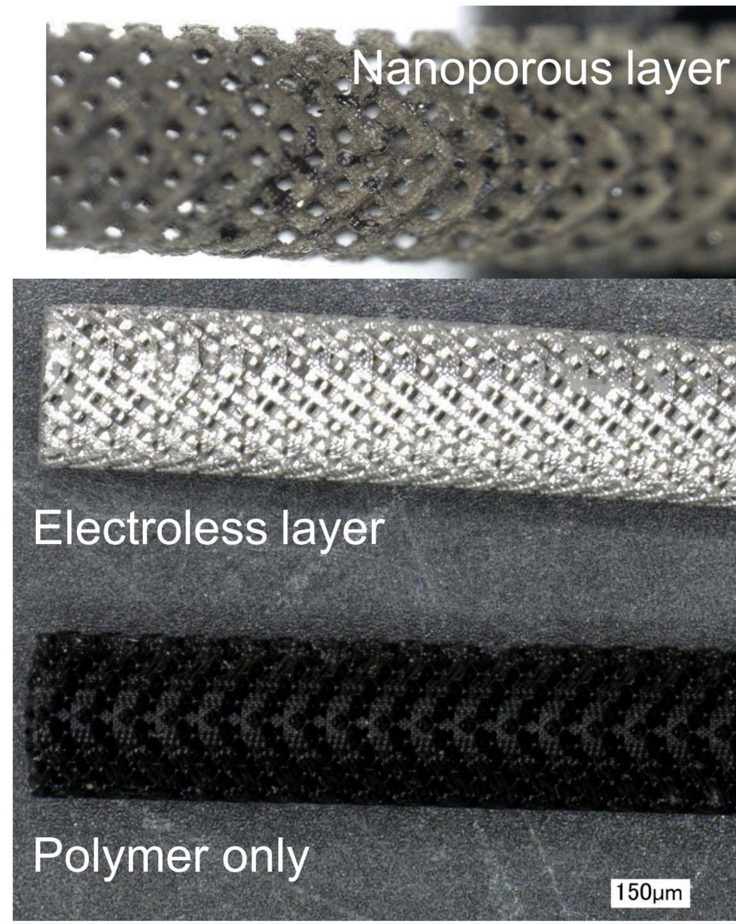
Pyramid base is 7.5 mm
Cylinders are 2 mm diameter, 20 mm long



Metal coating of Ember part

- We have grown conformal 1 µm scale Pd layers on Ember parts by electroless deposition. The layers can be thickened by subsequent electroless deposition or electrodeposition.

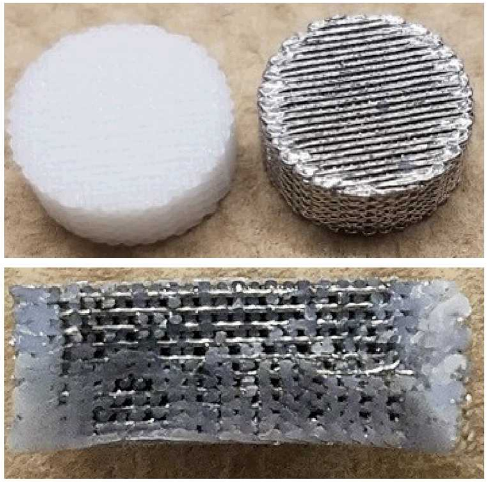




Electroless Pd layer

- Works well on polycarbonate filaments (extrusion 3D printers), acrylate photopolymers
- Create seed particles by sequential dips in Na_2PdCl_4, $NaBH_4$
- 2-24 h in $(NH_3)_4PdCl_4$ – N_2H_4 bath with excess NH_3, NH_4Cl
- Use isopropanol-water mix to aid wetting in seed dips
- Use flow or external agitation to aid mass transport in bath

