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Additive Manufacturing of Porous Materials

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3D Printing for Chemical Engineering

- Additive manufacturing can benefit more than just mechanical engineers.
- Chemical engineers often rely on randomly packed (or sintered) powders
  - Catalyst and separation columns
  - Battery and fuel cell electrodes
  - Filters and separator membranes
- Optimized geometries can yield major performance and efficiency improvements
  - Capillary gas chromatography
  - Microfluidic medical devices
  - “3D” batteries with microfabricated electrodes
- However, such improvements are not widespread because the appropriate fabrication techniques are not available in most situations.
- Our goal is to design, build, and test 3D-printed structures that demonstrate performance improvements for simple examples of chemical engineering devices.

Technology Gaps

- Limited access to the 1-100 μm length scale
  - Especially for inorganic materials
  - This length scale is needed for efficient fluid-solid contact
- Lack of parallelism in technologies that do exist
  - Tradeoff exists between part size and feature size
- Print time scaling:
  - Rastered laser or extruder: (part solid volume/voxel volume)^3
  - Projection: part height/layer height; area limits exist

Strategies

- Key technologies to overcome the gaps:
  - Photochemical methods that permit material deposition a plane at a time, with high-resolution optics
  - Chemical methods to deposit highly conformal layers of functional materials on photopolymer templates, with thickness comparable to feature size
  - Powerful computers and software for modeling and part design
  - Small-scale platforms for high-throughput characterization
  - Ongoing rapid advances in the scalability, resolution, and practicality of these methods
- As test cases, we are investigating:
  - 3D gas chromatography columns
  - 3D metal hydride battery and supercapacitor electrodes
  - 3D heat exchangers

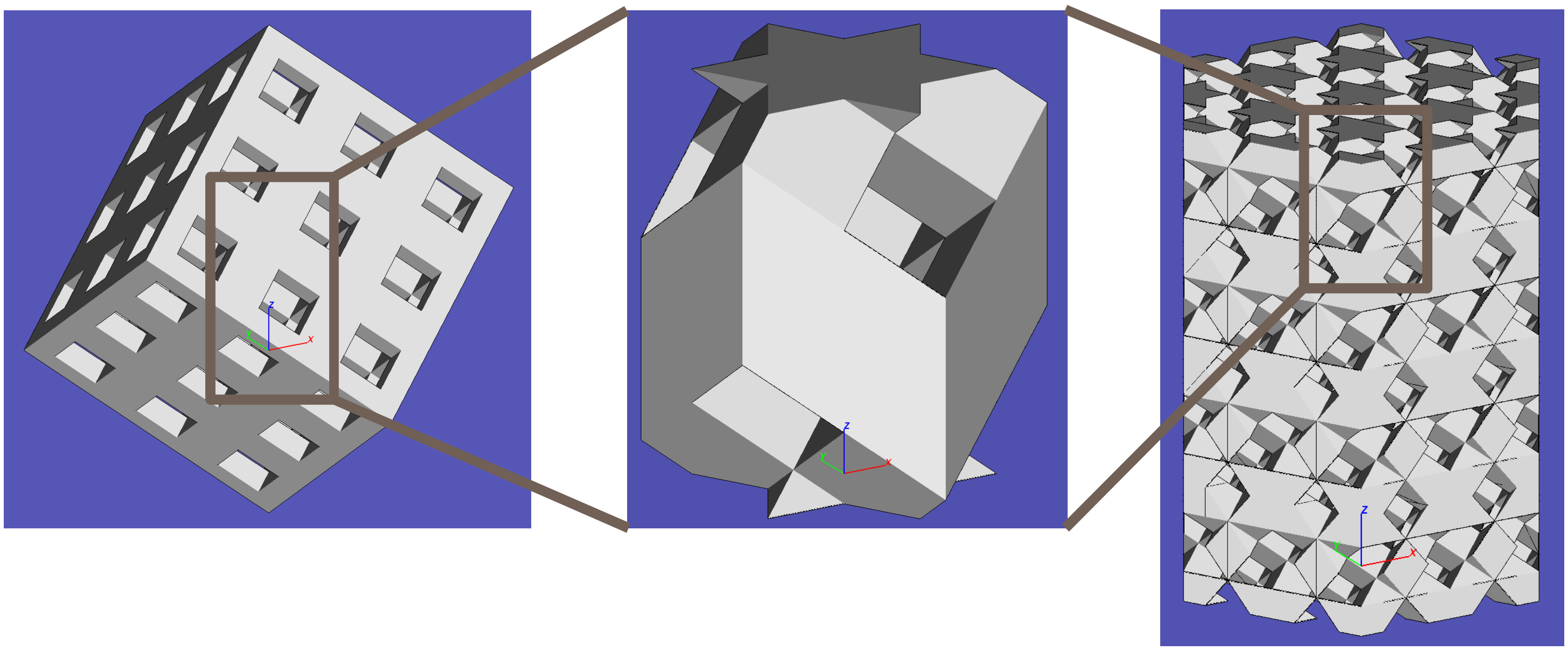
High-resolution 3D printers

- Nanoscribe
  - Rastered laser for two-photon polymerization
  - Sub-µm resolution
  - Requires days to print 1 mm cube
  - Sparse lattices can be much faster
  - $100k instrument, proprietary polymers and software
- Autodesk Ember
  - $7k projection microstereolithography, 50 µm pixels
  - Mostly open source polymers, software, and hardware
- Lawrence Livermore's large-area projection microstereolithography instruments
  - Resolution in low 10 µm range, prints cm^3 volumes in hours
  - Still undergoing instrument development

