SAND2016-2165C

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Nanoporous Metal Films and Powders Formed with Soft Templates

Presented by David B. Robinson

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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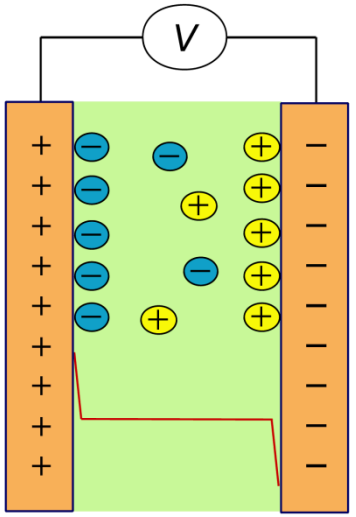
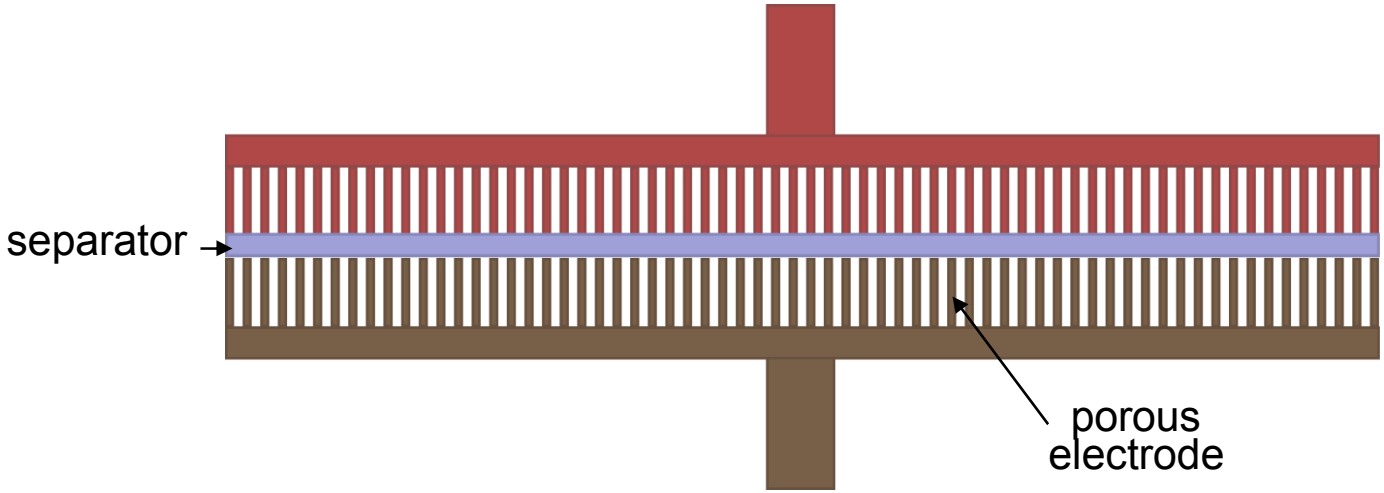
Porous materials for energy storage

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

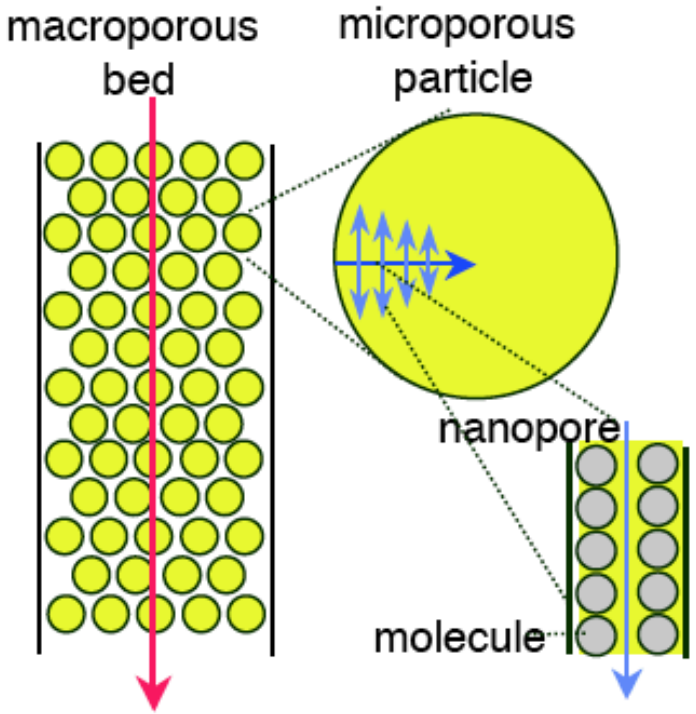




Robinson, J. Power Sources 195 3748 (2010)

Porous materials for chemical separations

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



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

Porous materials for catalyzed chemical reactions

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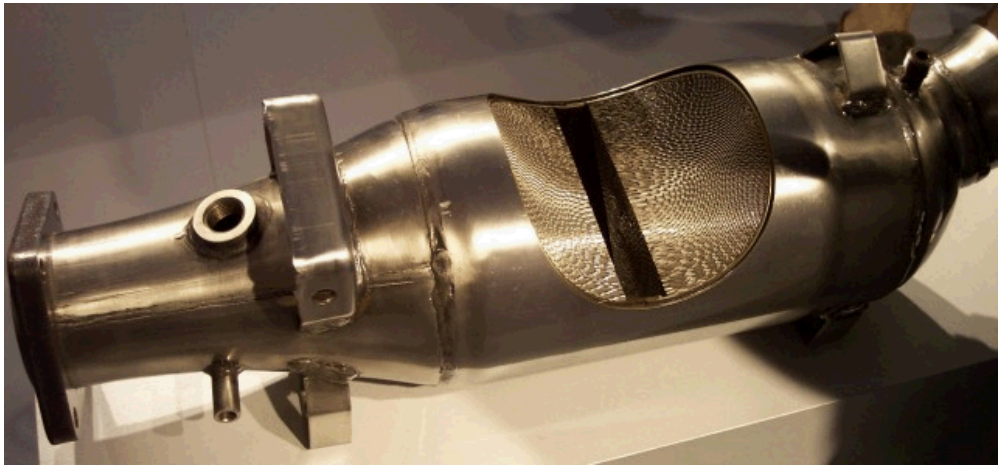
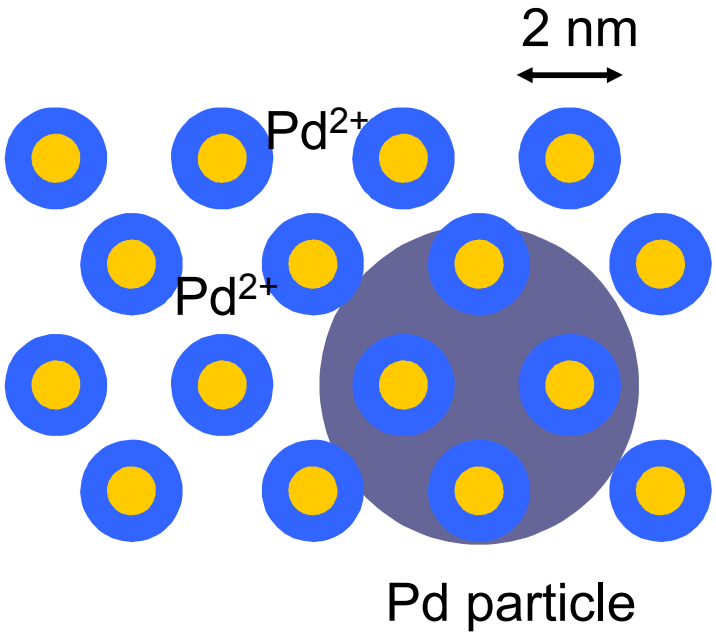
- Automotive catalytic converters, industrial flow reactors
- Needed: low flow resistance, thermal stability, optimized catalyst loading

