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Electrodeposition and Stacking to form 3D Hierarchically Porous Structures

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NNSA National Nuclear Security Administration

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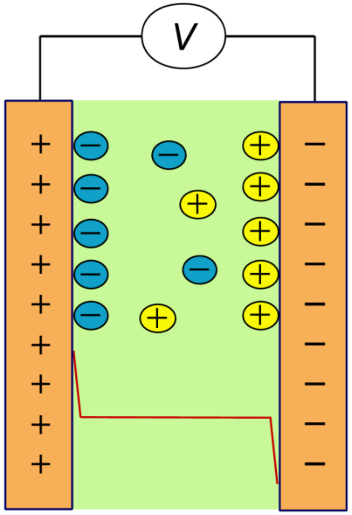
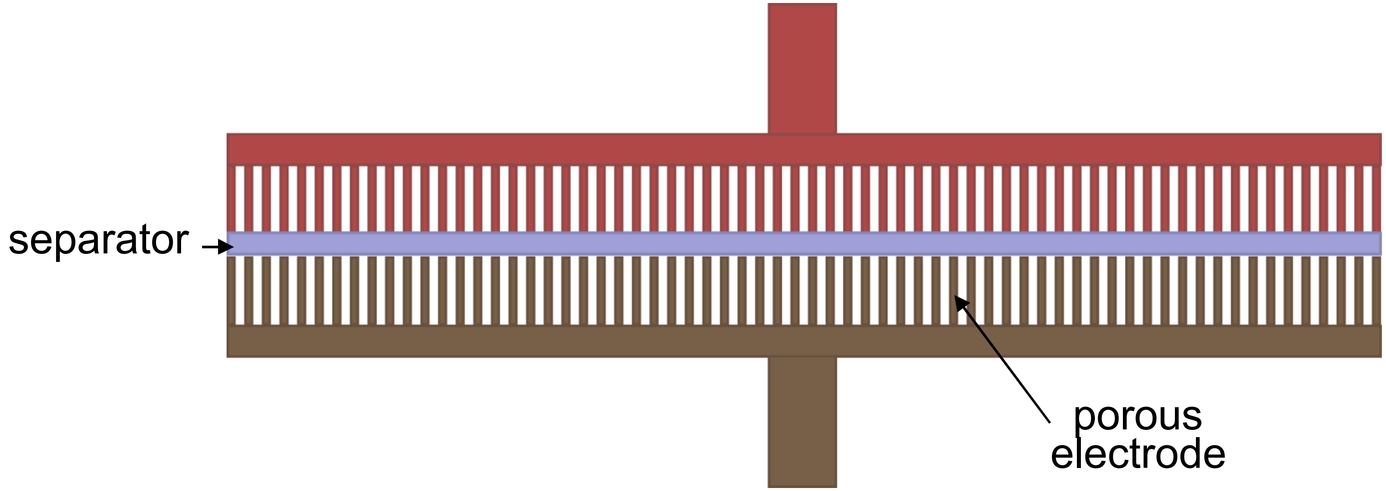
Porous materials for energy storage

- Battery electrodes
- Supercapacitors
- Hydrogen storage, fuel cells
- Needed: energy density, power density

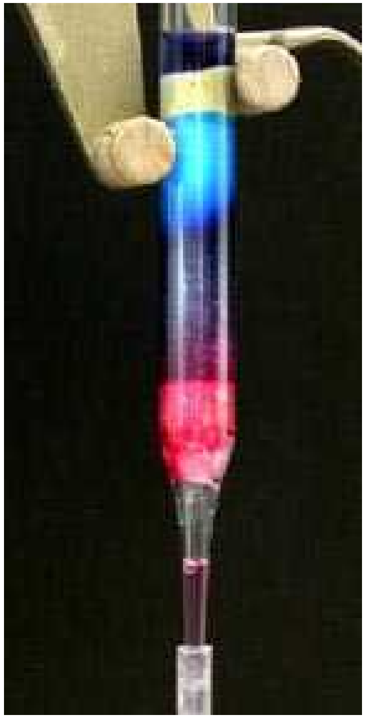




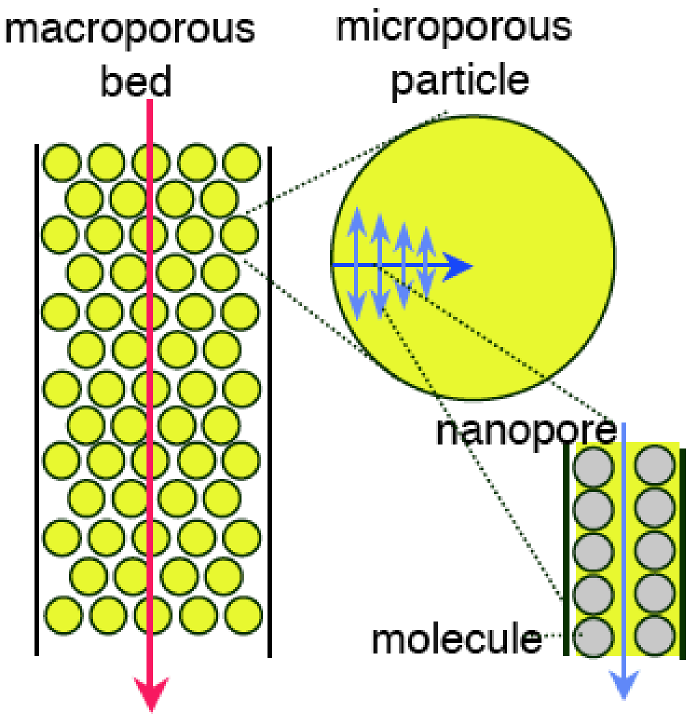
Robinson, DB. (2010). Optimization of power and energy densities in supercapacitors. Journal of Power Sources 195:3748.