Autodesk Ember

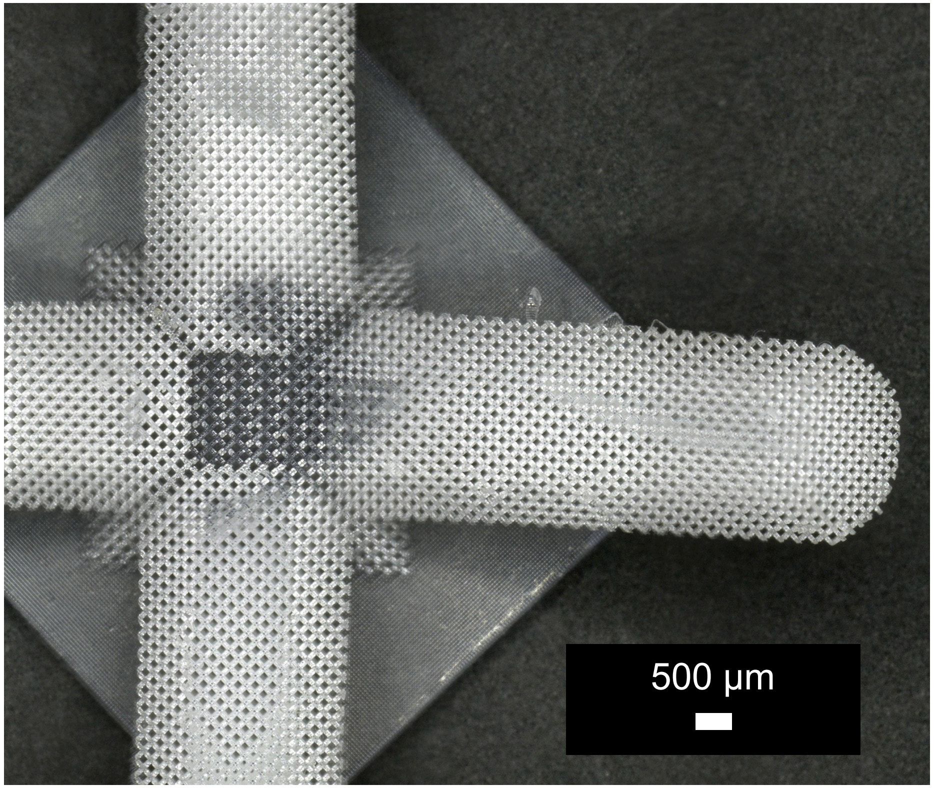
Lattice design

- 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



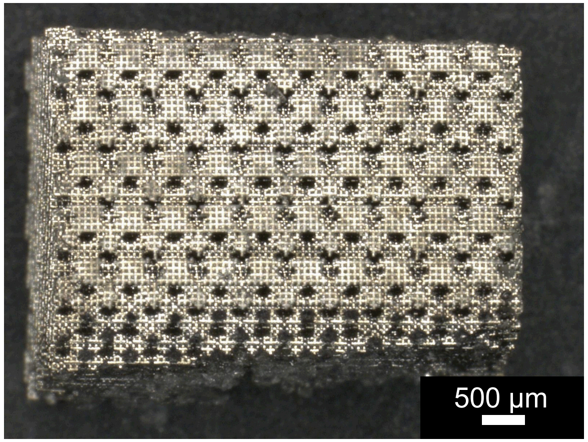
Ember lattice

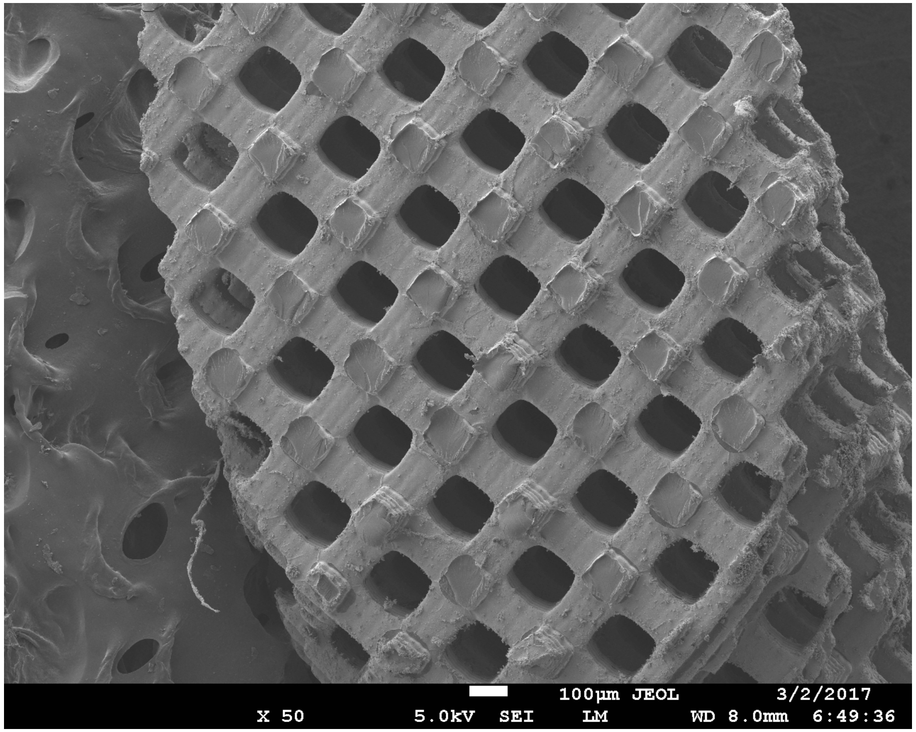
- This Ember part has 150 µm pores. The part is grown at an angle so that the cube-edge lattice is aligned with the growth direction, allowing full use of the printer's resolution.

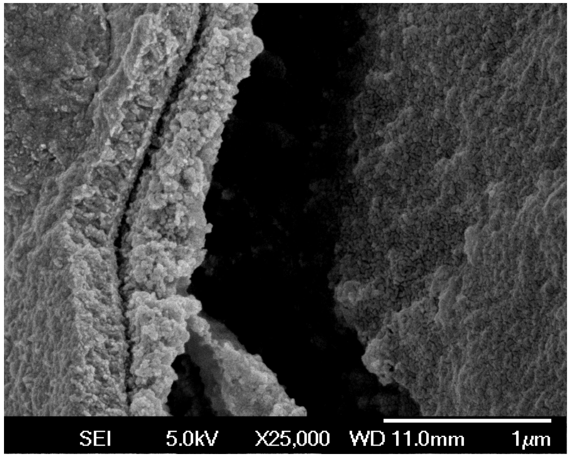


Metal coating of Ember part

- 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.
- Figures show some of each.

