

In Situ SAXS and GISAXS Studies of Polymeric Membranes for Energy Applications

Giselle Sandí

***Chemistry Division, Argonne National Laboratory,
9700 South Cass Ave., Argonne, IL 60439***

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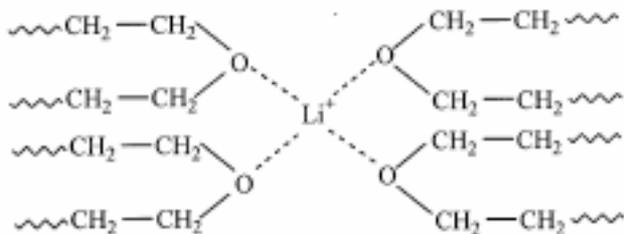


Two Types of Polymeric Membranes

- **Polymeric Membranes as solid electrolytes in lithium rechargeable systems**
- **Polymeric Membranes for catalytic and separation applications.**

Polymer Electrolytes

- **High Molecular Weight Polymers**
 - mechanical properties for solid state construction
 - better electrode interface than solid crystalline electrolytes
 - liquid like degrees of freedom at atomic level ⌚ amorphous
 - elimination of liquid electrolyte allows for use of lithium as electrode
 - small molecules can be reactive
- **Polyethylene oxide - polymer of choice to solvate lithium salt**



low glass transition temperature ~ -50 °C
low melting point ~ 60 °C

At RT $\sigma \sim 10^{-5}$ S/cm

At 80°C $\sigma \sim 10^{-3}$ S/cm

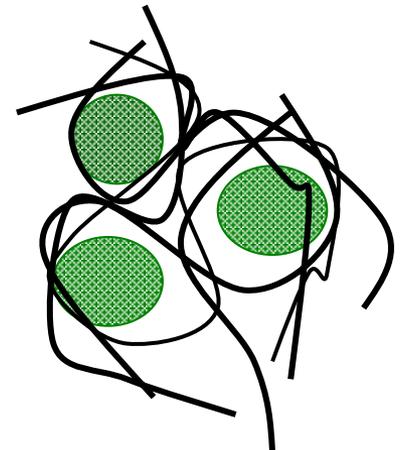
Polymer Nanocomposites

Lithium Conduction Dependent on Polymer Segmental Motion

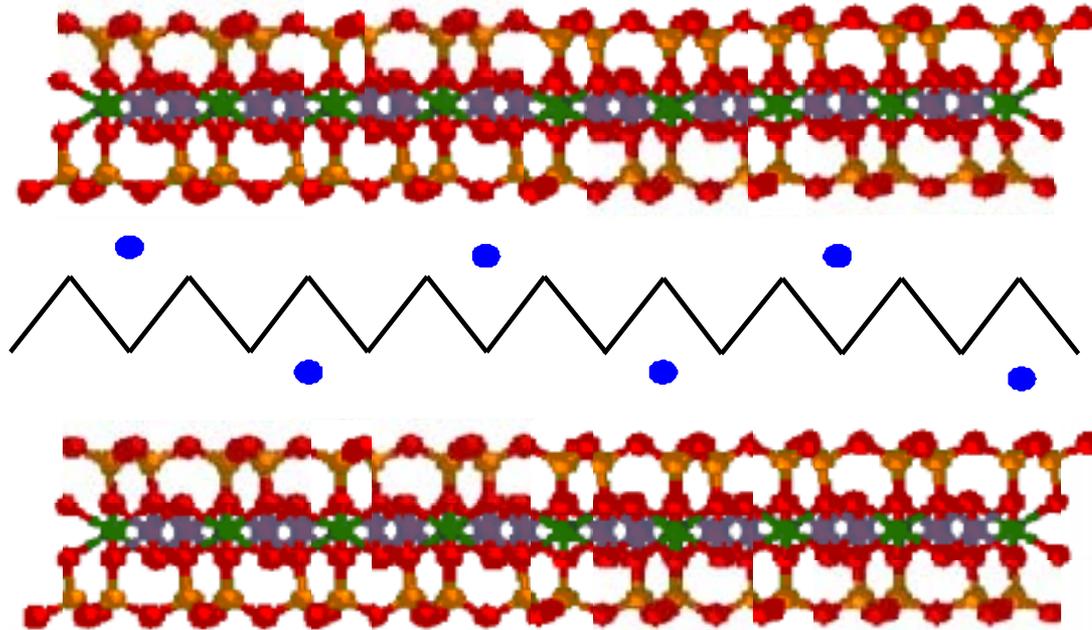
- performance of polymer electrolyte only good above melting point
- high T reduces mechanical stability of the material
- *desire single ion conductor*
- anion mobility can reduce net charge diffusion between electrodes
- exclusive motion of lithium cation ⌚ **transference number = 1**