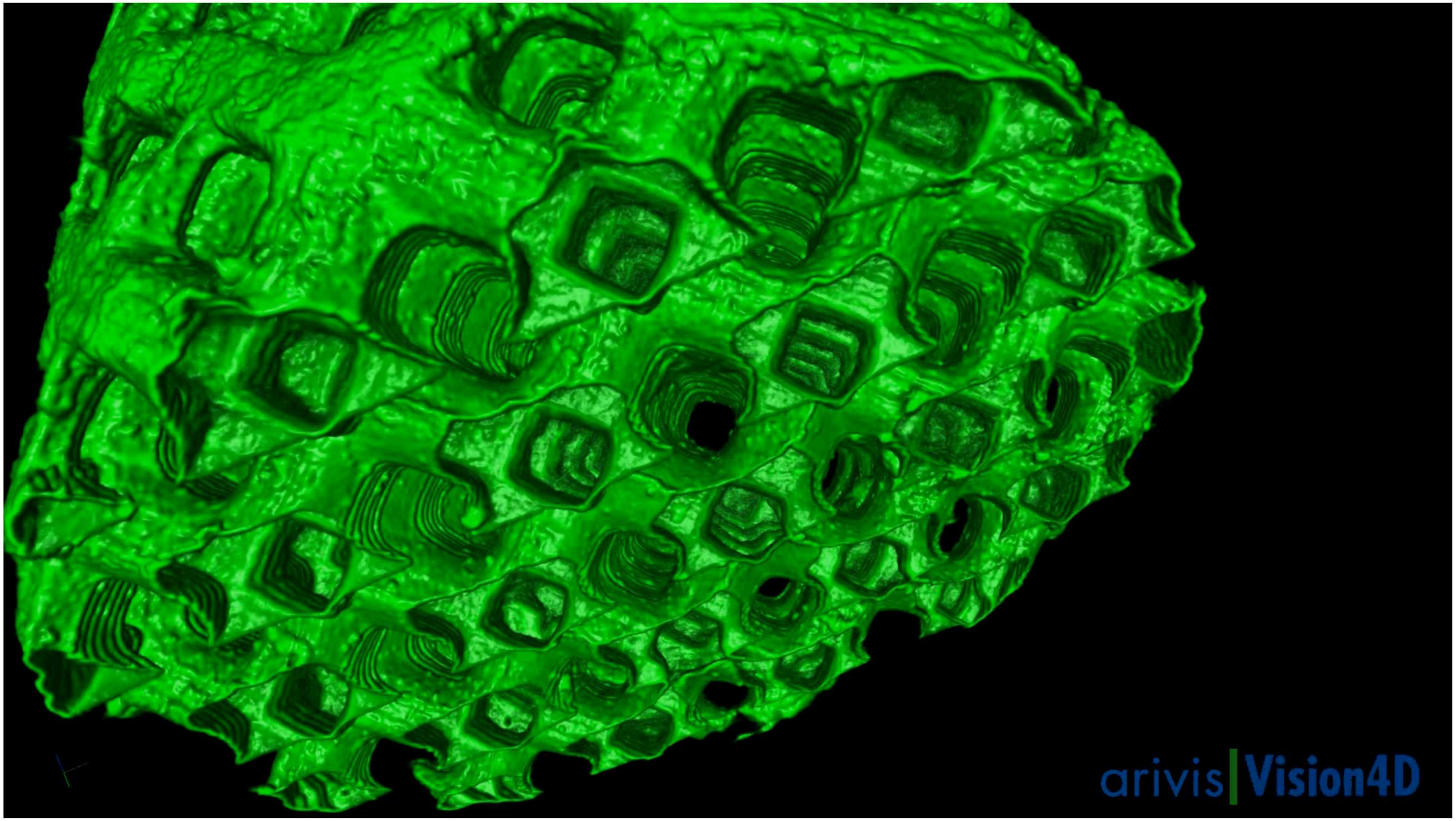
Polycarbonate lattice with and without electroless layer



Christopher G. Jones et al.
J. Electrochem. Soc. 2017, 164 (13) D867-D874
10.1149/2.1341713jes

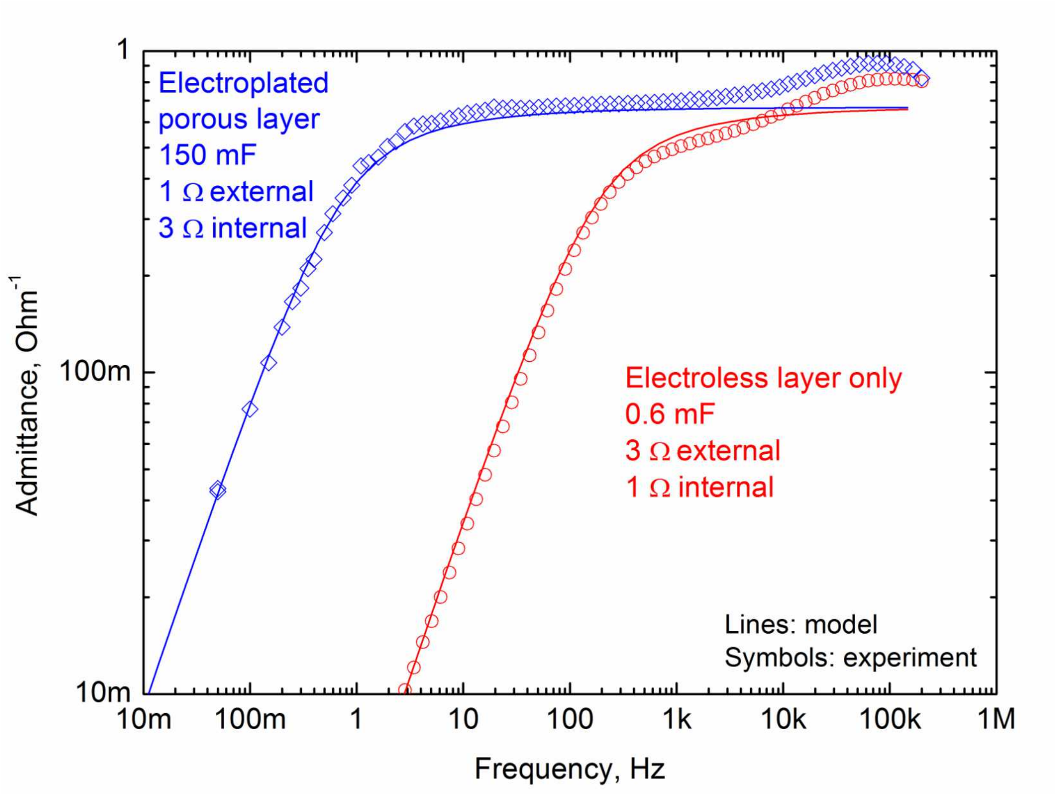
Ember x-ray tomography

- X-ray tomography has confirmed that the electroless deposition method evenly coats the part interior.