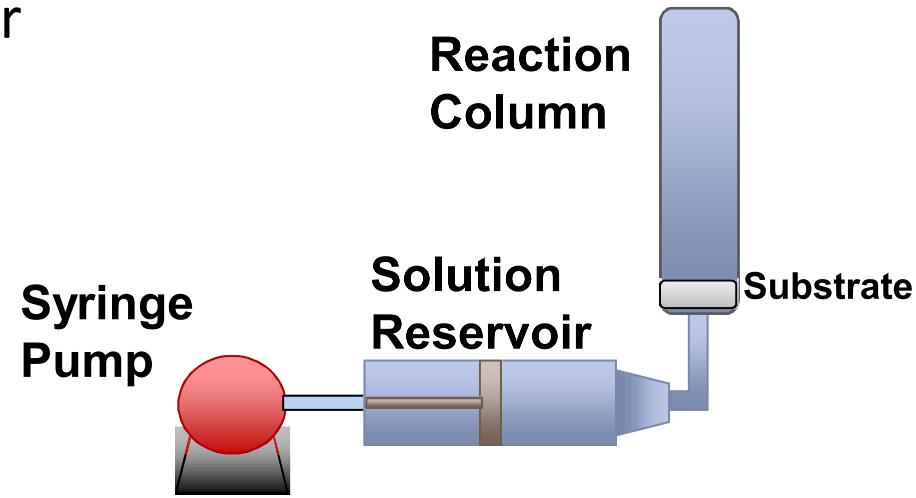




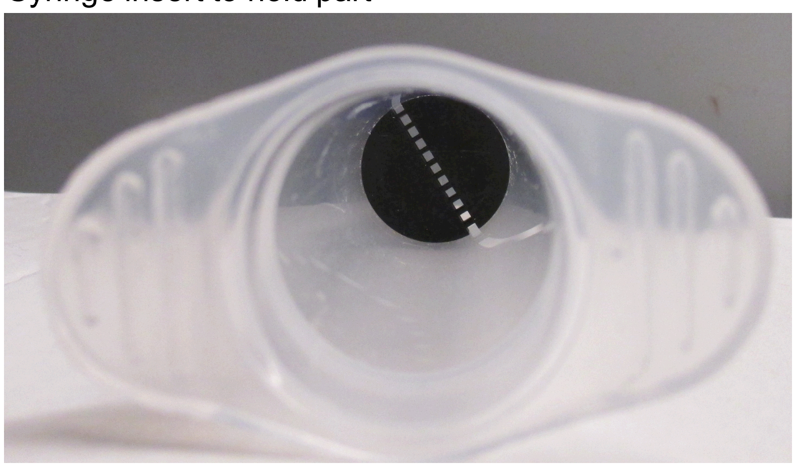


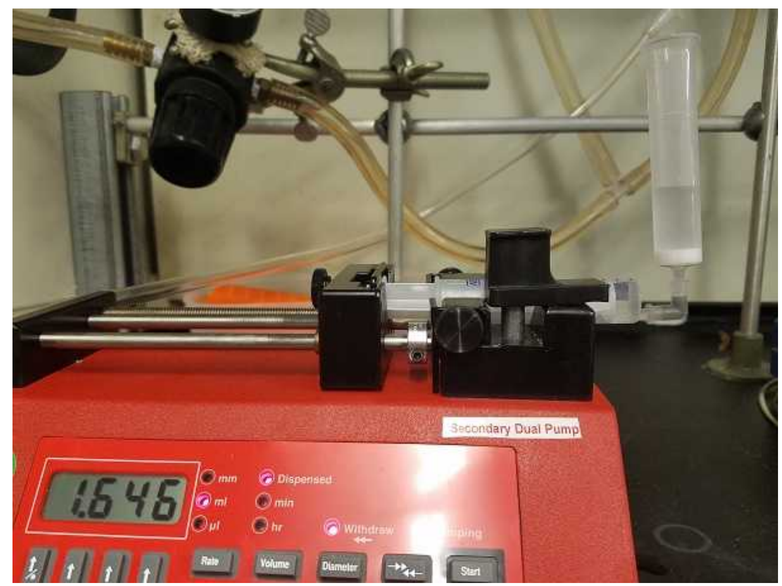
Conformality requires convection

- Not enough material in pores for thick coating
- Diffusion into pores is slow
- Option 1: rapid stirring
- Option 2: flow cell
- Hierarchical pores aid flow
- Flow through shortest dimension



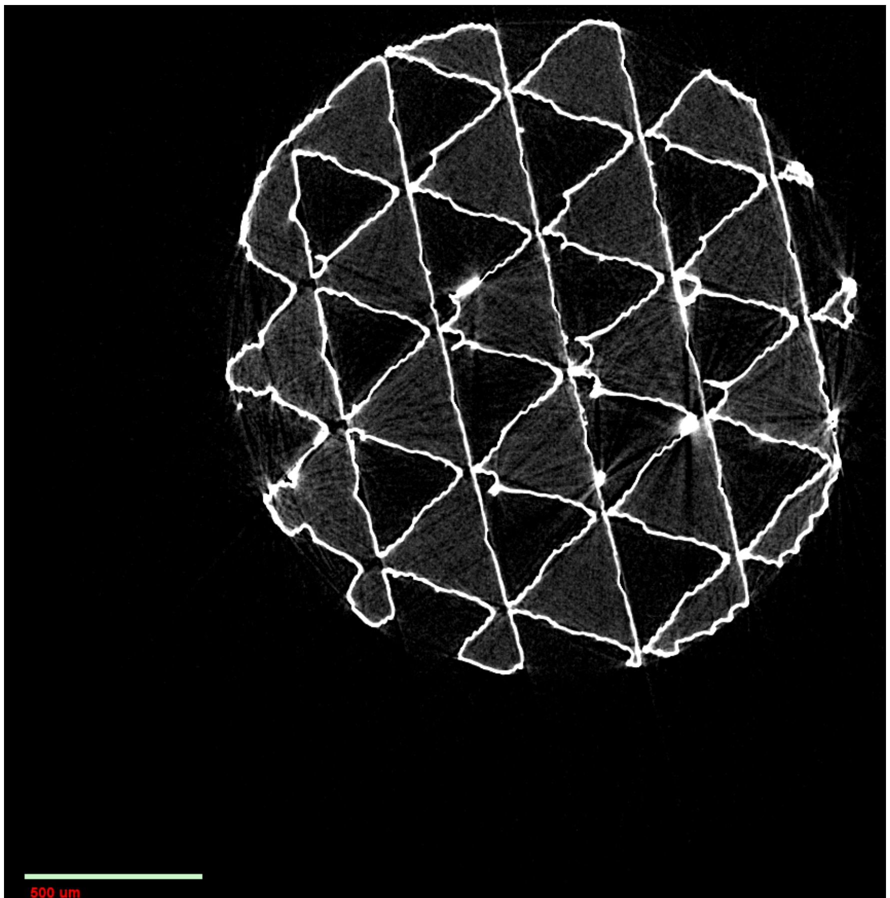
Syringe insert to hold part

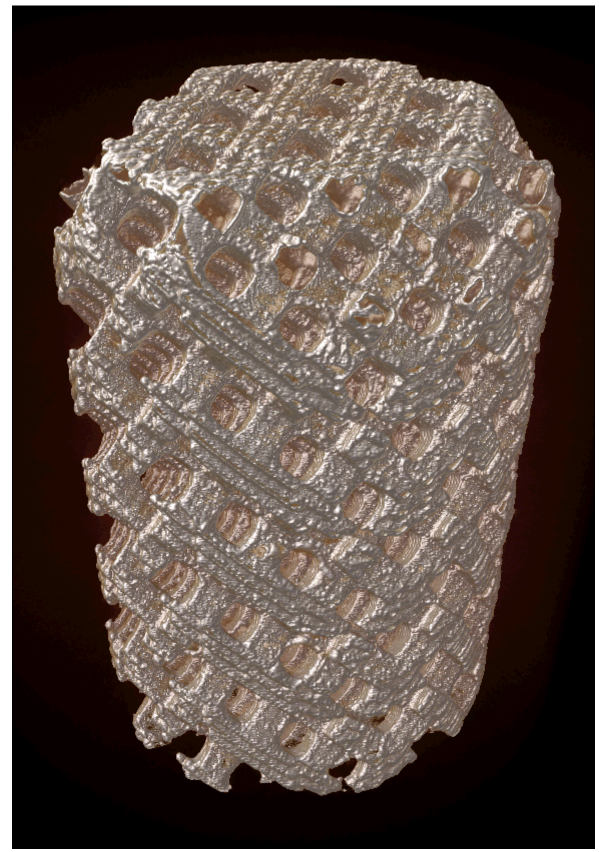




Ember x-ray tomography

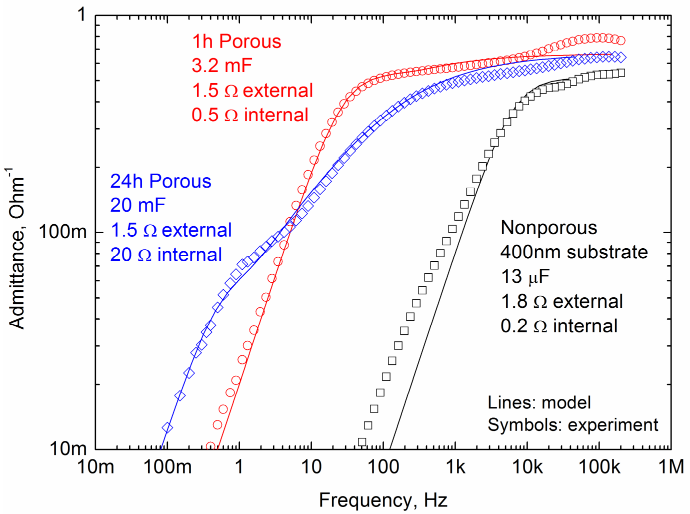
- X-ray tomography has confirmed that the electroless deposition method evenly coats the part interior.

