SAND2011-3108C

2011 MRS Spring Meeting, Apr. 25-29

Model Electrode Structures for Studies of Electrocatalyst Degradation

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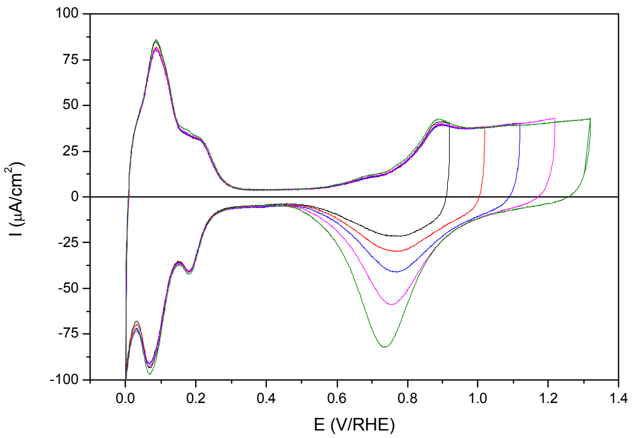
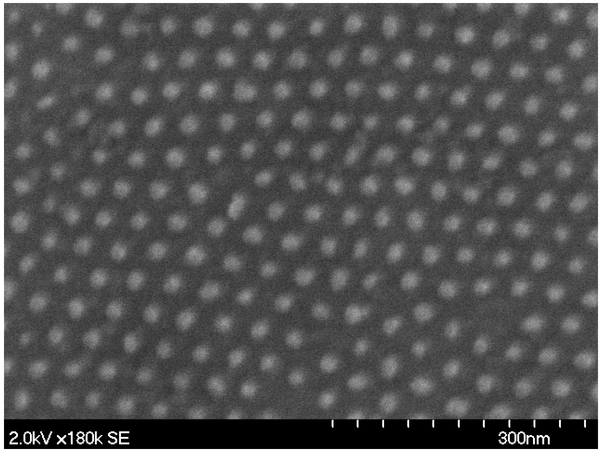




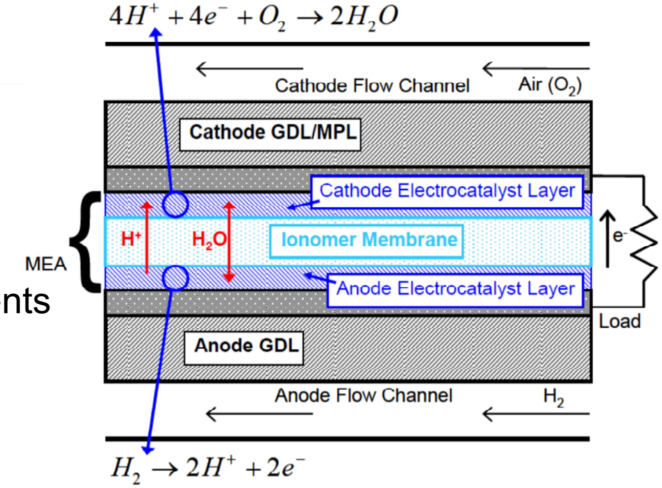
The University of New Mexico

Sandia National Laboratories

Fuel Cells

Polymer Electrolyte Membrane (PEM) Fuel Cells

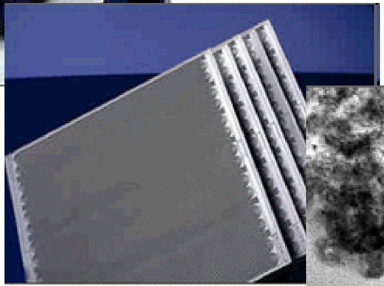
Potential replacement for the internal-combustion engine and portable power. - efficient, clean and low temperature ~80°C



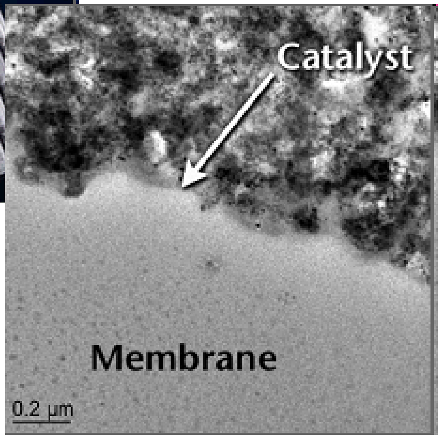
Borup, R., et al., Chem. Rev., 2007.

Limitations are primarily cathode requirements
Oxygen Reduction Reaction (ORR)
Pt most effective catalyst
Pt expensive (minimize)
Catalyst degradation

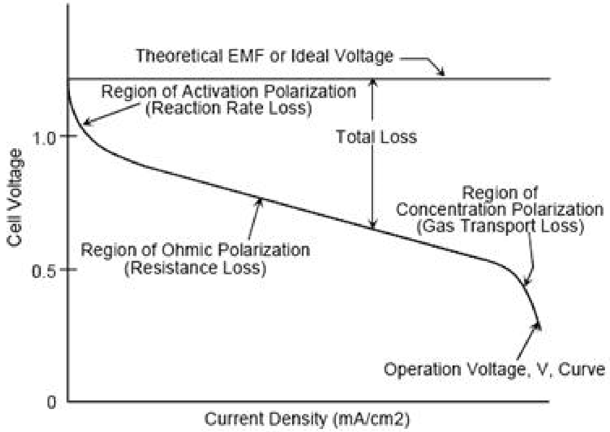
FC System



MEA stacks



Catalyst / Membrane



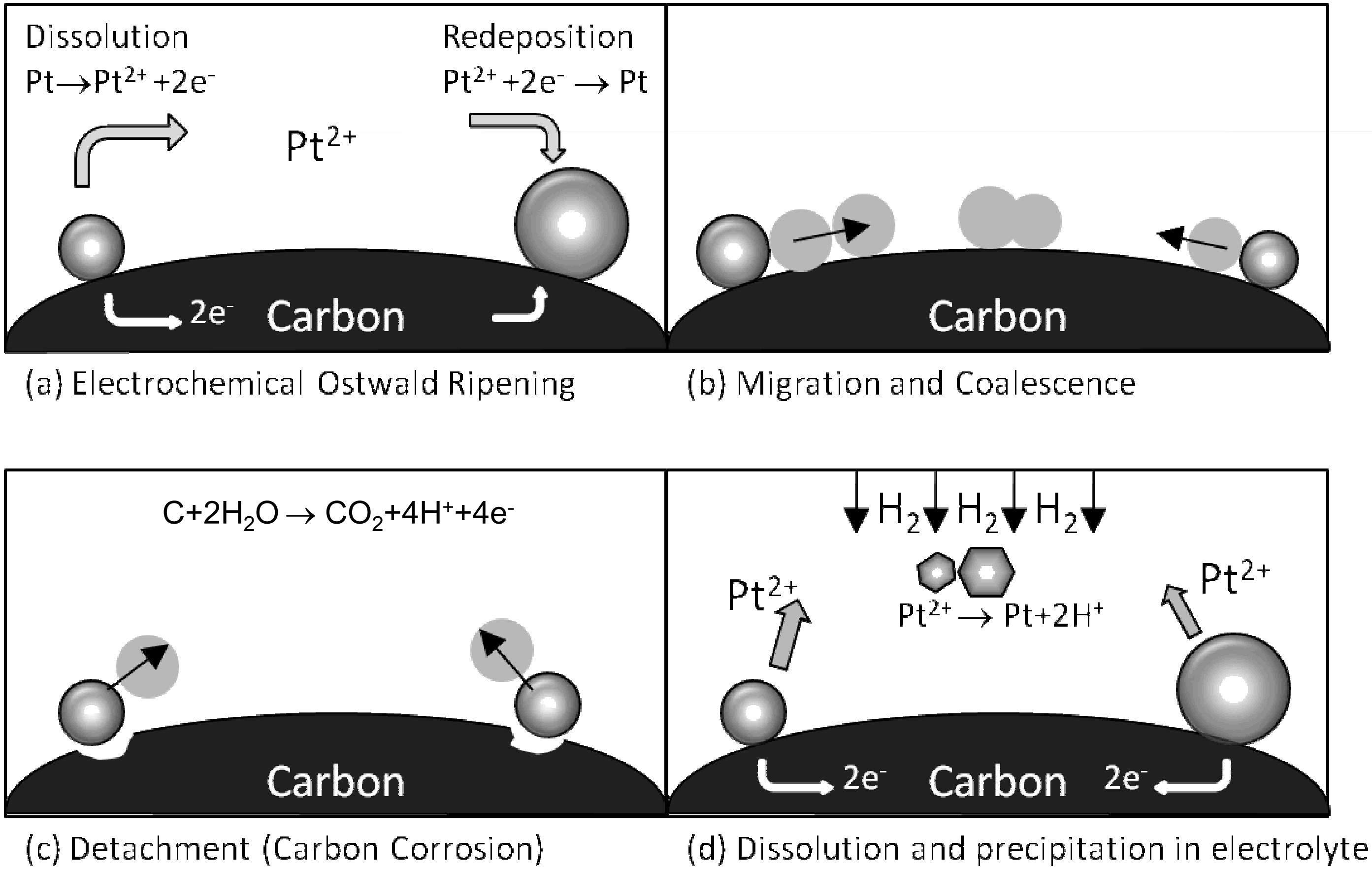
From DOE-EERE website

Larminie & Dicks Fuel Cell Sys. Exp., 2003

PEM Fuel Cells

Pt Catalyst Degradation Mechanisms

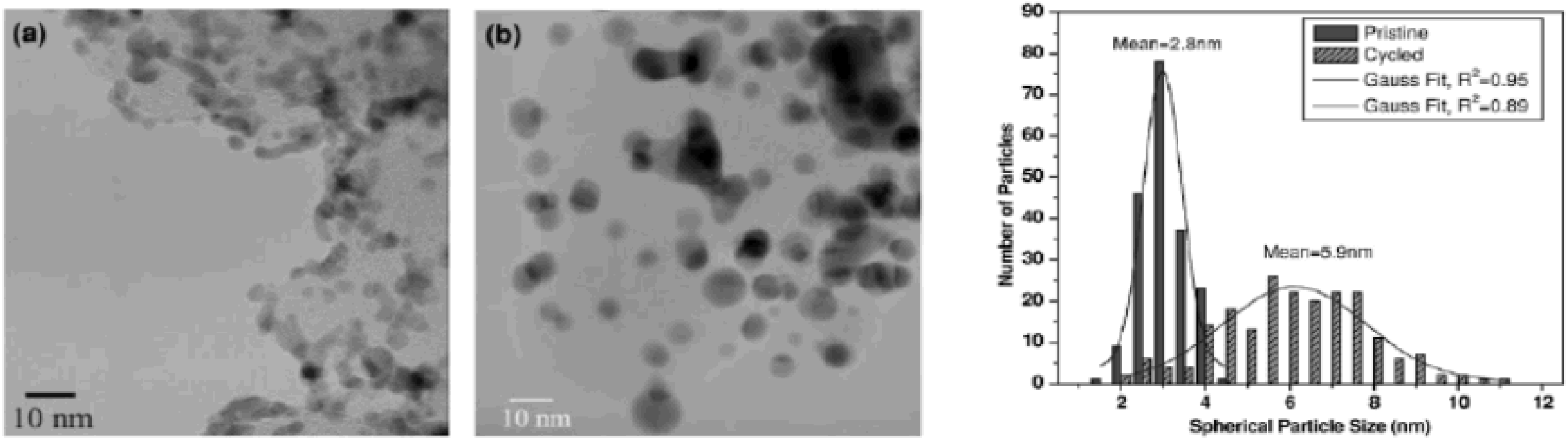
Sintering/Coarsening
Surface Area Loss



Corrosion (catalyst / support)
Material Loss

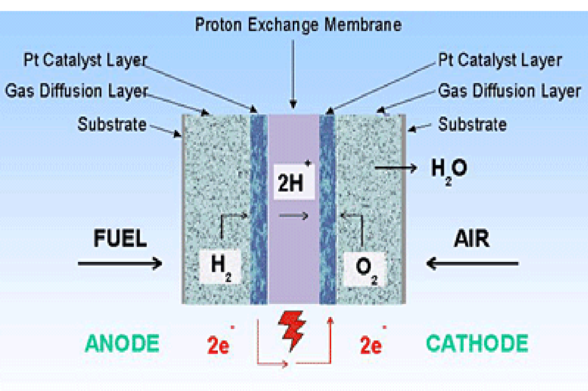
PEM Fuel Cells

Typical Catalyst Sintering Studies



P. J. Ferreira, et. al. *J. Electrochem. Soc* (2005)

- Average Particle size increased from 2.8 nm to 5.9 nm (0,000 cycles 0.6 – 1.0V) Sintering mechanism proposed by particle size distribution