Introduction of inorganic filler particles can improve mechanical properties

-high surface area of nanoparticles interacts with polymer preventing crystallization and sustaining mechanical properties at higher temperatures

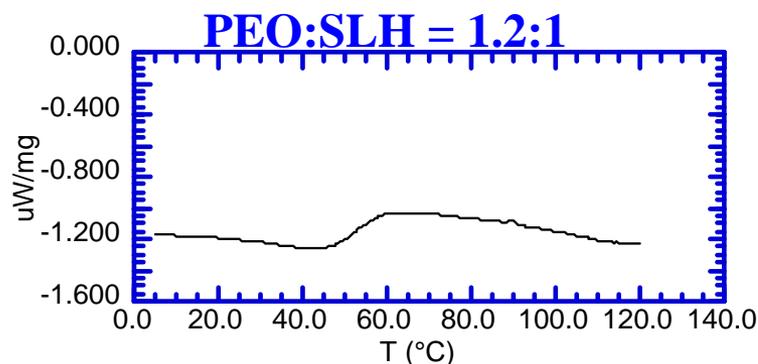
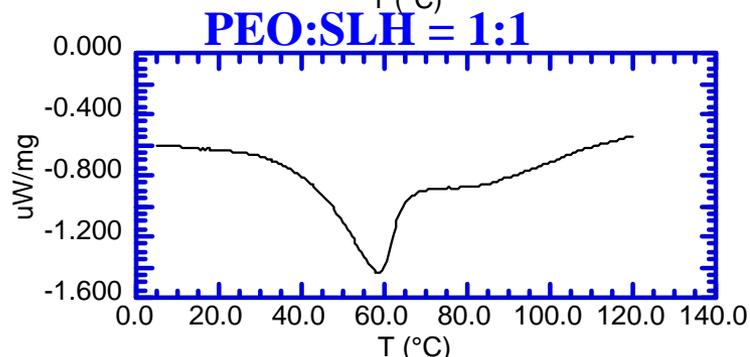
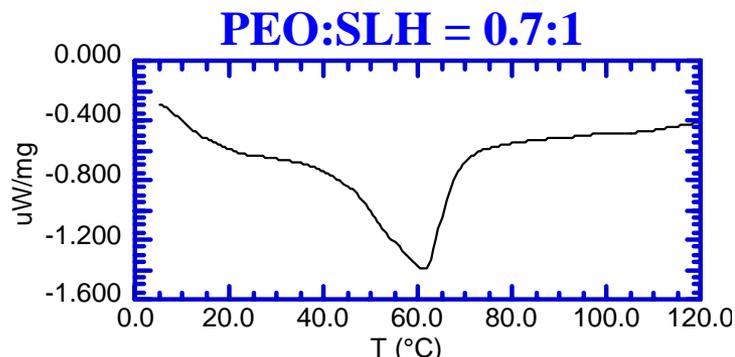


Nanocomposites Containing PEO and synthetic lithium hectorites (SLH) clays



They are composed of two tetrahedral silicate layers sandwiching a central octahedral layer in a so-called 2:1 arrangement. Isomorphous substitutions in the lattice of Li(I) for Mg (II) in the octahedral layers of hectorite cause an overall negative charge that is compensated by the presence of interlayer, or gallery, cations

DSC of Nanocomposite Films Made with PEO and SLH



Sample Ratio	Onset Temp. (°C)	ΔH (J/g)	Percent crystalline
0.7	22.8	-19.9	9
1.0	33.2	-57.8	27
1.2	43.5	-78.3	37

Intercalation of the PEO into the clay can disrupt the crystallization of the polymer and accounts for the reduction of the endothermic peak. From a comparison of the heat of melting in the polymer nanocomposites to the heat of melting in pure PEO, the amount of crystalline PEO in the composites was determined.



