Graphitic Carbon Thin Films for Neutron Reflectometry Investigations of Rechargeable Batteries and Fuel Cells

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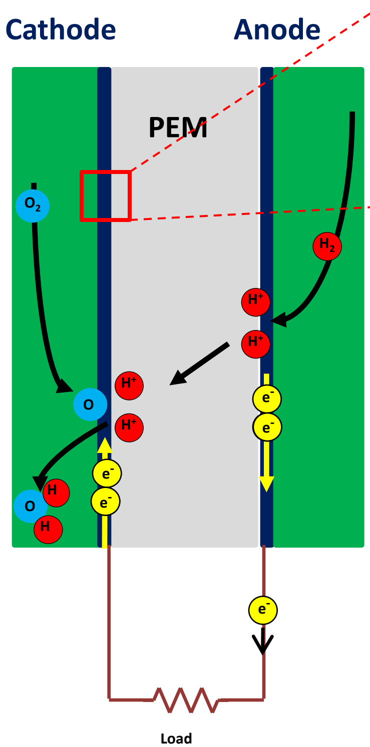
Neutron Condensed Matter Science Group
NIST Center for Neutron Research

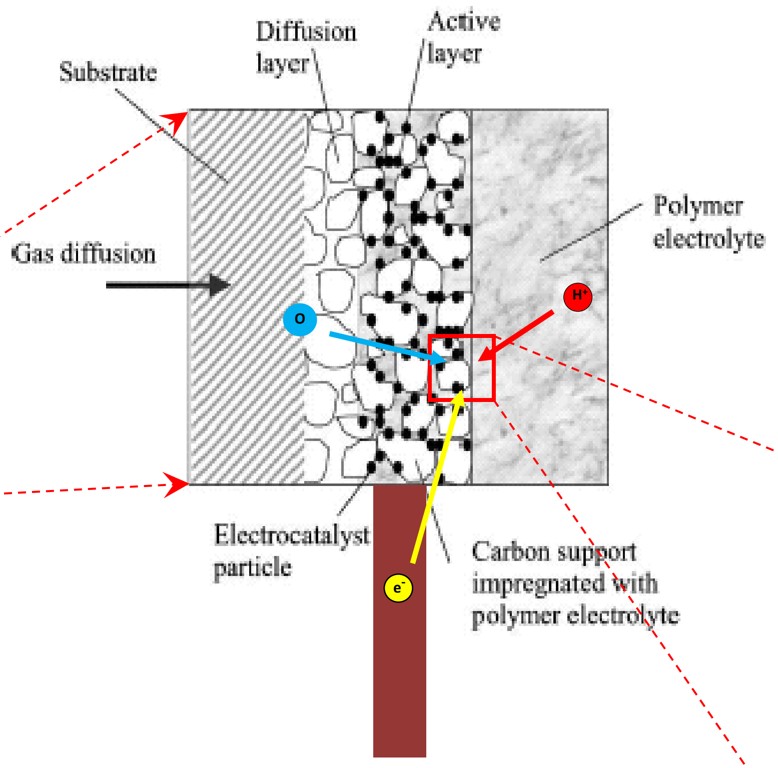
PEM Fuel Cells

(Polymer Electrolyte Membrane)

Membrane Electrode Assembly

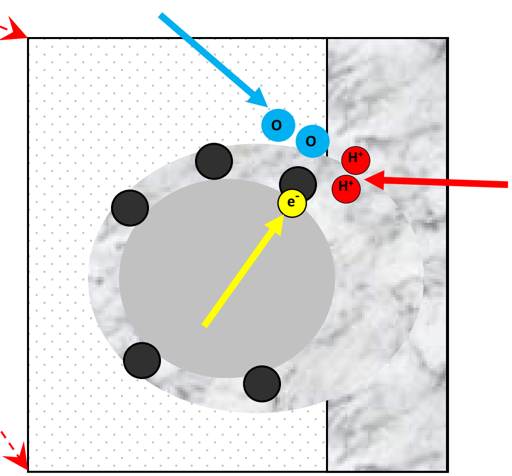


Gas diffusion layer

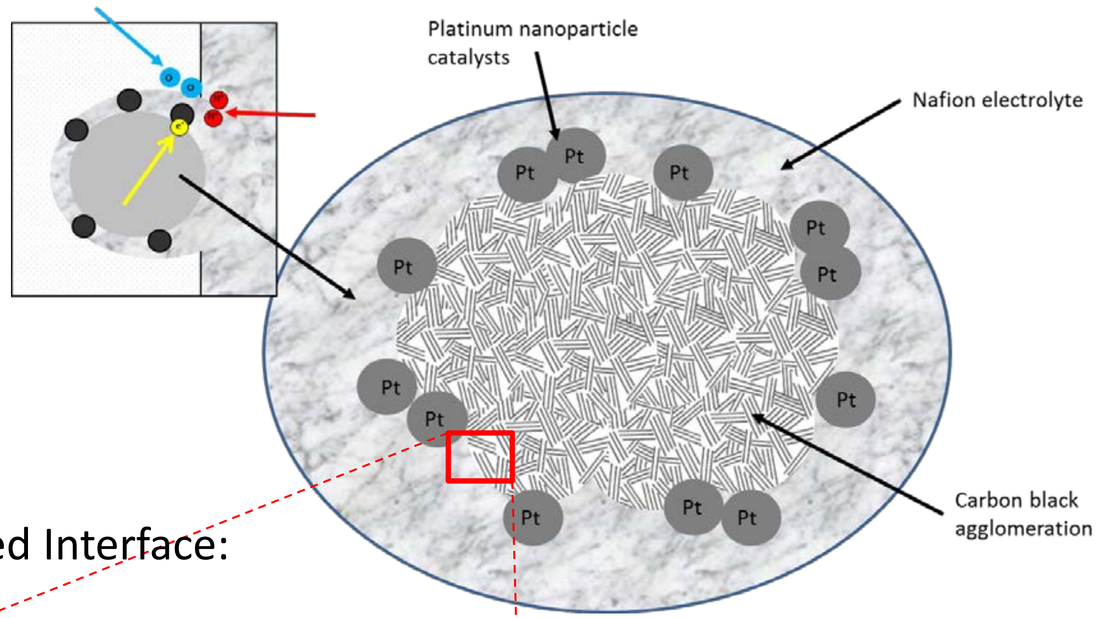


Three Phase Region

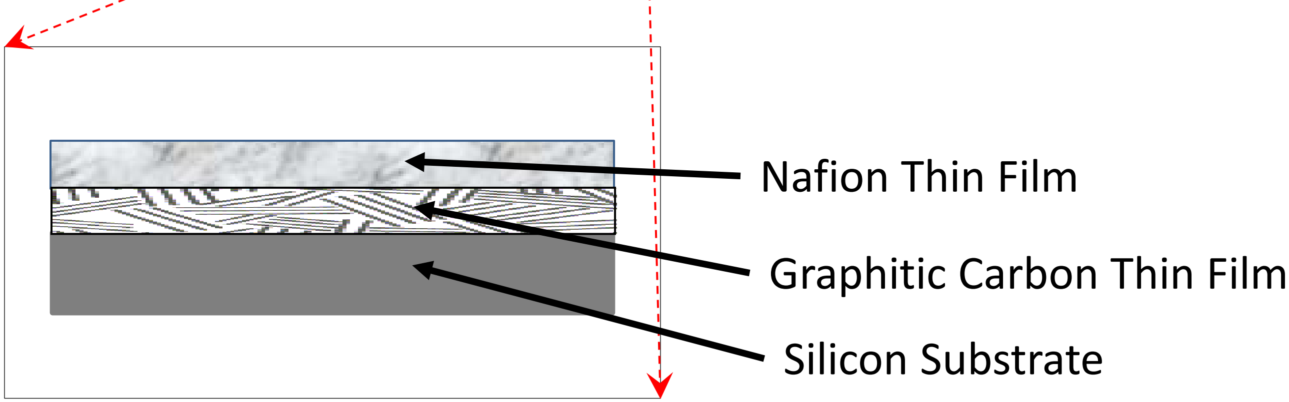
(where gasses, electrode, and PEM come together to allow the electrochemical reaction)



Why Carbon Thin Films?



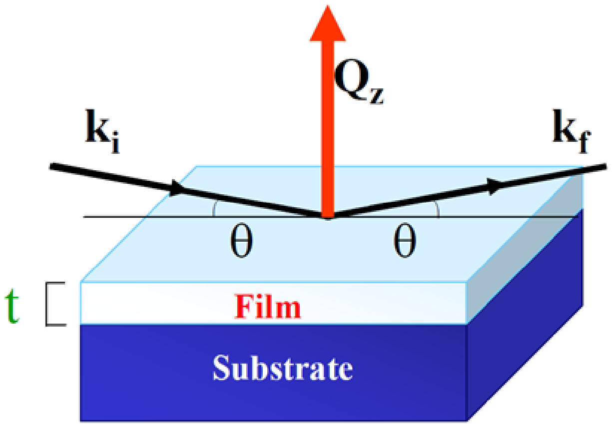
Idealized Interface:

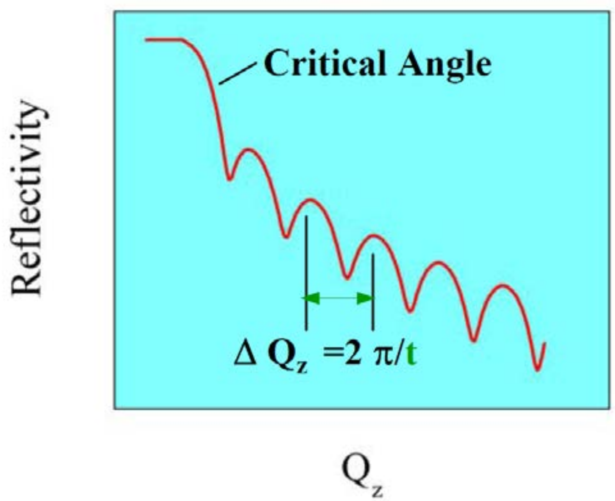


Interface Characterization:

Reflectometry
- High precision
- In situ
- Need flat surfaces

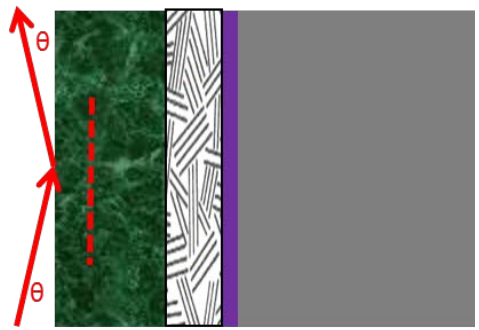
Neutron Reflectometry





- Reflectometry is a measure of the reflected intensity as a function of grazing angle
- Reflected neutrons interfere and average over the entire x-y plane, giving the z direction structure at a sub-Angstrom resolution
- When waves constructively interfere the pattern becomes oscillations related to layer thickness, which can provide a scattering length density profile