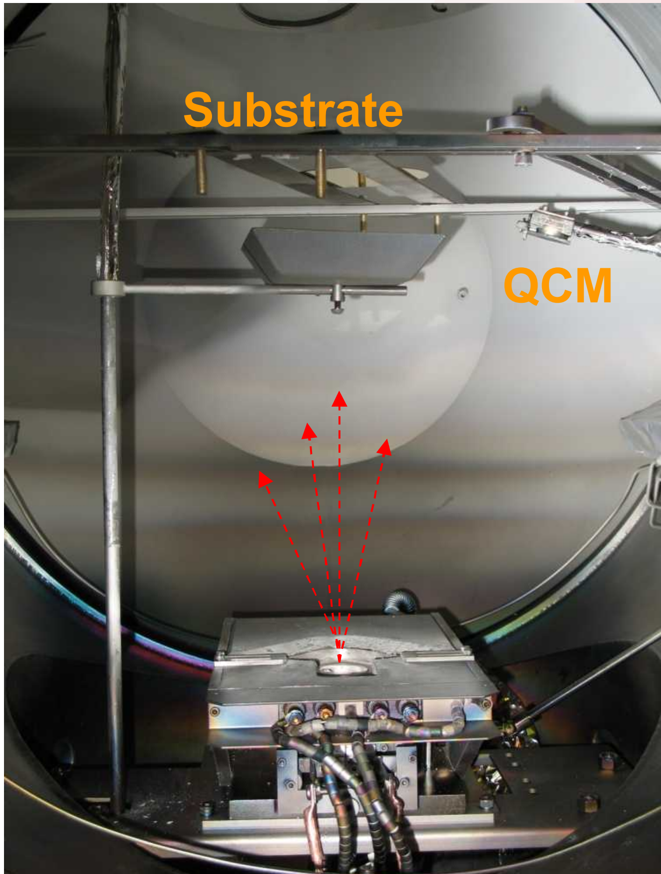


JM Johnson Matthey Fuel Cells
the power within

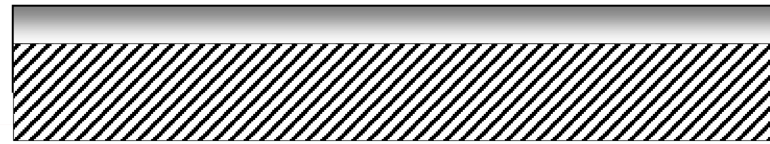
- Fuel cell catalyst are a complex mixture of metal particles, carbon support, gas diffusion layer and electrolyte.
- Destruction of the FC/MEAs are required to study the degradation process (statistical). Time consuming and costly
- A 2D Model Electrode is needed to bridge the gap between model single crystal surfaces and powder catalyst

Model Catalyst Fabrication

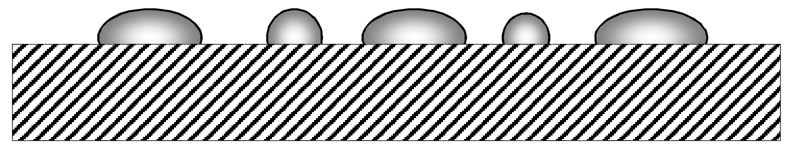
Ultra-thin Metal Deposition



Base Pressure: 1 x 10^{-7} torr
Evaporation rate 0.1 Å/s
Deposit directly on Electrode
Pt heated to ~ 1800ºC
Pt purity = 0.99999



Growth of wetting films (Layer by Layer growth)



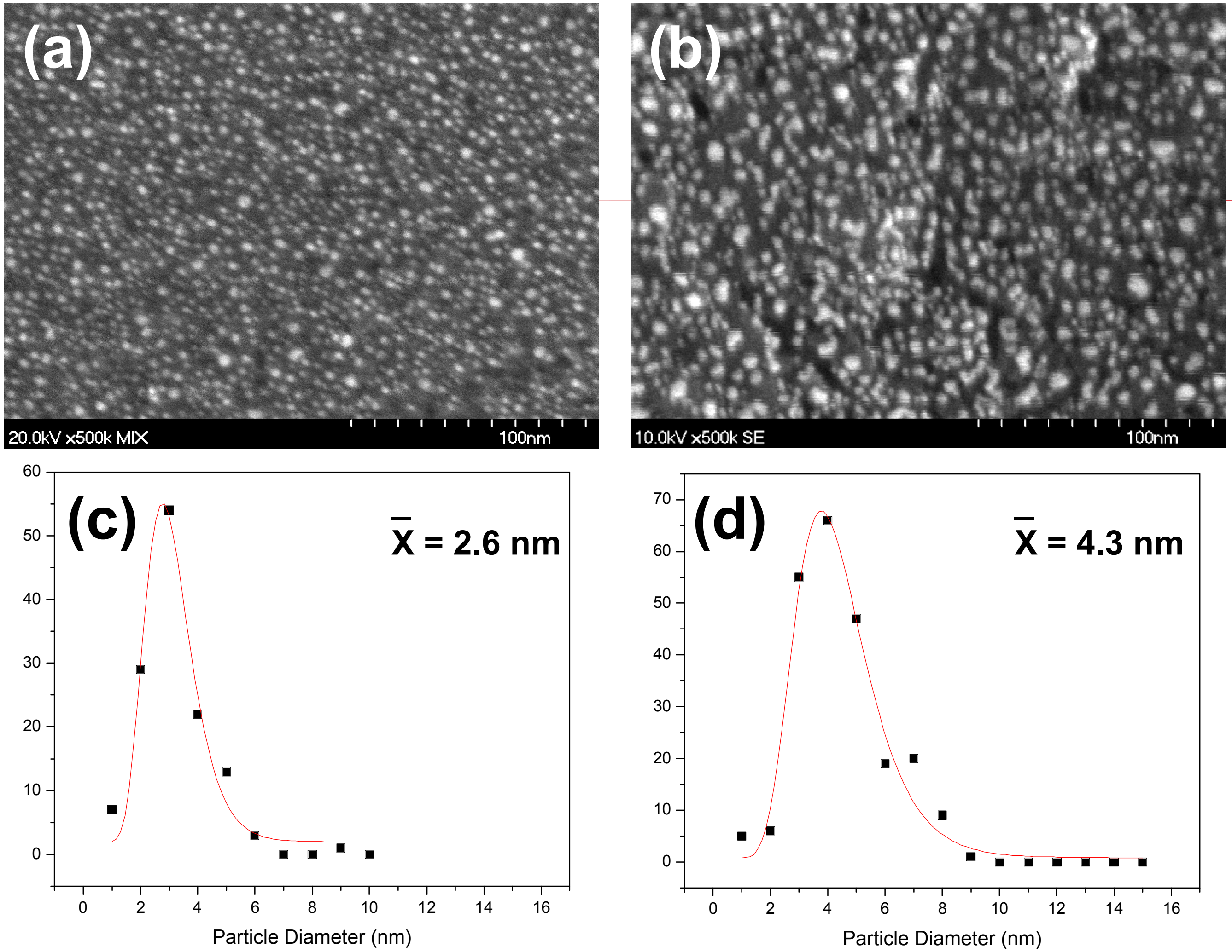
Growth of non-wetting films (Volmer-Weber growth)

Pt on Carbon is non-wetting
- mass/area loading will be utilized instead of film thickness

ρ_{Pt} = 21.4 g/cc → 1 nm film = 2.1 µg/cm^2

Pt particle Size Control on GC

Loading Affect PSD (800°C anneal)

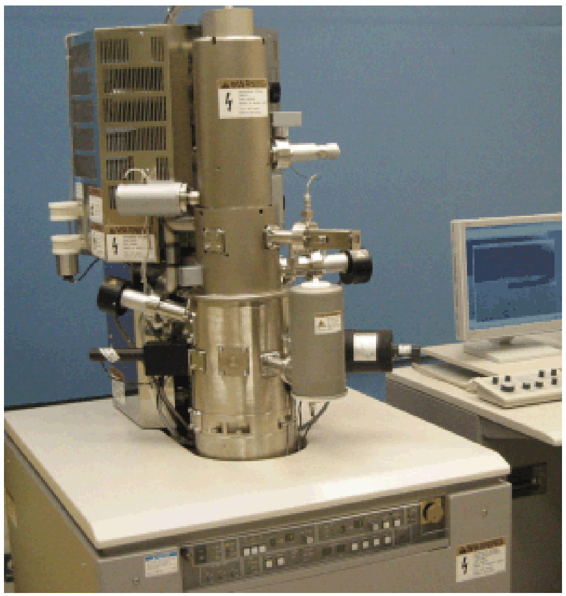


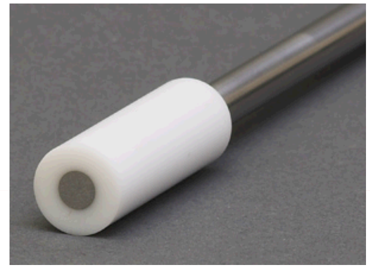
(1.1 µg Pt/cm²) **(2.1 µg Pt/cm²)**

Model Electrodes

Characterization Cycle

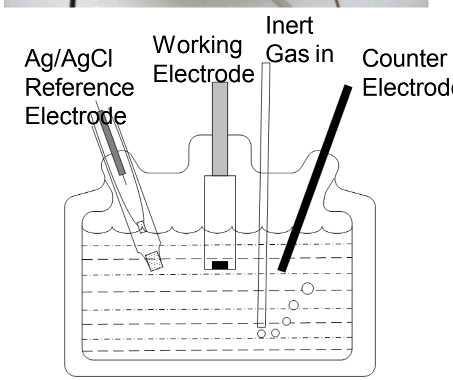
High Resolution
Field Emission
SEM imaging
Hitachi 5200

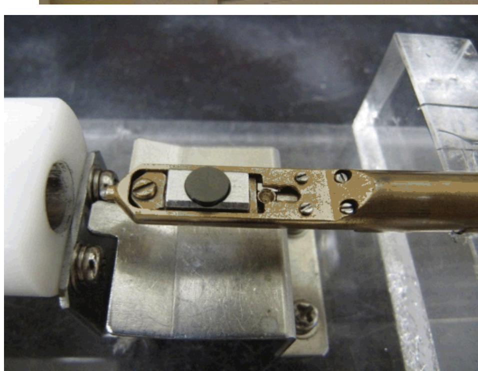


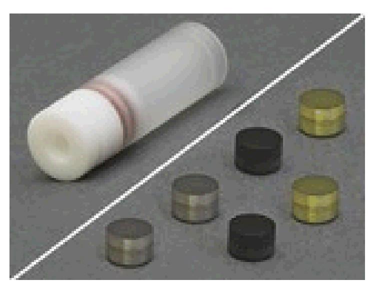


Electrochemical
Activity
Rotating Disk
Electrode (RDE)