Porous materials for chemical separations

- Chromatography columns
- Needed: narrow bands, faster band velocity, selectivity, shorter column, low flow resistance

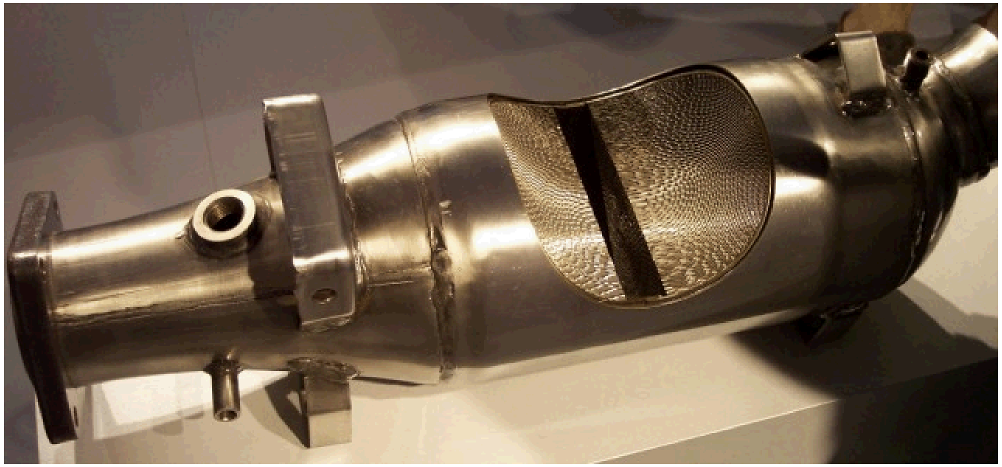


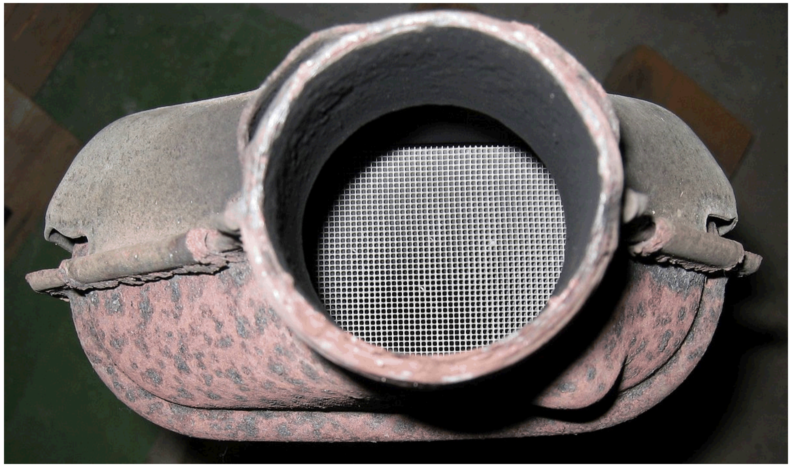
dynamicadsorbents.com



Porous materials for catalyzed chemical reactions

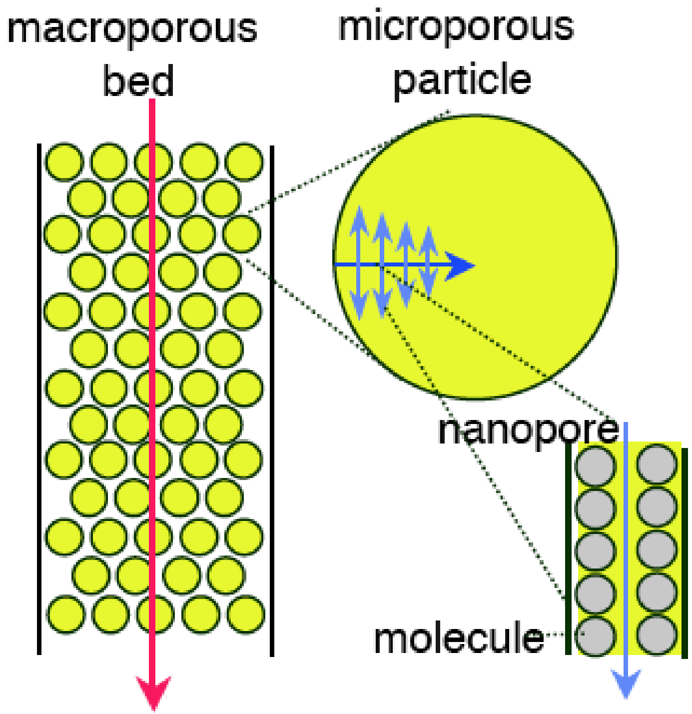
- Automotive catalytic converters, industrial flow reactors
- Needed: low flow resistance, thermal stability, optimized catalyst loading





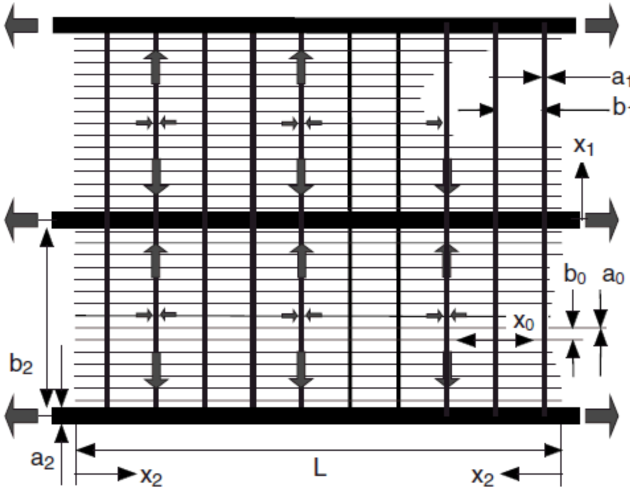
Physics and scaling

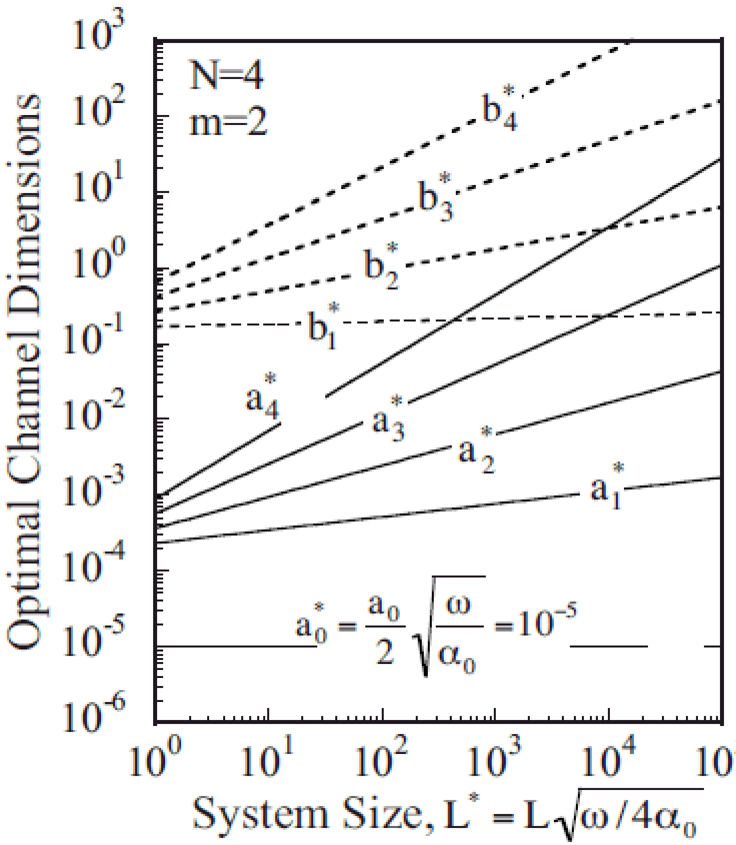
- Fluid flow
- Ion migration
- Fluid-phase diffusion
- Interfacial reactions
- Solid-phase diffusion
- Nonlinear aspects