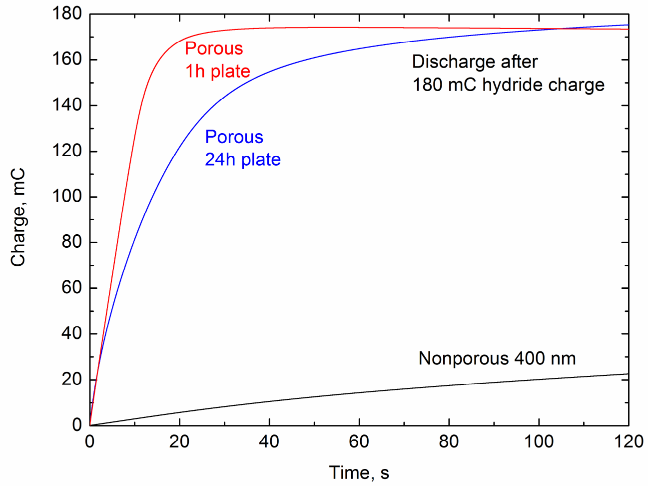


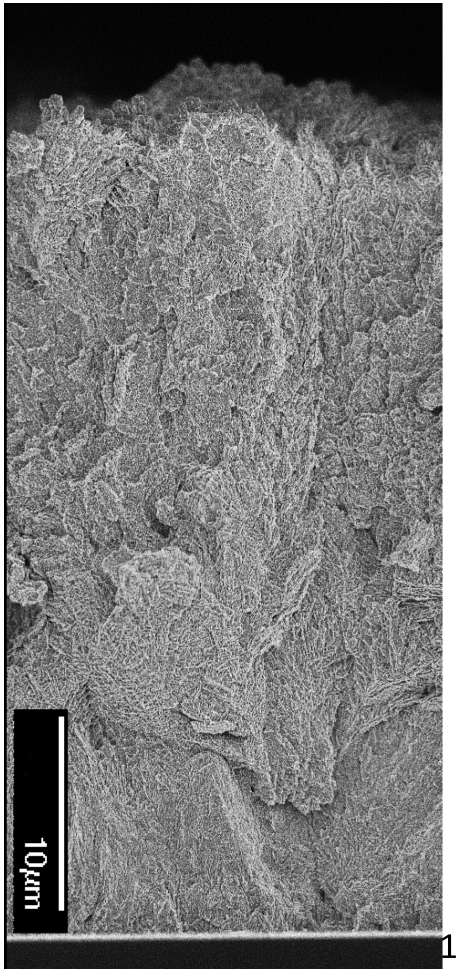


Electrodeposition of thick nanoporous Pd

- We electrodeposit 10 µm scale Pd films with 10 nm scale pores using block copolymer pore template
- Pd stores charge at surface (as a capacitor) and in the bulk (as a metal hydride battery).
- Nanopores increase capacitance, hydriding rate
- Results shown for 8mm diameter planar films
- Gives multiscale porosity in printed parts