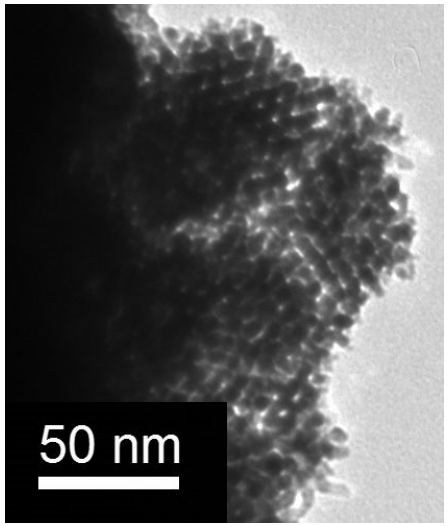


Reduction in lyotropic liquid crystals



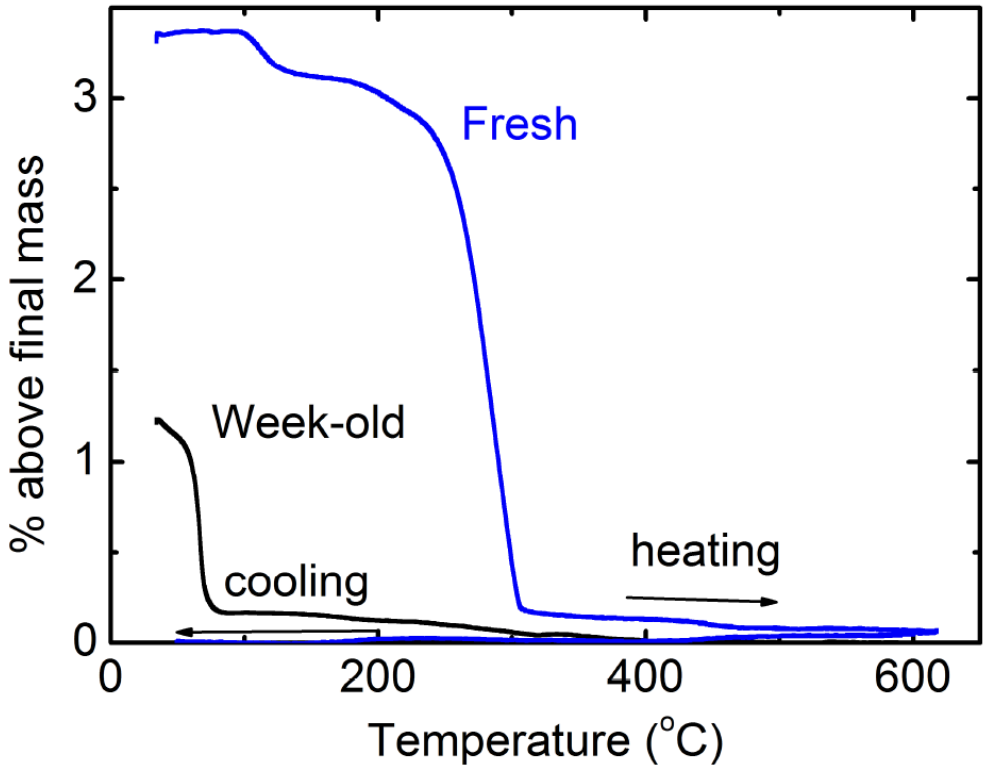
$(NH_4)_2\ PdCl_4 + H_2 \rightarrow Pd + 2\ NH_4Cl + 2HCl$

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



Surfactant removal

- Can require long soaks
- Easier with oxidized surfaces



Ong et al.
Chem Mater. 24 996 (2012)

Pd:Rh 9:1
4h ethanol-water soak

Thermal Stability Constrains Pore Size

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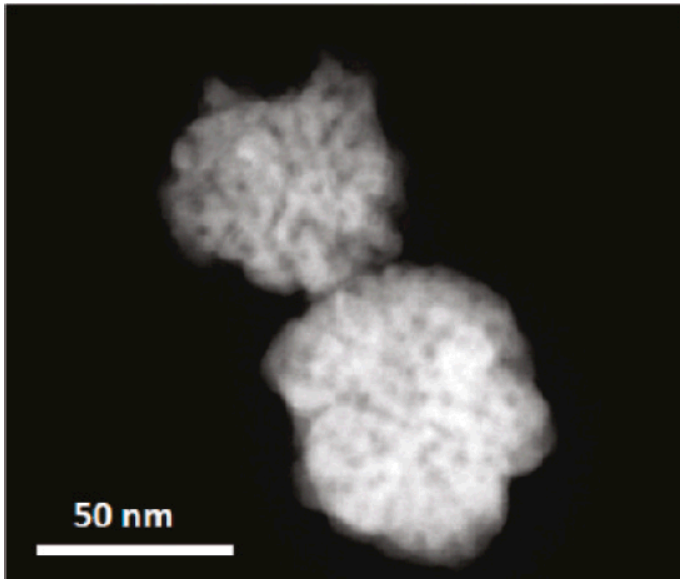
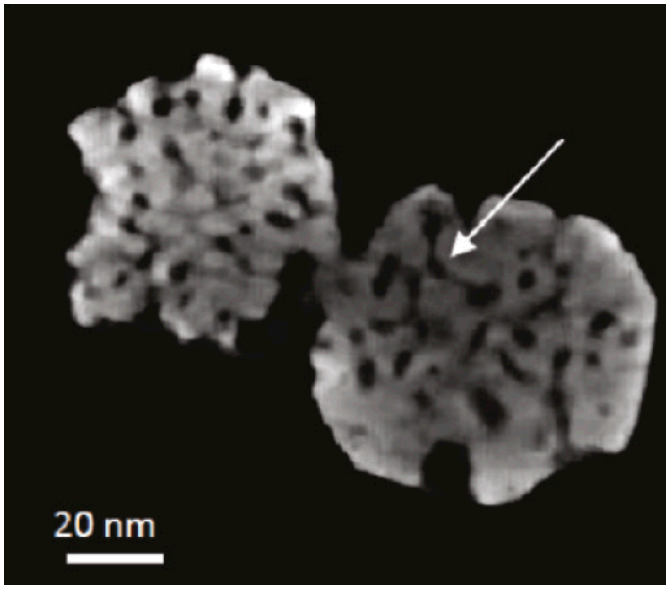
3 nm pores