Use a removable
5mm Glassy Carbon
Electrode
from Pine Research
Instrumentation

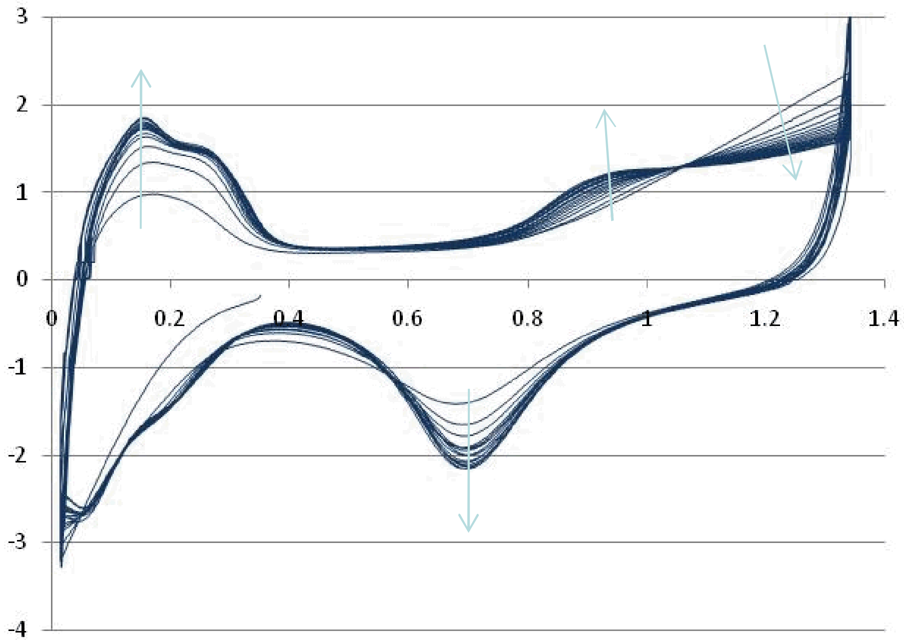




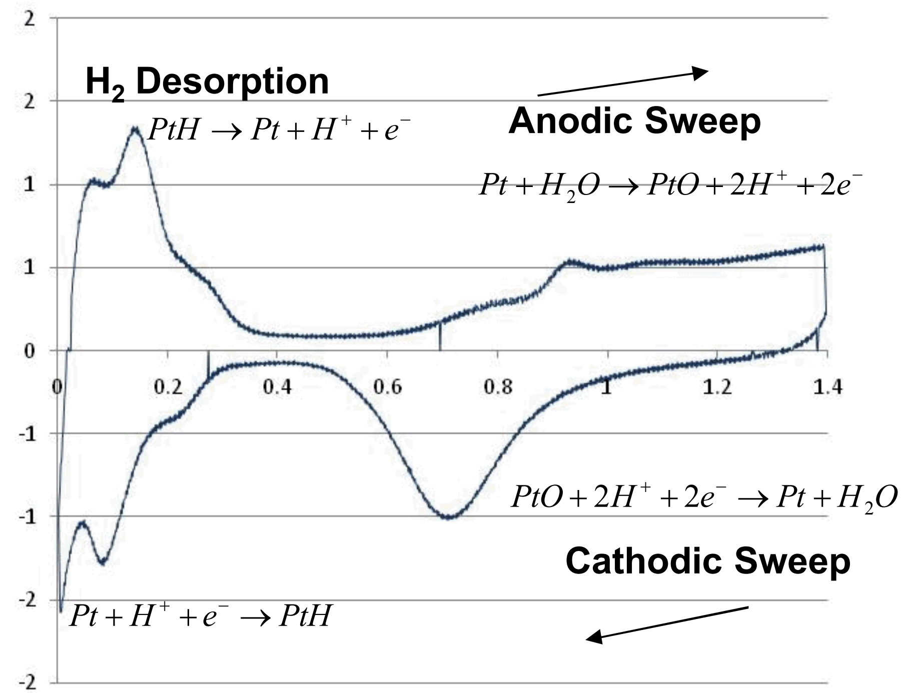


Electrode Cleaning Cycles

Initial Conditioning / Pt Cyclic Voltamogram



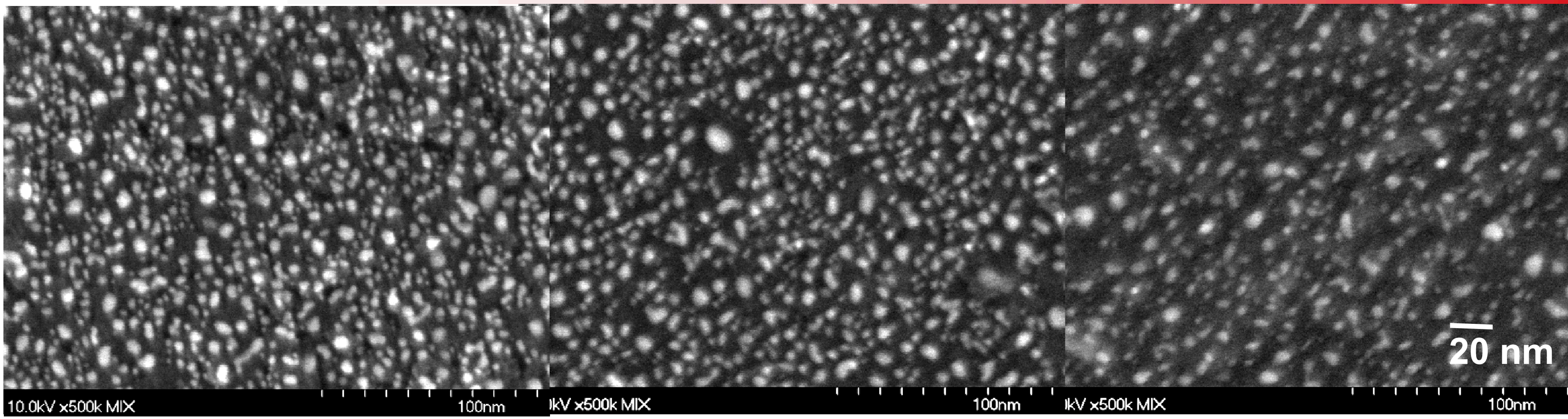
40 cycles, 0 → 1.4 RHE, 0.5V/s



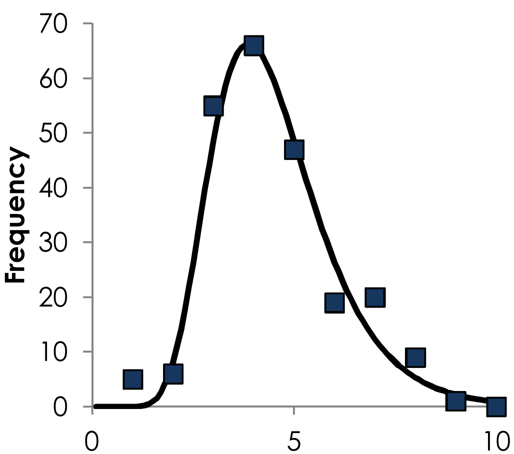
Ar saturated 0.1M $HClO_4$ at 20°C
500 mV/sec

Pt (2.1 µg/cm²) 800°C Anneal

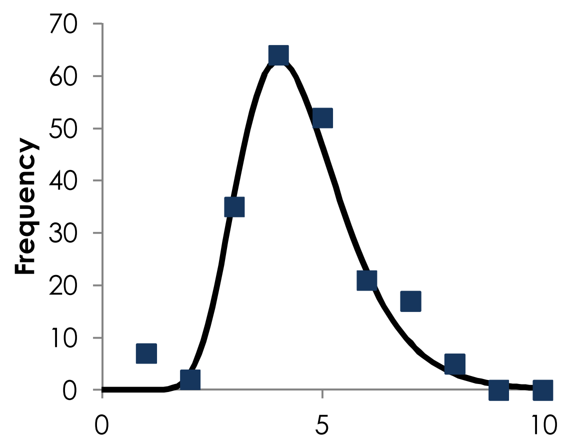
Aged in Ar saturated 0.1M $HClO_4$ at 20°C



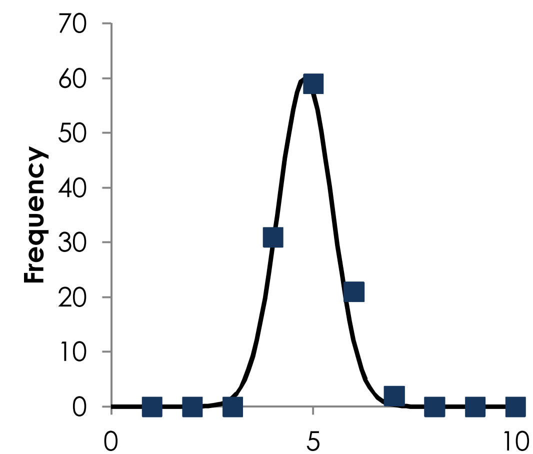
After 800°C anneal | **Initial Conditioning** | **500 cycles 0.6 – 1.2V RHE**