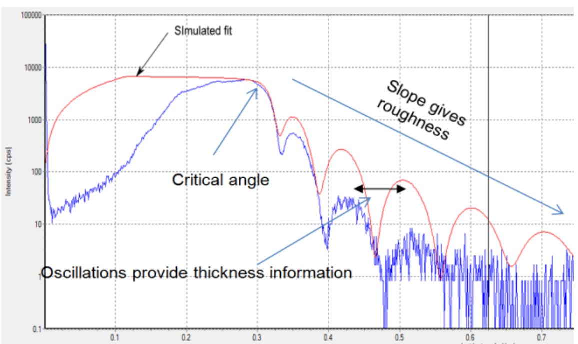
Scattering Length Density Profile



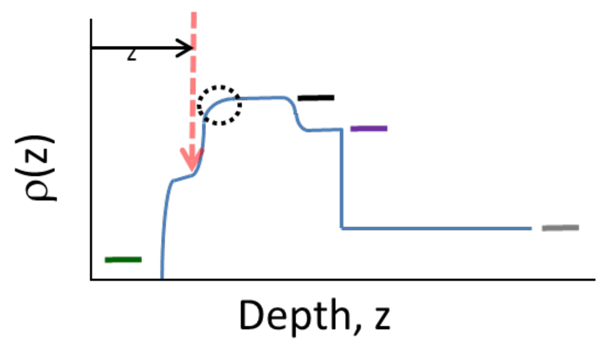
$$SLD(z) = \Sigma_i\, b_n(i)\, n_i(z)$$

$b_n(i)$ = neutron scattering length of isotope i

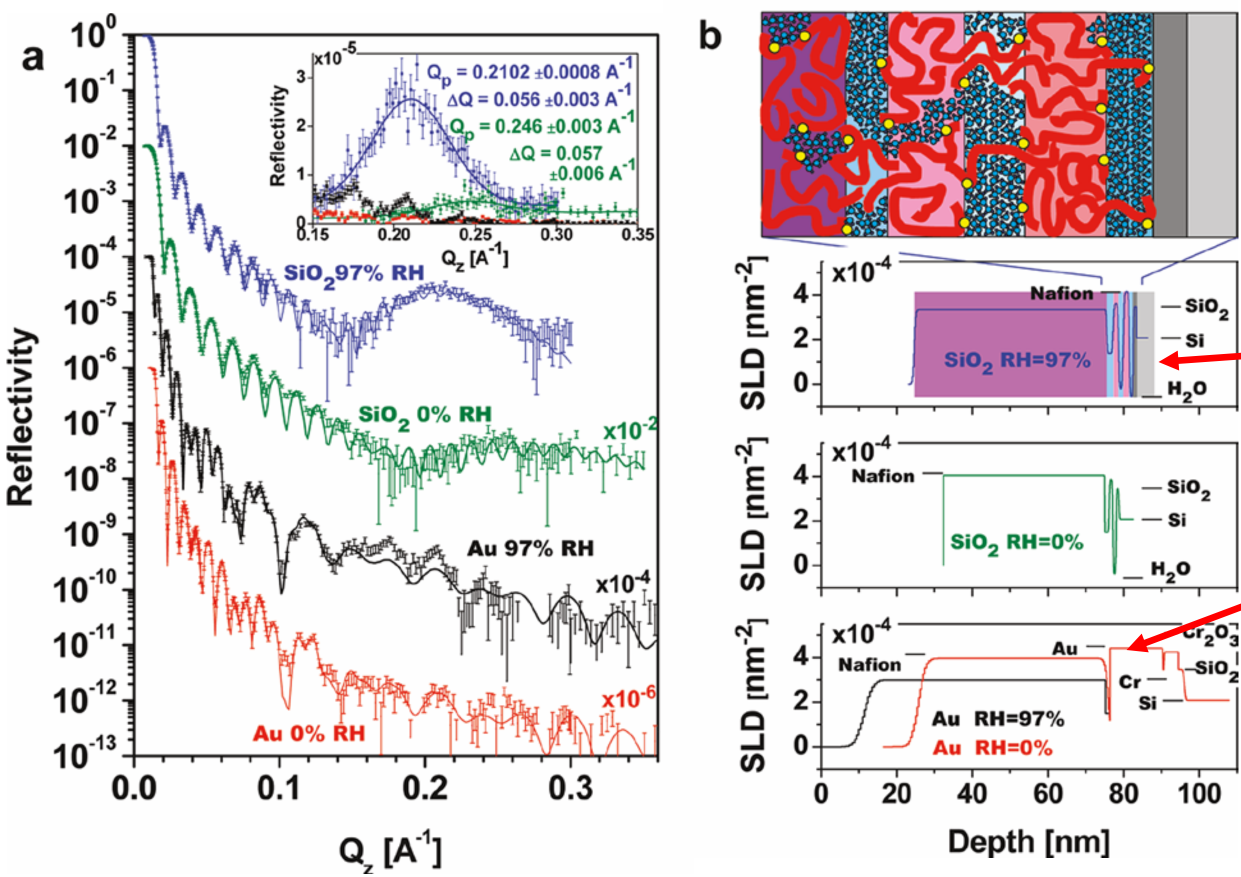
$n_i(z)$ = number density of isotope i as a function of depth



Thin-film thickness and density determination from X-ray reflectivity data using a conventional power diffractometer
HUANG T. C. ; GILLES R. ; WILL G.

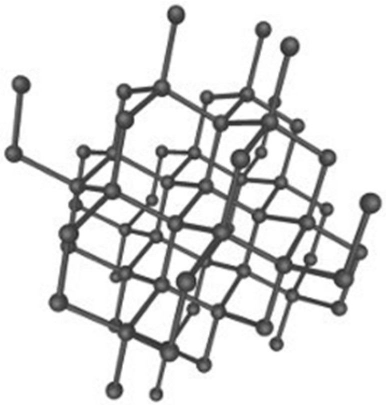


Previous Research

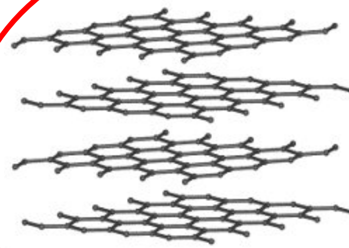


- Nafion on silicon or gold substrates
- Silicon substrate:
  - Lamellar structure with water layers
- Gold substrate:
  - Single water-rich layer
- Similar structure on a carbon surface could have important implications for fuel cell function

NIST Center for Neutron Research

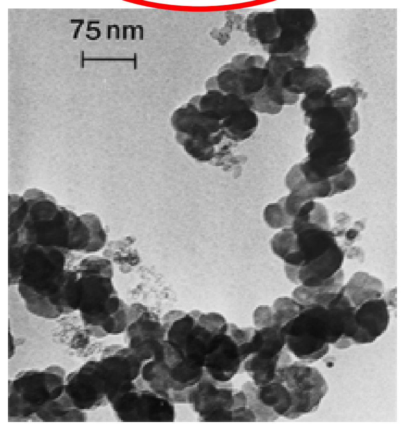


Diamond



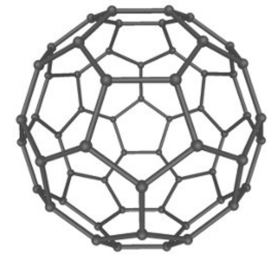
Graphite

Graphene



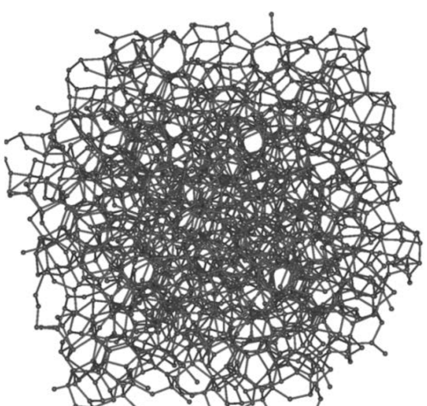
Biological Issues in Materials Science and Engineering: Interdisciplinarity and the Bio-Materials Paradigm; L.E. MURR

Carbon Black

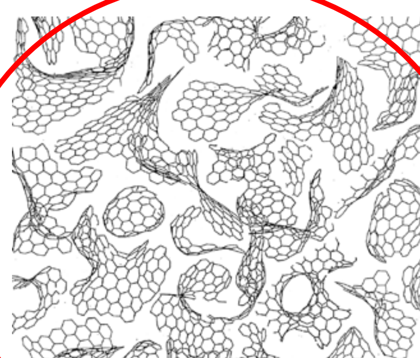


C60, Buckminsterfullerene

WIKIMEDIA COMMONS, MICHAEL STROCK

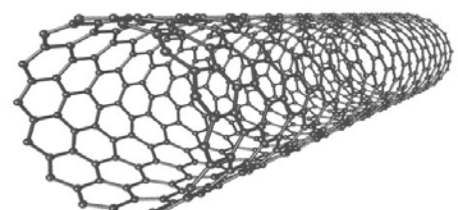


Amorphous Carbon



Glassy Carbon

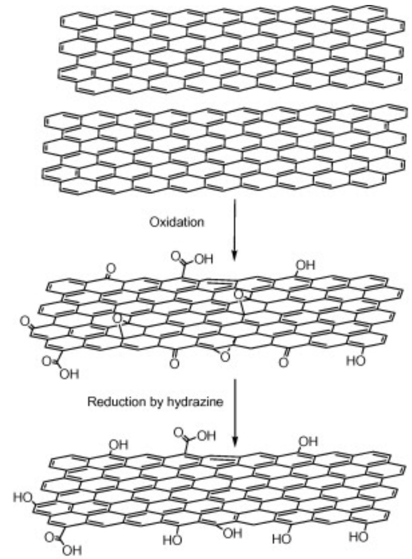
New Perspectives on the Structure of Graphitic Carbons PETER J. F. HARRIS



Carbon Nanotube

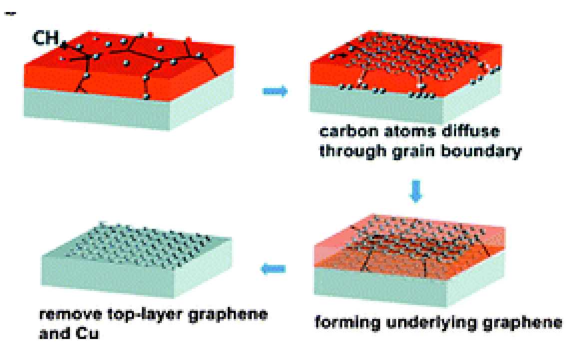
Current Materials

- Reduced oxidized graphene
  - Well understood process
  - Graphene oxide must be reduced by hydrazine
  - Reduction is never complete and produces rough samples with high oxygen content



Graphene based materials: Past, present and Future VIRENDRA SINGHA, DAEHA JOUNGA, LEI ZHAIA

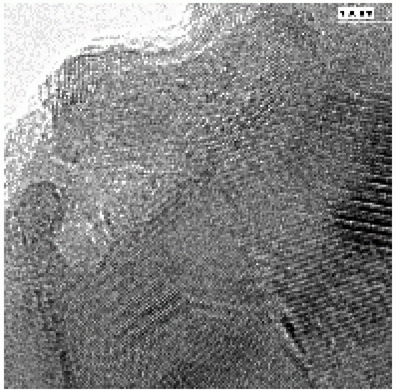
- Chemical Vapor Deposited graphene
  - Expensive
  - Complex process, but well understood
  - Also produces rough samples



Graphene transfer: key for applications JUNMO KANG, DOLLY SHIN, SUKANG BAE A AND BYUNG HEE HONG

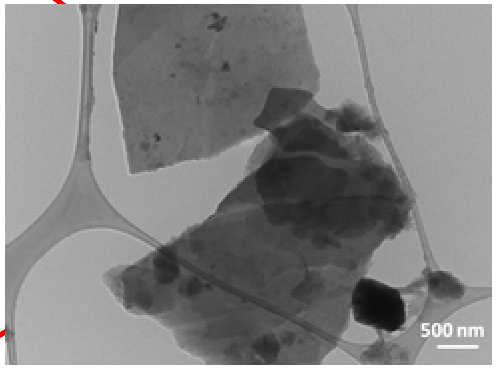
Two Possibilities

- Pyrolized Photoresist (PPR)
  - Relatively easy to fabricate
  - Very similar to glassy carbon, smoother surface
  - Slightly rougher than reflectometry resolution



http://mmadou.eng.uci.edu/Research/CMEMS.htm CHUNLEI WANG, BENJAMIN YONG PARK, RABIH BACHIR ZAOUK, KARTIKEYA MALLADI, GENIS TURON TEIXIDOR, FRANCESC GALOBARDES JORNET

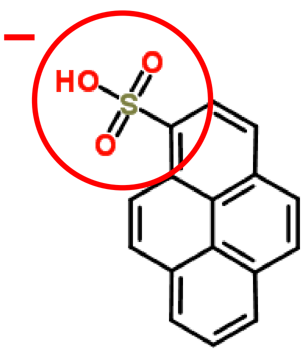
- Deposited Aqueous Graphene
  - Fabrication process has not yet been performed
  - If it forms graphite, the surface should be very similar to carbon black
  - Is only stable at very dilute concentrations
  - Is only dissolved in water, difficult to process

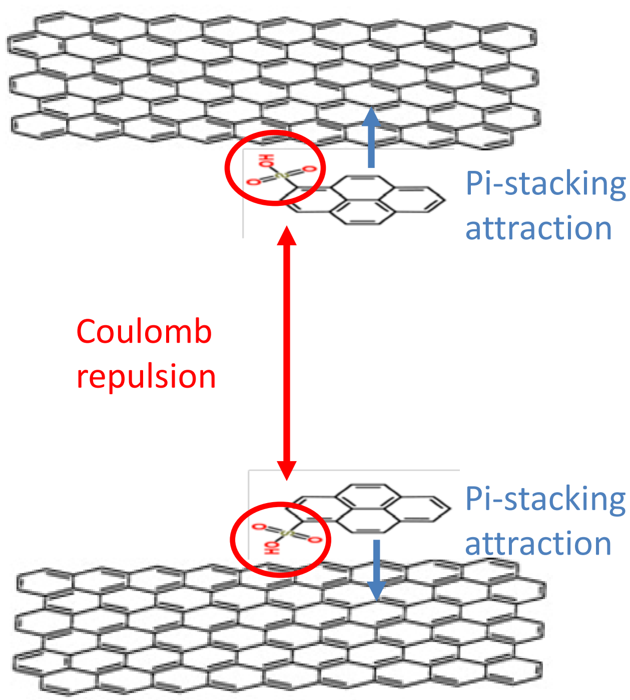


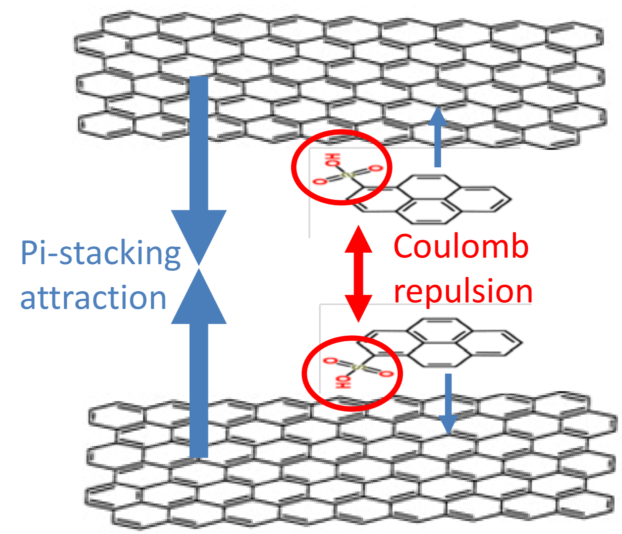
Dispersions of Non-Covalently Functionalized Graphene with Minimal Stabilizer DORSA PARVIZ, SRIYA DAS, H. S. TANVIR AHMED, FAHMIDA IRIN, SANJOY BHATTACHARIA, AND MICAH J. GREEN