Room Temperature



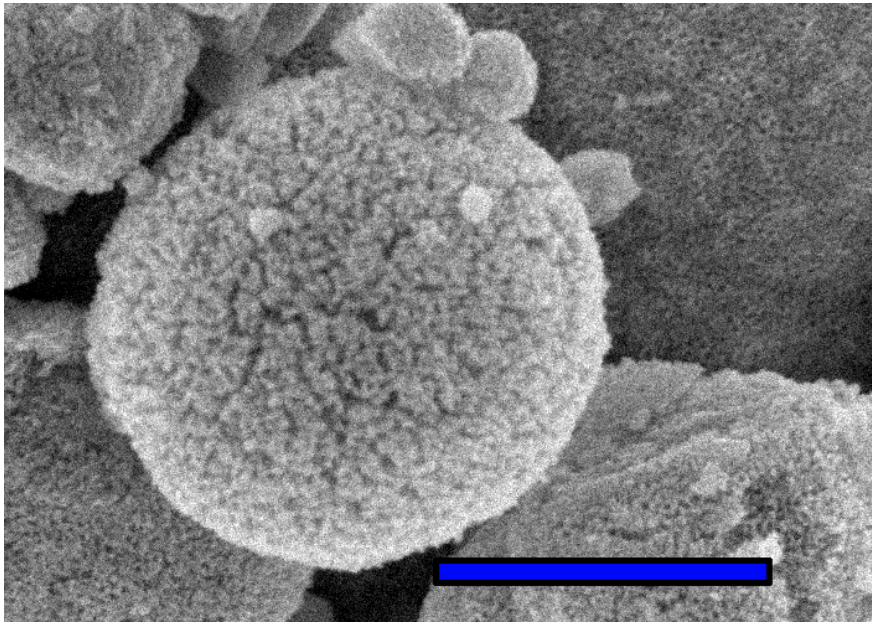
600°C

- STEM and STEM-tomography show that pores begin to collapse at 200°C
- By 600°C Pores have coalesced into large voids
- Larger pores should be more stable

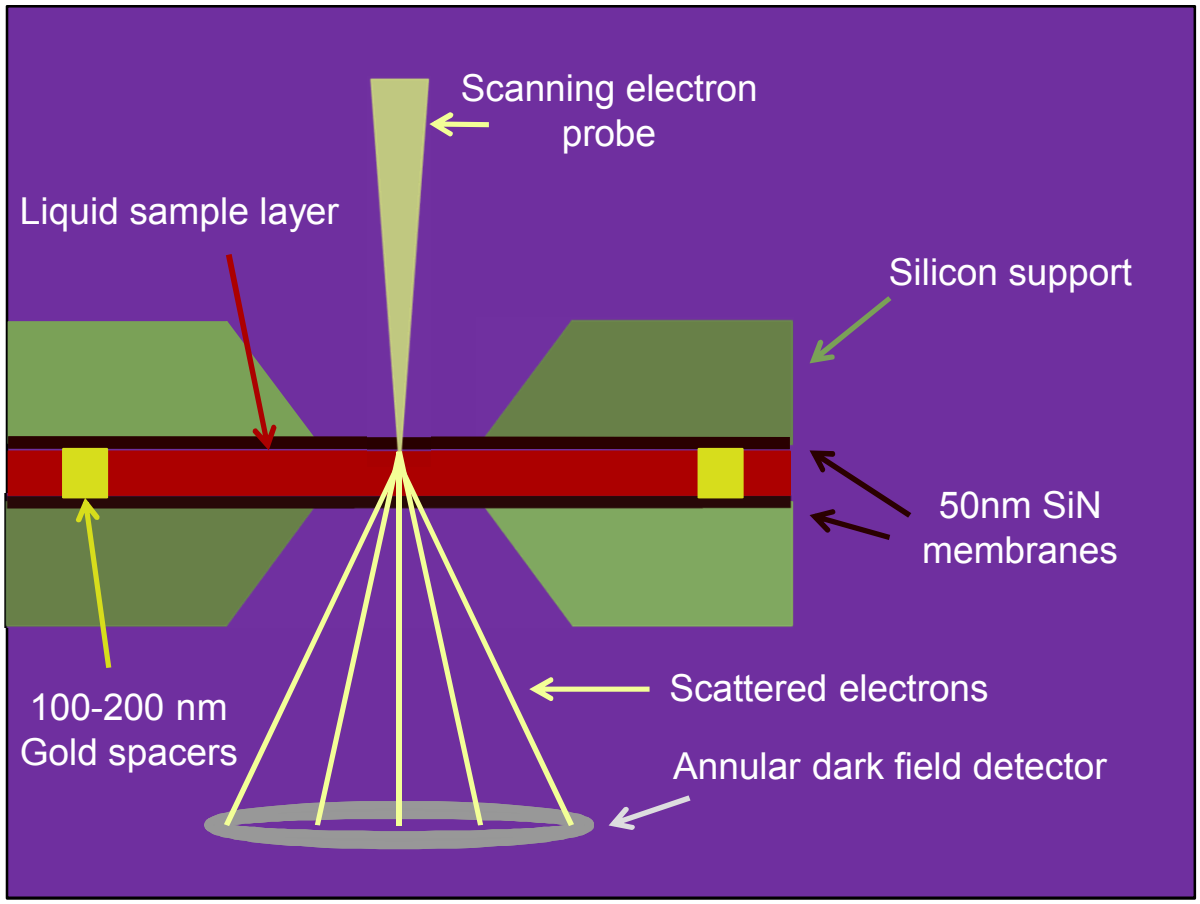
Klein, *et al.*, J. Am. Chem. Soc. 2011, 133, 9144–9147

Block copolymer gels

- Prior work: Pt films from Block copolymer gels
  Yamauchi et al., Angew. Chem. 47 5371 (2008)
  Takai et al., JACS 132 209 (2010)
- Pores in SEM range
- Gram scale, H_2-reduced Pd
  Cappillino et al. J. Mater. Chem. A 1 602 (2013)



Liquid stage STEM



Lucas R. Parent et al., ACS Nano, 6 3589 (2012)

Reduction of $(NH_4)_2PdCl_4$ in water + (bcp-3.8,5k)