Optimizing channel geometry

- Aperture and spacing of transport channels increase with normalized system size and frequency
  - power law scaling arises from variation of bulk pore diffusivity with channel aperture
- Impedance is comparable in each level of optimized hierarchy





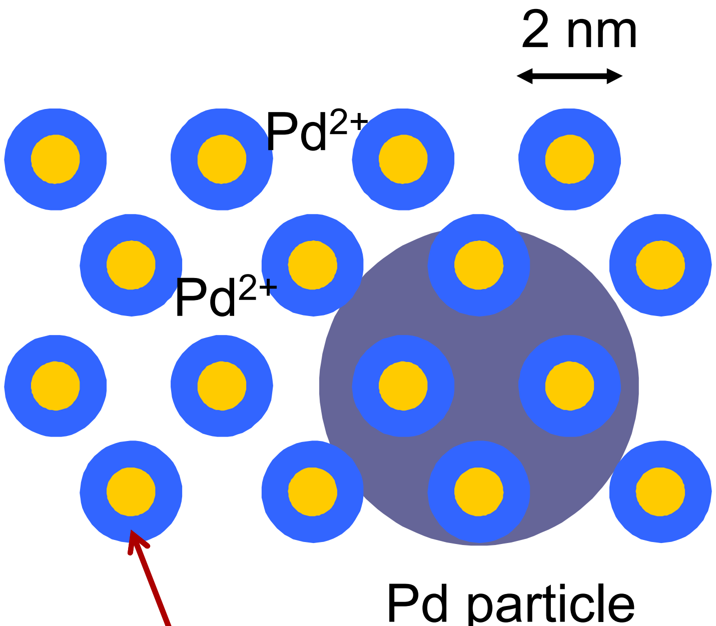
Bob Nilson and Stewart Griffiths
Phys Rev E 79 036304 (2009)
Phys Rev E 80 016310 (2009)

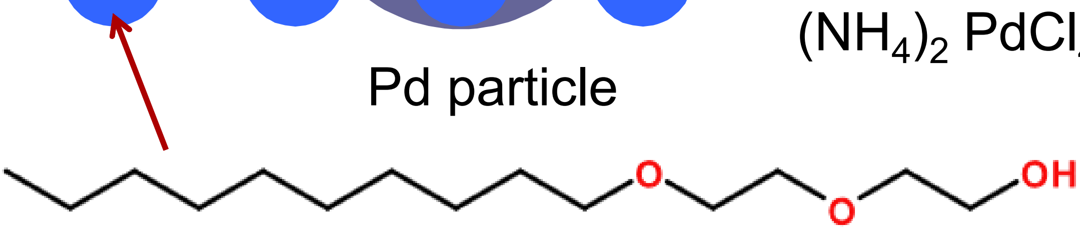
Design questions

- What is the optimal pore architecture to achieve design goals? (energy density, power density, etc.)

- What can actually be built?
  - Electrodeposition of block copolymer-templated nanoporous metals
  - 50 µm scale woven wire mesh substrates
  - Photoresist-patterned substrates
  - Stacked 3D structures
  - 3D printed structures

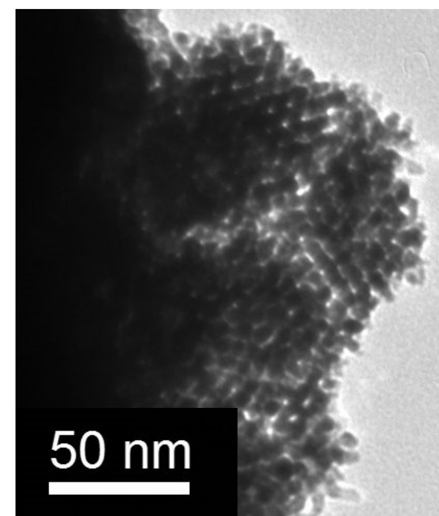
Synthesis of nanoscale pores





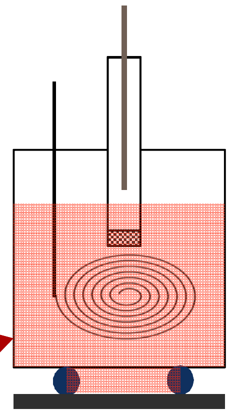
$(NH_4)_2\,PdCl_4 + H_2 \rightarrow Pd + 2\,NH_4Cl + 2HCl$

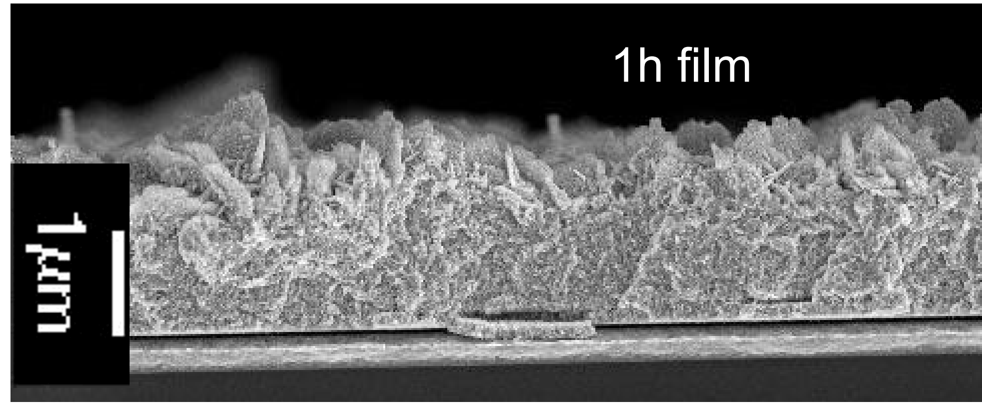
- Robinson et al.,
  Int. J. Hydrogen Energy 35 5423 (2010)
- Particles grow around surfactant phase
- Pd and PdRh alloys
- Prior work: Attard et al., Science 278 838 (1997)