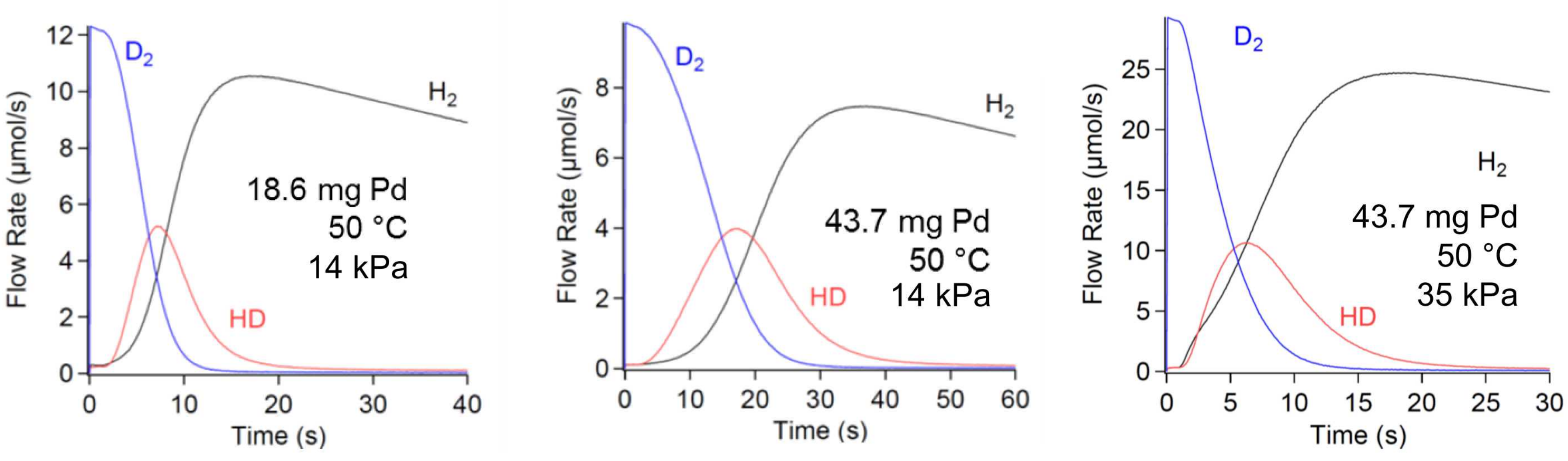
Ember part as capacitor

- Part shows high capacitance with internal resistance comparable to external resistance
- 10 µm layer thickness estimated from this
- 150 µm pores increase surface area 5x vs. nonporous cylinder



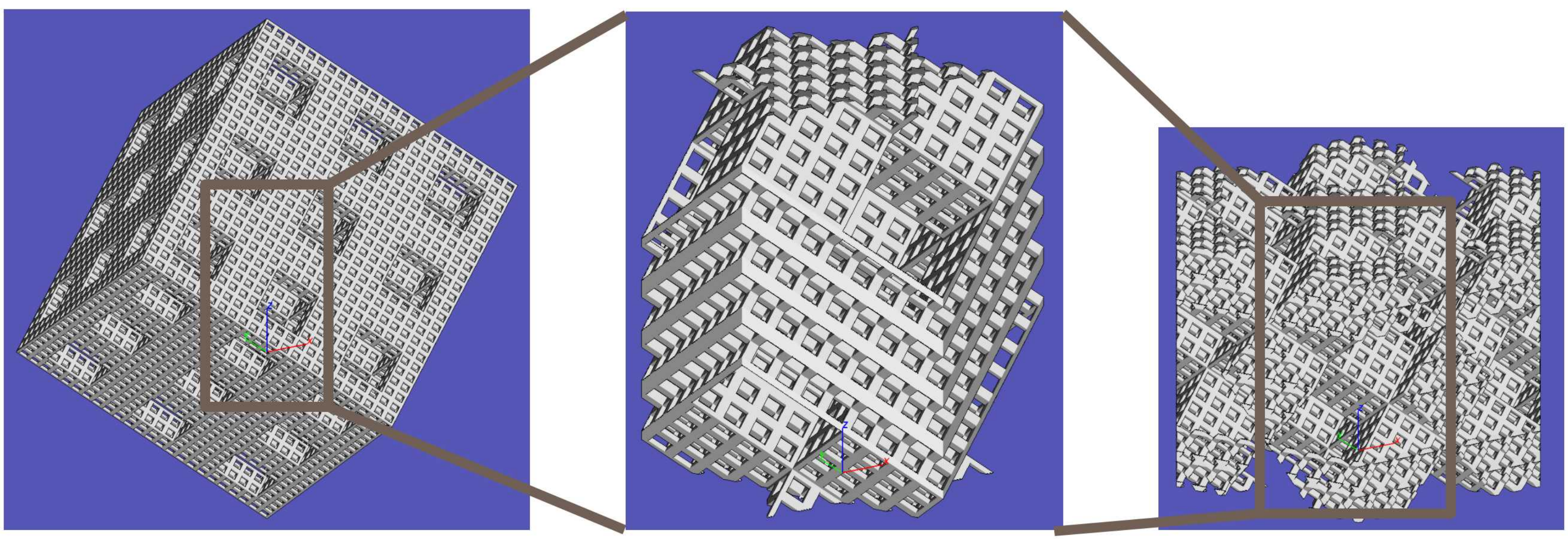
3D-printed column performance

- Electroless layer +
  porous electrodeposited layer
- Peak width approximately equals elution time
- Some nearly pure D_2 elutes
- Should improve with more Pd, lower polymer volume fraction
- Pressure drop as noted