d = 4.3 nm
Log normal distribution



d = 4.4 nm
Log normal distribution

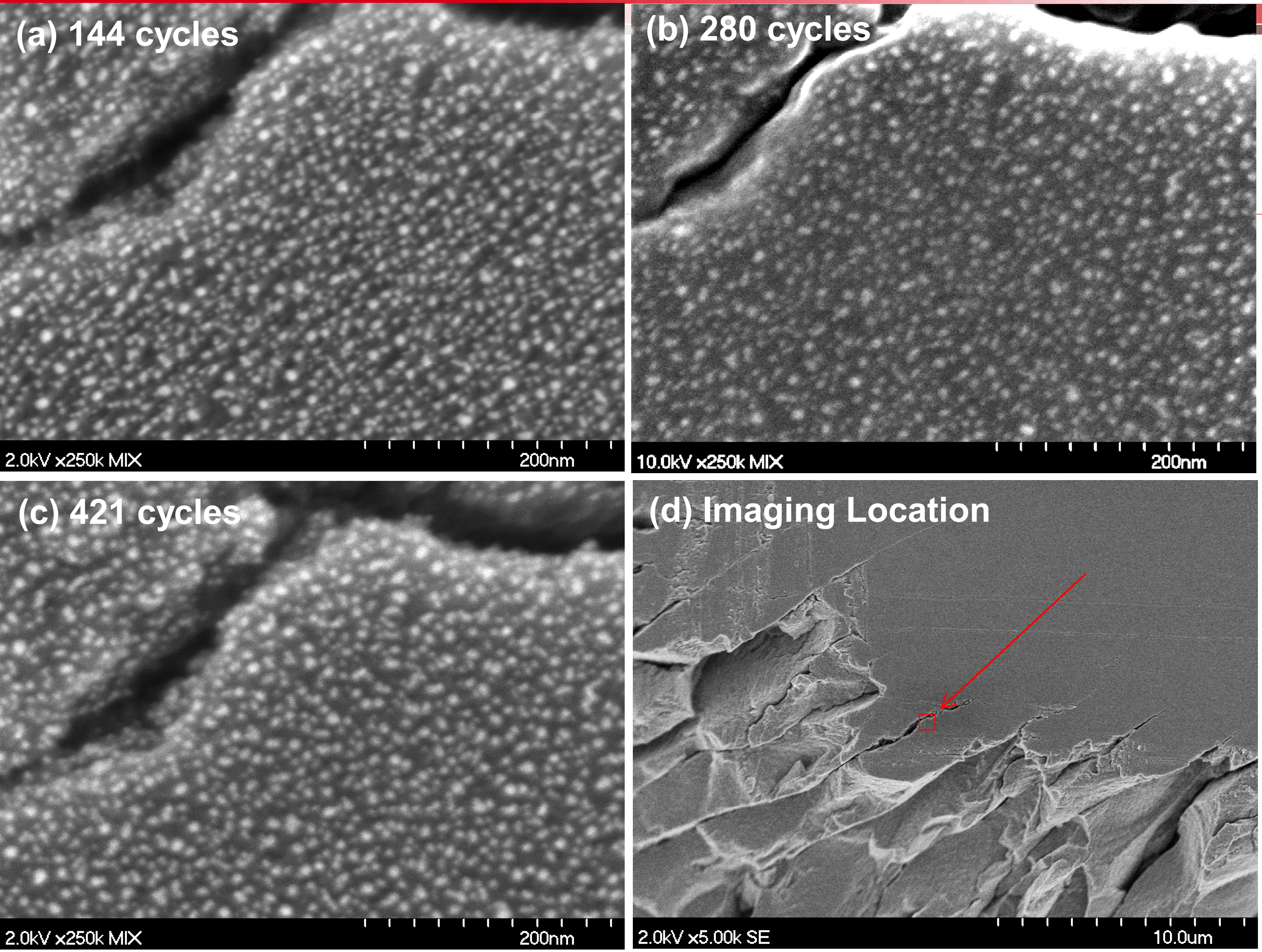


d = 4.9 nm
normal distribution

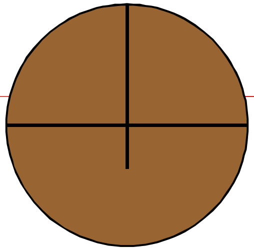
Ostwald Ripening & dissolution?

Fixed Location Study

Aging (cycled 0.6 – 1.2 VRHE)



Diamond scribed reference marks

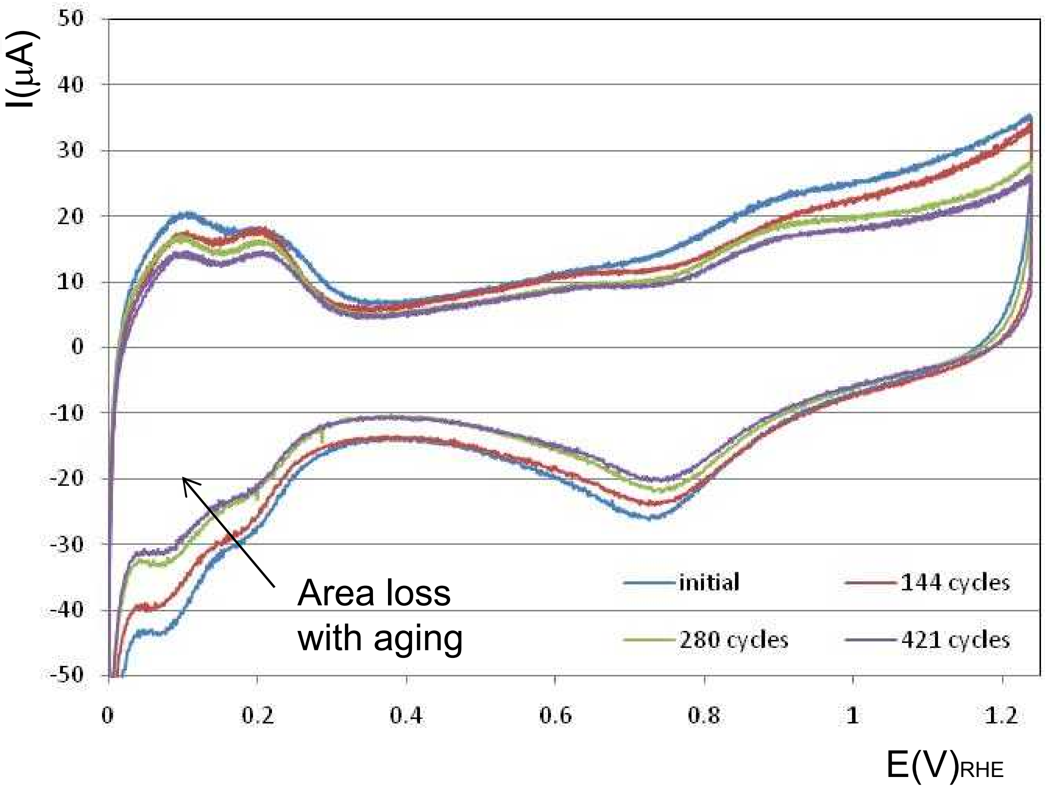


In Ar purged
0.1M $HClO_4$
50 mV/s

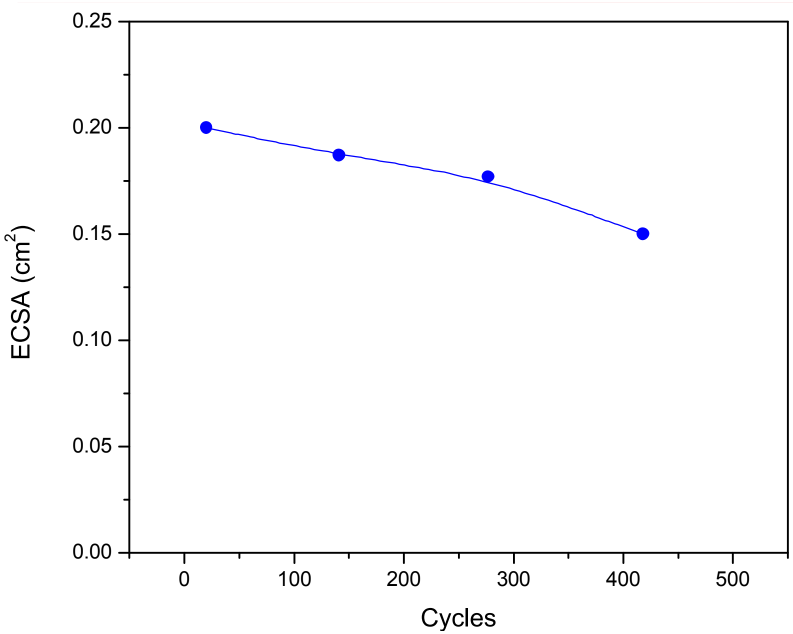
Pt/GCE Repeat Cycling

Aging (cycled 0.6 – 1.2 V_{RHE}) Ar

Cyclic Voltamograms show area loss



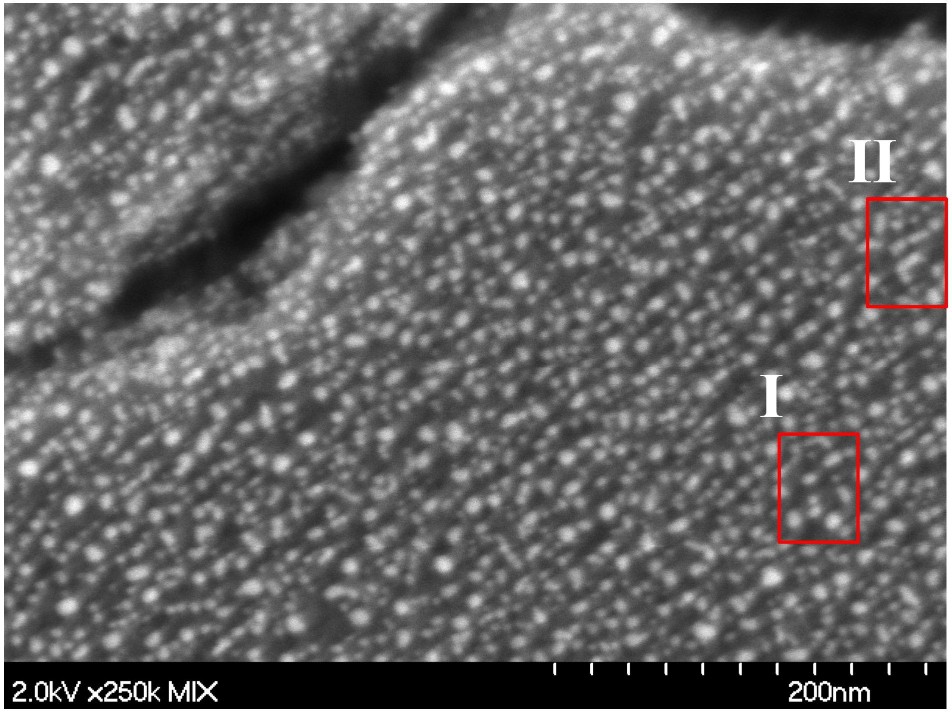
Electrochemically Active Surface Area (ECSA) from CO stripping