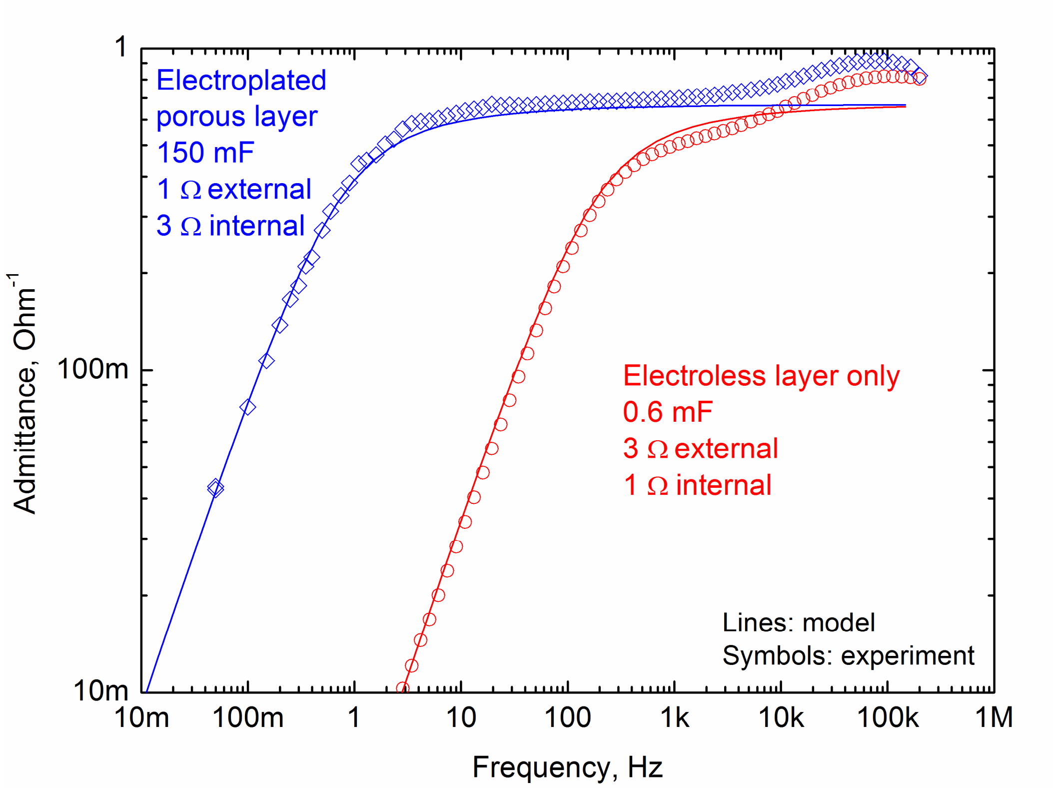






Ember part as capacitor

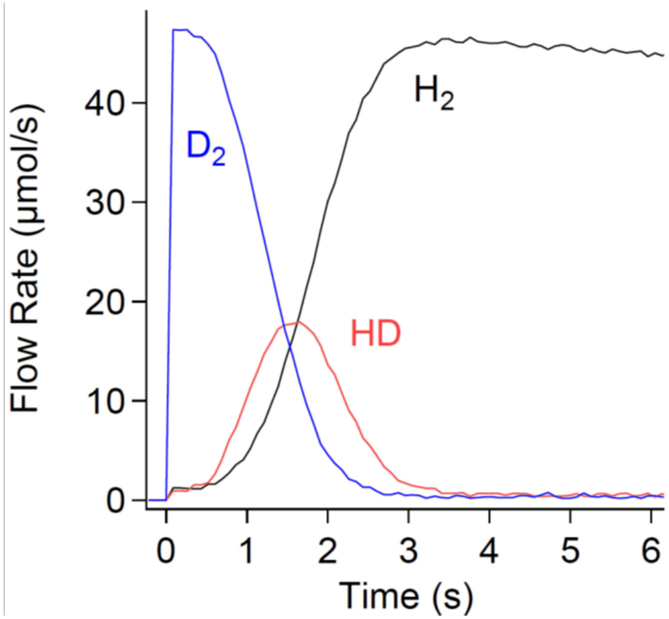
- Porous film was electrodeposited on electroless layer with pulse deposition and stirring.
- 2mm dia x 20mm long cylinder, 0.15mm pores
- 10 µm layer thickness estimated from this
- mm-scale porosity increases surface area 5x



Gas isotopic displacement column

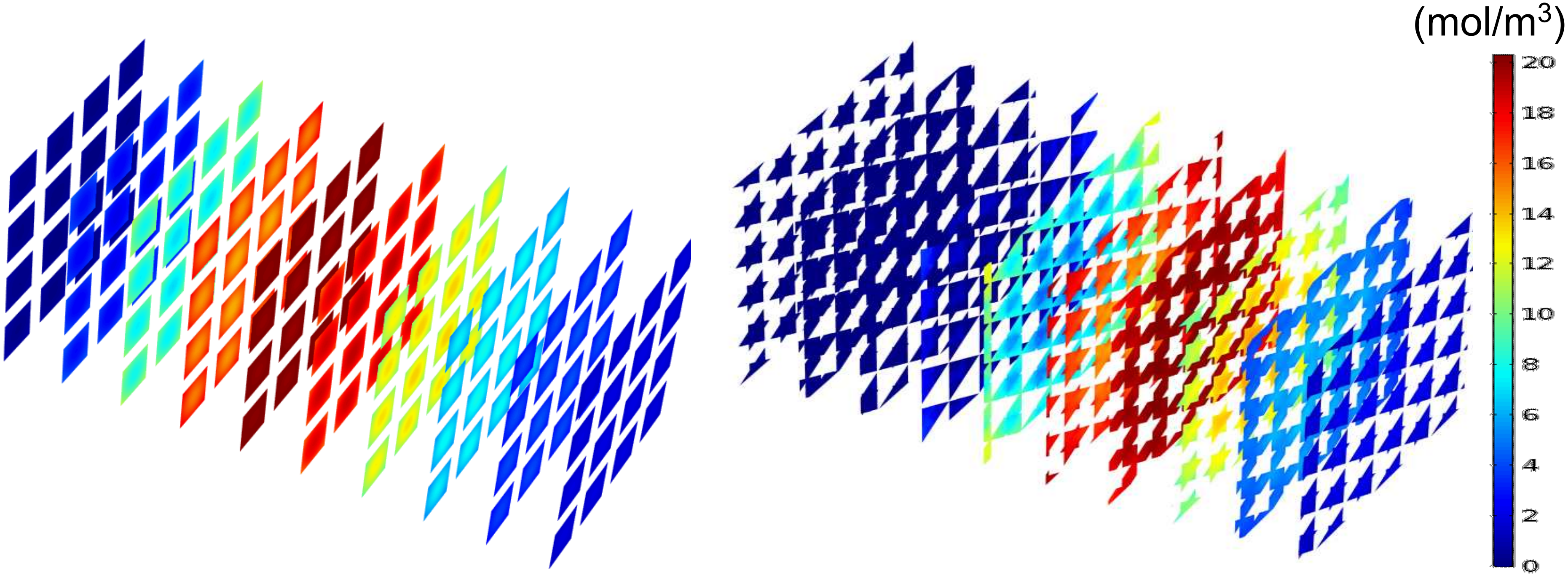
- Faster timescale than electrochemical dehydriding
  - No rearrangement of Pd atoms
- $H_2 + PdD_{0.6} \text{ -> } D_2 + PdH_{0.6}$
- Second-order kinetics: sharp composition boundary
- Elute with H_2, measure eluate with mass spectrometer
- HD peak width indicates broadening mechanisms
  - Reaction kinetics
  - Gas-phase axial, radial diffusion
  - Solid-phase diffusion
- Peak width is comparable to elution time
- 9.9 mg Pd on column