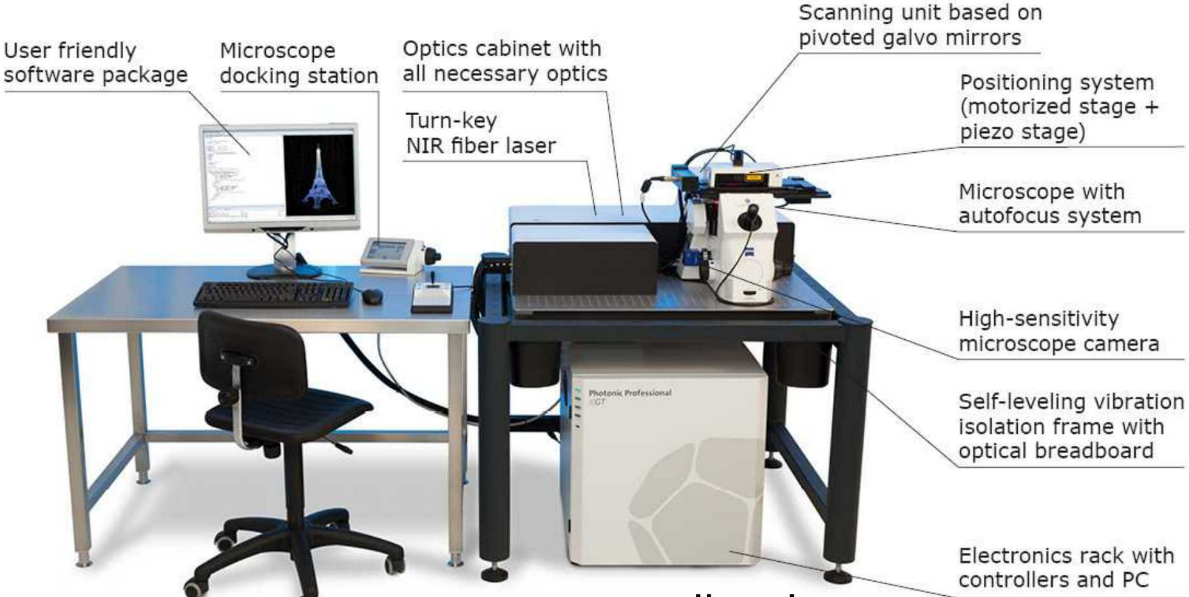
Hierarchical lattices

- Can finer porosity be 3D printed?
- Example: finer lattice is also a cube-edge lattice oriented along the cube space diagonal
- Finer lattice increases the surface area of the solid phase, allowing for increased fluid-solid contact.
- Metal layer can be electroless only, without nanoporous layer
- Requires high-resolution 3D printer



Nanoscribe 3D printer

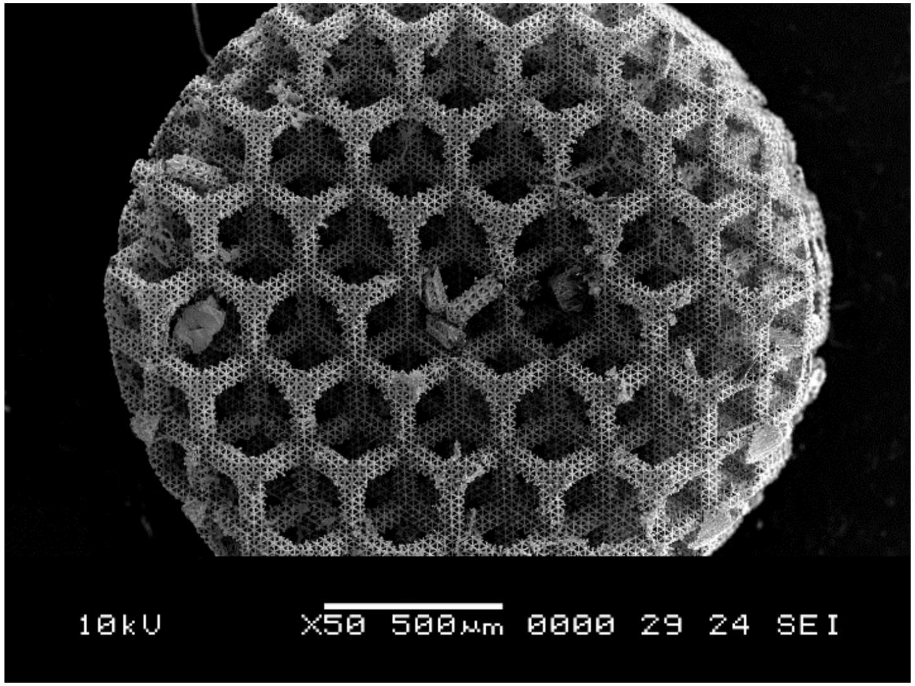
- Rastered laser for two-photon polymerization
- Sub-µm resolution
- Requires 1 day to print 1 mm solid cube
- Sparse lattices can be much faster
- $500k instrument, proprietary polymers and software

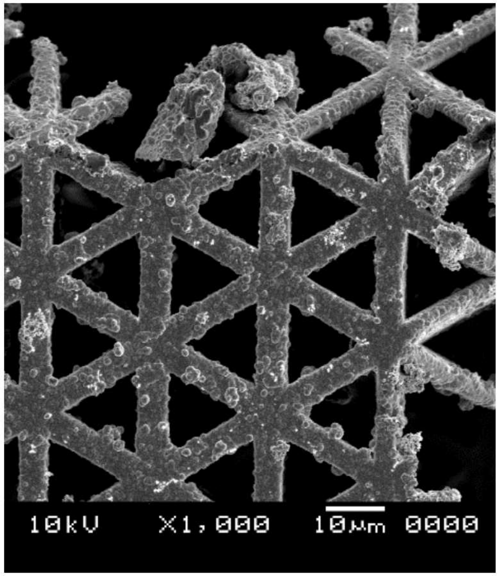


nanoscribe.de

Sparse Nanoscribe sublattice

- We have designed sparse sublattices that can print as two 2 mm diameter, 2.8 mm tall cylinders overnight (9 mm^3).
- Left image is a polymer structure in an optical microscope. Other images are electroless Pd-coated parts in the electron microscope.