Aqueous Dispersion of Graphene

- Pyrenesulfonic acid as a dispersion agent in water
- Limiting concentration for dispersion
  - Pi-stacking is short-range vs. Coulomb repulsion is long-range
  - As concentration increases, graphene flakes becomes close enough together than pi-stacking between them can overcome the coulomb repulsion

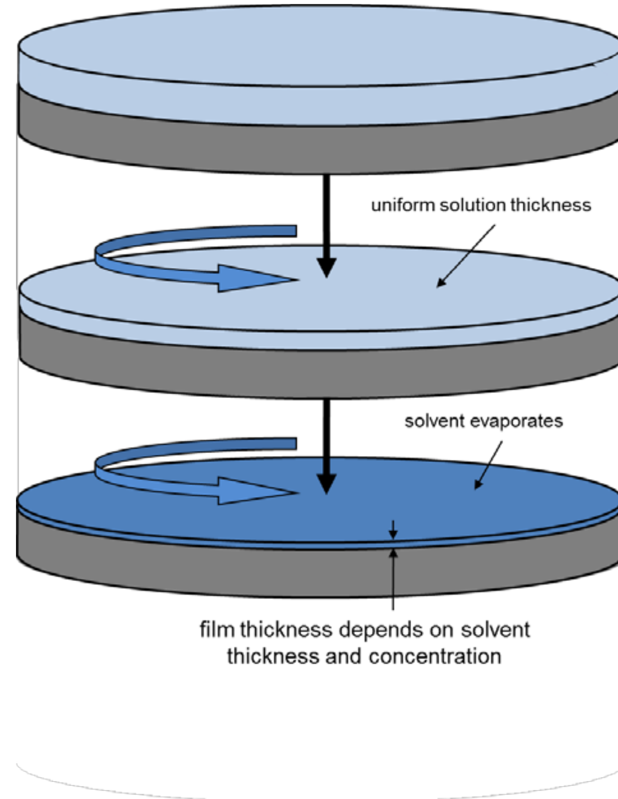


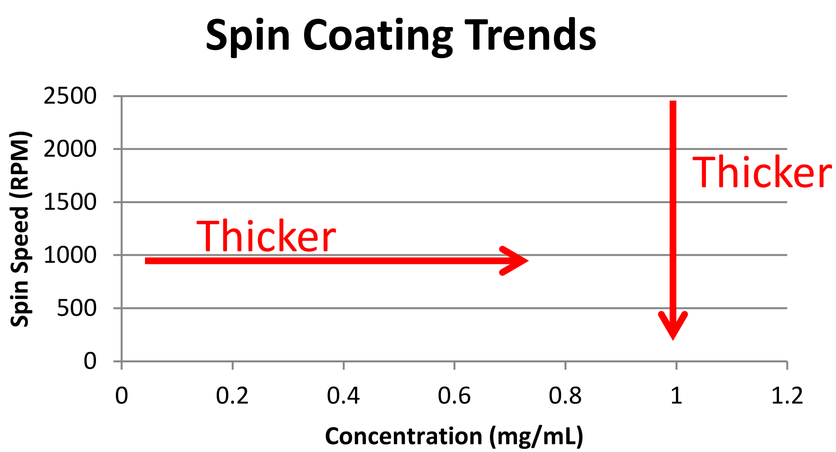




Spin Coating

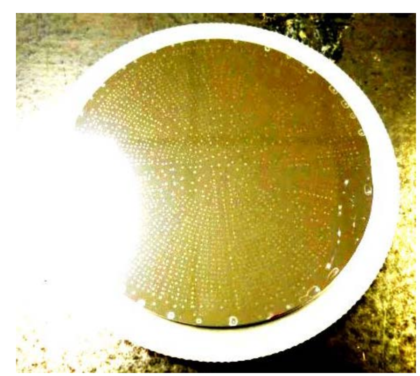
- Solution is ejected onto the substrate, which is then spun
- Centrifugal force produces a uniform solution film
- Solution film thickness is inversely proportional to spin rate and also depends on substrate hydrophobicity and solution viscosity
- The solvent then evaporates, depositing a uniform film of solute
- The final film thickness is proportional to solution concentration and solution film thickness





Unfortunately…

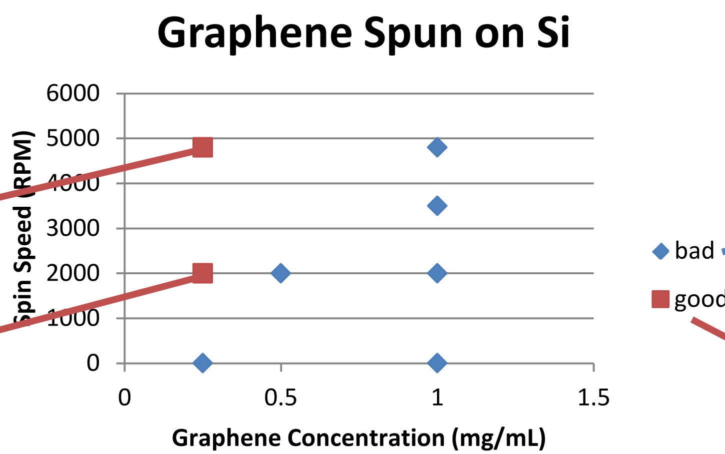
- As the water evaporates away, the graphene concentration increases
- The graphene precipitates out of solution
- Forms a pattern of spots on the substrate

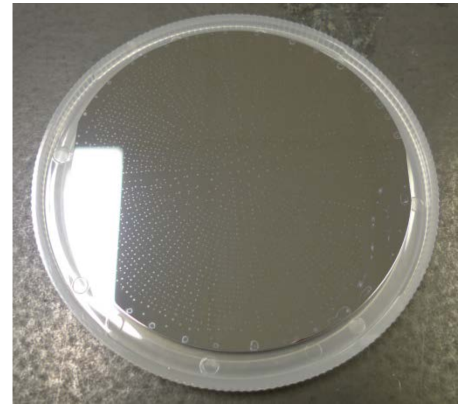


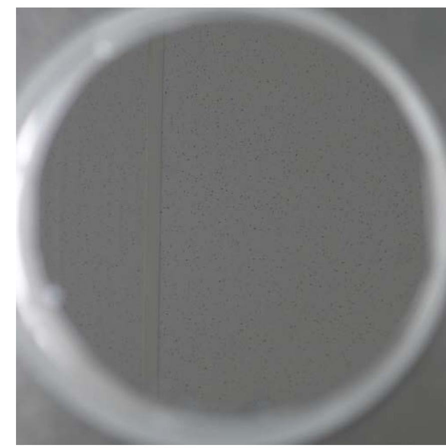
Process Phase Diagram

~ 6 Ang.

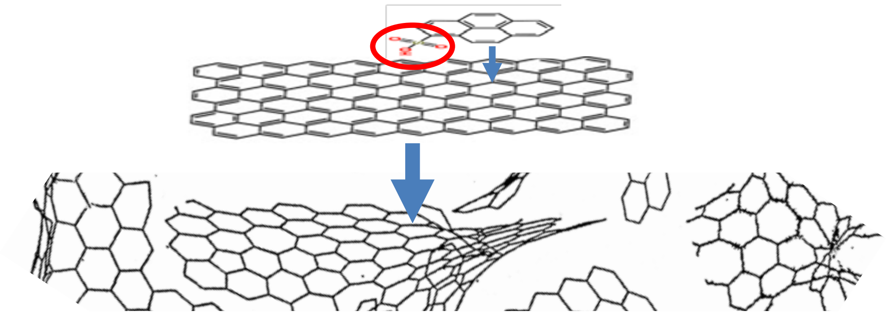
~ 30 Ang.

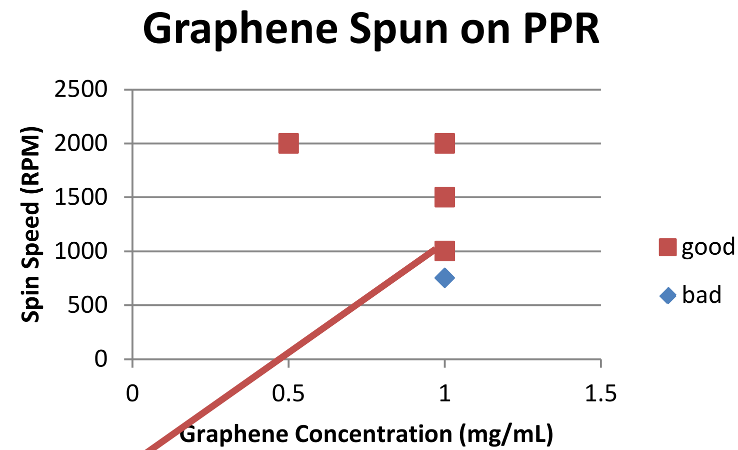


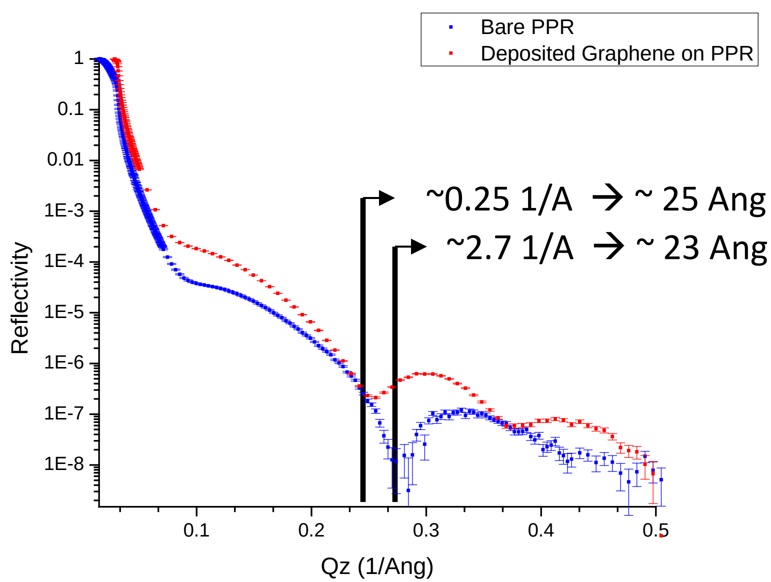


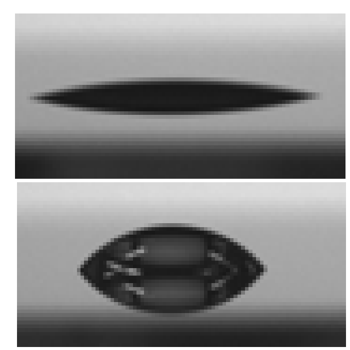


X-ray Reflectometry Data





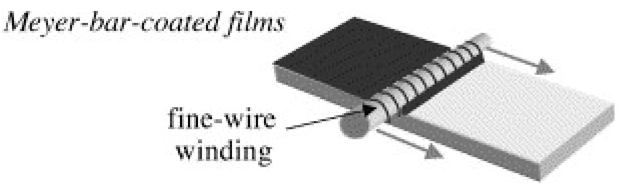




Water on Si/SiO_2

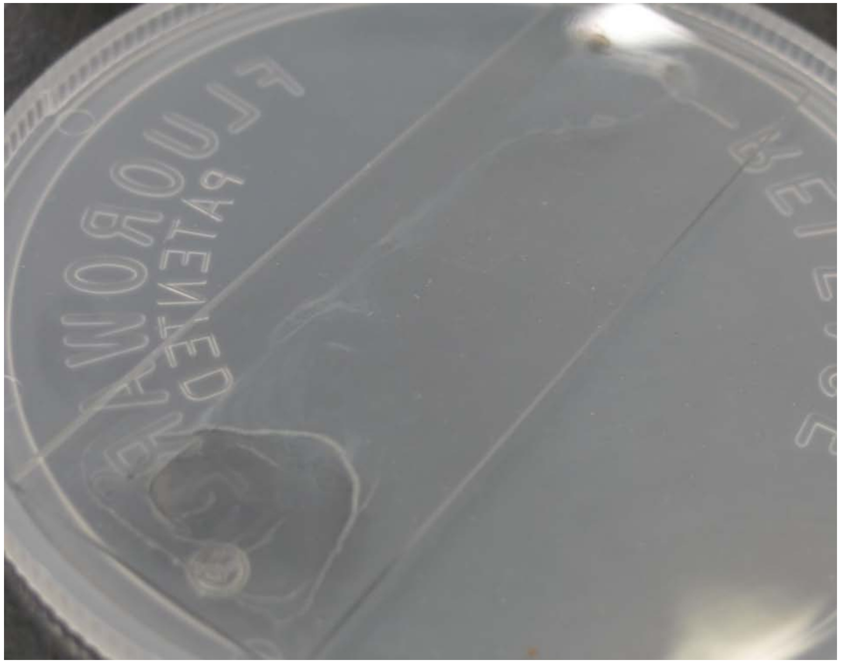
Water on PPR on Si/SiO_2

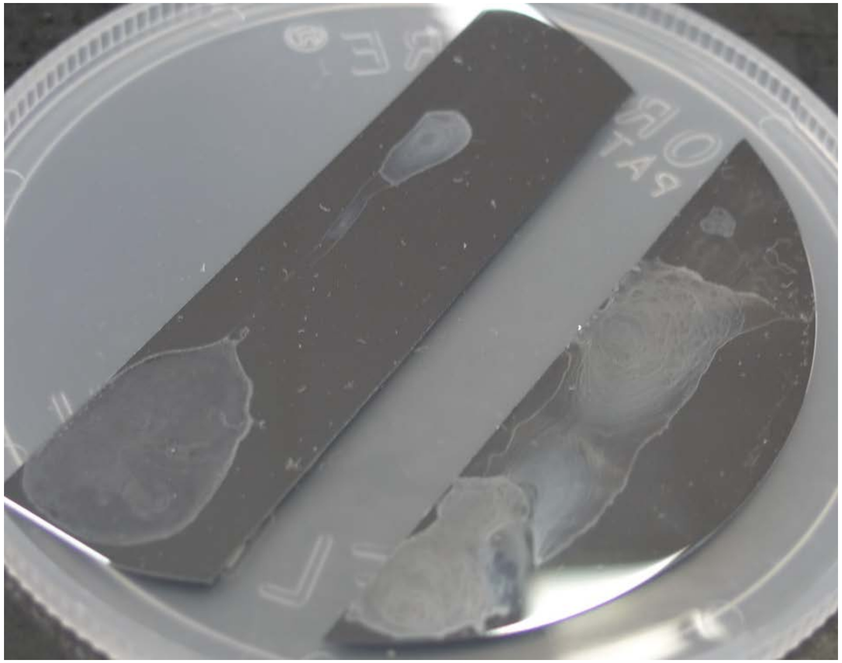
Bar Coating



Orientationally ordered and patterned discotic films and carbon films from liquid crystal precursors KENGQING JIAN, HAIQING XIANYU, JAMES EAKIN, YUMING GAO, GREGORY P. CRAWFORD, ROBERT H. HURT