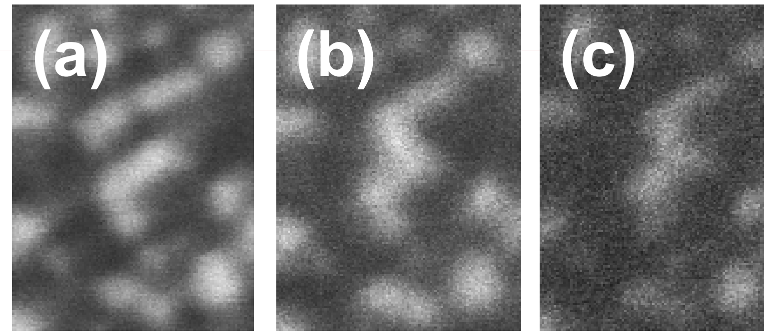
2.1 μg Pt/cm^2 and 800°C anneal

Particle Migration/Coalescence

Sintering Observations



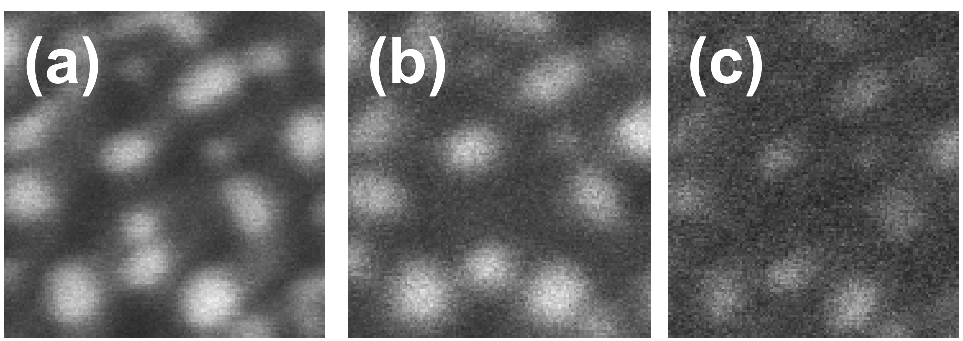
Region II



Formation of elongated shapes

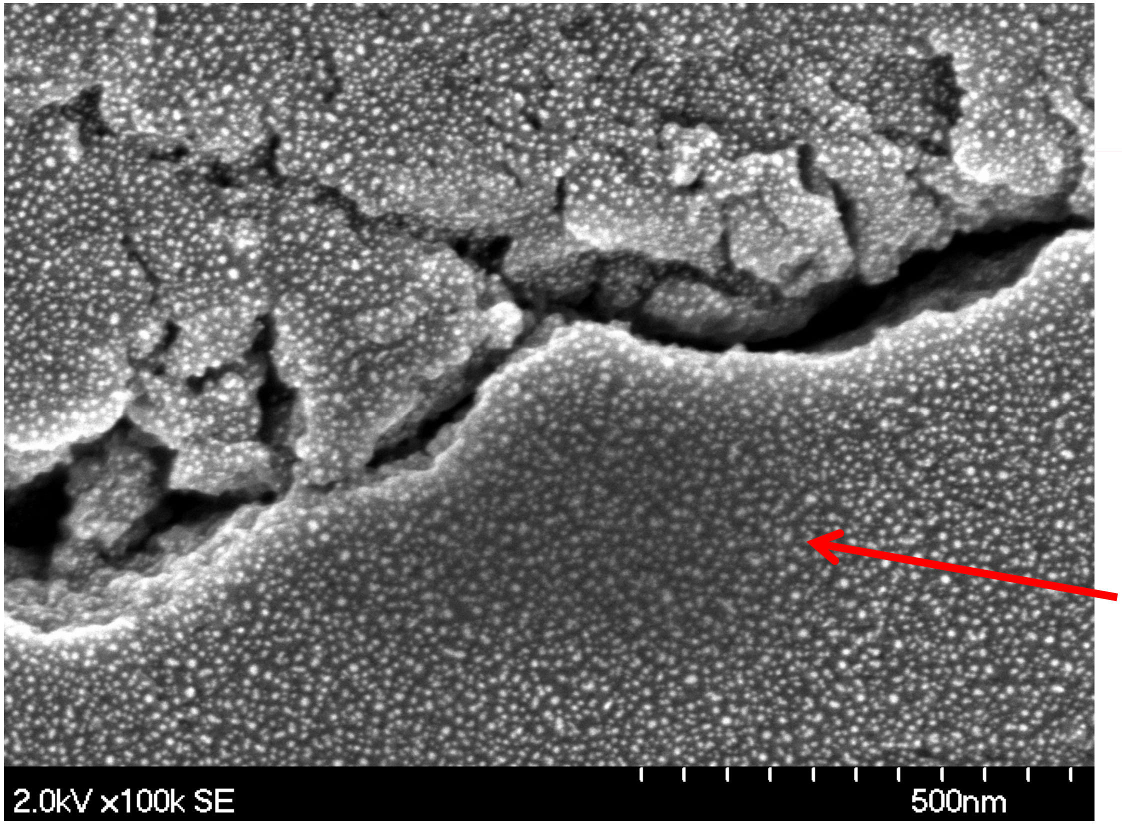
Agglomeration, followed by slow sintering

Region I



SEM imaging residue

Residue limits imaging cycles



Previous imaging location still evident after testing

Does this affect future sintering?

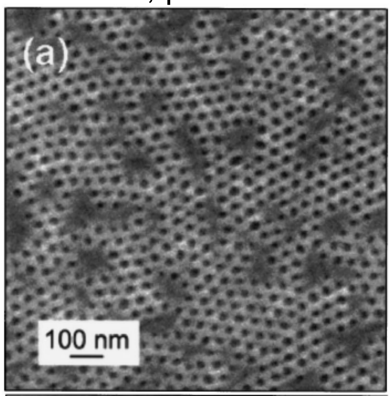
Control over initial particle position and size required to eliminate repeat imaging of the same location!

Diblock Copolymers

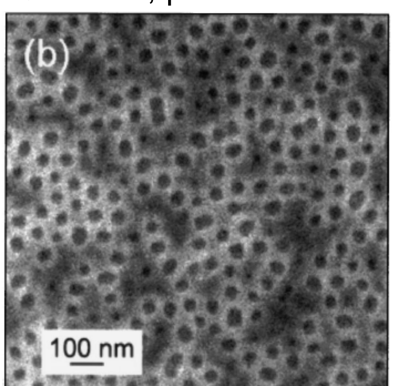
Particle Size and Spacing Control

Utilize diblock copolymer templates developed for nano-scale patterning on silicon

M_n=67100 g/mol
Ø 24 nm, pitch 50 nm

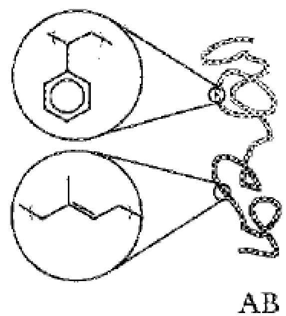


M_n=131800 g/mol
Ø 40 nm, pitch 70 nm

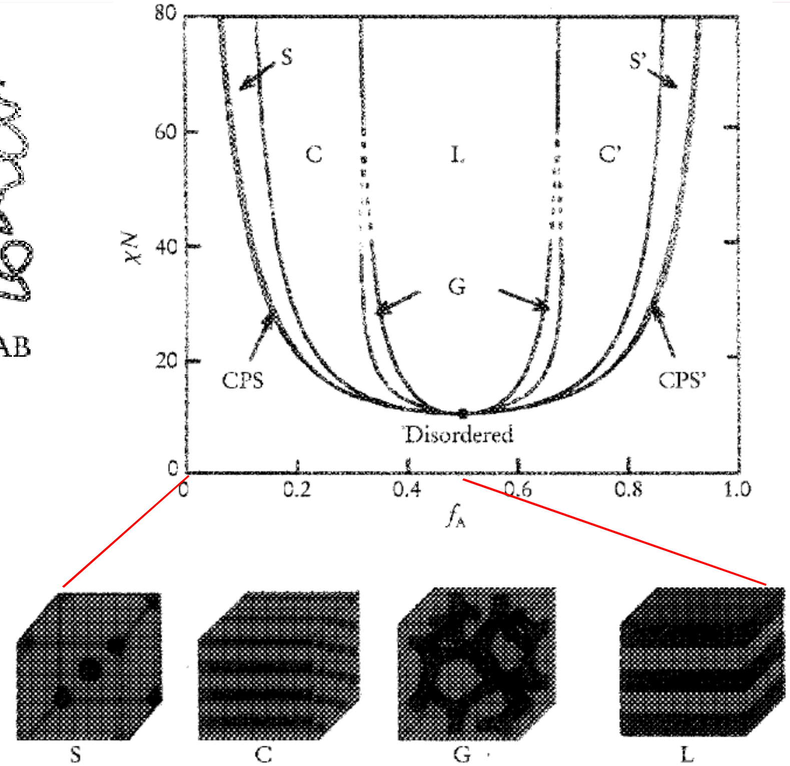


Polystyrene

PMMA



SEM images of the exposed and developed polymer template for different PS-PMMA diblock copolymer molecular weights, demonstrating how pore size and spacing can be controlled.



K. W. Guarini, C. T. Black, et. al, JVST (2001)

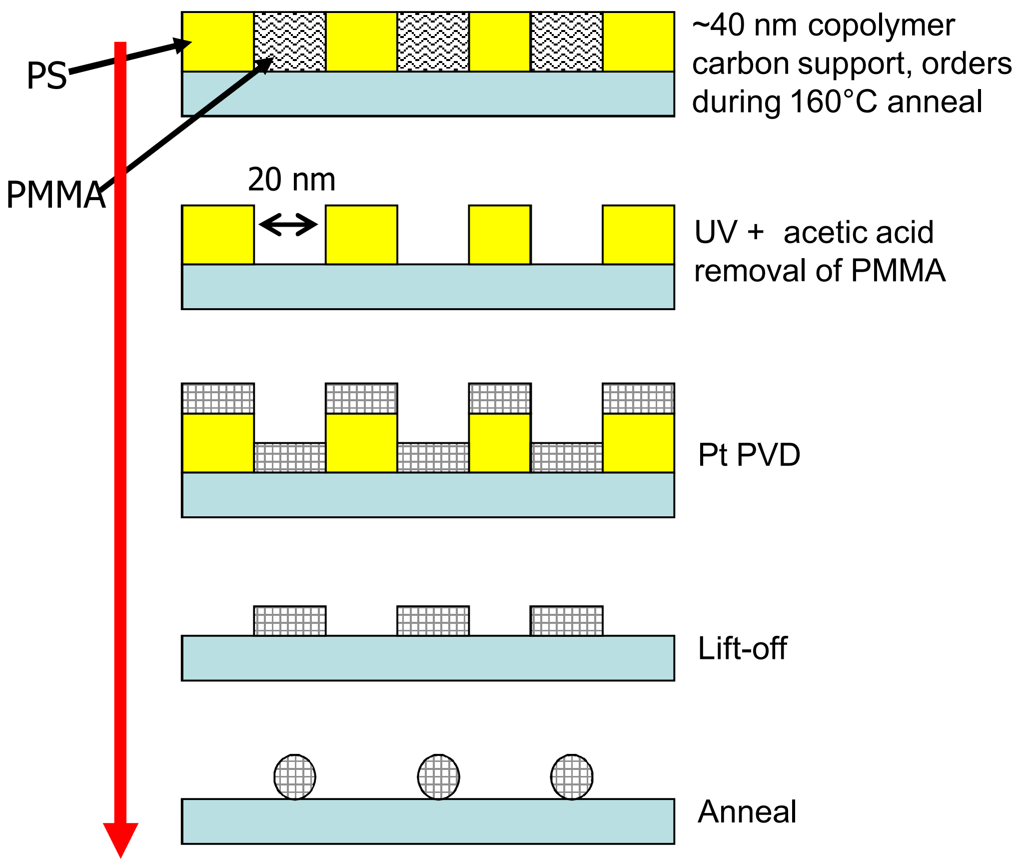
F.S. Bates and G.H. Fredrickson, Physics Today (1999)

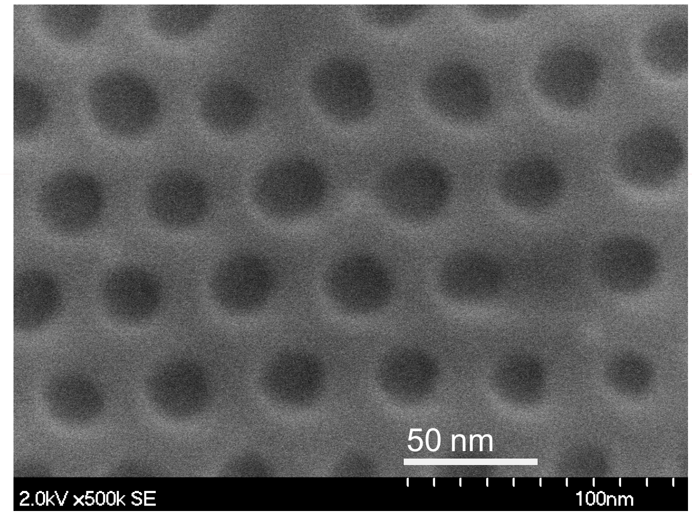
Template Process

20 nm Pores in Polystyrene on Si Wafer

•Thin random brush copolymer is first created on substrate by spin coating from toluene solution. Brush bonding occurs to hydroxyl groups.