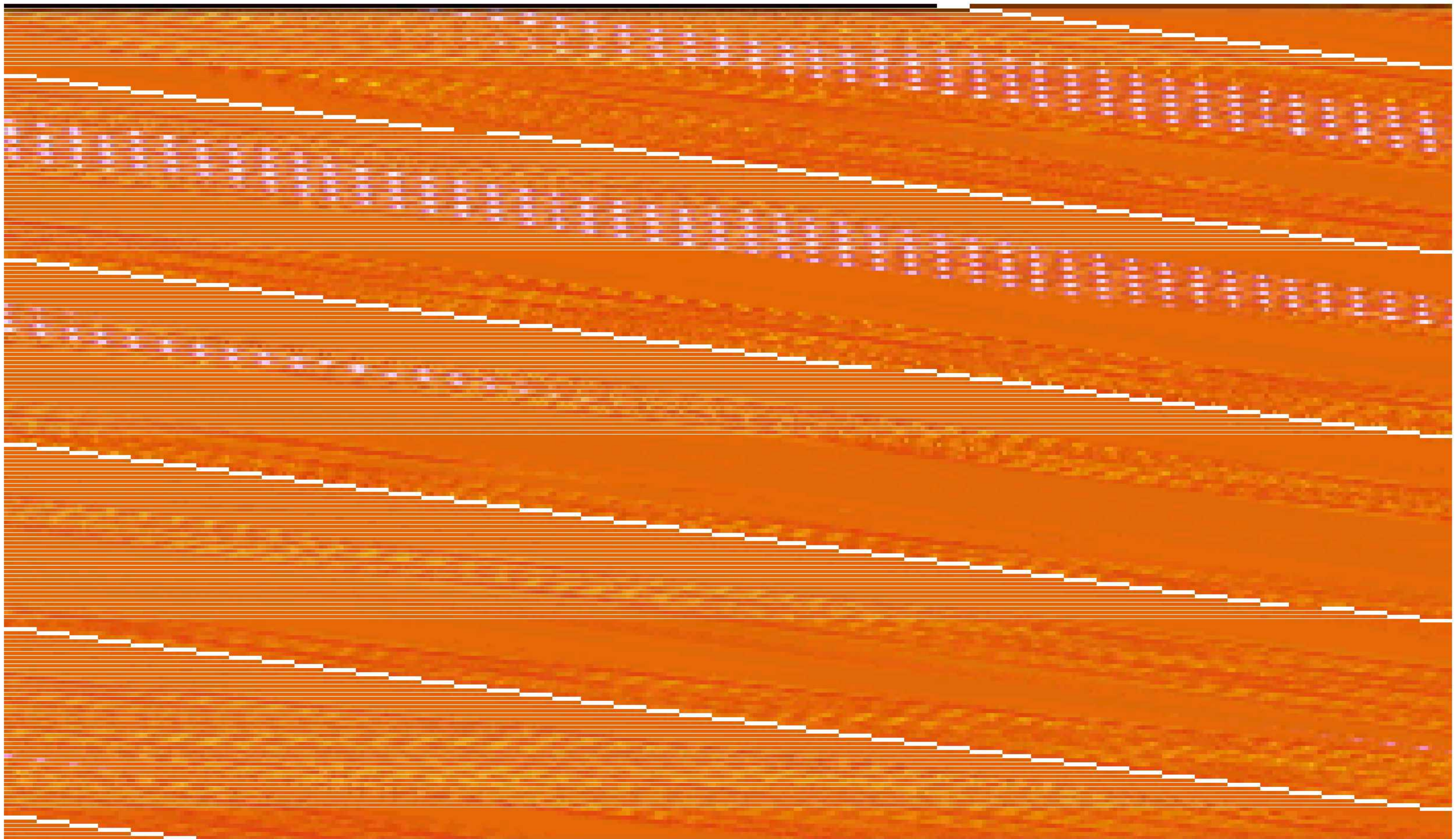




133 µm flow channels

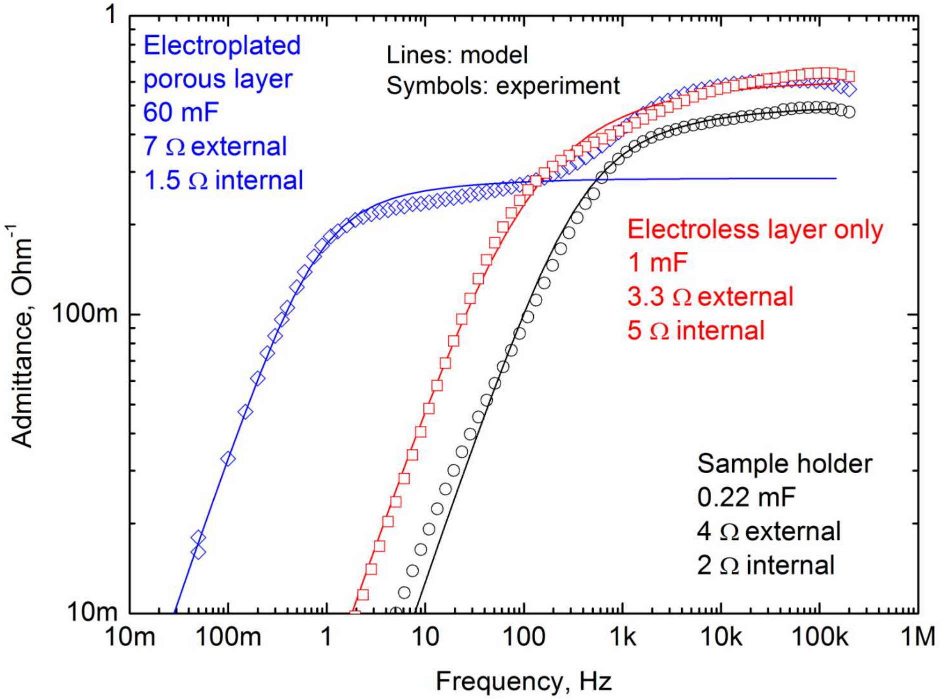
Nanoscribe movie

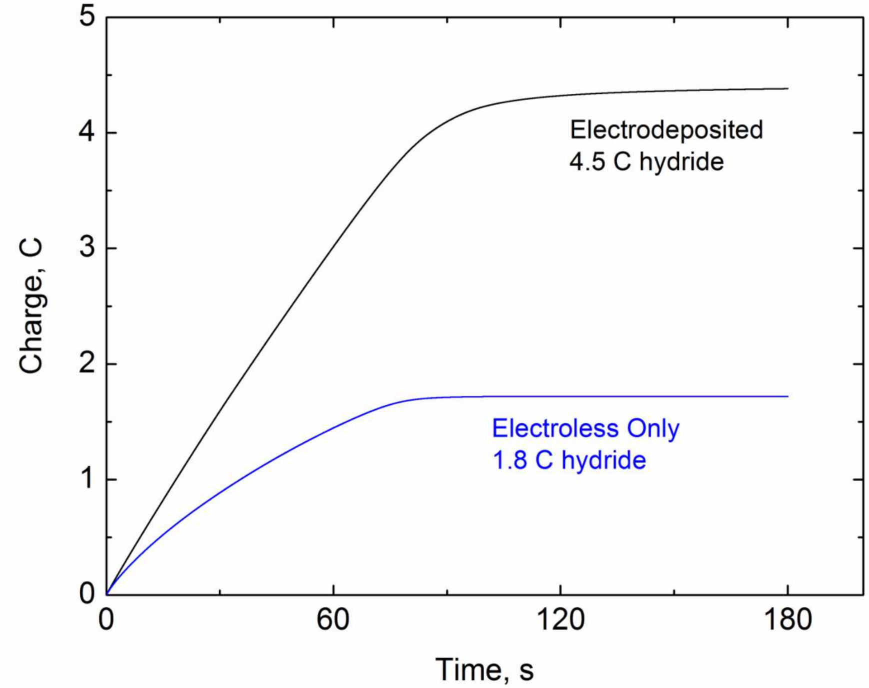
- Rastered laser solidifies polymer
- µm-scale overhangs are accommodated



Nanoscribe electrochemistry