Electrodeposition: Wafer cell

Double junction Ag/AgCl reference electrode
Coiled Pd wire counter electrode





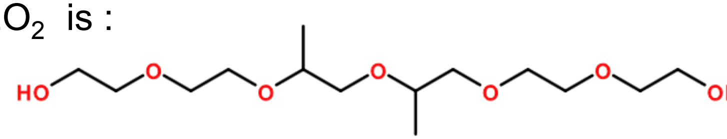
400nm sputtered Pd on Si wafer
10nm Ti adhesion layer
Surface area: $0.4 cm^2$

- Dilute micelles adsorb during plating
- Eliminates slow, messy pastes, gels
- Pores less ordered
- Prior work with Pt:
  Wang et al., Chem. Mater. 24 1591 (2012)

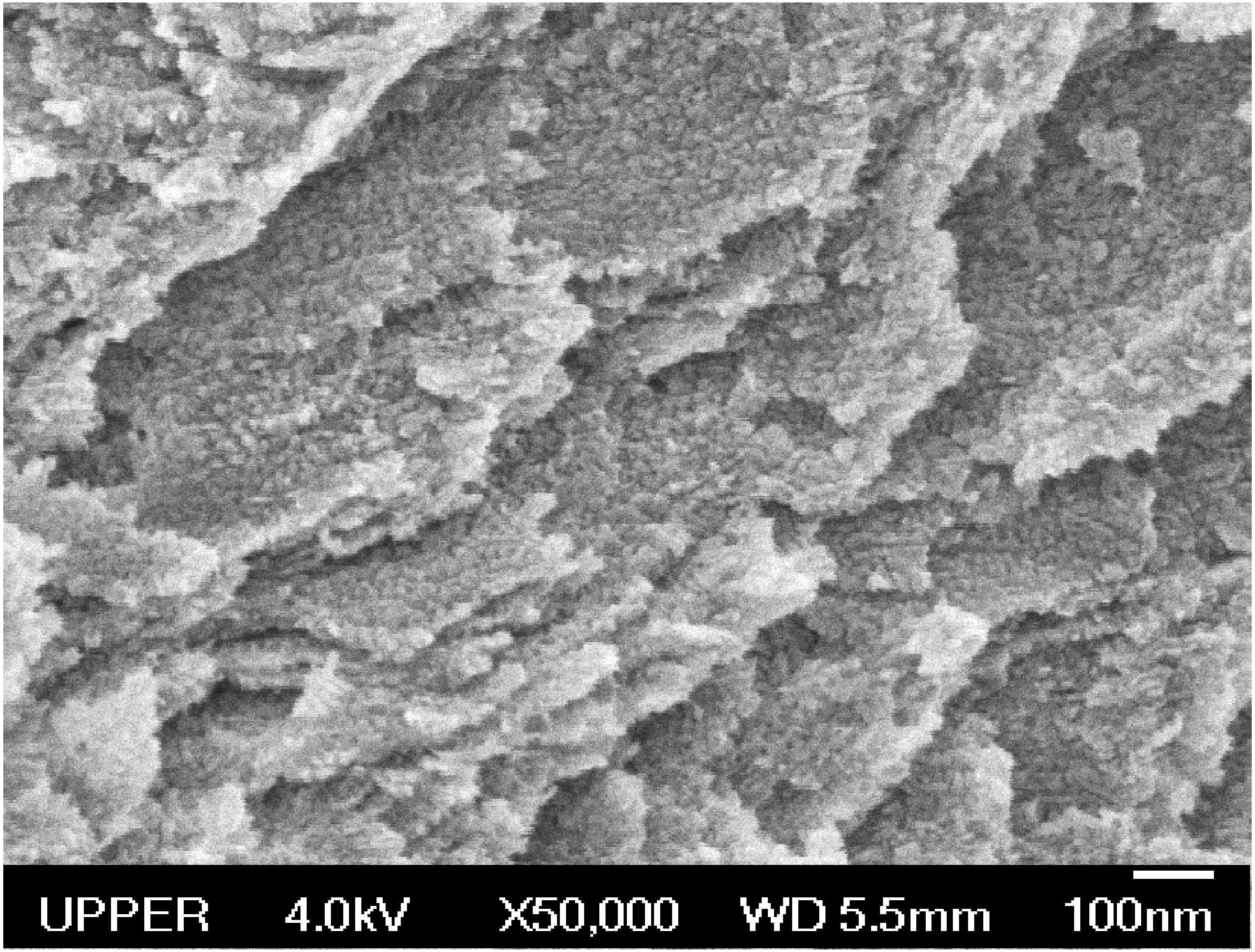
plating solution:
200µl 0.25M-1M Na_2PdCl_4
200µl 1m HCl
200µl 10% F127

Plate at -0.4 to -1 mA 1-24 hours

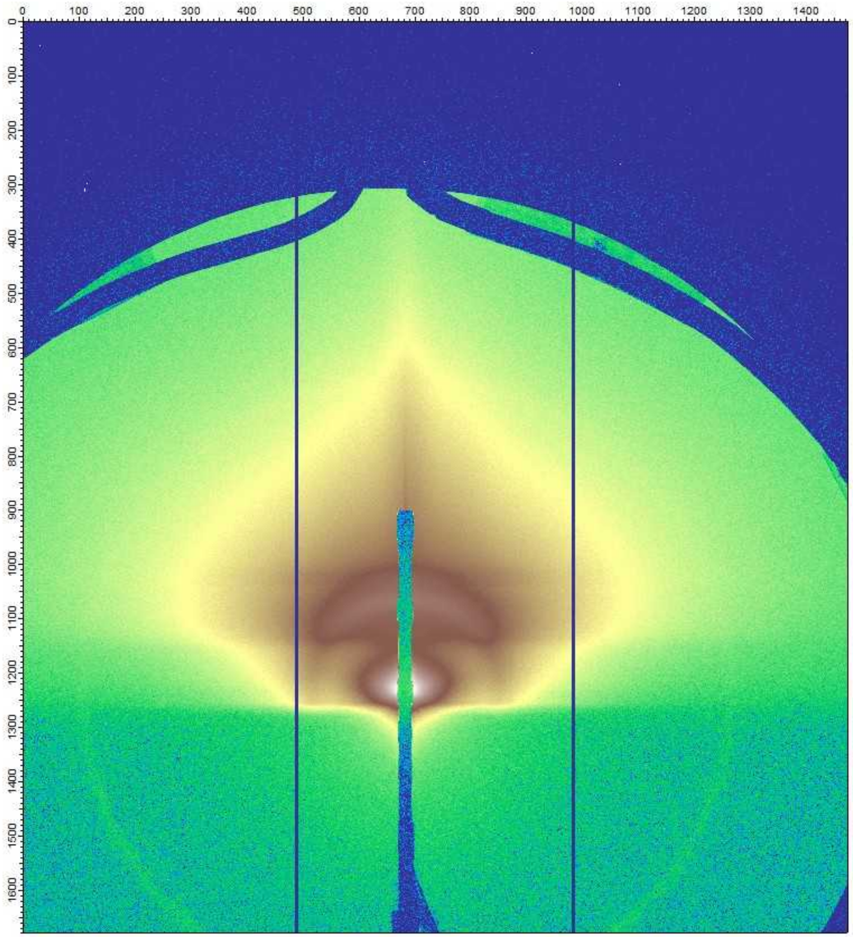
Pluronic F127 is EO_{101} PO_{56} EO_{101}
$EO_2PO_2EO_2$ is :