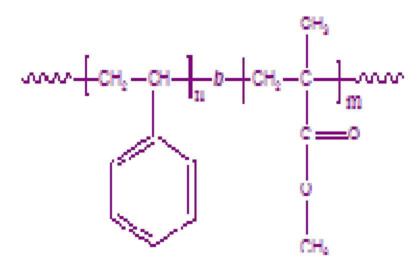
•Block co-polymer is then added by spin coating a 1% PS-b-PMMA solution in toluene





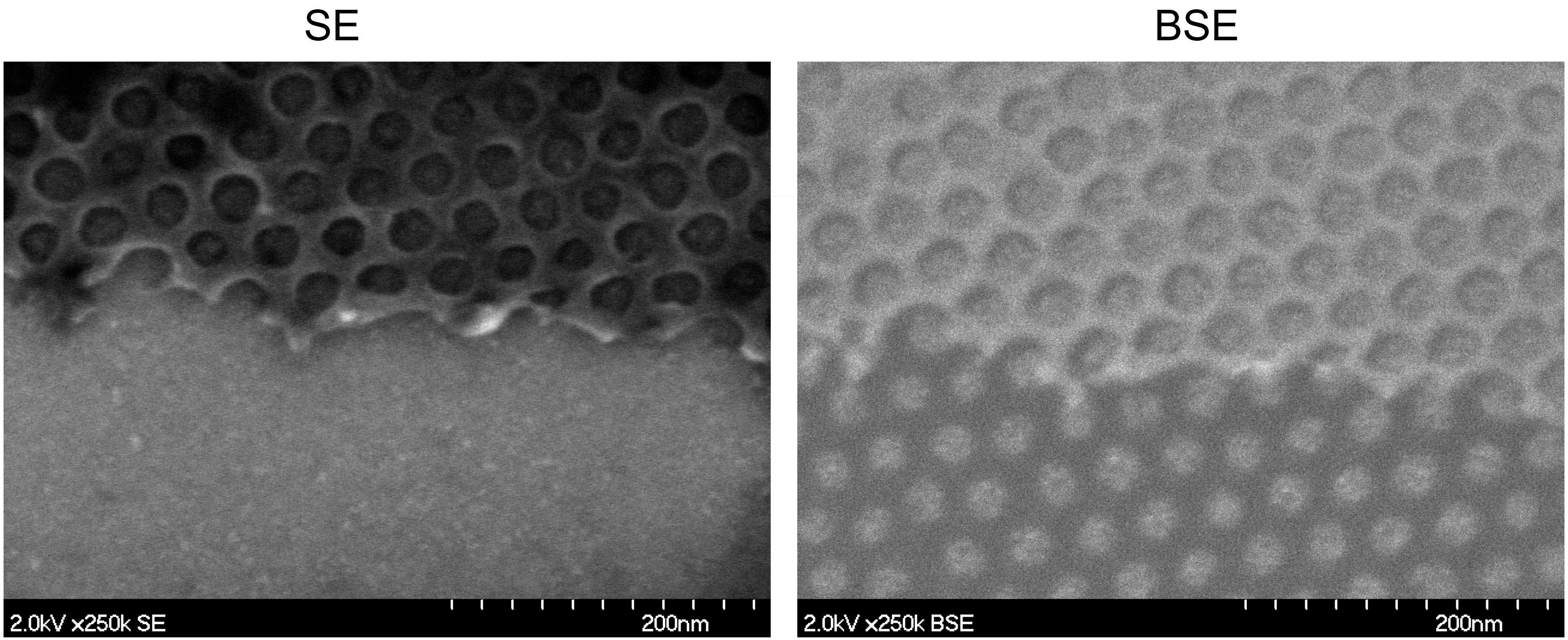
101.5 kDa (68.0-b-33.5)
67.1 kDa (46.1-b-21.0)
31.5 kDa (21.5-b-10.0)

Poly(styrene-b-methyl methacrylate)

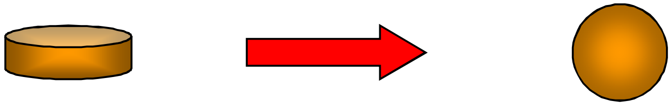


Template Results

Pt Lift-Off



- Partial lift-off of PS template after 5 minutes in toluene with ultra-sonic agitation.
- 20 nm islands ~ 1 ML thick, visible in lifted areas

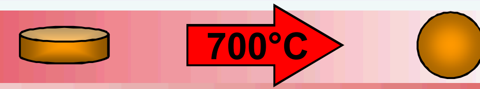


Volume of Cylinder = $h(\pi D^2)/4 \rightarrow$ Sphere = $(\pi d^3)/6$

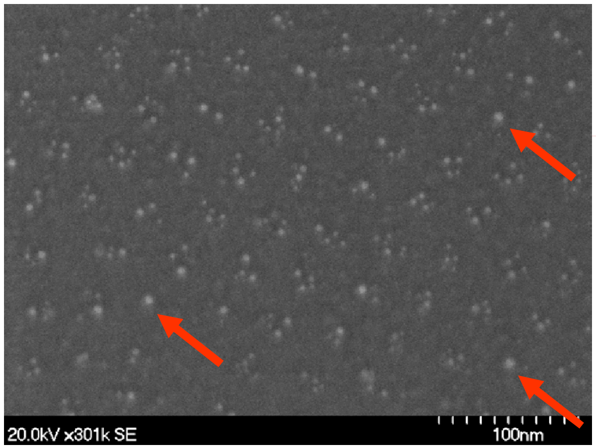
(5 nm particles from 20nm pores, h=0.21 nm ~ 0.44 μg/cm2)

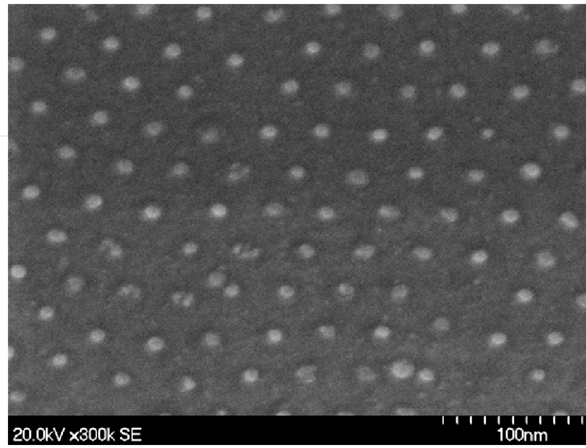
Particle Size Control

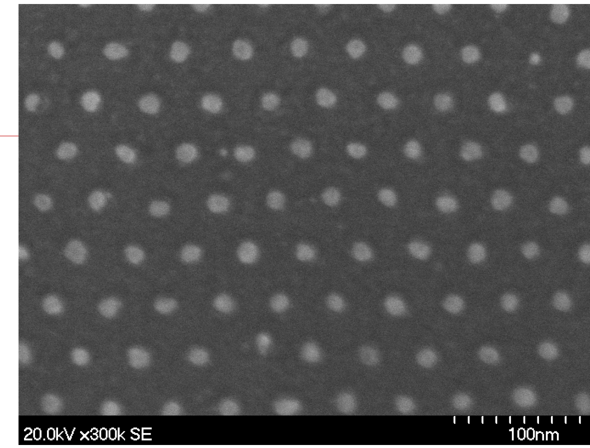
Size Control Demonstrated on Silicon



Polymer Template with 20 nm pores limited to > 7nm particles



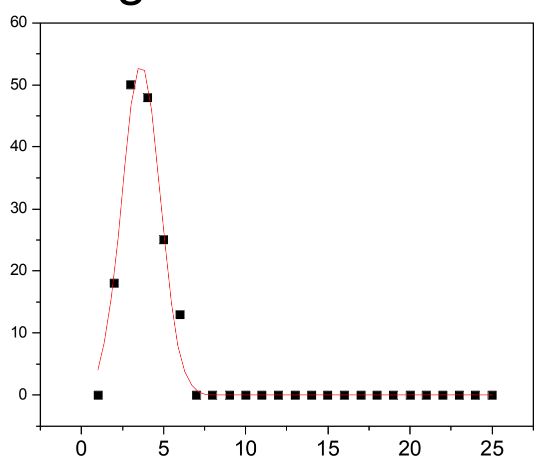


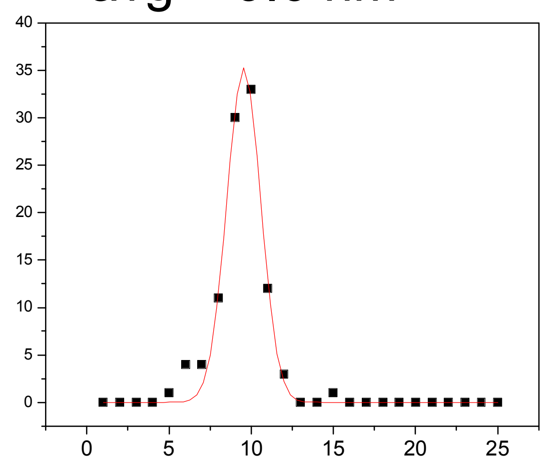


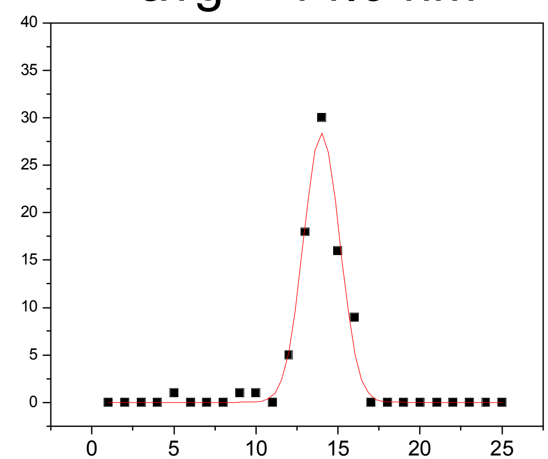
1.3 µg/cm^2 ~ 2ML
exp d = 7.1 nm
avg = 3.6 nm