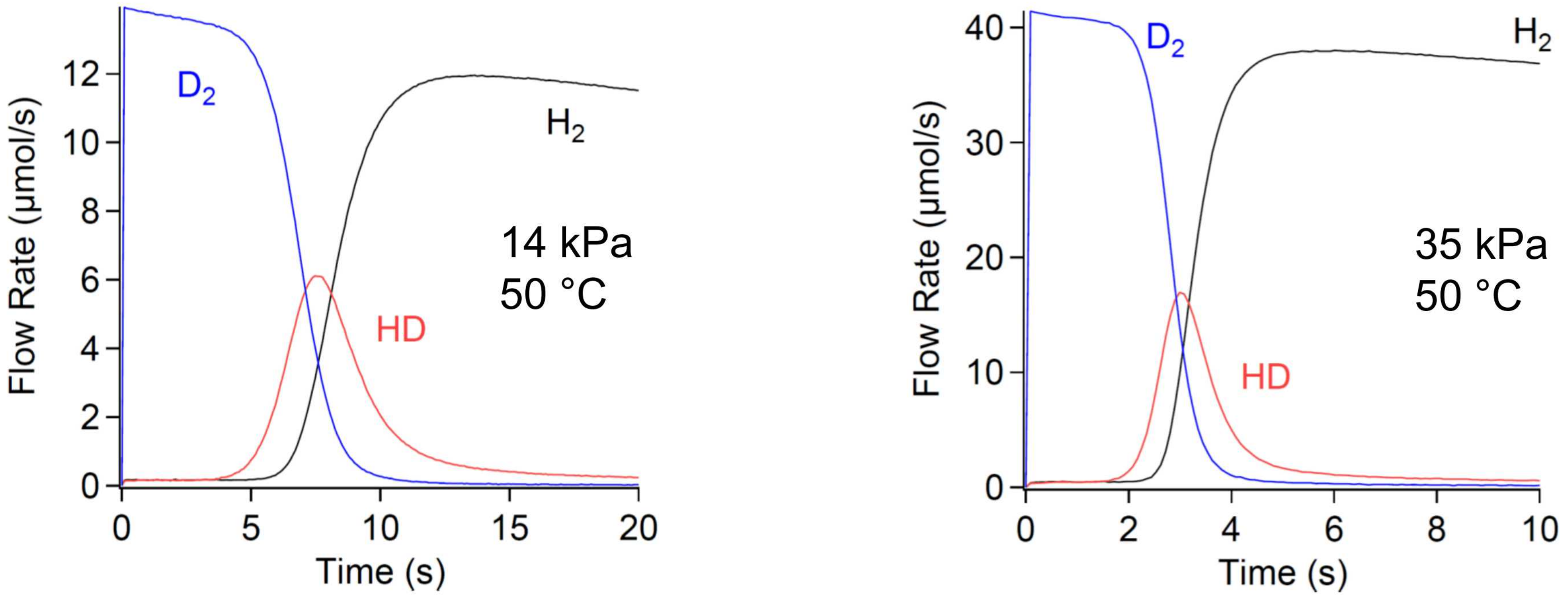
- A Nanoscribe part shows high capacitance when coated with nanoporous layer, and resistance that is mostly external. It stores more hydrogen and releases it more quickly with the nanoporous layer when charged at constant current near about -0.25 V for 180 s.