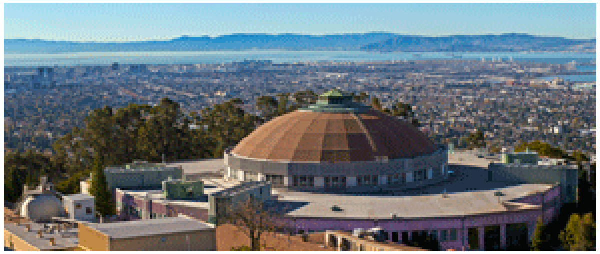
SEM cross section shows nanoporosity



Small-angle X-ray scattering



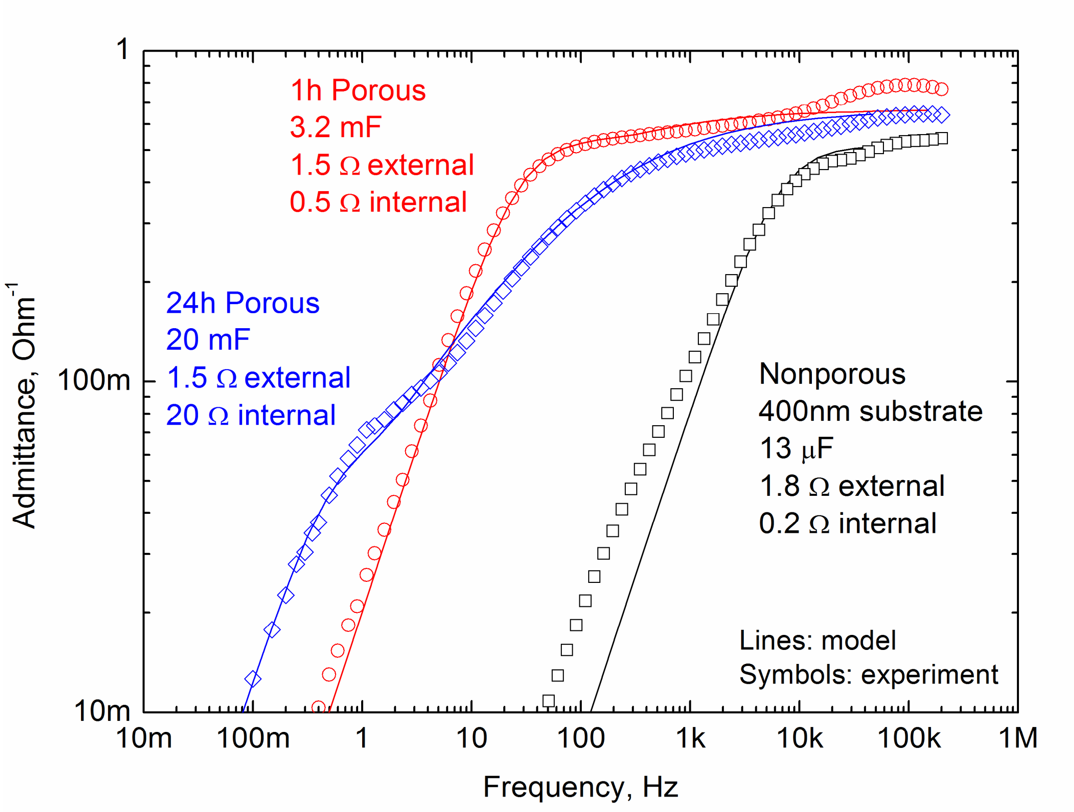
- Ring indicates presence of bulk porosity
- Crescent indicates pore orientation
- Advanced Light Source beamline 7.3.3
- Grazing incidence