- Tends to produce thicker films than spin coating
- Produced thicker films,
- But cohesion forces made the film shrink like a droplet instead of uniform drying across the film
- The final surfaces were unsuitable for reflectometry





Two Possibilities

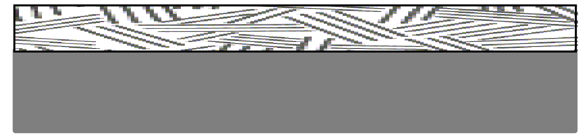
- Pyrolized Photoresist (PPR)
  - Relatively easy to fabricate
  - Glassy carbon structure similar to bulk carbon black
  - Different surface from carbon black
- Deposited Aqueous Graphene
  - ~~Fabrication process has not yet been performed~~

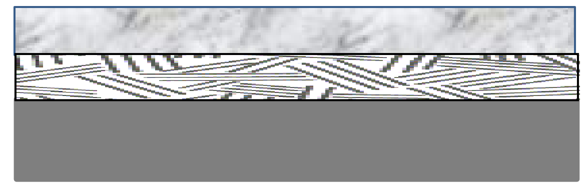
(Has been shown to be too thin due to limitations on concentration in the solution)

  - Structure is not well known
  - If it forms graphite, the surface should be very similar to carbon black

Pyrolized Photoresist (PPR)

- Two samples:
  - PPR on silicon
  - Nafion on PPR on silicon





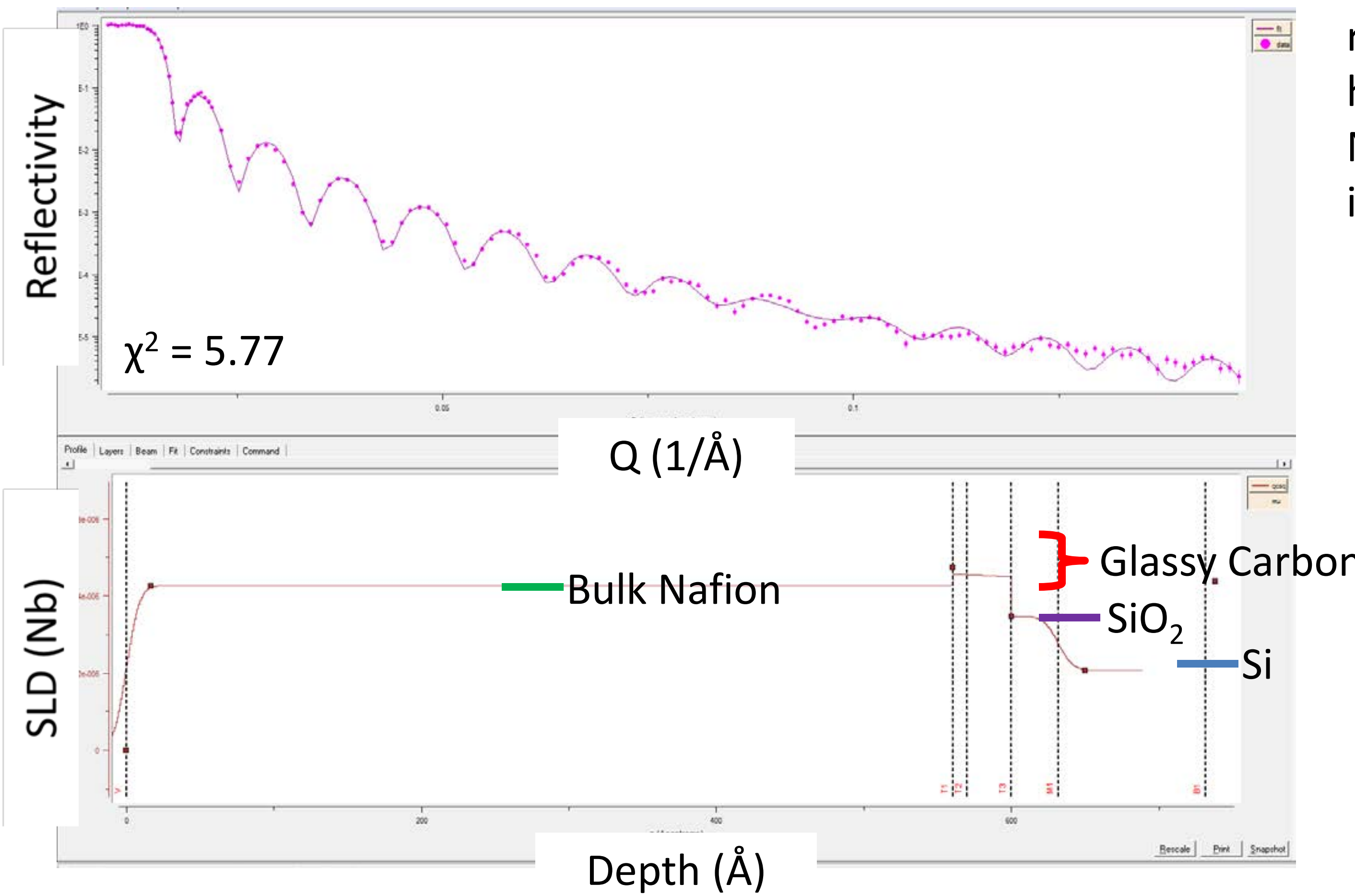
- Three experimental systems:
  - Dry (argon)
  - H_2O vapor (highest contrast for water)
  - D_2O vapor (alternative water contrast)

	Scattering Lengths		Scattering Cross Sections		
	Coherent	Incoherent	Coherent	Incoherent	Absorption
Element	b_c Fermi	b_i Fermi	σ_c Barn	σ_i Barn	σ_a Barn
H-1	-3.739	25.278	1.757	80.30	0.333
D-2	6.671	4.04	5.592	2.05	0.000
C-12	6.646	0	5.550	0.001	0.003
N-14	9.36	2.0	11.01	0.50	1.90
0-16	5.803	0	4.232	0.000	0.000
F-19	5.654	0	4.232	0.001	0.000
Na-23	3.63	3.59	1.66	1.62	0.530

1 Fermi = 10^{-13} cm.
1 Barn = 10^{-24} cm^2.

Fit Neutron Data

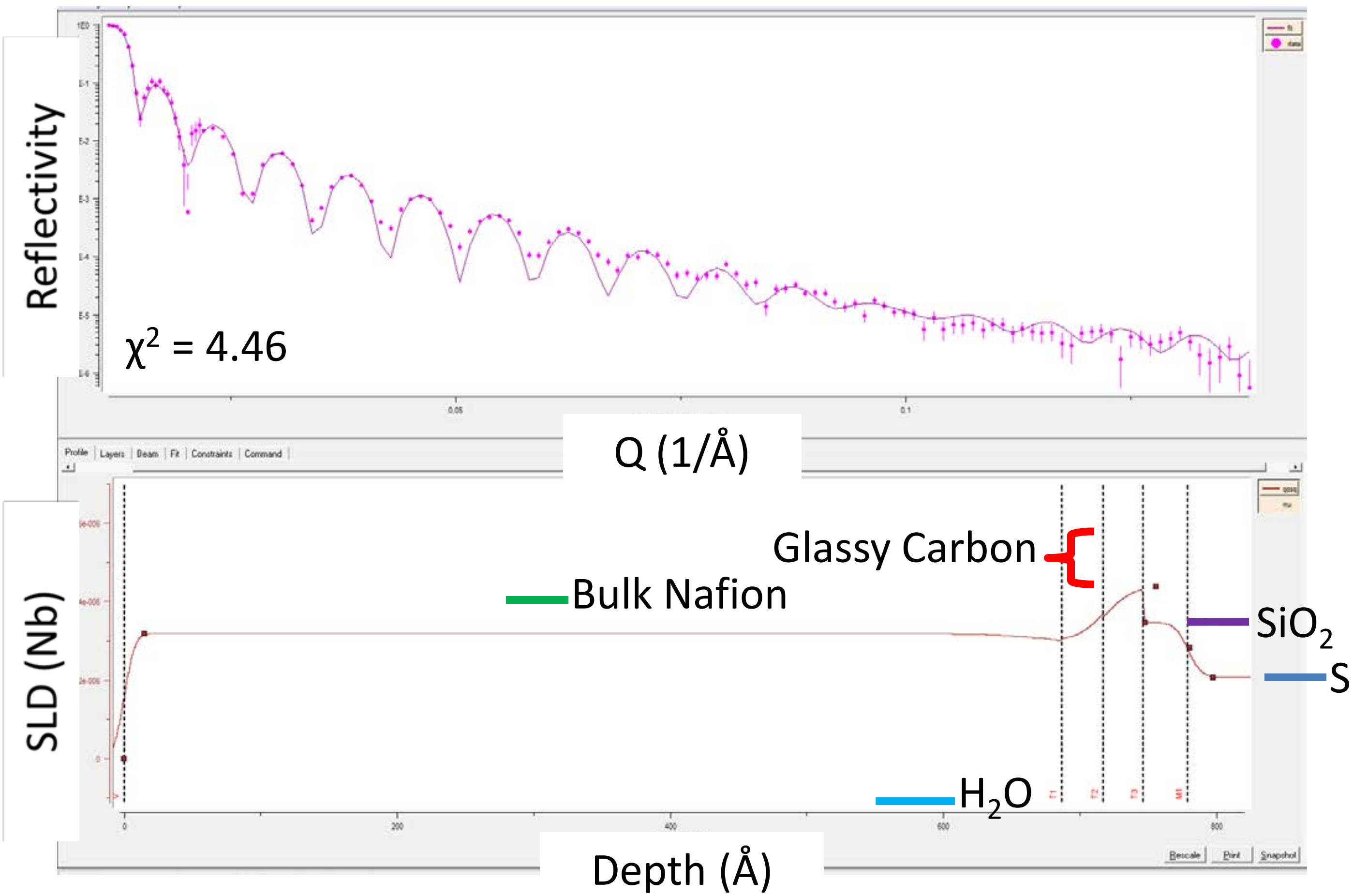
Dry Nafion/PPR



Dry Nafion on PPR reveals a thin layer of high sld under the bulk Nafion with a sharp interface