Nanoscribe chromatography

- 20.5 mg Pd on 6 stacked parts
- More pure D_2 elutes than for analogous Ember part
- HD peak may be limited by detector rise time



Conclusions

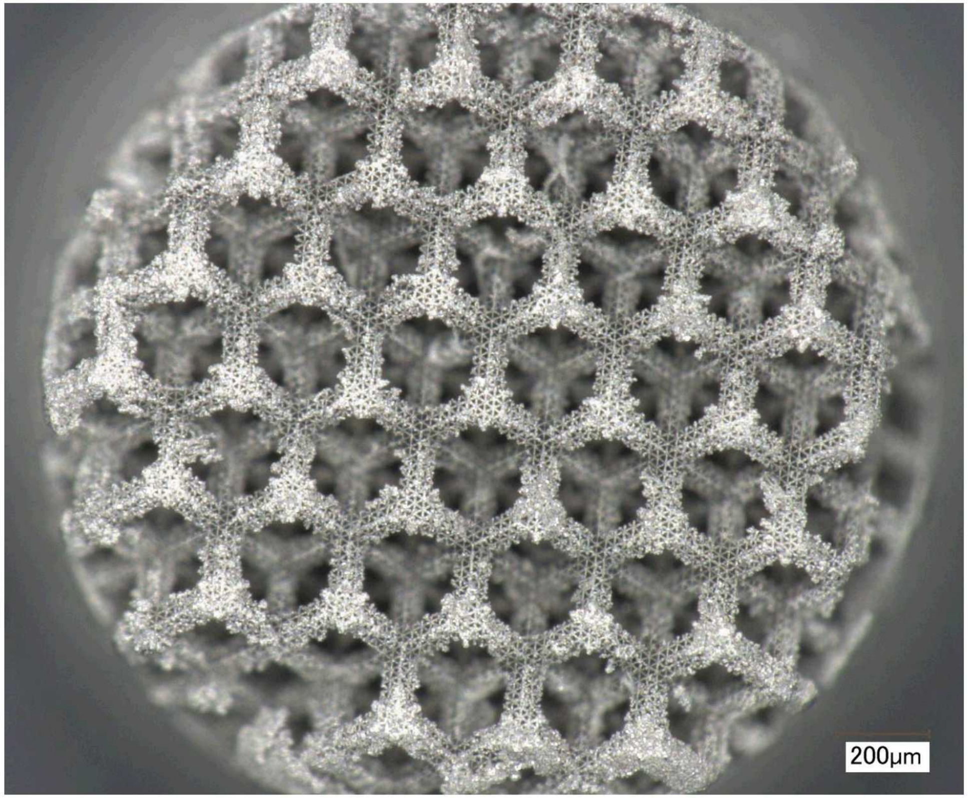
- Projection stereolithography and two-photon lithography can efficiently print macroscopic lattice parts with features on the 1-100 μm scale.
- Polymer parts can be uniformly metallized by electroless deposition.
- Thick nanoporous layers can be deposited within polymer lattices.
- Thick hierarchically porous electrodes show higher power density than thick planar electrodes.
- Sharp reaction boundaries can be obtained in exchange chromatography columns.

Team members

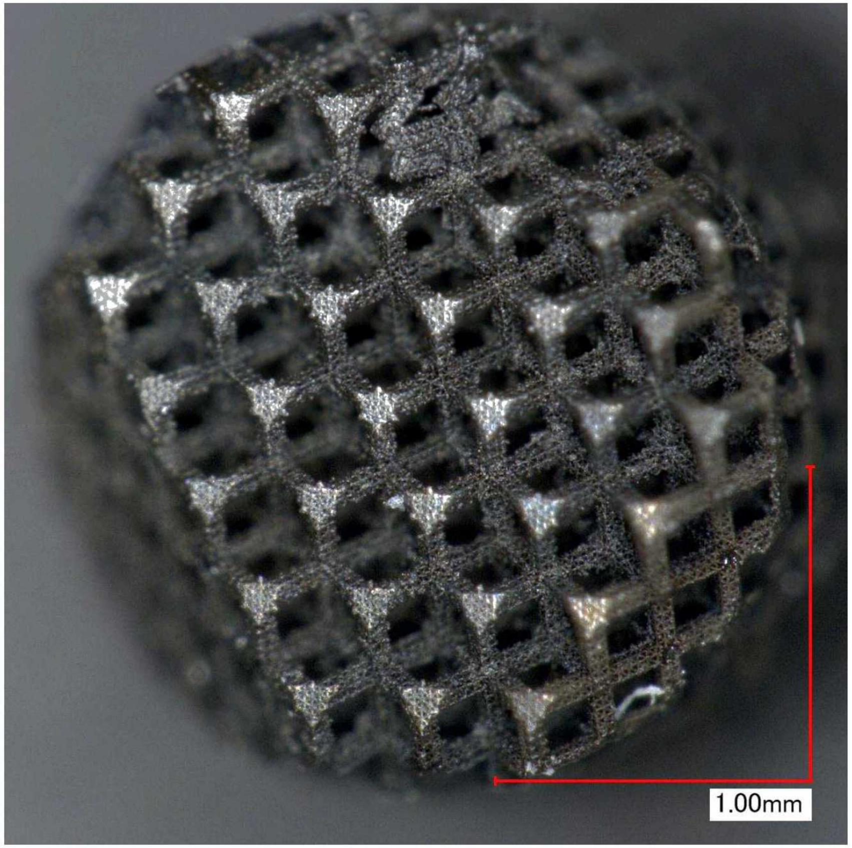
- Dave Robinson (PI)
- Maher Salloum (modeling)
- Bryan Kaehr (Nanoscribe)
- George Buffleben (flow tests)
- Ryan Nishimoto (electron microscopy)
- Bernice Mills (X-ray tomography)
- Chris Jones (metal deposition)
- Gail Garcia (electrochemistry)
- Victoria Lebegue (Ember printer)
- Aidan Higginbotham (Ember printer)
- Roopjote Atwal (Ember printer)