The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

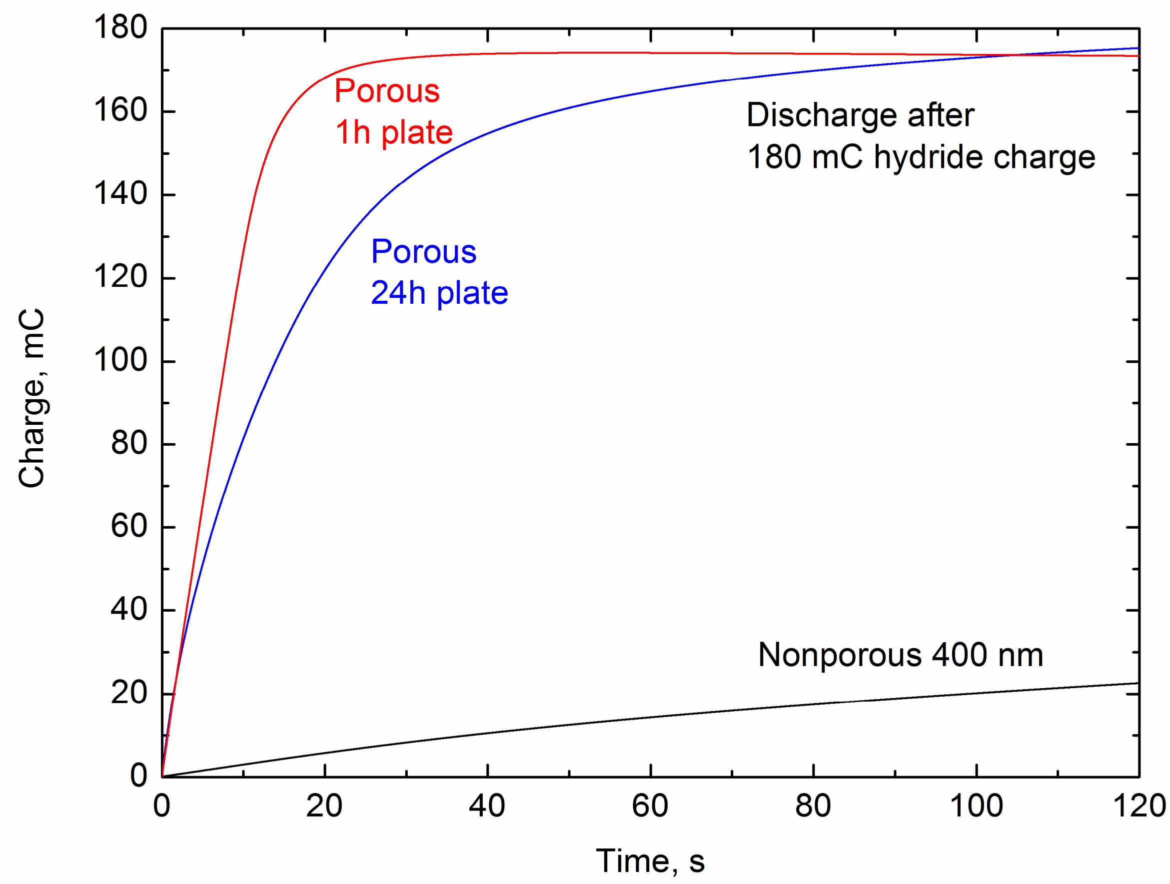
Electrochemical admittance

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

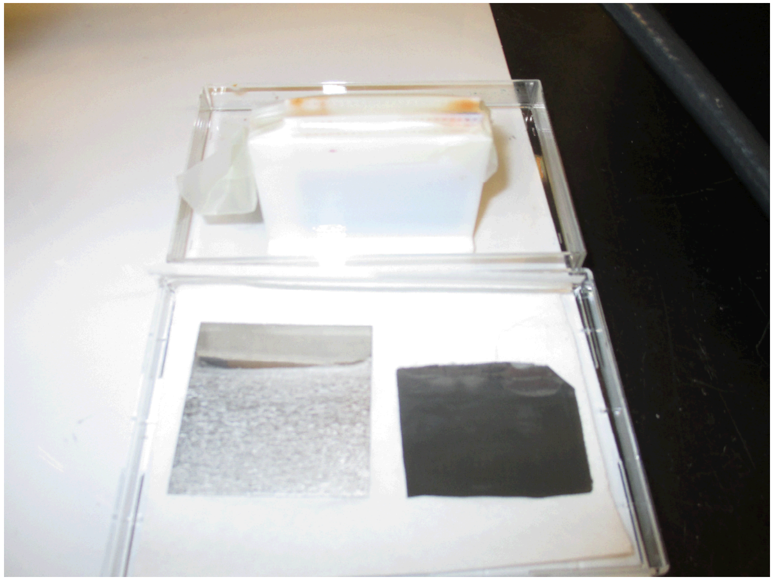


Electrochemical hydriding rates

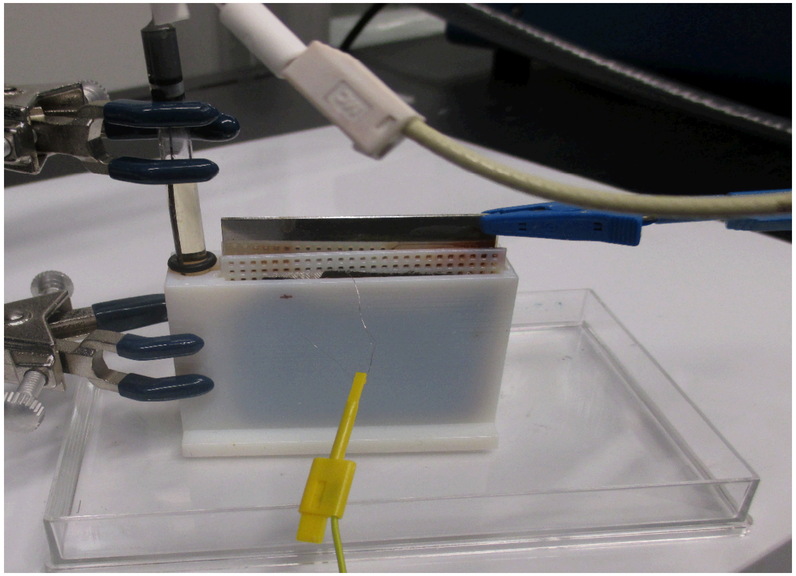
- Apply negative current for fixed time: $Pd + H^{+} + e^{-} \longrightarrow PdH$
- Then step to positive potential, observe reverse reaction