Fit Neutron Data

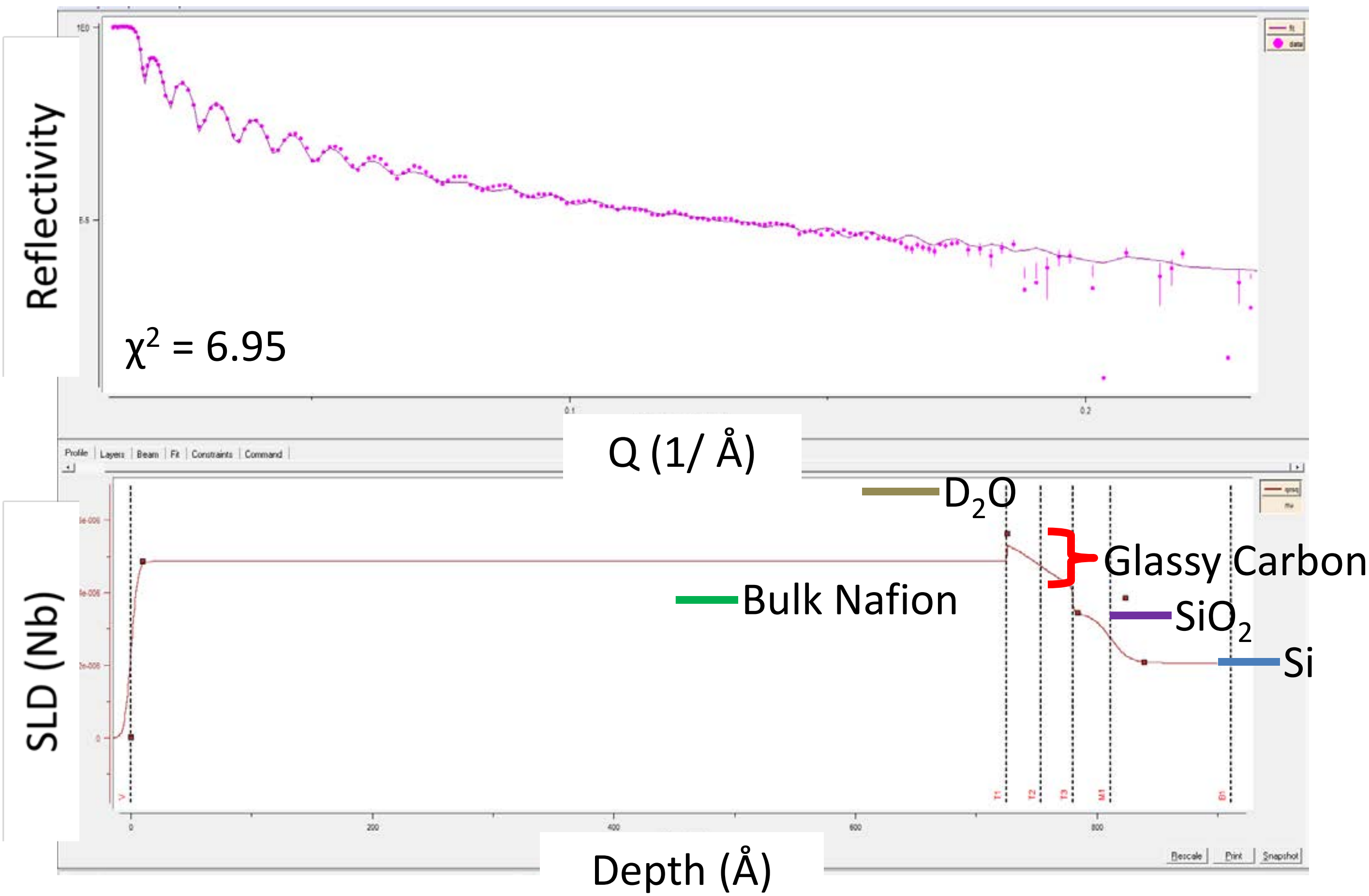
Nafion/PPR in H_2O vapor, RH = 90%



H_2O vapor reveals a strong dip in sld between Nafion and the PPR layer, corresponding to a single water-rich layer at the interface

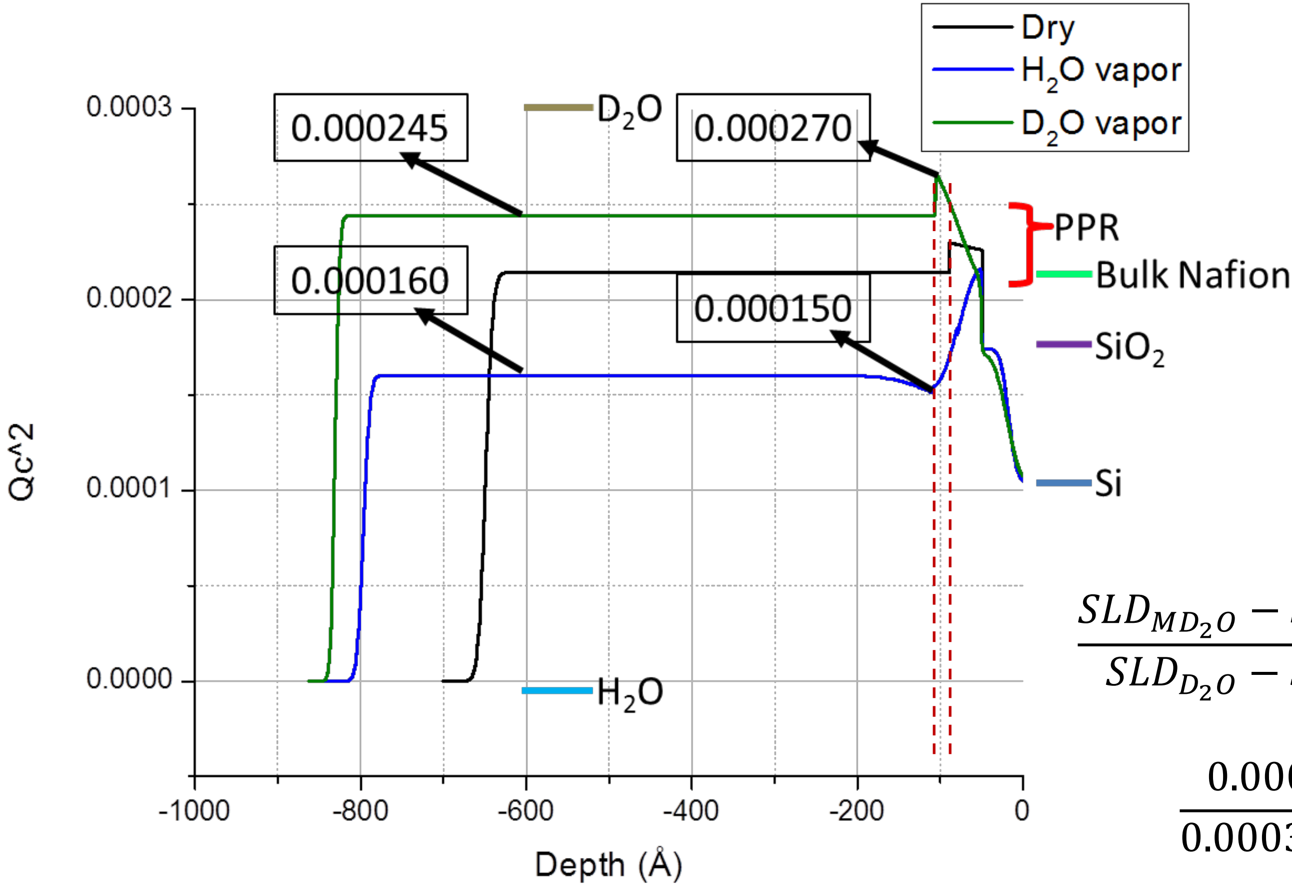
Fit Neutron Data

Nafion/PPR in D_2O vapor, RH = 90%



D_2O reveals a strong peak in sld between the Nafion and PPR layers, also corresponding to a single water-rich layer at the interface

Conclusions



$$\frac{SLD_{MD_2O} - SLD_{MH_2O}}{SLD_{D_2O} - SLD_{H_2O}} = V_{liquid\ (bulk\ Nafion)}$$

$$\frac{0.000245 - 0.00016}{0.00032\ - (-0.00006)} = 0.22$$

$$V_{liquid\ (bulk\ Nafion)} = 0.22$$

$$V_{liquid\ (interface)} = 0.32$$

Conclusions

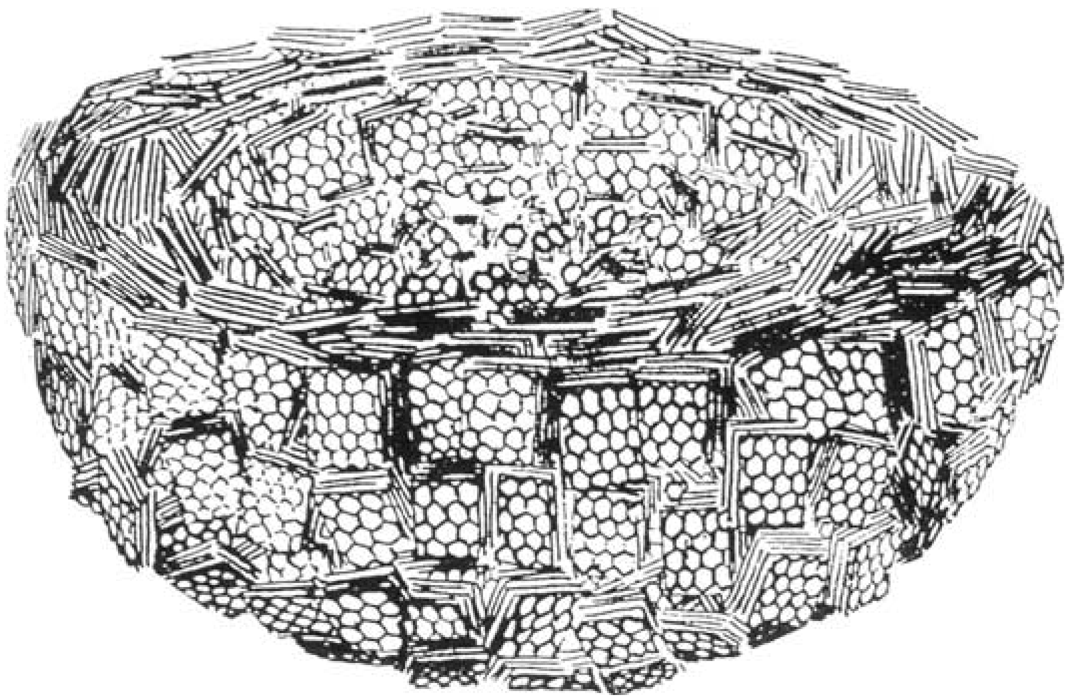
- We have proven that aqueous dispersions of graphene can not easily produce thick enough films to be useful for reflectometry studies
- We found that Nafion on PPR does not contain lamellar structures at the interface, like a silicon substrate
- We found that Nafion on PPR does contain a single water-rich layer at the interface, like a gold substrate

Acknowledgements

- Joe Dura (SURF advisor)
- Dorsa Parviz and Micah Green, Texas Tech. university (aqueous dispersion of graphene)
- Michael Thompson, Research Experience for Teachers (RET) Intern (PPR fabrication and neutron data)
- CNST Nanofab Staff:
  - Robert Newby and Jerry Bowser (pyrolization)
  - Kerry Siebein (SEM)
  - Lei Chen (AFM)
  - Gerard Henein (sputtering and profilometry)
- Nina Verdal (tube furnace carbonization)
- Dan Pajerowski (FTIR)
- Rob Dimeo, Dan Neumann, Julie Borchers
- The rest of the SURF Directors
- NIST and the NCNR
- NSF CHRNS

Questions?

Carbon Black Structure



New Perspectives on the Structure of Graphitic Carbons PETER J. F. HARRIS

Carbon Black Particle

Spectral properties of carbon black C. JÄGERA, TH. HENNINGA, R. SCHLÖGLB, O. SPILLECKEB

Polymer Electrolyte Membrane: Nafion

$(-CF_2-CF_2-CF_2-CF_2-CF-CF_2-CF_2-CF_2-CF_2-CF_2-CF_2-CF_2-CF_2-CF_2-CF_2-)_n$

$$
\begin{array}{c}
CF \\
| \\
O \\
| \\
CF_2 \\
| \\
F_3C\text{-}CF \\
| \\
O \\
| \\
CF_2 \\
| \\
CF_2 \\
| \\
SO_3^-H^+
\end{array}
$$

Teflon–like Backbone
- Provides Structure
- Impervious to e^-, H_2, O_2
- Hydrophobic