Nanoscribe optical images

With electroless layer



With nanoporous layer



Ember x-ray tomography

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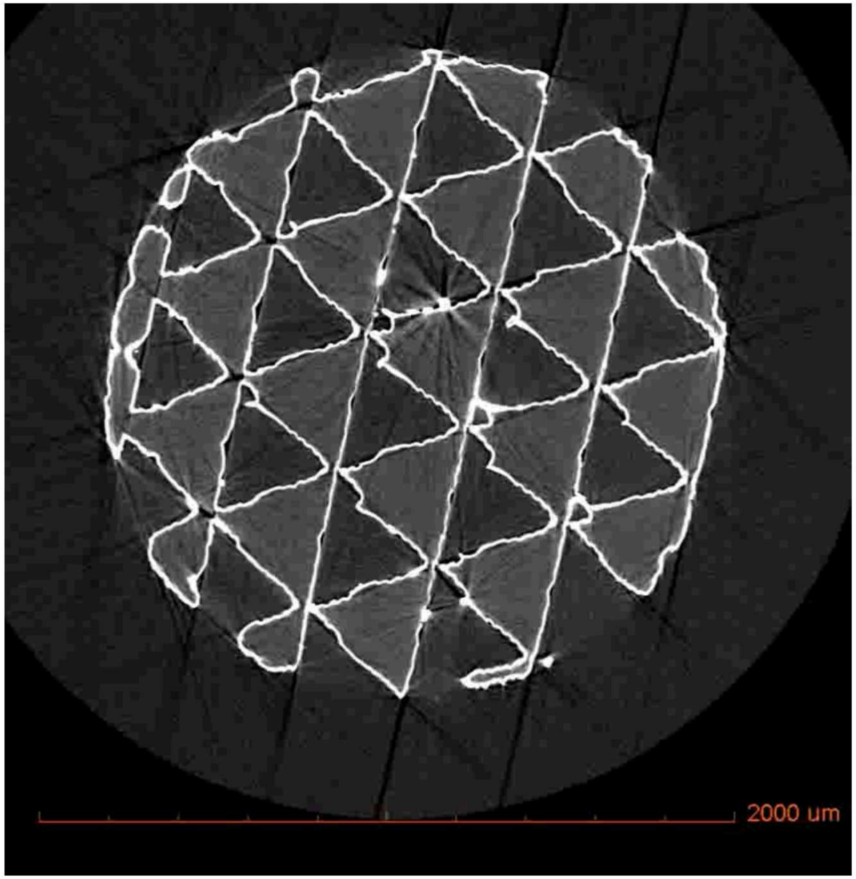

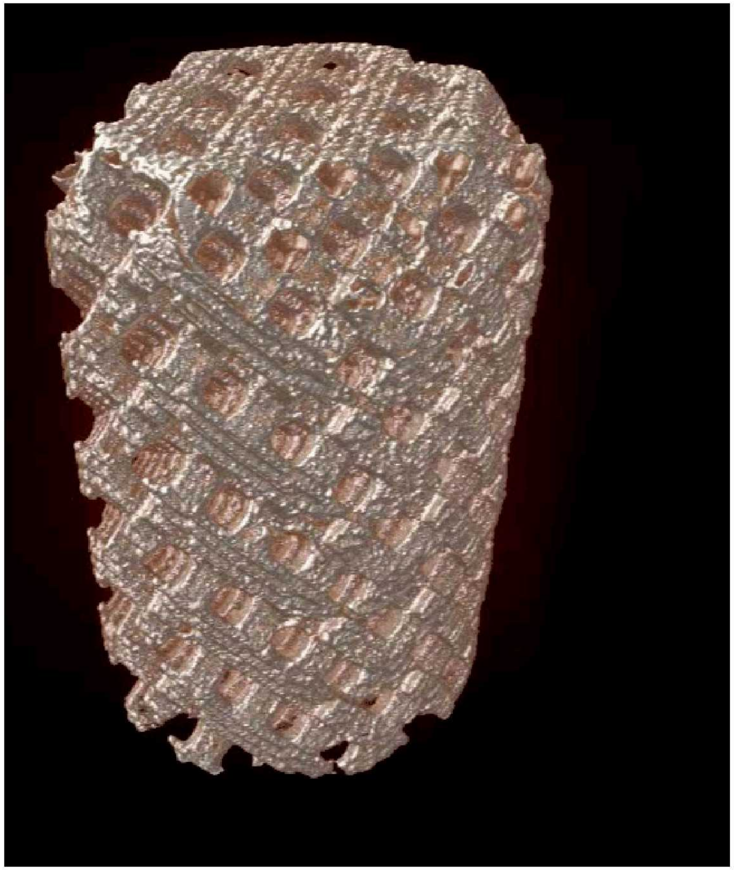

Software used

- Lattices and parts to STL: OpenSCAD*
- Voxel lattices, STL-voxel interconversion: GNU Octave*
- Routine STL to voxels: Autodesk Print Studio
- STL to toolpaths: Nanoscribe DeScribe
- STL checks: MeshLab*
- Modeling: COMSOL and Matlab
- STL imaging: Cravesoft STL viewer*
- PLY/OFF overhang removal: GNU Octave*

*open source