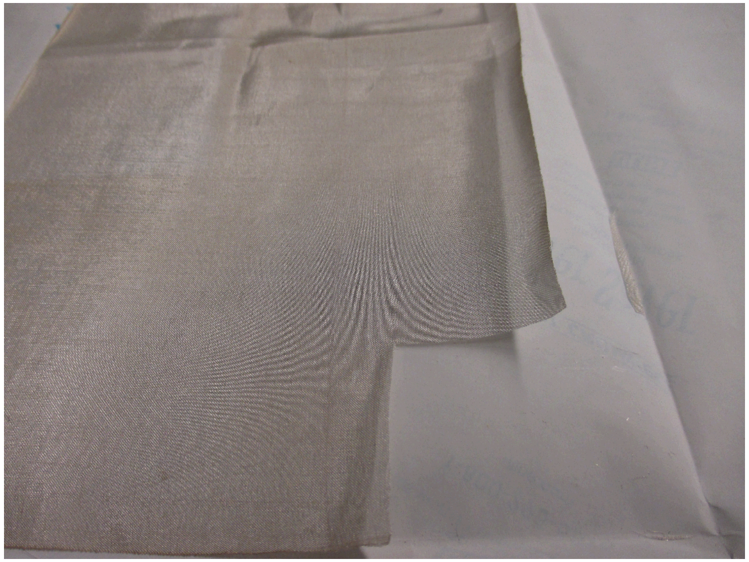


Mesh plating for pore hierarchy

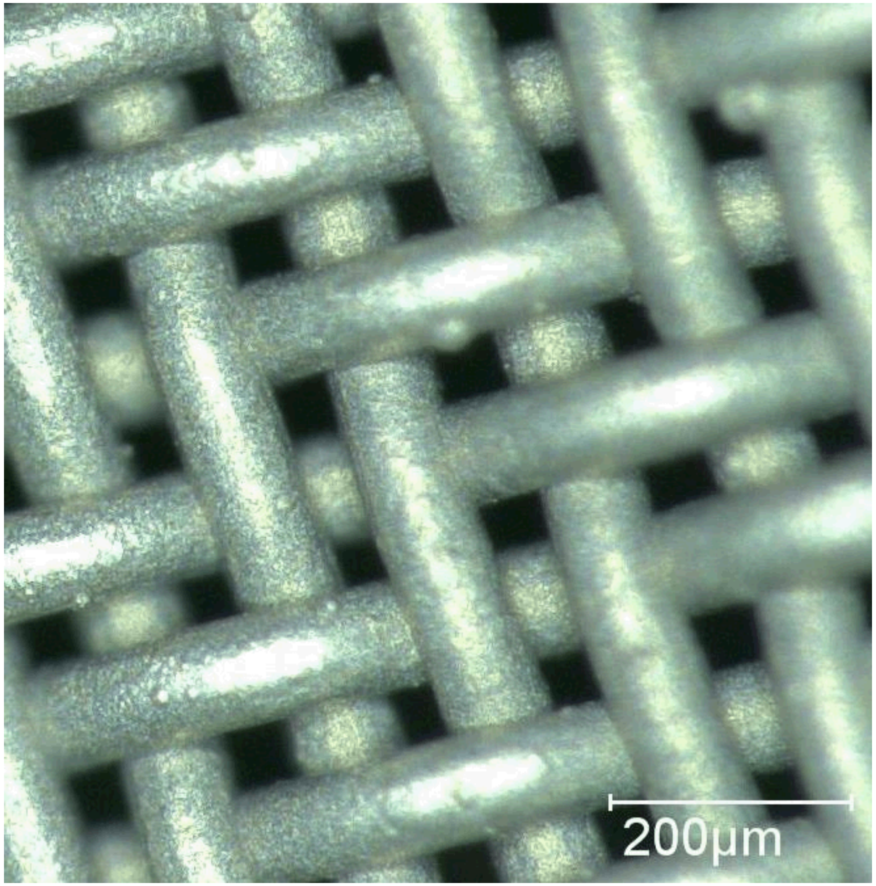


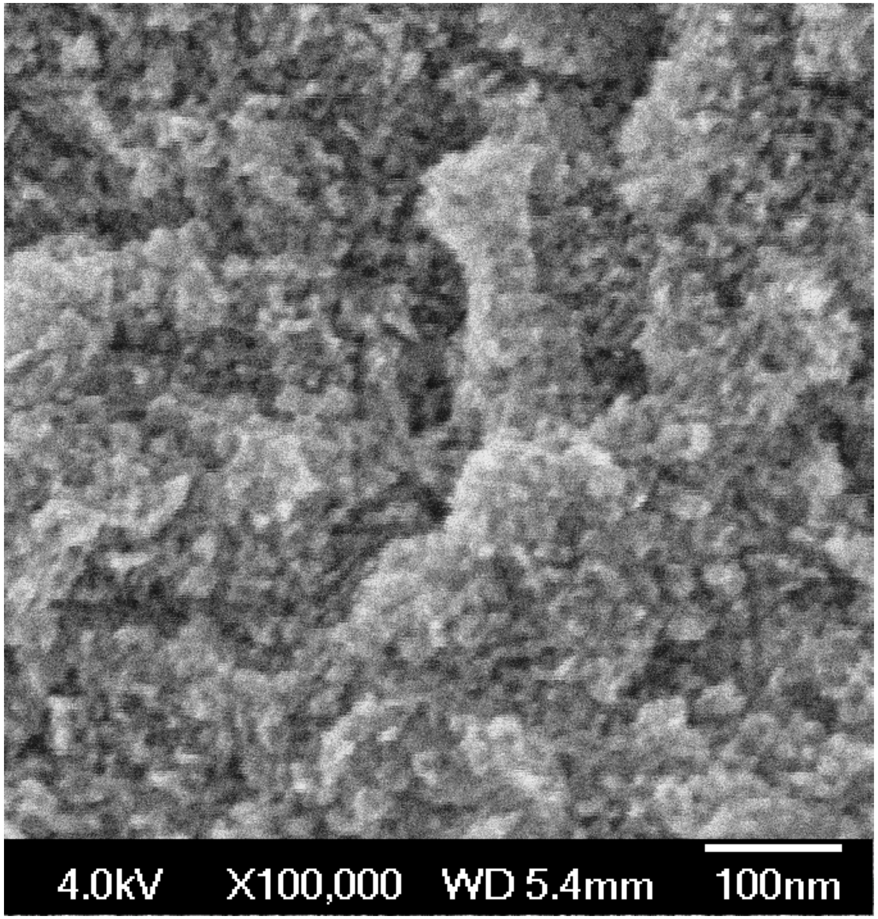
- 3D printed cell to optimize geometry
- 99.99% Pd anode plates 50x50x1mm
- Ag mesh: 50 μm wire, 127 μm pitch