Phase Segregation

Sulfonic Acid Side Chain
- Hydrophilic
- Absorbs H_2O
- Passes H^+ ions

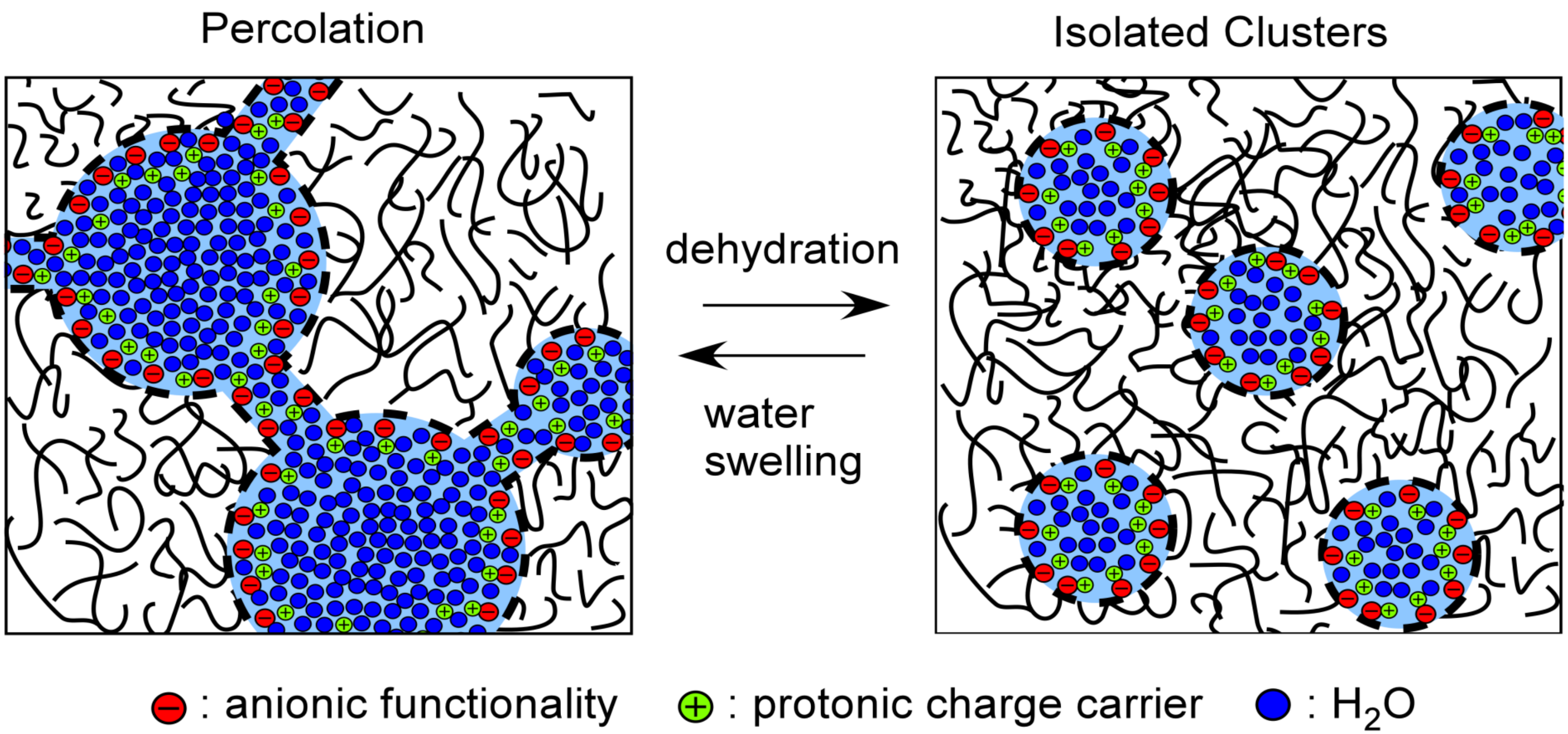
PEM – also Polymer Electrolyte Membrane

Passes H^+ ions

Impervious to e^-, H_2, O_2

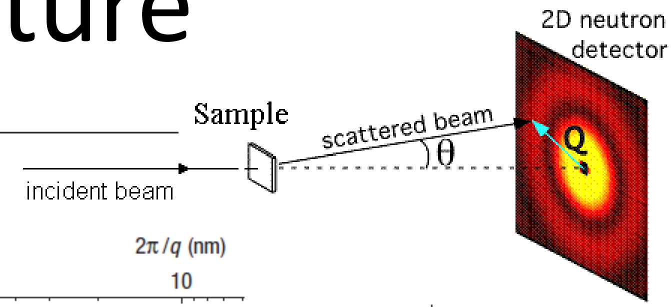
Absorbs H_2O

Ionic Conduction Via Water Channels



But too much water floods the electrodes - Blocking H and O to the PEM

Bulk Nafion Structure



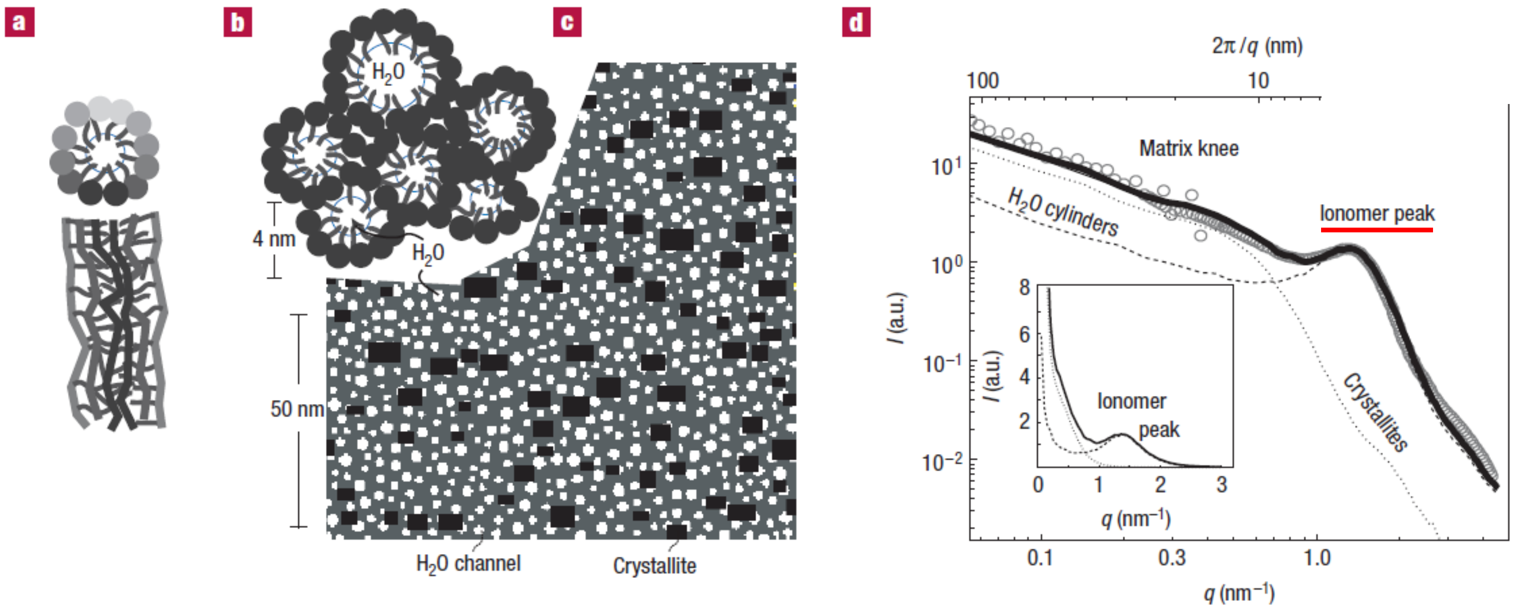
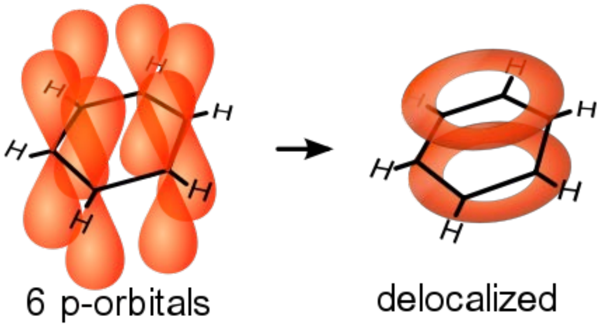


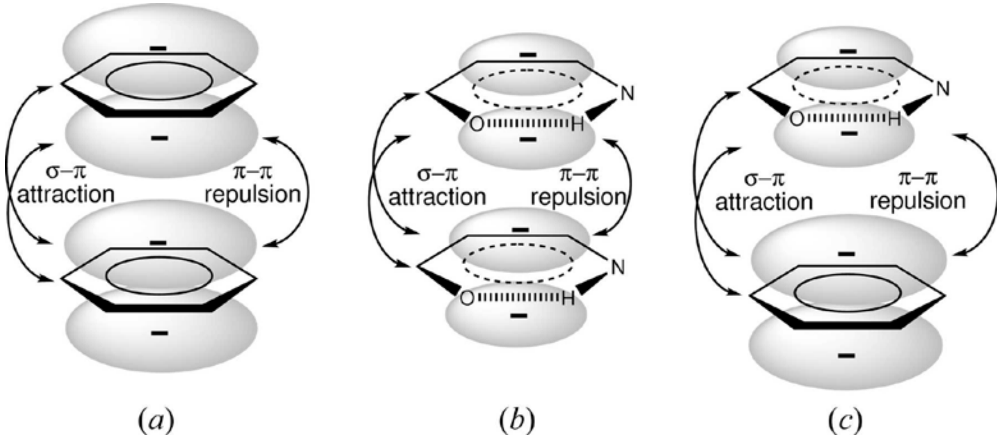
Figure 2 Parallel water-channel (inverted-micelle cylinder) model of Nafion. a, Two views of an inverted-micelle cylinder, with the polymer backbones on the outside and the ionic side groups lining the water channel. Shading is used to distinguish chains in front and in the back. **b**, Schematic diagram of the approximately hexagonal packing of several inverted-micelle cylinders. **c**, Cross-sections through the cylindrical water channels (white) and the Nafion crystallites (black) in the non-crystalline Nafion matrix (dark grey), as used in the simulation of the small-angle scattering curves in **d**. **d**, Small-angle scattering data (circles) of Rubatat *et al.*[17] in a log(I) versus log(q) plot for Nafion at 20 vol% of H_2O, and our simulated curve from the model shown in **c** (solid line). The inset shows the ionomer peak in a linear plot of $I(q)$. Simulated scattering curves from the water channels and the crystallites by themselves (in a structureless matrix) are shown dashed and dotted, respectively.

Parallel cylindrical water nanochannels in Nafion fuel-cell membranes
Klaus Schmidt-Rohr and Qiang Chen
Nature Materials **7** pp. 75-83 January 2008
[doi:10.1038/nmat2074]

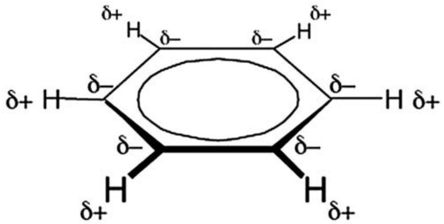
Pi-stacking interactions

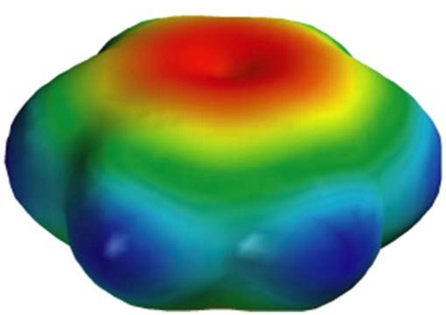


http://proteopedia.org/wiki/images/2/22/Benzene_Orbitals.png



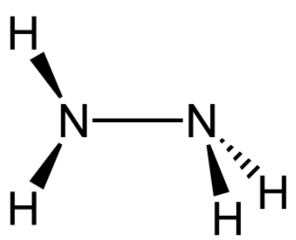
http://journals.iucr.org/b/issues/2012/01/00/ry5040/ry5040fig7.html





http://jn.nutrition.org/content/137/6/1504S.full.pdf+html

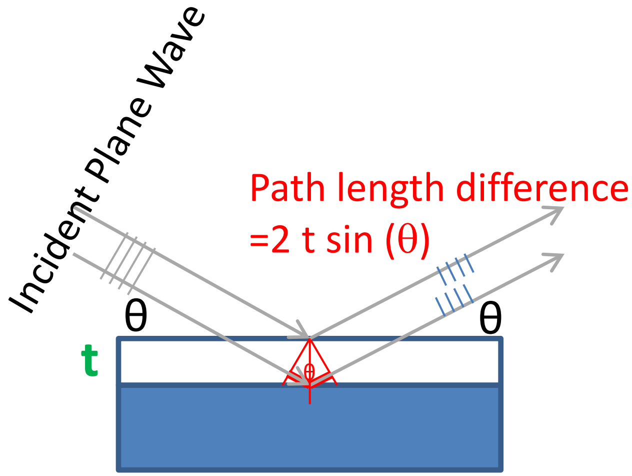
Hydrazine

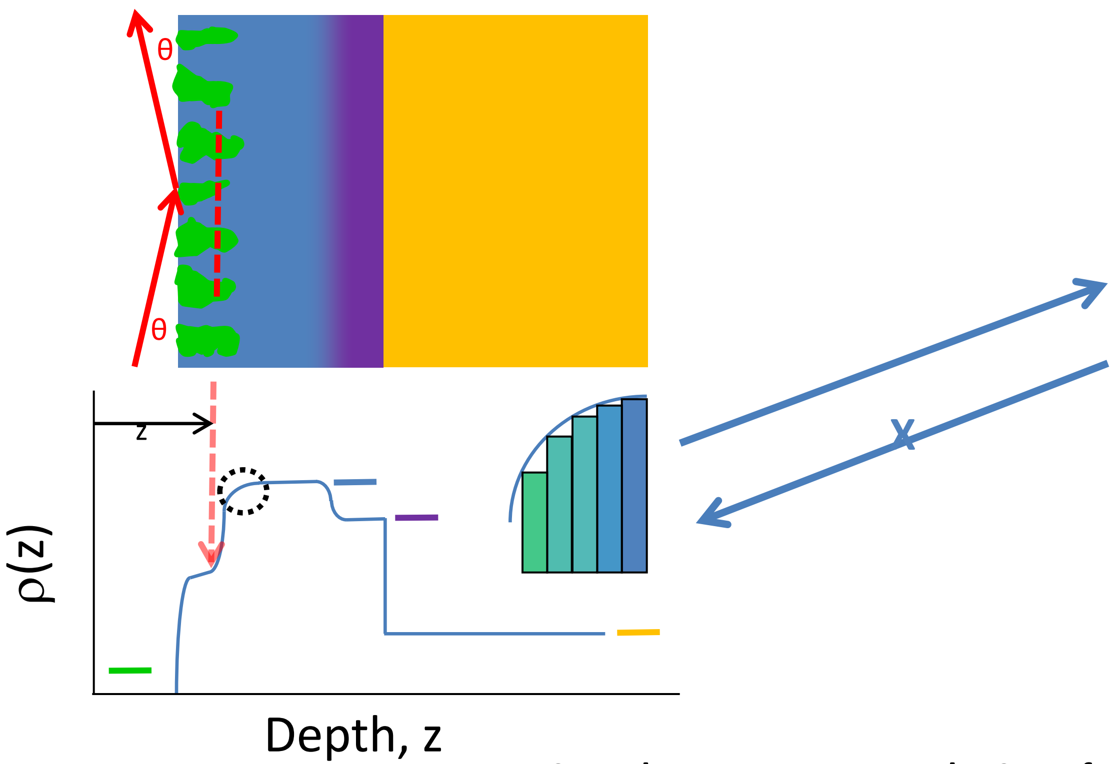


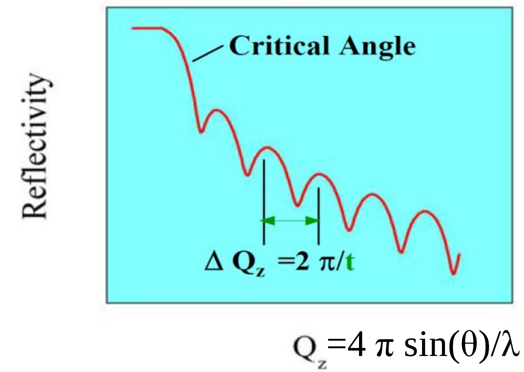
GHS Classification
Signal: Danger
Flammable liquid and vapor
Fatal in contact with skin
Fatal if inhaled vapor
Toxic if swallowed
Causes severe skin burns and eye damage
May cause an allergic skin reaction
Suspected of causing genetic defects
Suspected of causing cancer
Causes damage to liver and central nervous system
Causes damage to the liver, the lungs, the kidneys and the central nervous system through prolonged or repeated exposure
Very toxic to aquatic life with long lasting effects