NMR Characterization: Variable Temperature Static ^7Li NMR Spectra of PEO:SLH = 1.2 Sample

T = -30 °C



T = 0 °C



T = 10 °C



T = 30 °C



20000.0 0.0 -20000.0

Freq (Hz)

T = 50 °C



The increasing mobility of the Li cation and motion of PEO inside the clay causes the narrowing of the spectra.

T = 70 °C



T = 90 °C

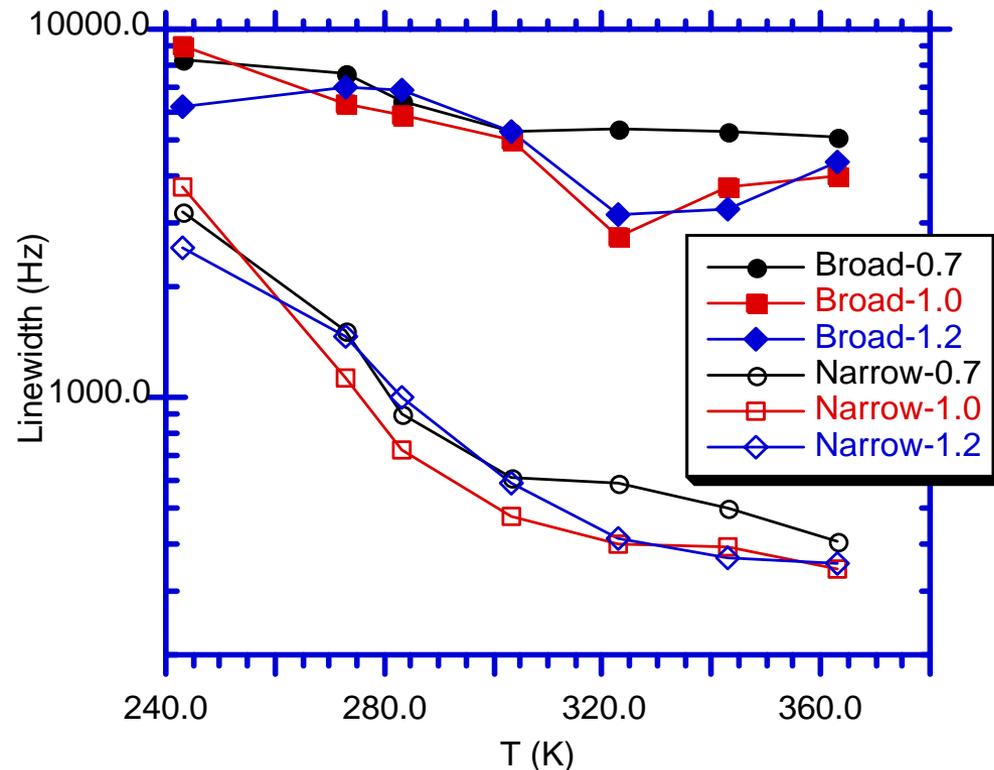


20000.0 0.0 -20000.0

Freq (Hz)



NMR Characterization



The static ${}^7\text{Li}$ spectra could be deconvoluted into two components: a narrow component due to mobile cations and a broad component due to static cations. The linewidth of the broad component does not change substantially with temperature. The narrow component becomes increasing narrower as the cation mobility increases with temperature.