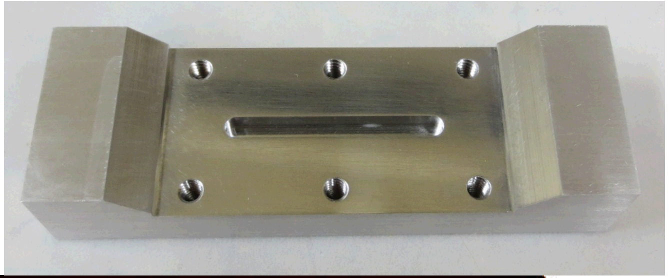
Porous on 10 µm and 10 nm scales

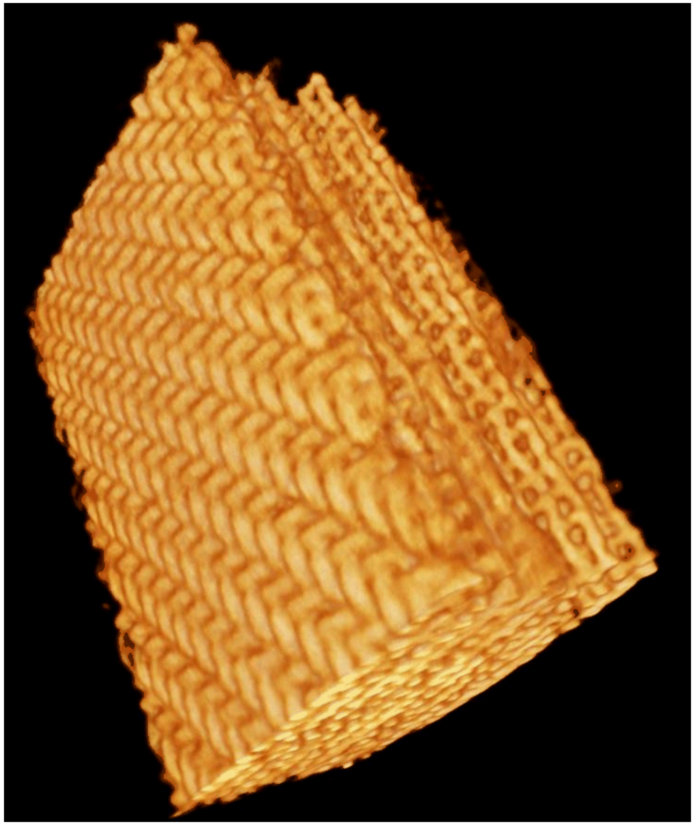


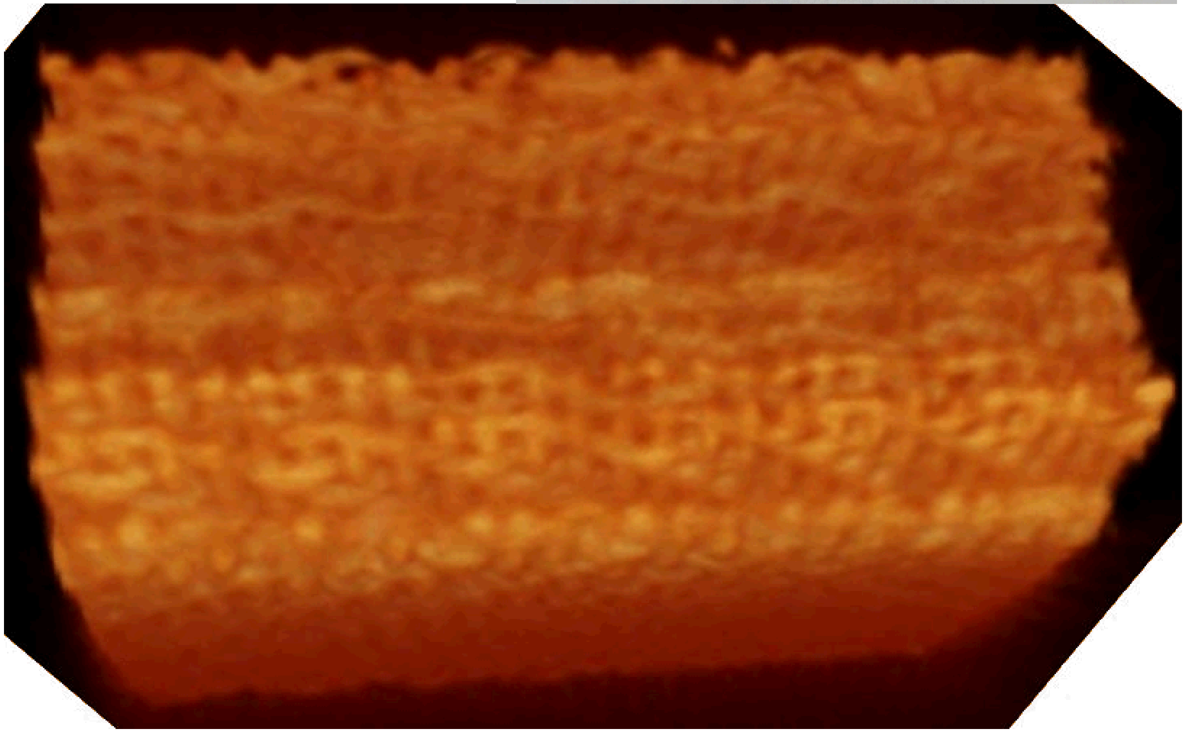


Stack mesh for 3D porosity

- Cut into strips, pack into 3 x 3 x 30 mm flow column
- Image by X-ray computed tomography

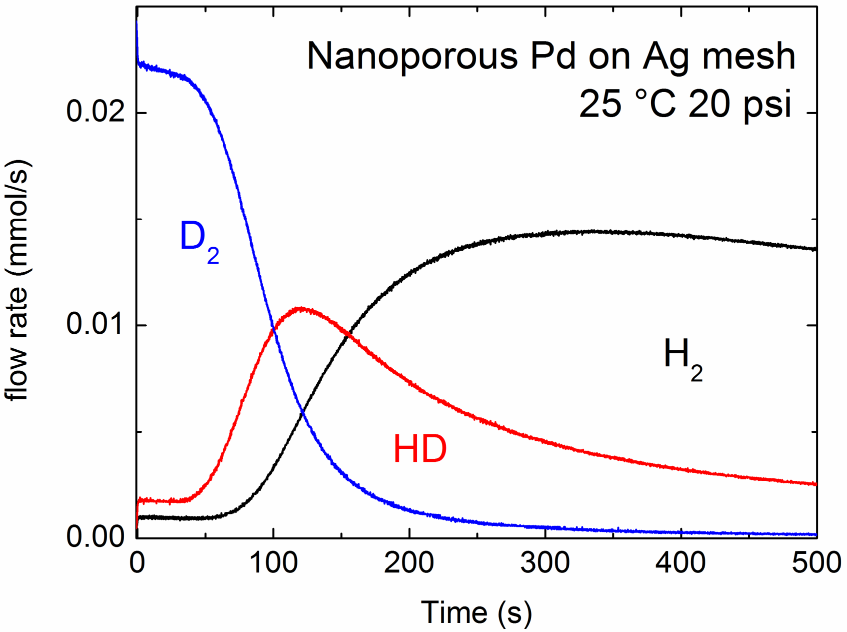






Gas isotopic displacement column

- Faster timescale than dehydriding
  - No rearrangement of Pd atoms
- $H_2 + PdD_{0.6} \rightarrow D_2 + PdH_{0.6}$
- 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
- Asymmetric peak suggests solid-phase diffusion limit



Summary and Conclusions

- Polymer-templated electrodeposition yields porosity on 10nm scale
  - Film thickness can be 10 μm scale, porous throughout
- Stacked woven mesh substrates yield porosity on 10 μm scale
- Porous films show high surface area, fast dehydriding
- Nanoporous stacked meshes allow fast isotopic displacement
- Tailoring multiscale porosity could potentially benefit:
  - metal hydride batteries
  - supercapacitors
  - gas chromatography
  - fuel cell membranes

Acknowledgements

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