Specular X-Ray Reflectometry (2)

- One can calculate the reflectivity from the SLD, but not invert the reflectivity since phase information is not measured
- Therefore we must fit the data to models

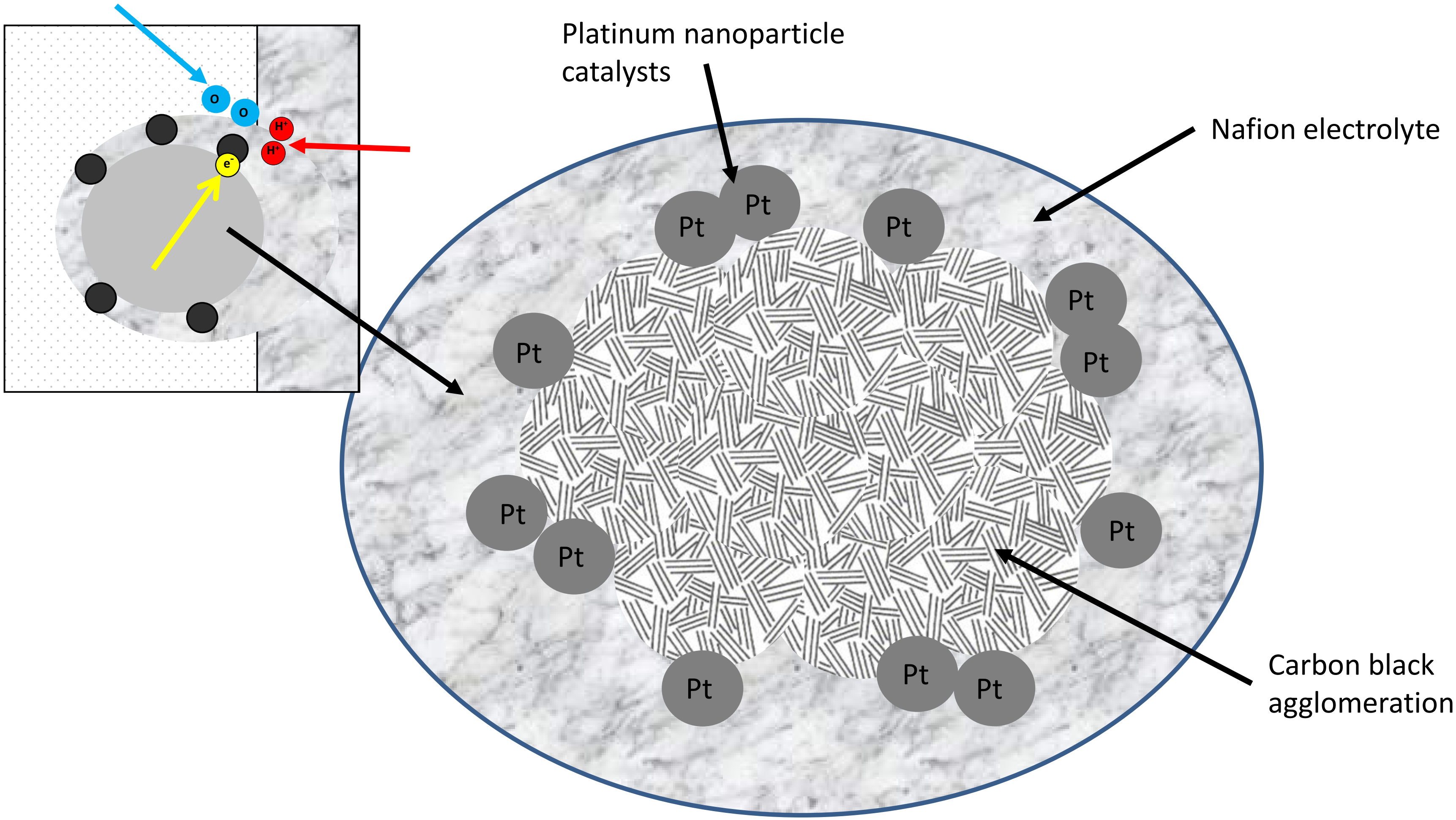




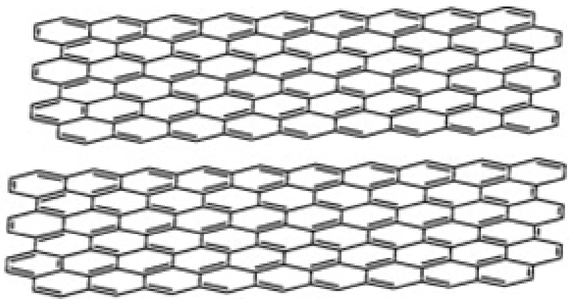


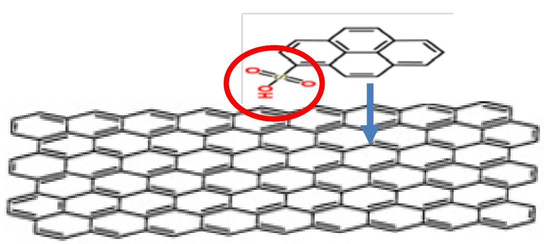
- Specular X-Ray Averages the SLD of materials in the plane
- Gradients can be approximated by a set of uniform slabs
- Can determine the ratio of two known components

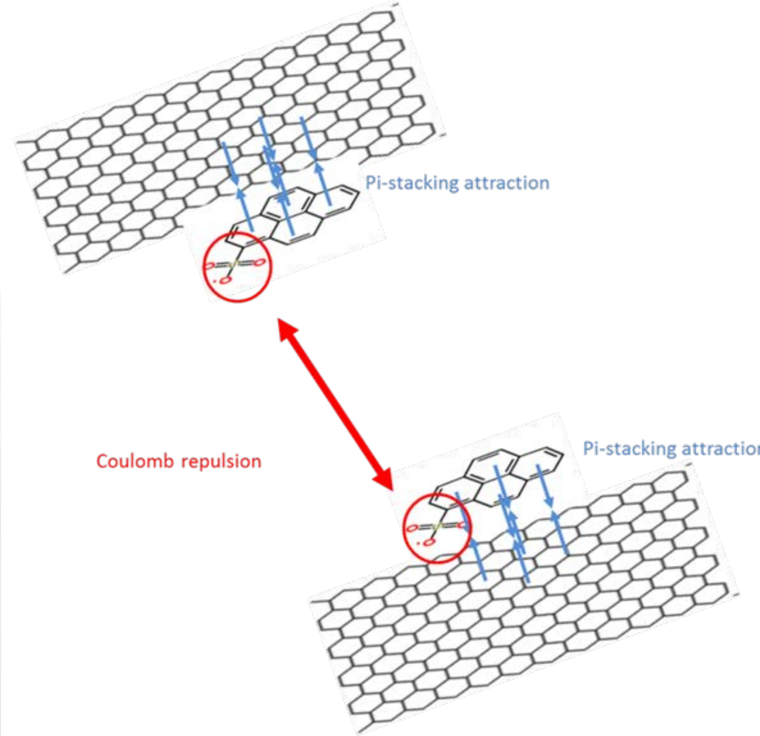
Image work

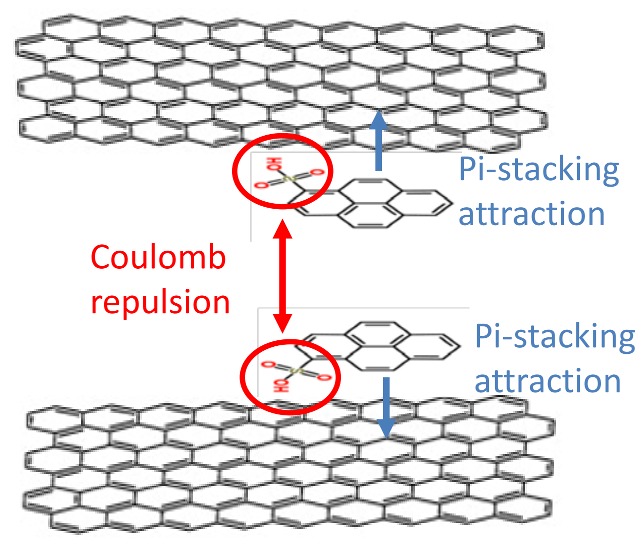


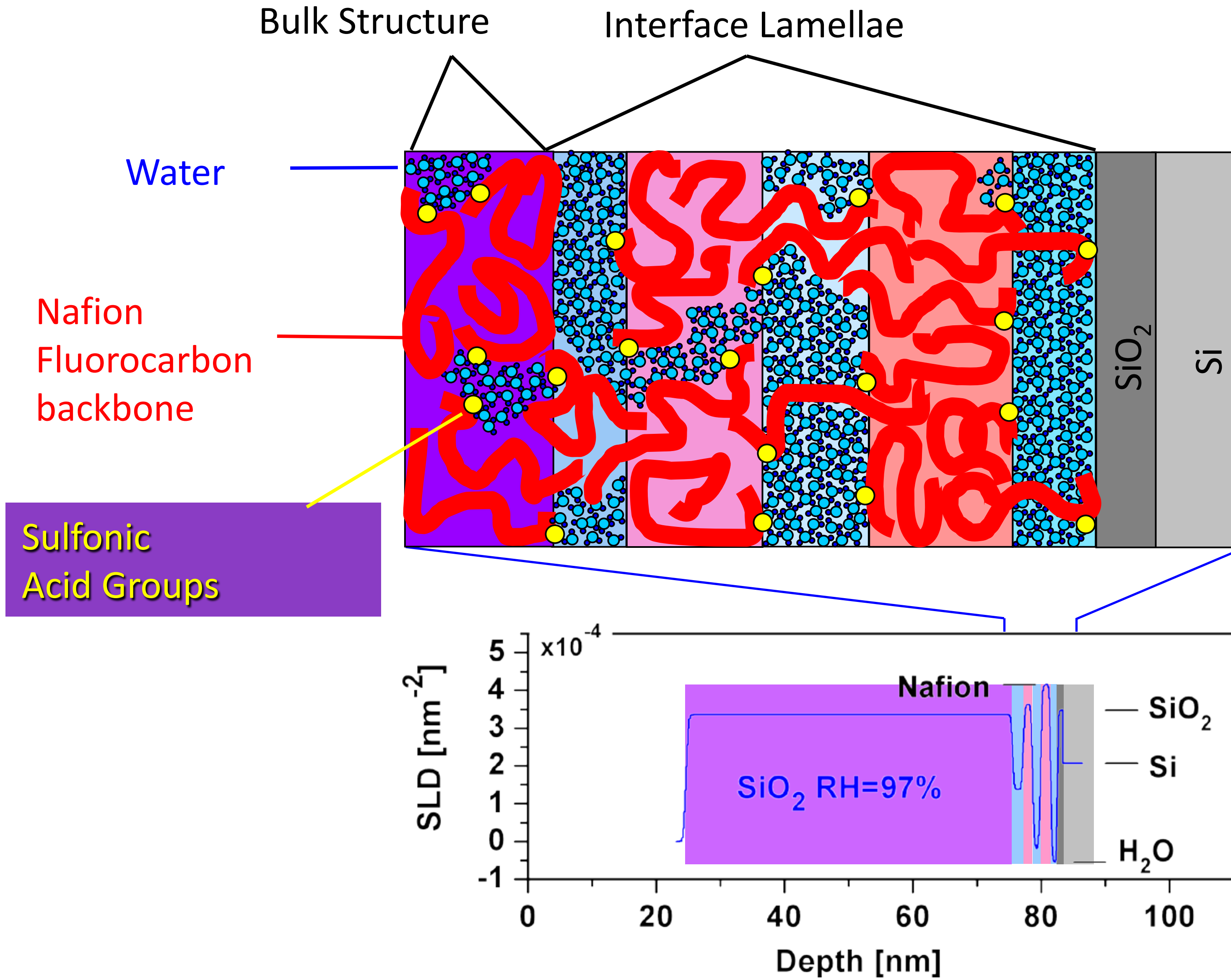
O
O
H+
H+
e-
Platinum nanoparticle catalysts
Nafion electrolyte
Pt
Pt
Pt
Pt
Pt
Pt
Pt
Pt
Pt
Pt
Pt
Pt
Pt
Carbon black agglomeration