H_2 →  → D_2



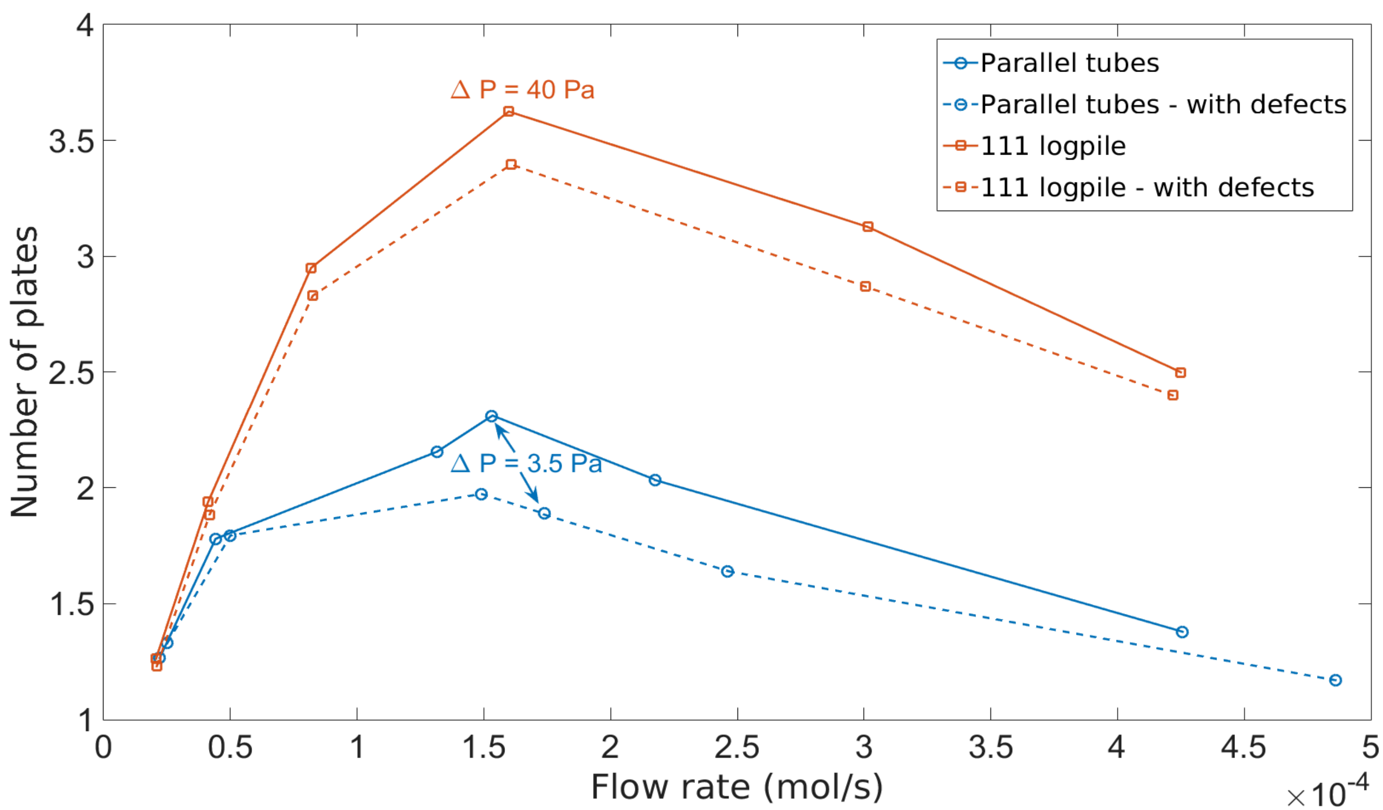
Flow modeling

- A reactive flow COMSOL model predicts improved performance for 3D vs. 1D structures, including defect tolerance.
- This plot shows sharper HD peak for the 3D structure (right) vs. an array of straight channels (left).



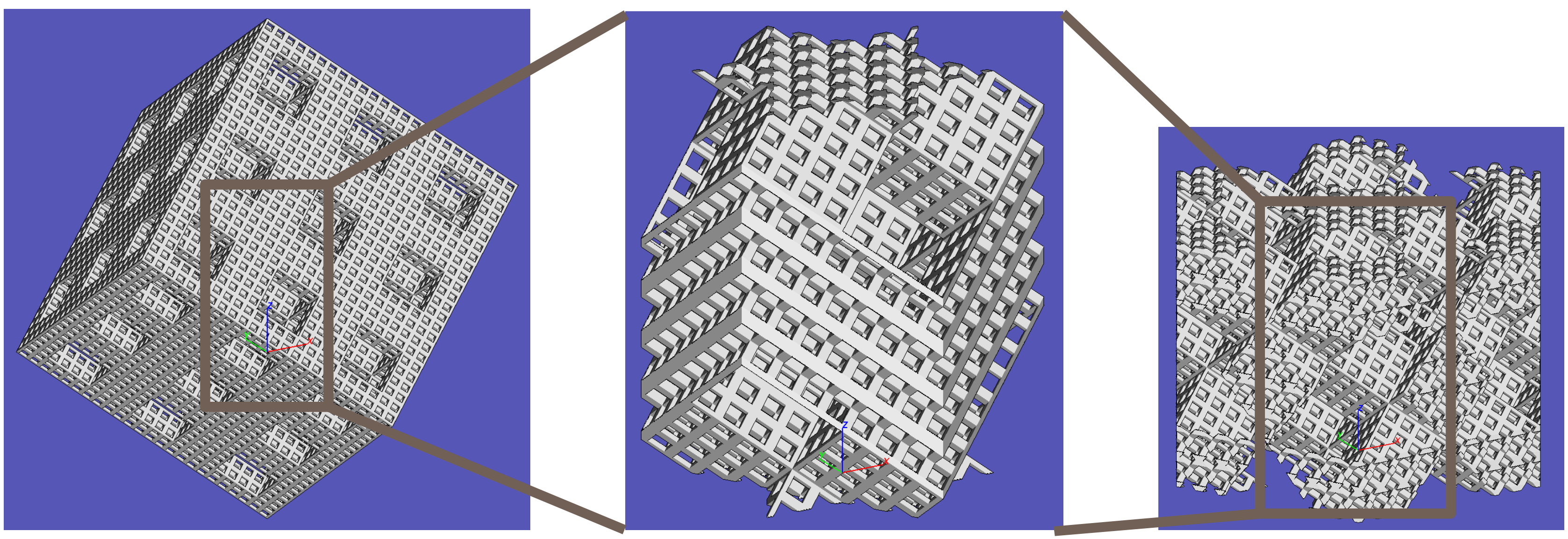
Flow modeling

- “Plates” (column length/HD peak width) quantifies performance vs. pressure, structure.
- 3D structure outperforms 1D, even with defects present.



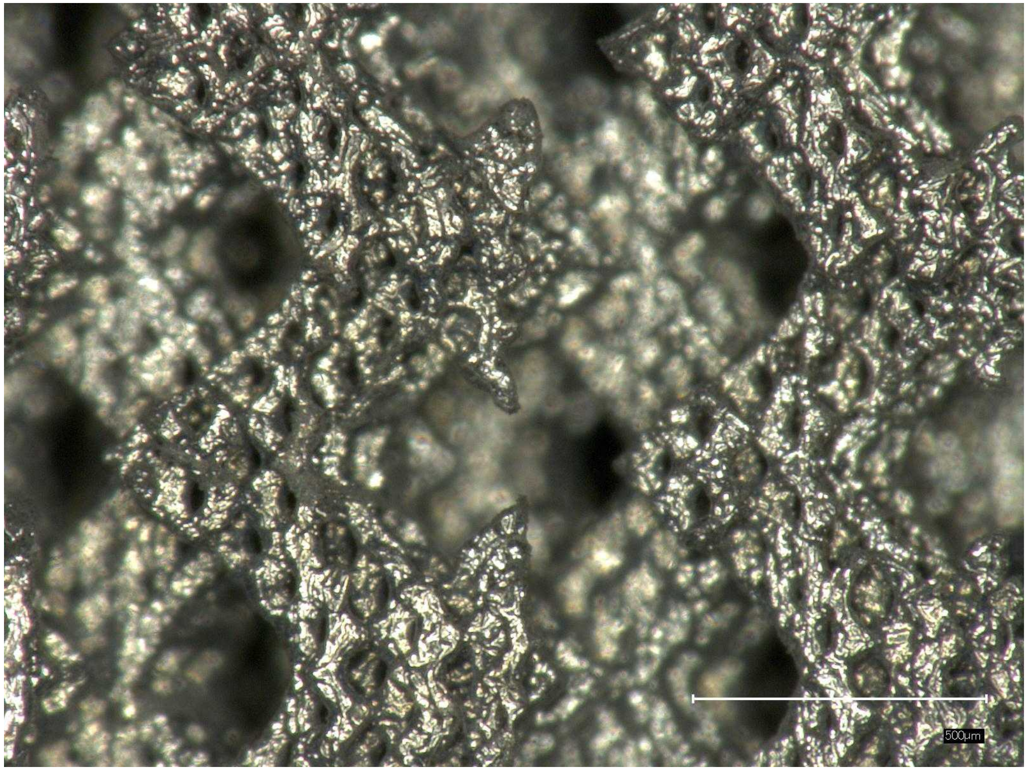
Hierarchical lattices

- Can finer porosity be 3D printed?
- For example, a finer lattice is also a cube-edge lattice oriented along the cube space diagonal.
- The 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