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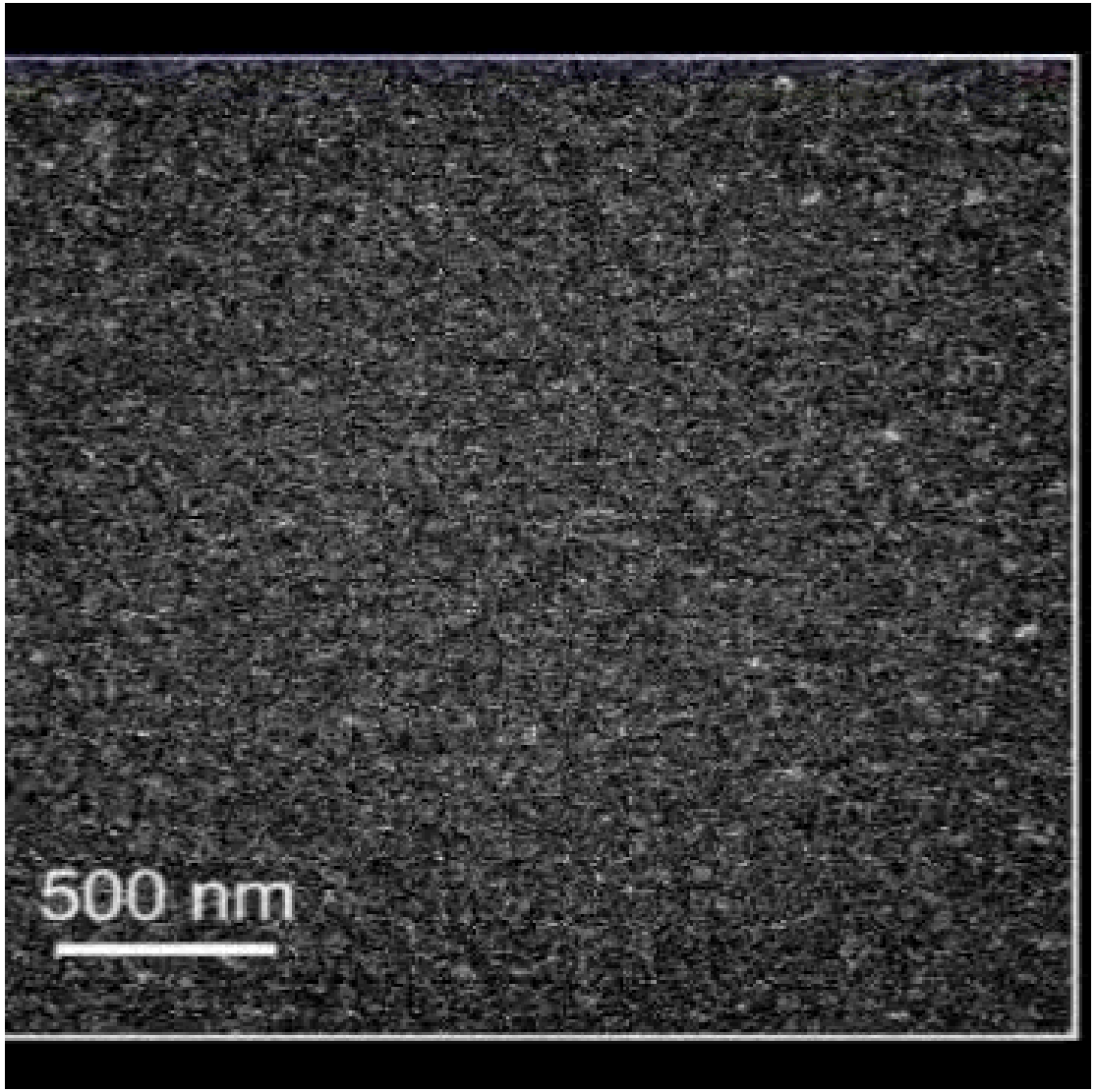
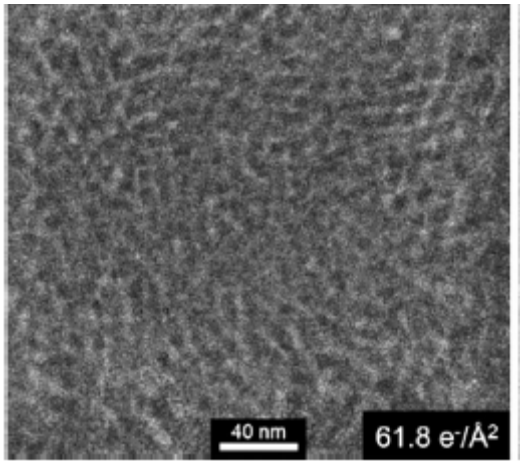
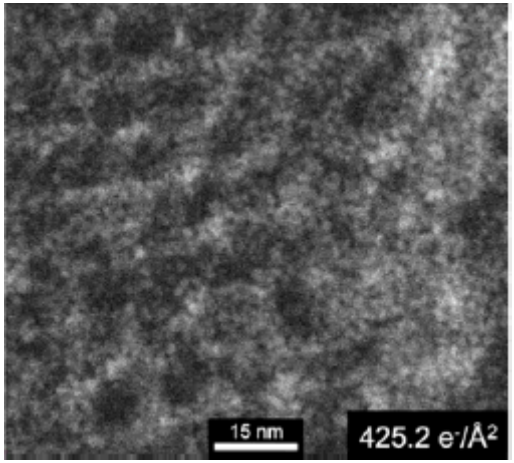


Nanoparticles nucleate, grow, and fuse to form porous structure

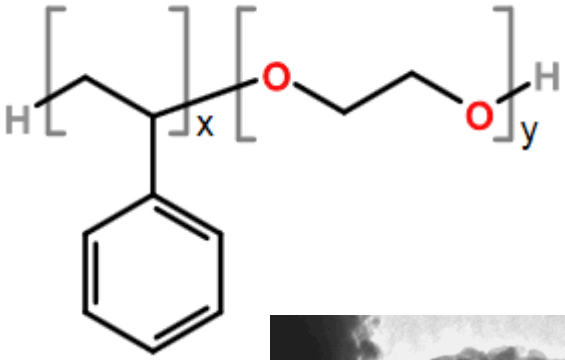




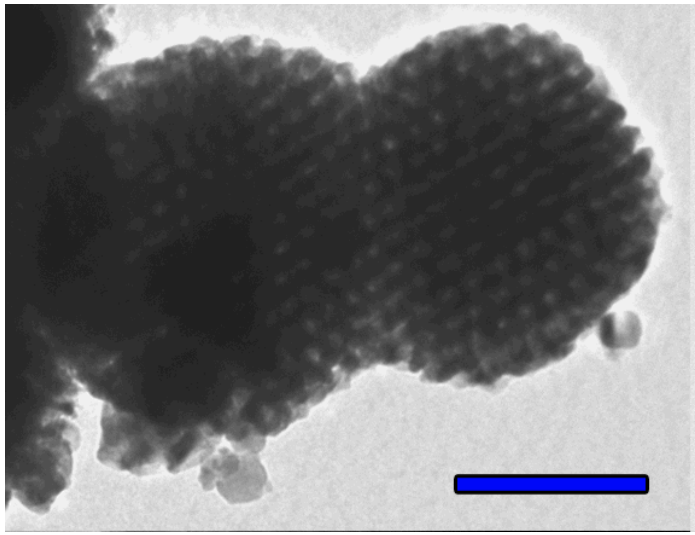
Lucas R. Parent et al., Chem. Mater. 26 1426 (2014)