3.6 µg/cm^2
exp d = 10.1 nm
avg = 9.6 nm

9.7 µg/cm^2
exp d = 14 nm
avg = 14.0 nm





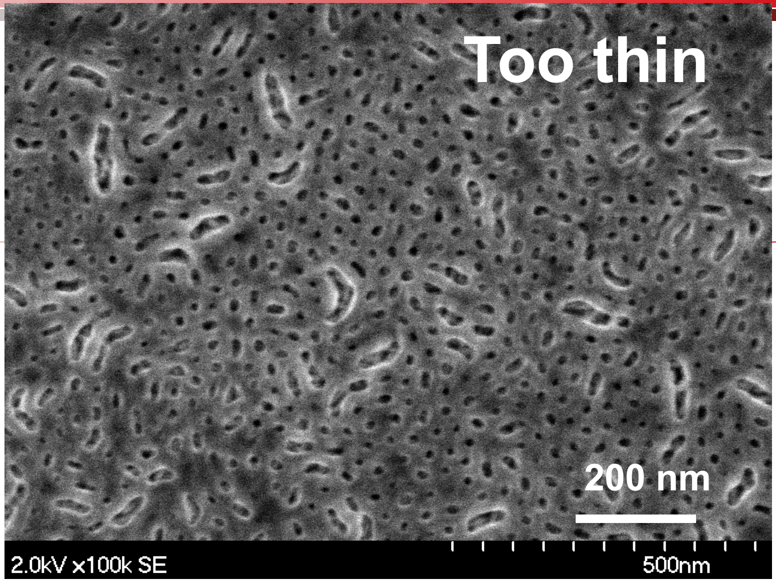


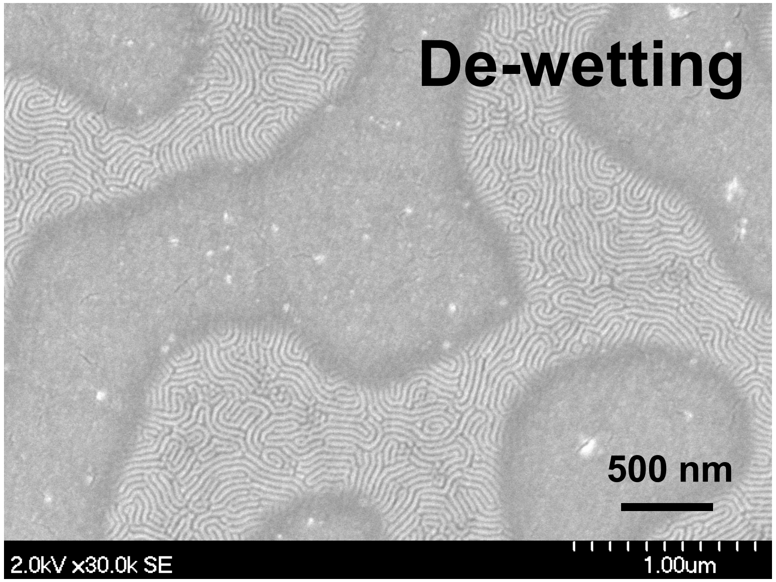
Template on Glassy Carbon

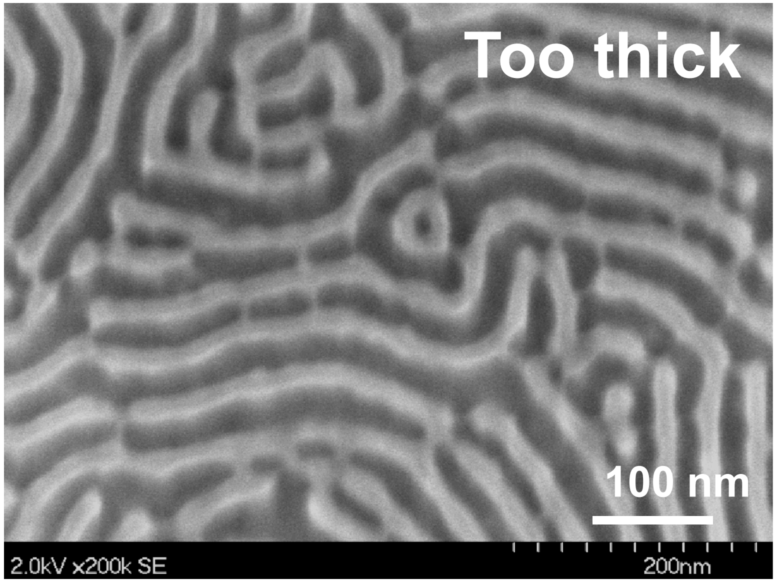
Polymer challenges on small electrode

Application to 5mm glassy carbon electrodes has been challenging

Spin uniformity on small size
Adhesion of random brush layer





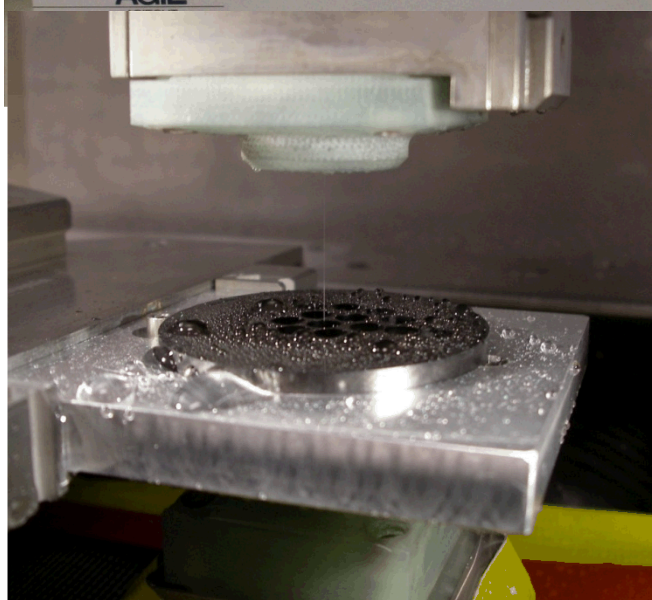


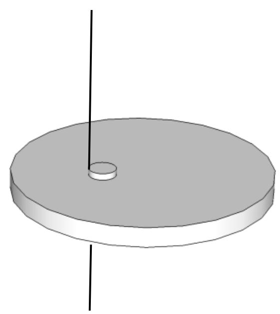
µWire EDM

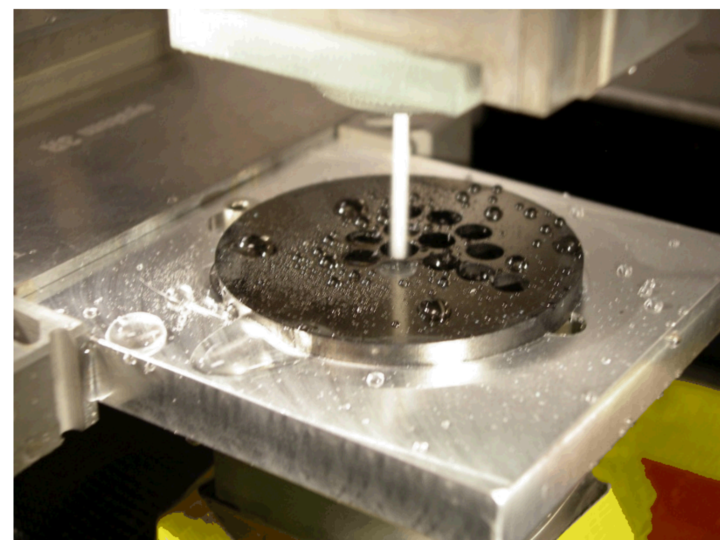
Glassy carbon wafer for polymer processing

Micro-Wire Electrical Discharge Machining (EDM) using a 50 µm tungsten wire

5 mm electrodes cut from a glassy carbon wafer, 50 mm diameter, after application of polymer template

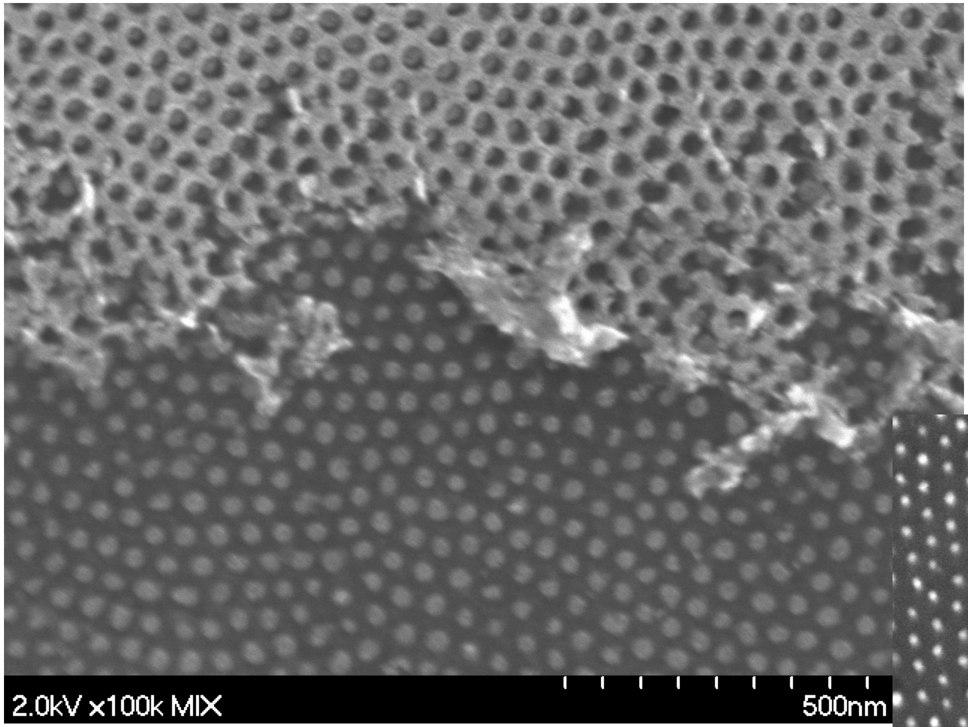






Pt Array on Glassy Carbon

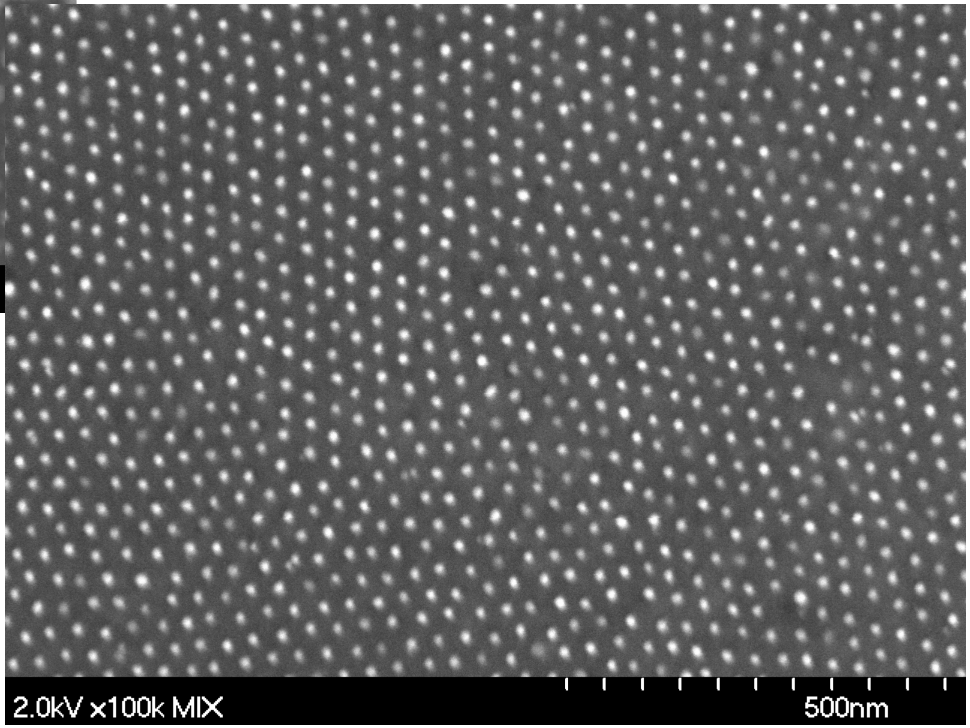
X-linked random mat on carbon



Cross-linked random polymer mat created by Univ. of Wisconsin Prof. Nealey's group