Hierarchical LLNL part

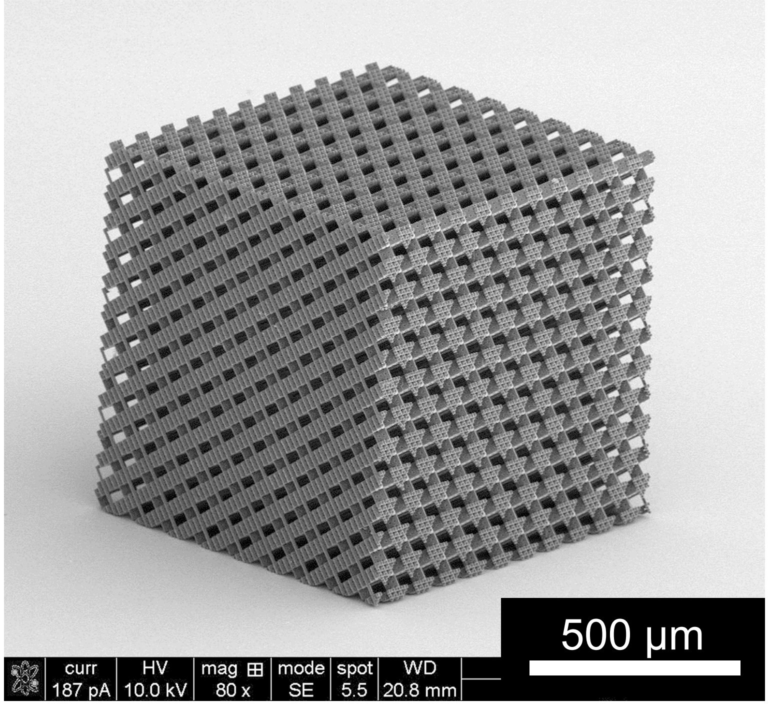
- We have received a test part from LLNL with 50 µm pores.
- Despite having 50 µm projector pixels, the Ember must cure a larger polymer volume to ensure part cohesion.
- We have coated the LLNL part with Pd.

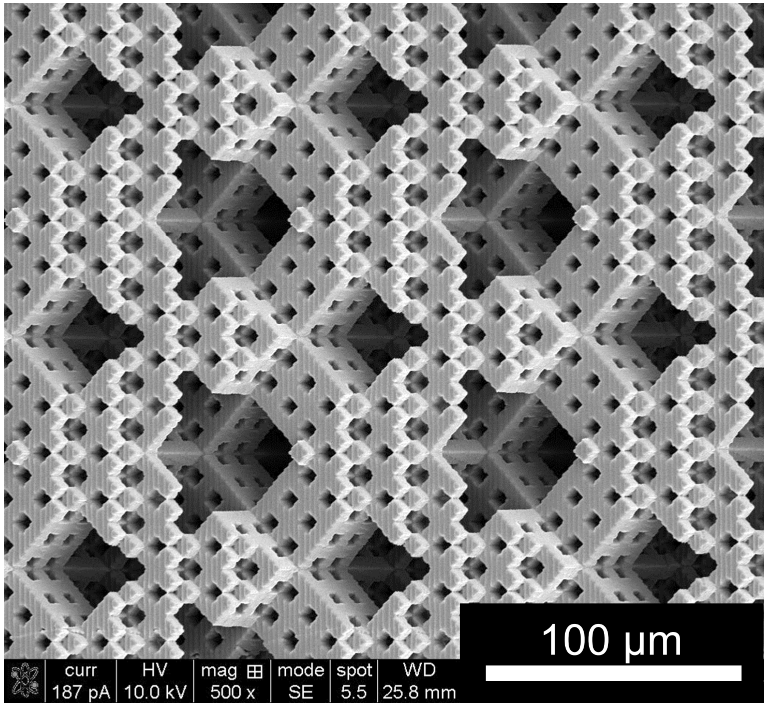


500 µm scale bar

Hierarchical Nanoscribe lattice

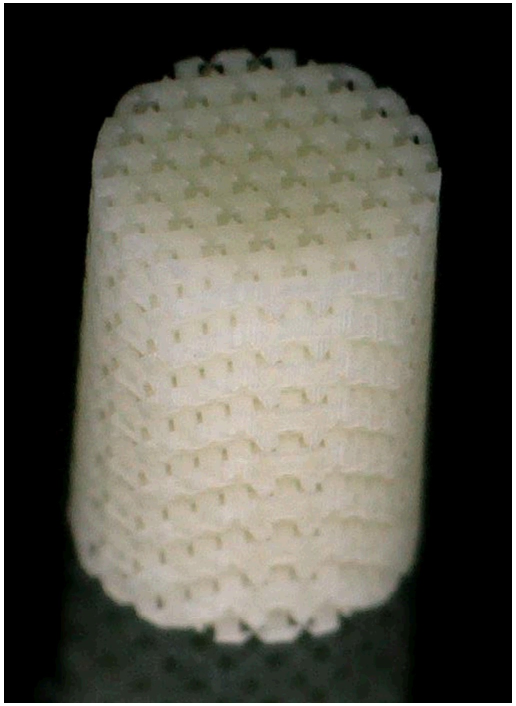
- The Nanoscribe can create a sublattice with 8 μm pores, but this 0.5 mm cube required more than a day to print.

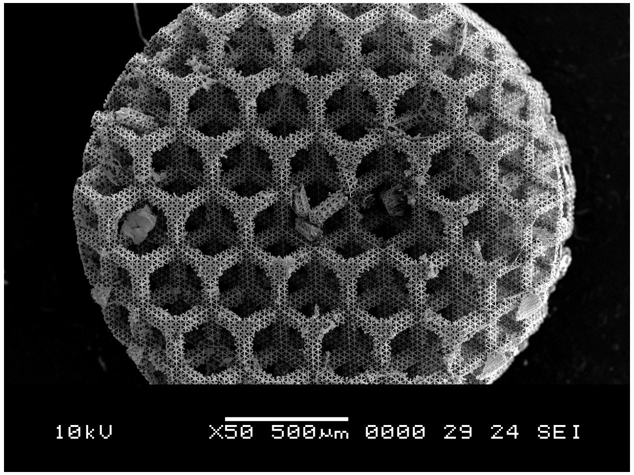


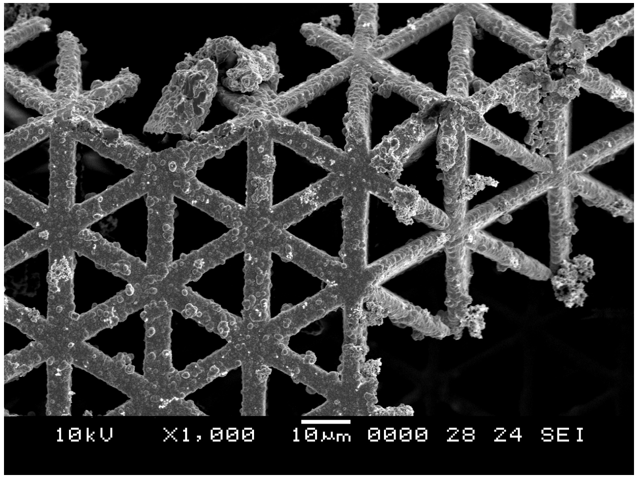


Sparse Nanoscribe sublattice

- We have designed a sparser sublattice that can print as a 2 mm diameter, 2.8 mm tall cylinder in about 12 hours.
- Left image is the polymer structure in an optical microscope. Other images are electroless Pd-coated parts in the electron microscope.