Size tuning with block copolymers

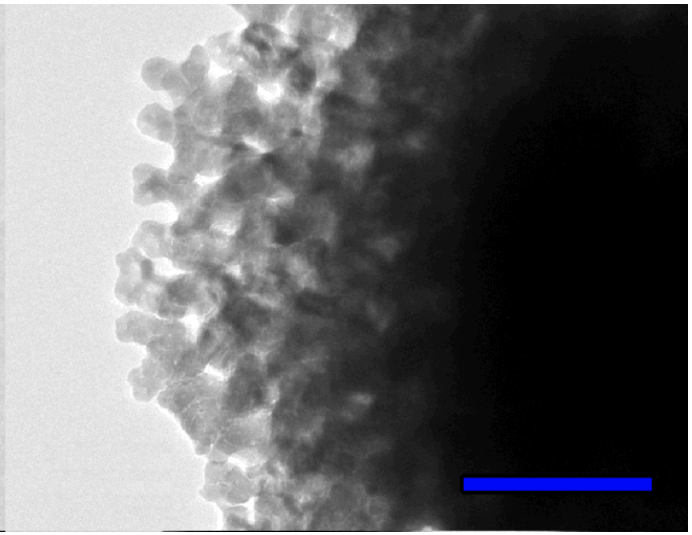
- Cappillino et al. J. Mater. Chem. A 1 602 (2013)
- Poly (styrene-block-ethylene oxide)



Name	x	y	Pore, nm	Pitch, nm
Pd_S	22	70	7	15
Pd_L	36	113	12	30



100 nm



100 nm

7 & 13 nm pores stable to > 600° C

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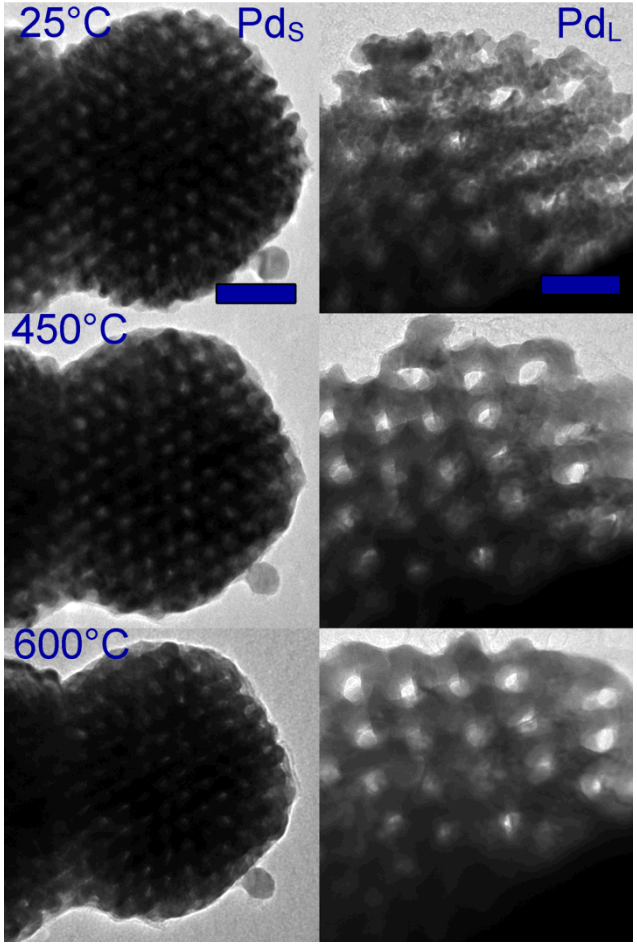
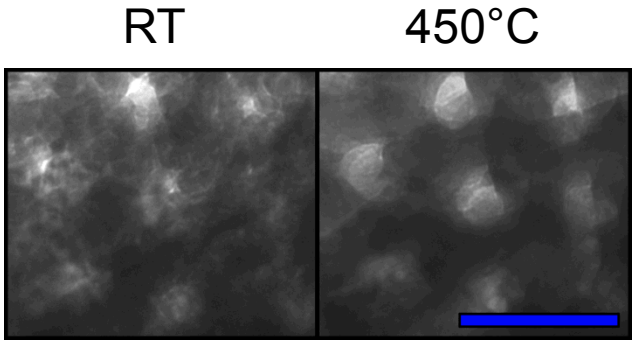
Both 7 nm (left) and 13 nm (right) pores are intact to 600°C. Collapse occurs by 700°C





NP forming ligaments fuse upon annealing (small voids collapse)

Pore structure remains intact

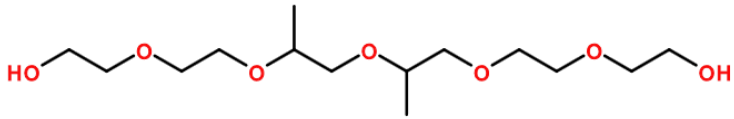
Cappillino *et al.*, J. Mater. Chem. A (2013) p. 602

50 nm scalebars

Plating from dilute micellar phase

- Eliminates slow, messy pastes, gels; pores less ordered
- Prior work: Pt + F127, aqueous: Wang et al., Chem. Mater. 24 1591 (2012)
- Prior work: Au + PS-PEO, mixed solvent: Li et al., Nature Comm. 6 6608 (2015)
- Our work: Pd, 20x thicker films