During Lift-Off in NMP at 100°C

10nm particles after 800°C

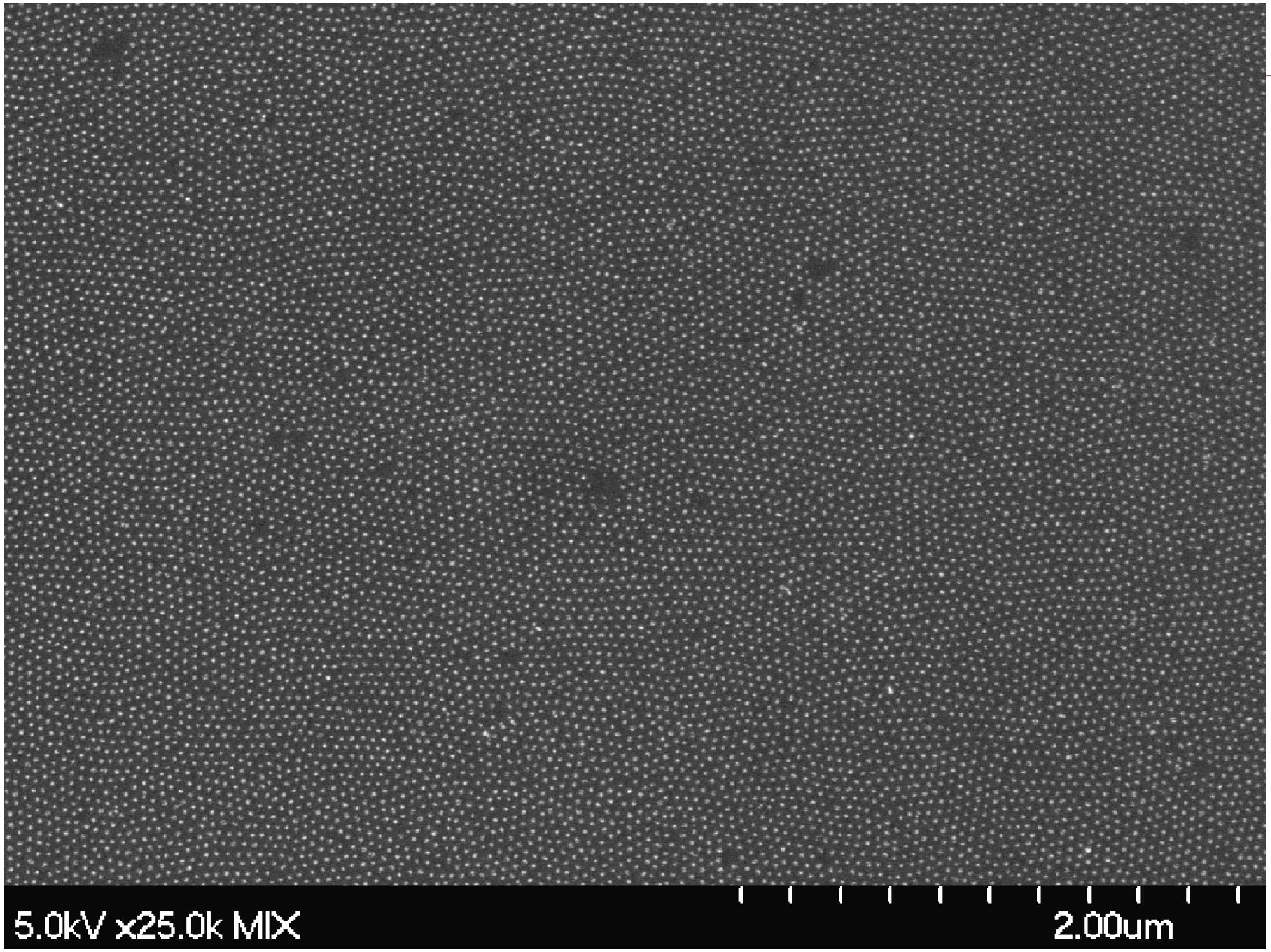


After Lift-Off and 800°C Anneal

Nano-Particle Array on GC Electrode

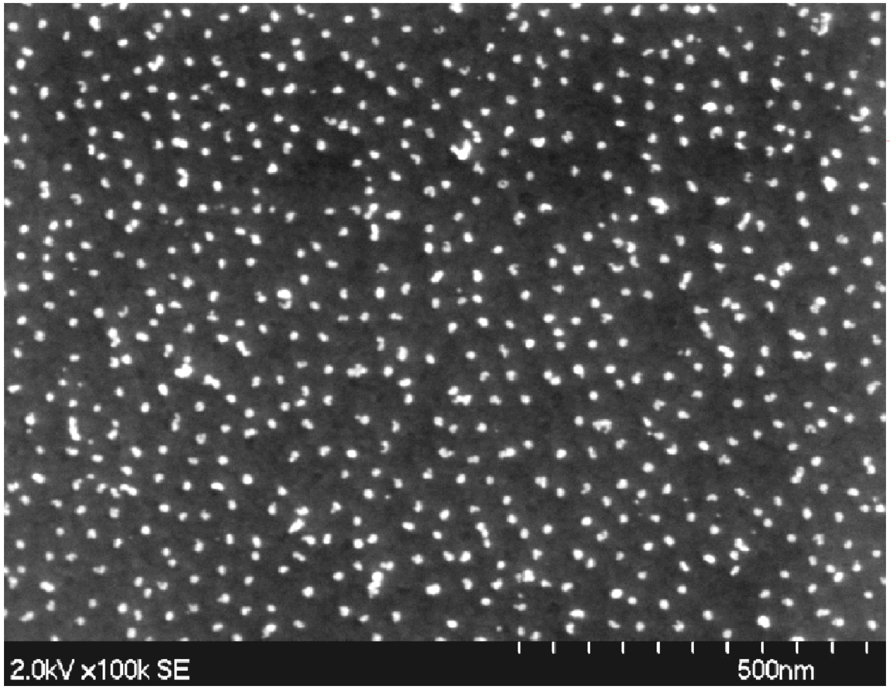
Uniformity to electrode edge

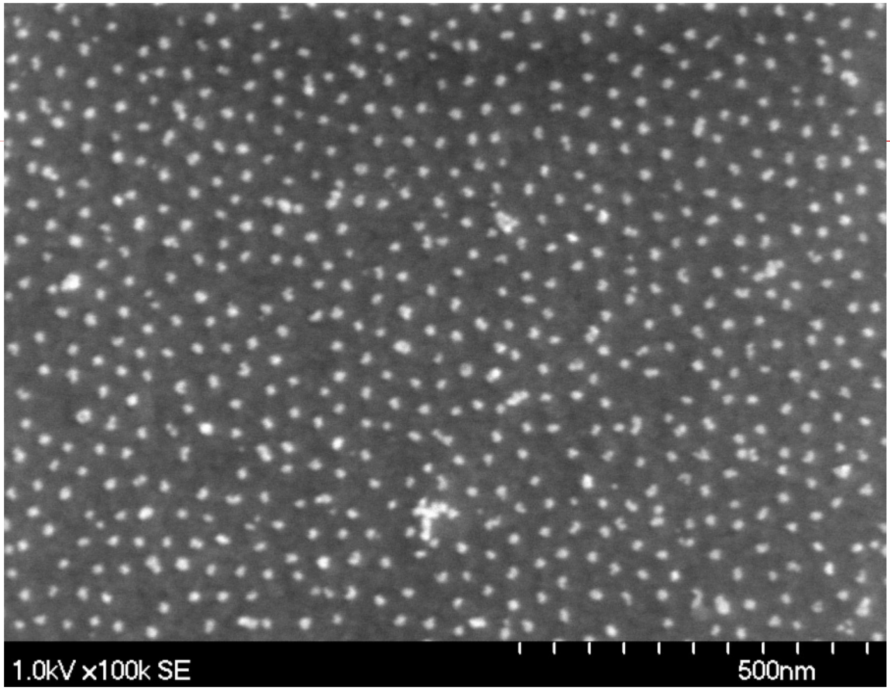
Ordering visible over large area (entire surface covered with only minor defects)



Conditioning CVs on Pt Array

Pt particle agglomeration from detachment



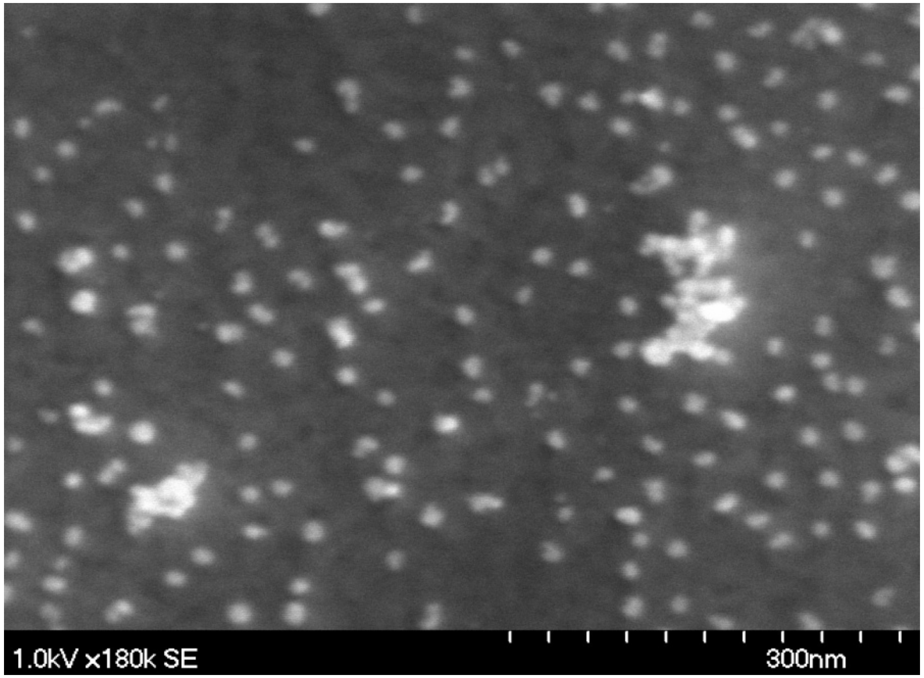


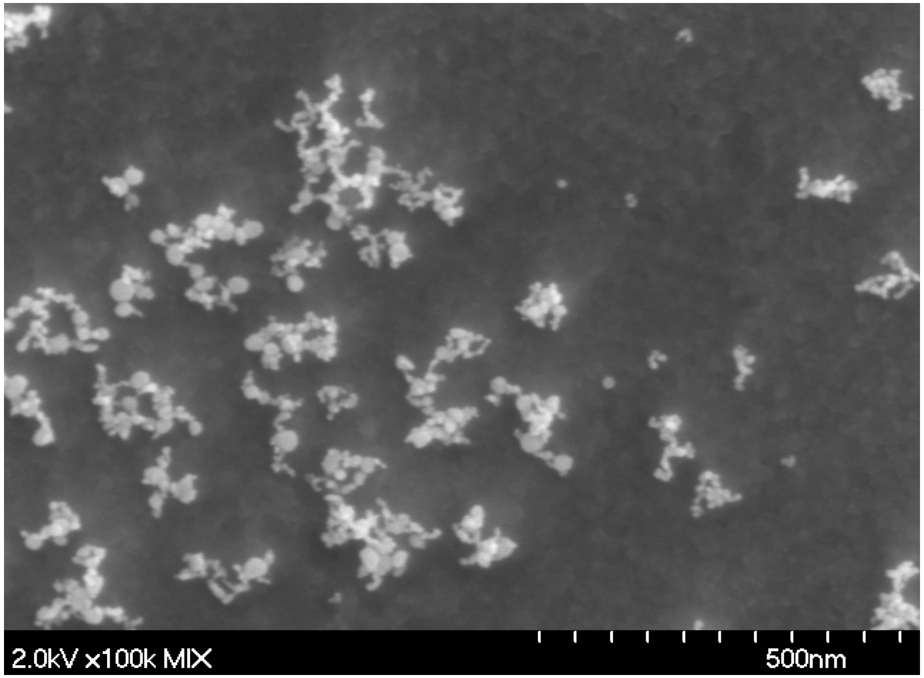
Agglomeration from detachment
- clusters not next to missing particles

Initial Conditioning: 0 – 1.4V_{RHE} 500mV/s (40 cycles)
in Ar purged 0.1M $HClO_4$

Pt particle Agglomeration

Significant agglomeration in some regions





Particle agglomeration & disorder in particle array

Particle clusters slowly begin to sinter

Expect future PSD to be log-normal

Conclusions

- Model electrode structures have been developed using PVD Pt on RDE electrodes
- Cycling between RDE experiments and SEM imaging demonstrated with out damaging electrode structures
- Catalyst degradation mechanisms by Ostwald ripening, dissolution and particle detachment/agglomeration observed
- Template approach developed for application of catalytic particles to glassy carbon electrodes
  - control of particle size and spacing
  - Smaller pore templates will be required for particles < 7nm

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