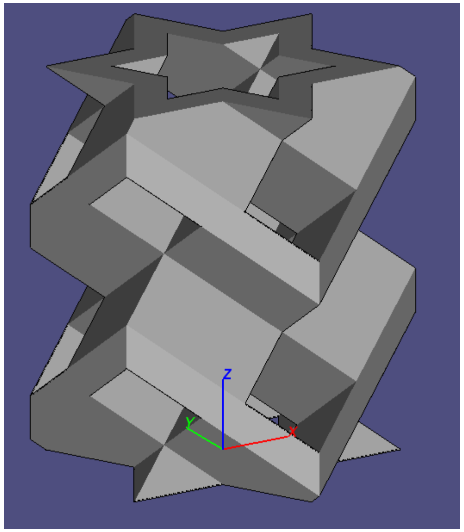


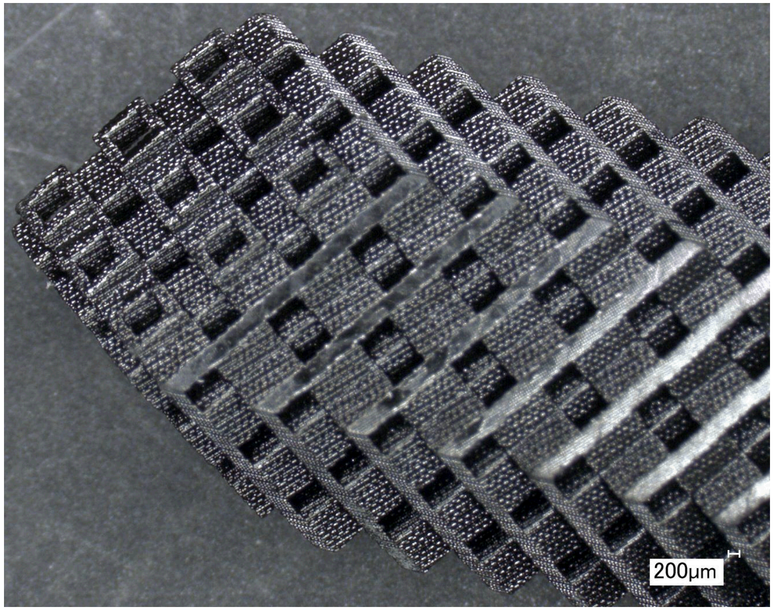


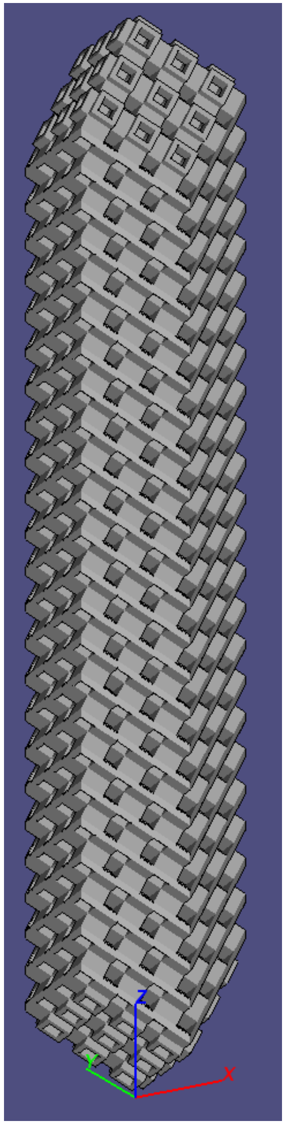
These parts can be stacked for flow testing.

Bicontinuous lattices

- Hollow out solid phase to create non-mixing second fluid phase
- Heat or chemical species could be made to cross the boundary
- Permits design of heat exchangers and filters





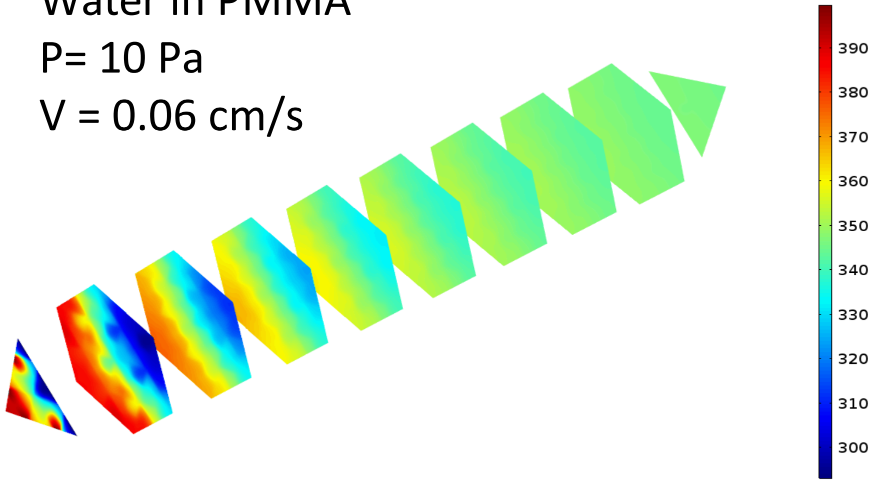


Heat exchange modeling

- We use a COMSOL model to evaluate whether our geometry results in an efficient heat exchanger even though most 3D printing materials have poor thermal conductivity.
- Co-current flow is best test of this. Apparently the answer can be yes, depending on flow rates and geometry details.

Air in Stainless steel
P= 10 Pa
V = 0.03 m/s

Water in PMMA
P= 10 Pa
V = 0.06 cm/s



Temperature,°C

Conclusions and next steps

Conclusions:

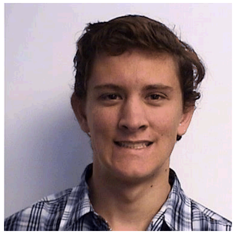
- Projection stereolithography and similar photopolymerization techniques can efficiently print macroscopic parts with features on the 10-100 μm scale.
- Polymer parts can be uniformly metallized.
- Models predict improved performance and defect tolerance for 3D versus 1D structures.
- Gas flow and electrochemical tests show consistency with models.

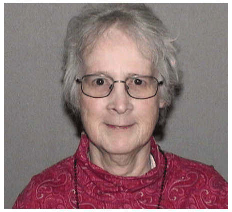
Next steps:

- Gas flow tests on hierarchical 3D-printed parts
- We are working to increase Pd layer thickness.
- We are funded through September.
- We are seeking sponsors for further development of this and similar technologies for high-resolution 3D printing for chemical engineering applications.

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)
- Joshua Deotte (LLNL printers)





Software used

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

*open source