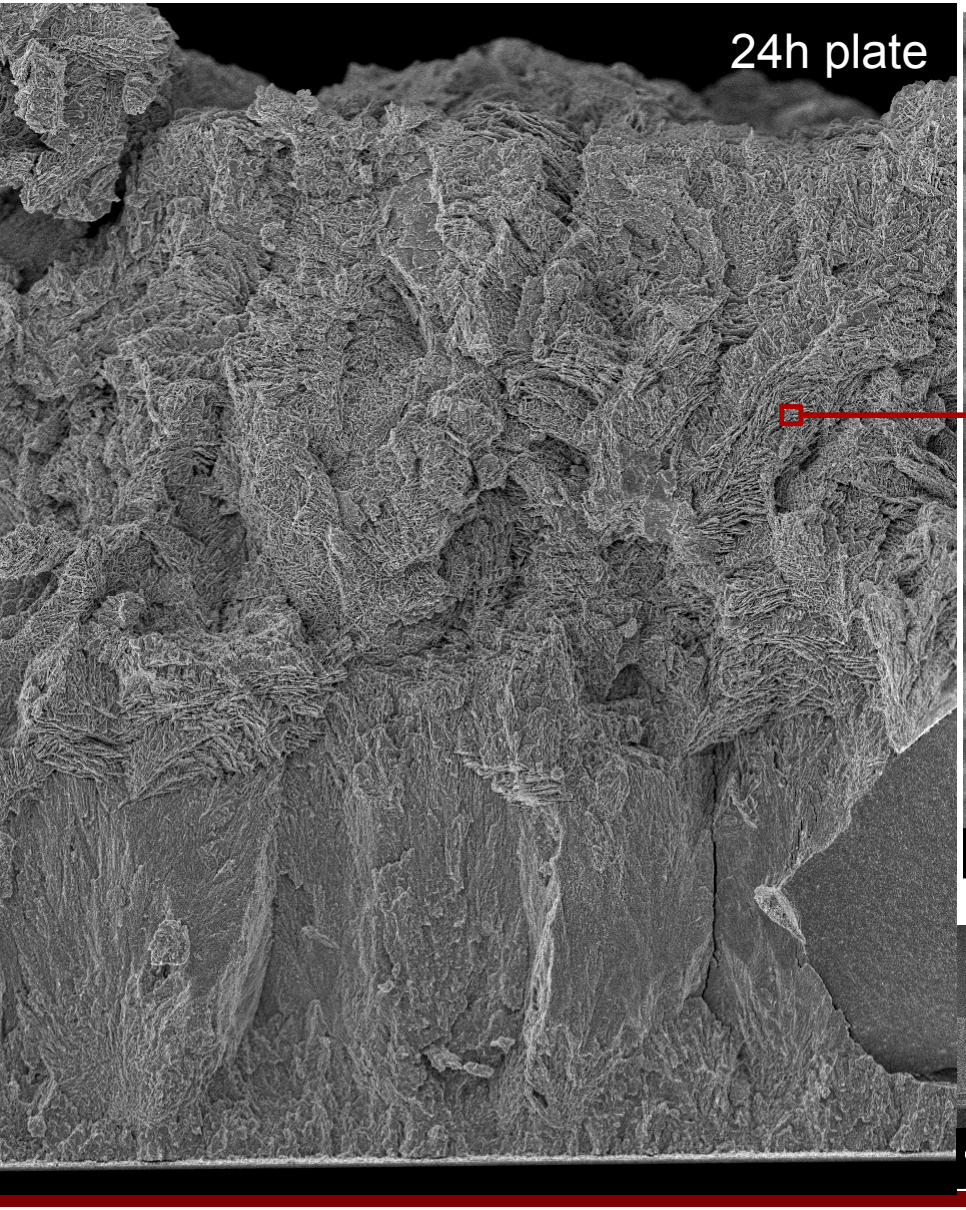
Pluronic F127 is $EO_{101}\ PO_{56}\ EO_{101}$
$EO_2PO_2EO_2$ is :

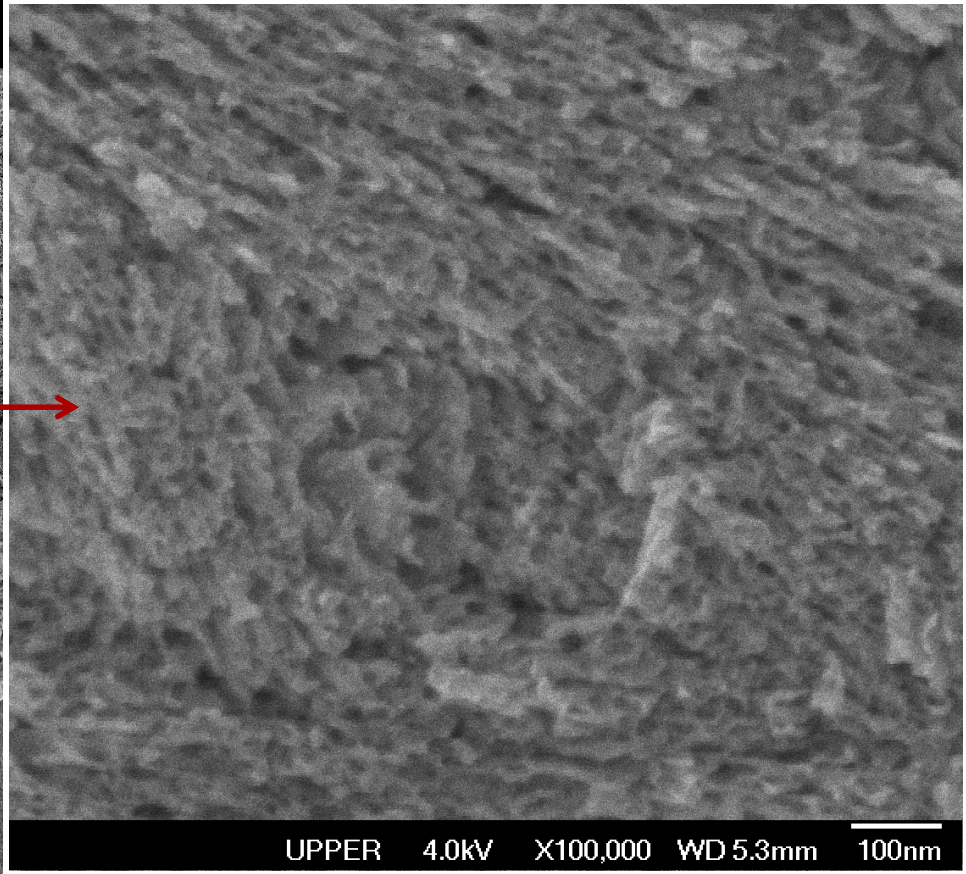


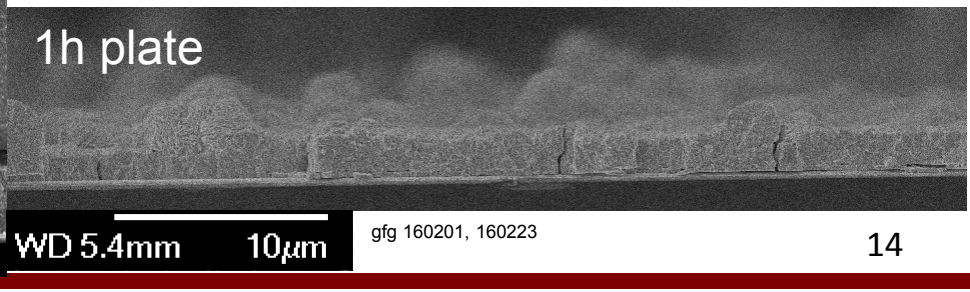
Tricks:

- Similar working-, counter-electrode areas
- Double junction Ag/AgCl reference electrode
- Pd^{2+}, HCl concentration > 0.1M
- F127 > 1 wt %
- Current density near 1 mA/cm^2