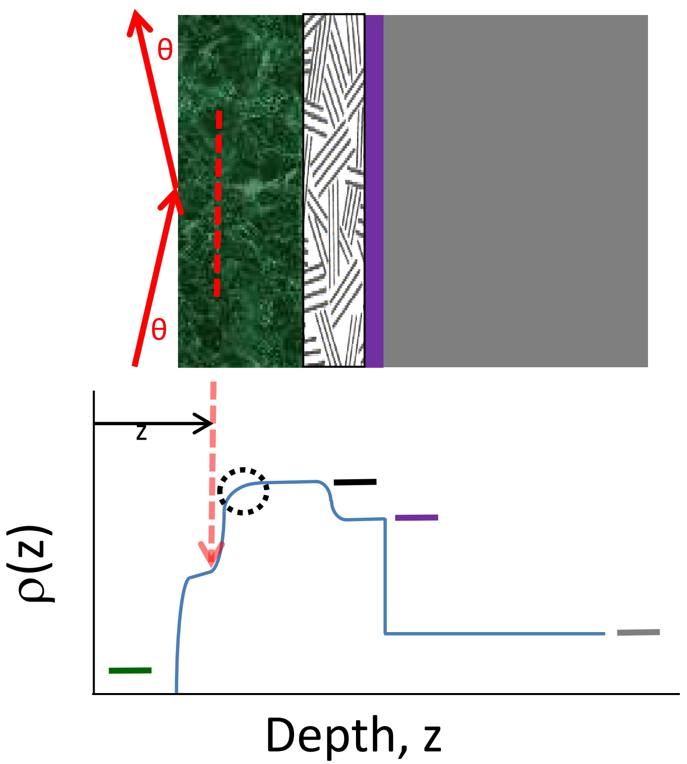


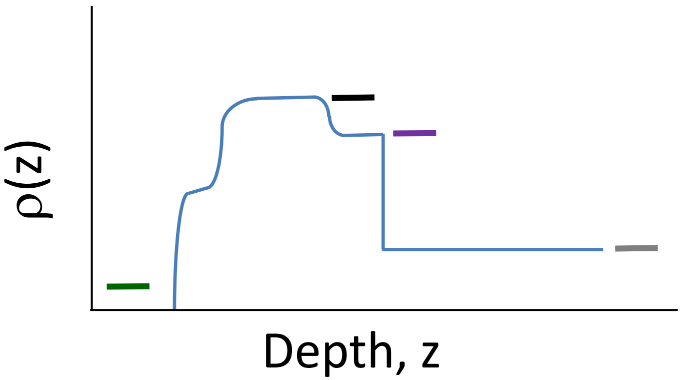



Pi-stacking attraction
Coulomb repulsion
Pi-stacking attraction


Pi-stacking attraction
Coulomb repulsion
Pi-stacking attraction

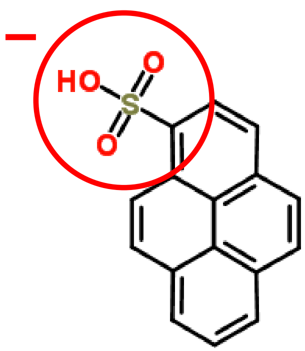

Bulk Structure
Interface Lamellae
Water
Nafion
Fluorocarbon
backbone
Sulfonic
Acid Groups
SiO2
Si
x10^-4
SLD [nm^-2]
Nafion
SiO2
Si
H2O
SiO2 RH=97%
Depth [nm]

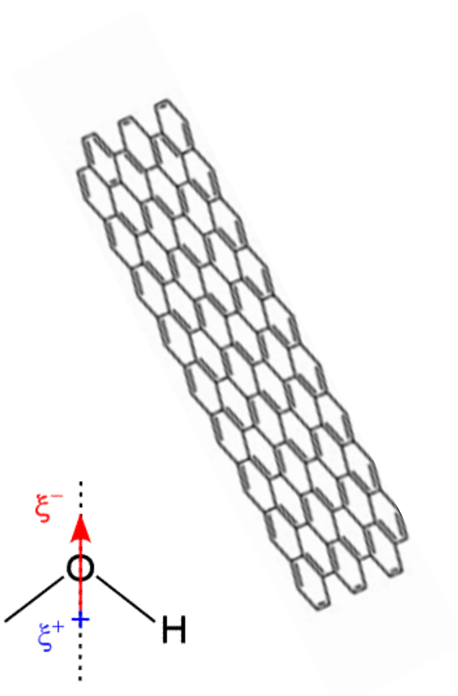

θ
θ
z
ρ(z)
Depth, z

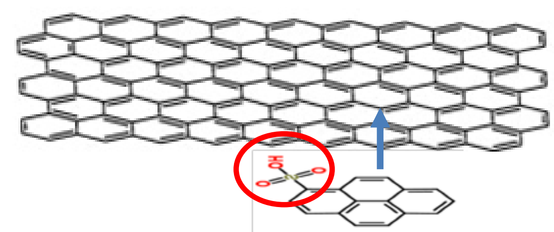

ρ(z)
Depth, z

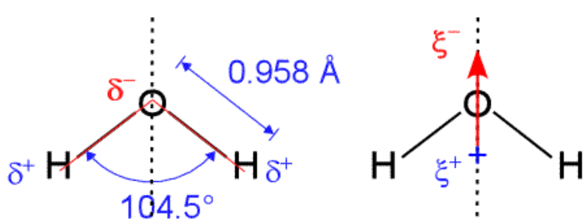
Aqueous Dispersion of Graphene

- Monopole(sulfonic acid) vs dipole (water) vs pi-stacking (pyrene and graphene) interactions



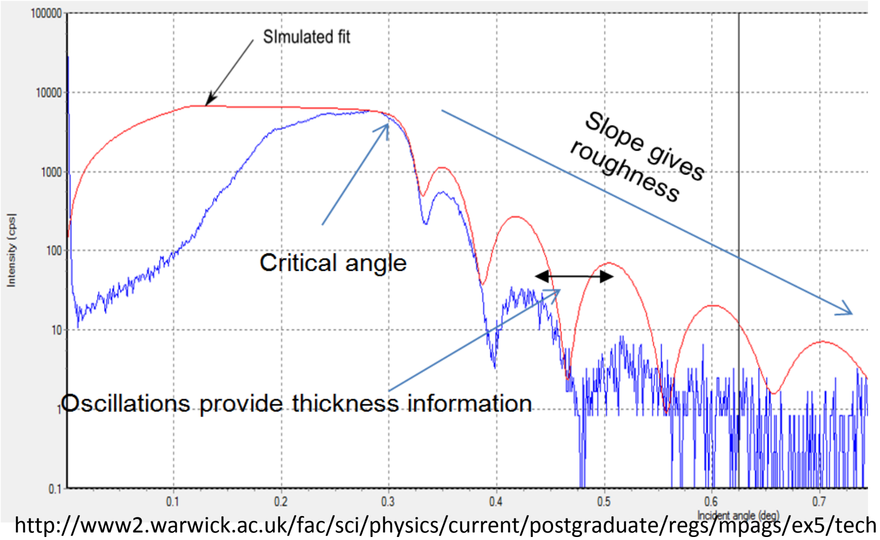






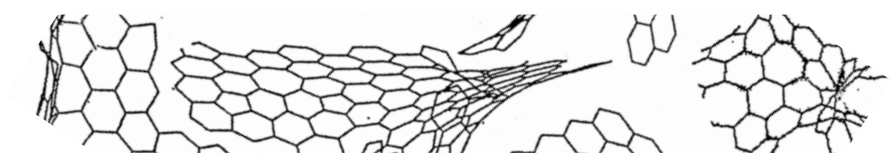
	Scattering Lengths		Scattering Cross Sections		
	Coherent	Incoherent	Coherent	Incoherent	Absorption
Element	b_c Fermi	b_i Fermi	σ_c Barn	σ_i Barn	σ_a Barn
H-1	-3.739	25.278	1.757	80.30	0.333
D-2	6.671	4.04	5.592	2.05	0.000
C-12	6.646	0	5.550	0.001	0.003
N-14	9.36	2.0	11.01	0.50	1.90
0-16	5.803	0	4.232	0.000	0.000
F-19	5.654	0	4.232	0.001	0.000
Na-23	3.63	3.59	1.66	1.62	0.530

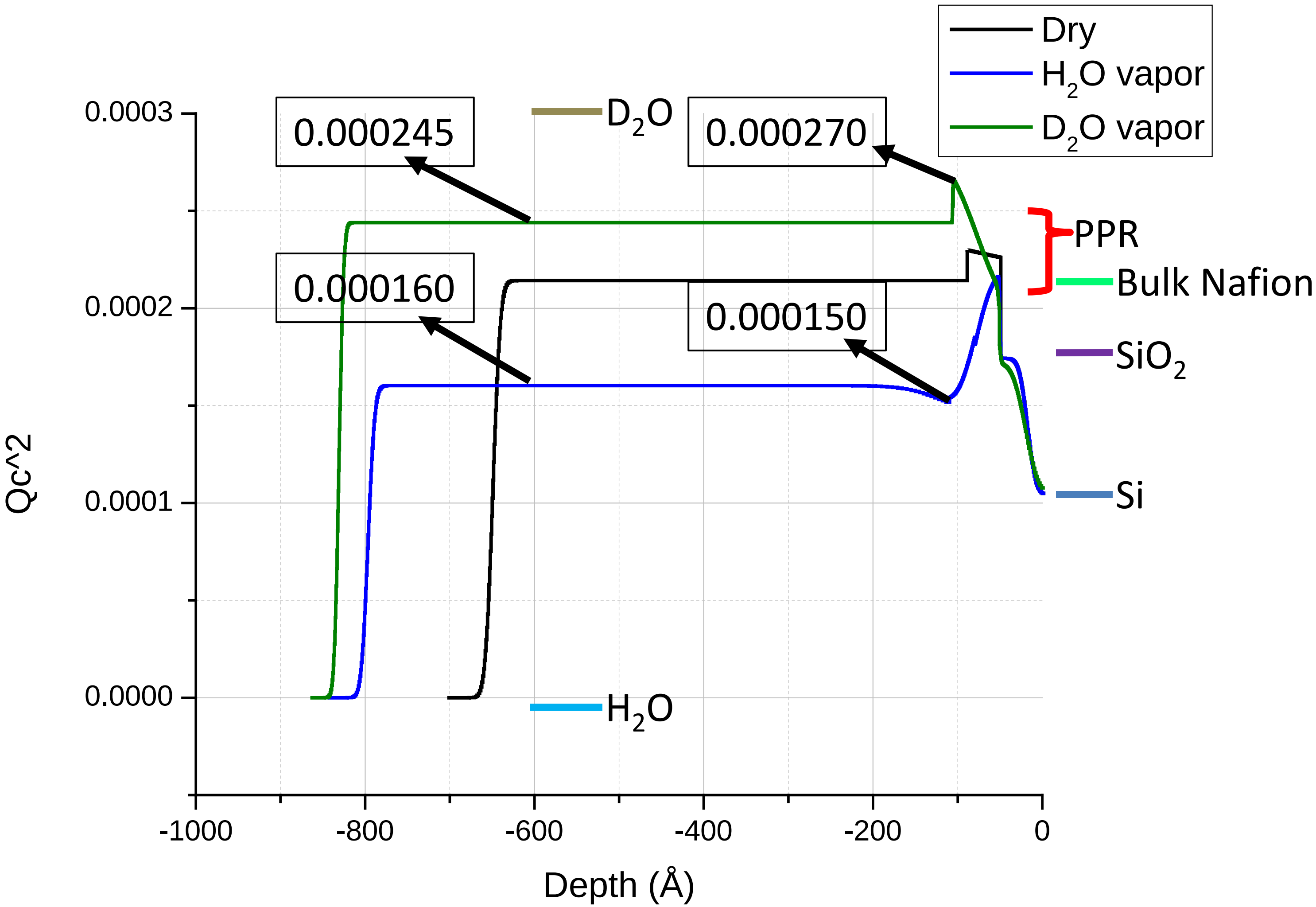
1 Fermi = 10^{-13} cm.
1 Barn = 10^{-24} cm^2.



http://www2.warwick.ac.uk/fac/sci/physics/current/postgraduate/regs/mpags/ex5/techniques/structural/gixrd/

$$SLD(z) = \Sigma_i \, b_n(i) \, n_i(z)$$





Dry
H_2O vapor
D_2O vapor
0.000245
0.000270
0.000160
0.000150
D_2O
H_2O
PPR
Bulk Nafion
SiO_2
Si
Qc^2
0.0003
0.0002
0.0001
0.0000
-1000
-800
-600
-400
-200
0
Depth (Å)