SEM cross section shows nanoporosity

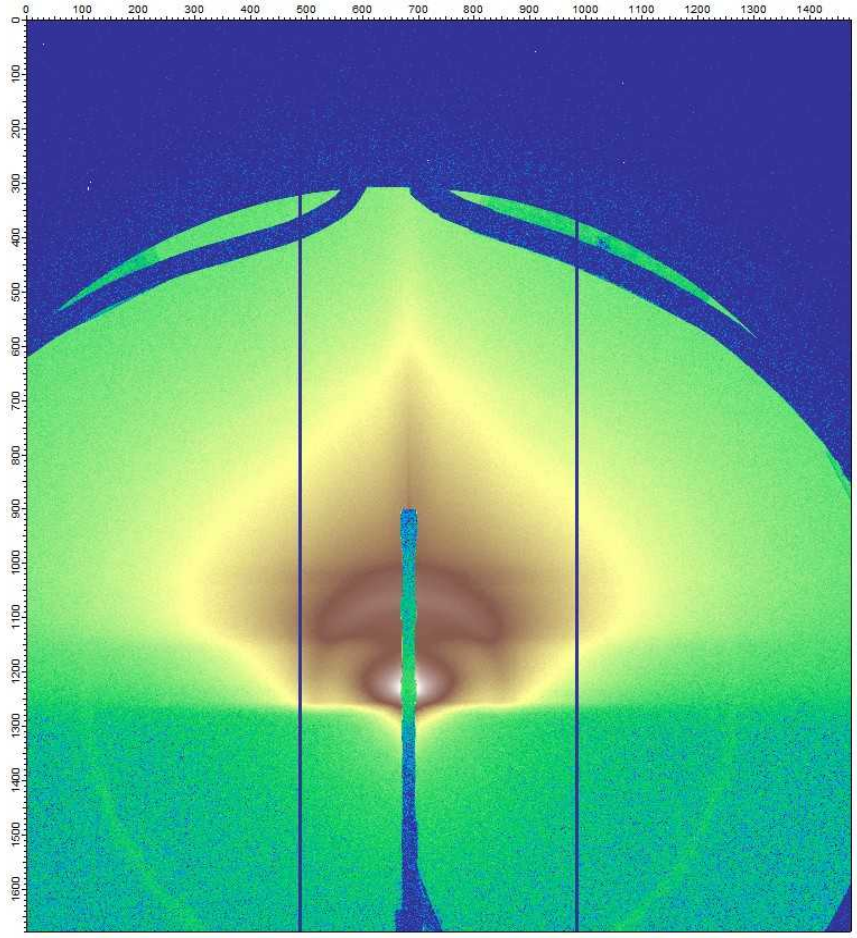






gfg 160201, 160223

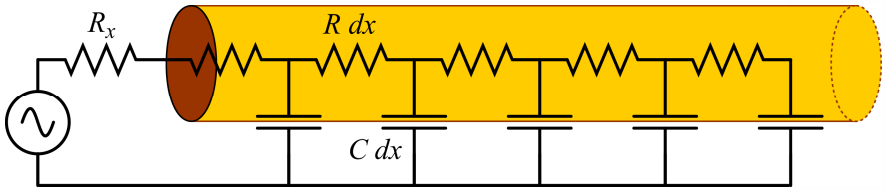
Small-angle X-ray scattering



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

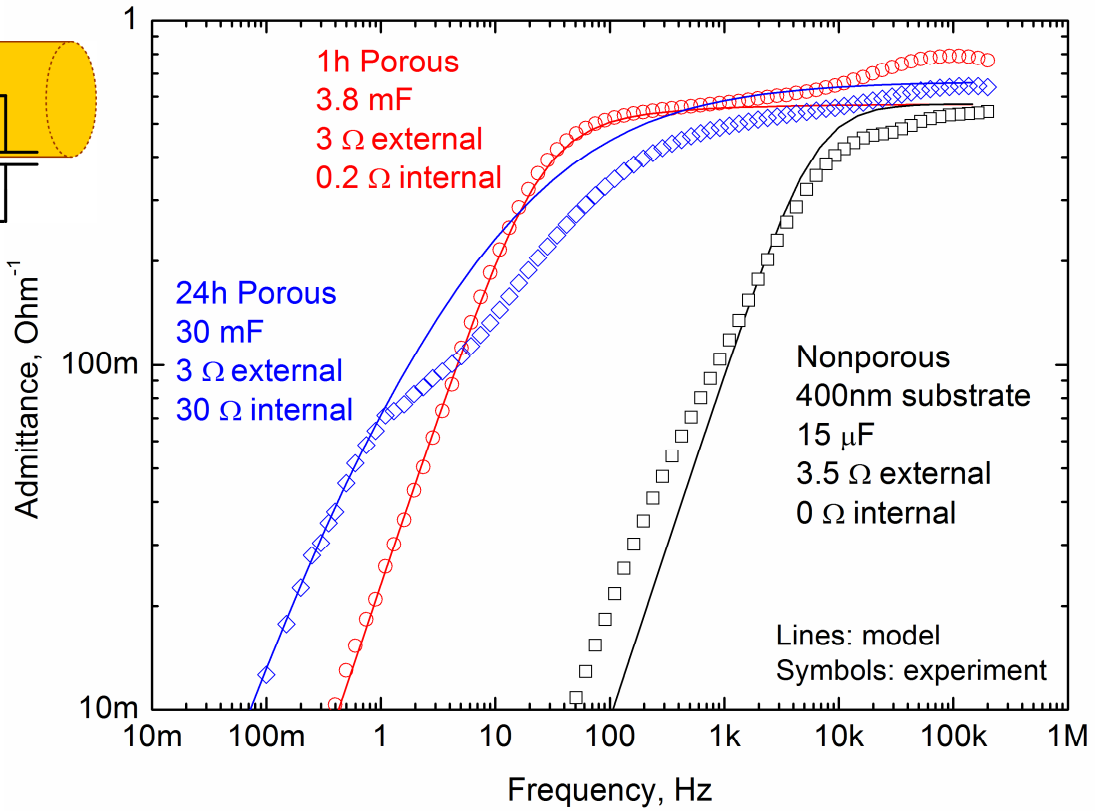
Electrochemical capacitance

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



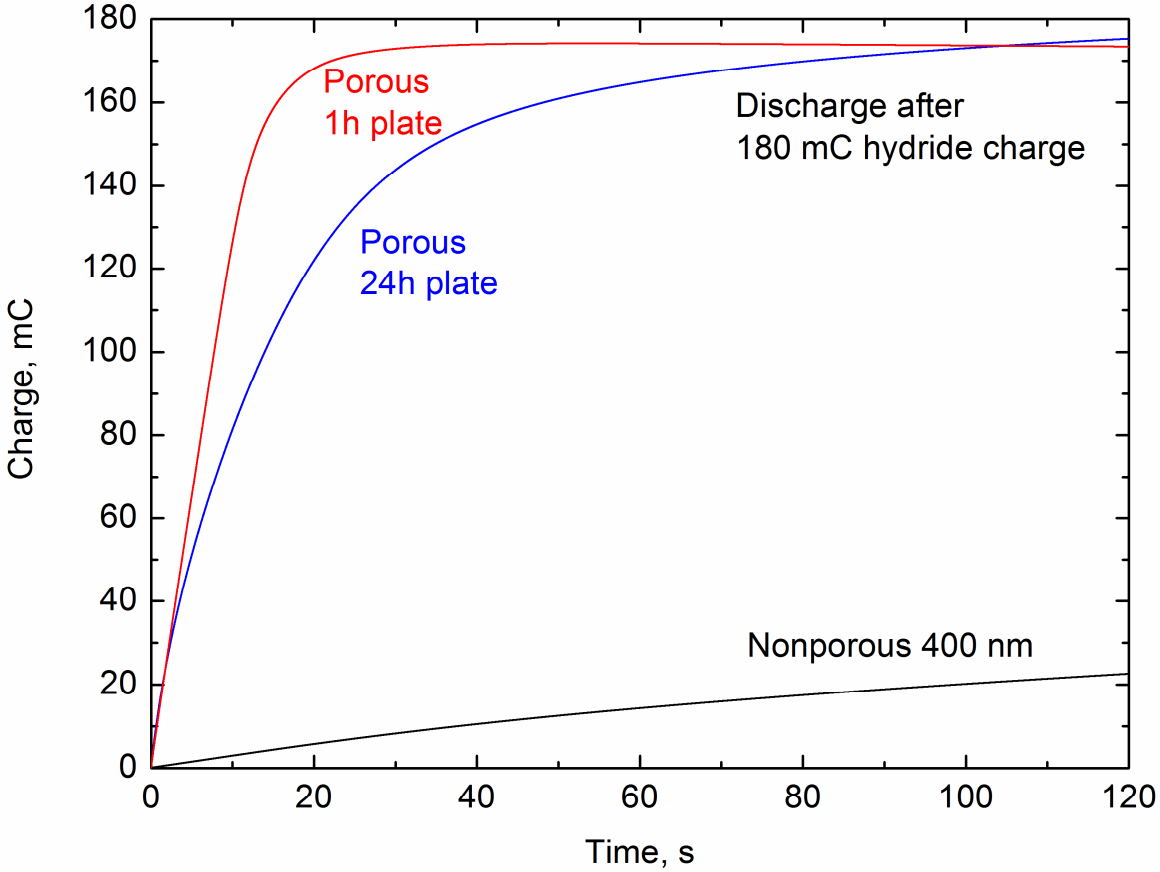
Robinson et al.,
Langmuir 26 6797 (2010)

Chae et al.,
ACS Appl Mater. Interf.
4 3973 (2012)



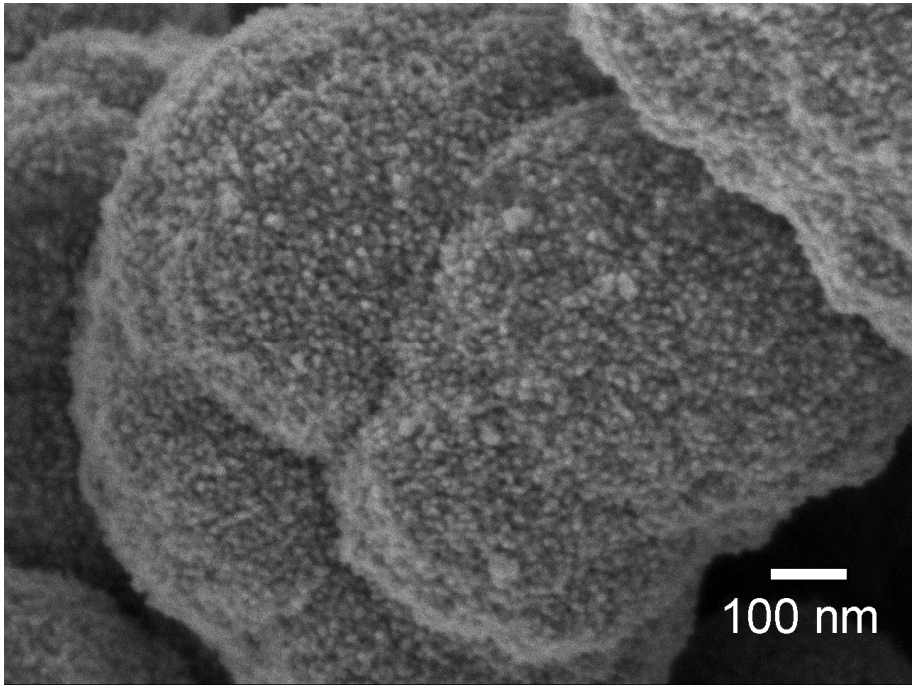
Electrochemical hydriding rates

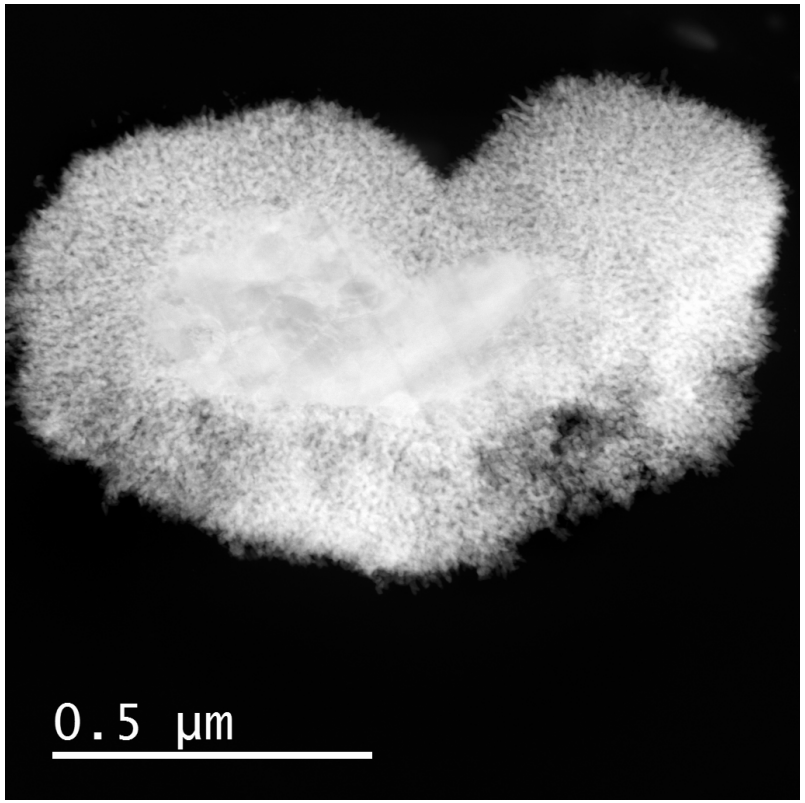
- Apply negative current for fixed time: $Pd + H^+ + e^- \longrightarrow PdH$
- Then step to positive potential, observe reverse reaction



Iterative Electroless Porous Pd

- Stepwise growth of nanoporous Pd from dilute F127
  - $Pd + H_2 \rightarrow PdH_{0.6}$
  - $PdH_{0.6} + Na_2PdCl_4 + F127 \rightarrow$ porous Pd + HCl
- Films or powders





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