NMR Characterization

External PEO Activation Energies

Sample Ratio	E_a (kJ/mol)	τ (ps)
0.7	27.2 ± 3.5	0.0062 ± 0.0078
1.0	28.7 ± 1.0	0.0047 ± 0.0015
1.2	28.6 ± 2.8	0.0019 ± 0.0018
PEO bulk	~ 28	

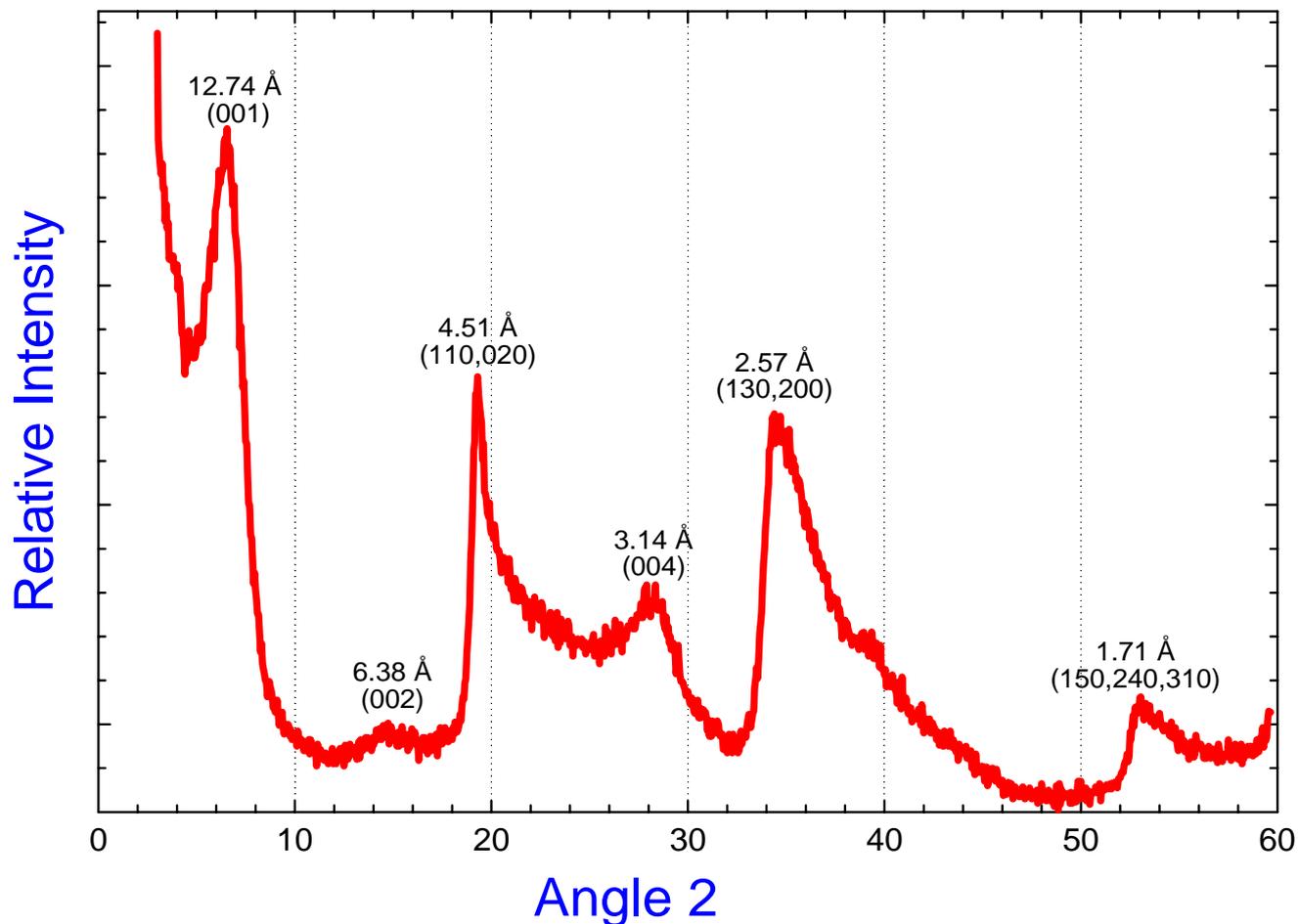
External PEO has activation energies similar to bulk PEO.

Internal PEO Activation Energies

Sample Ratio	E_a (kJ/mol)	τ (ps)
0.7	23.1 ± 1.4	0.16 ± 0.08
1.0	21.2 ± 1.0	0.31 ± 0.11
1.2	23.3 ± 1.9	0.14 ± 0.09
PEO bulk	~ 28	

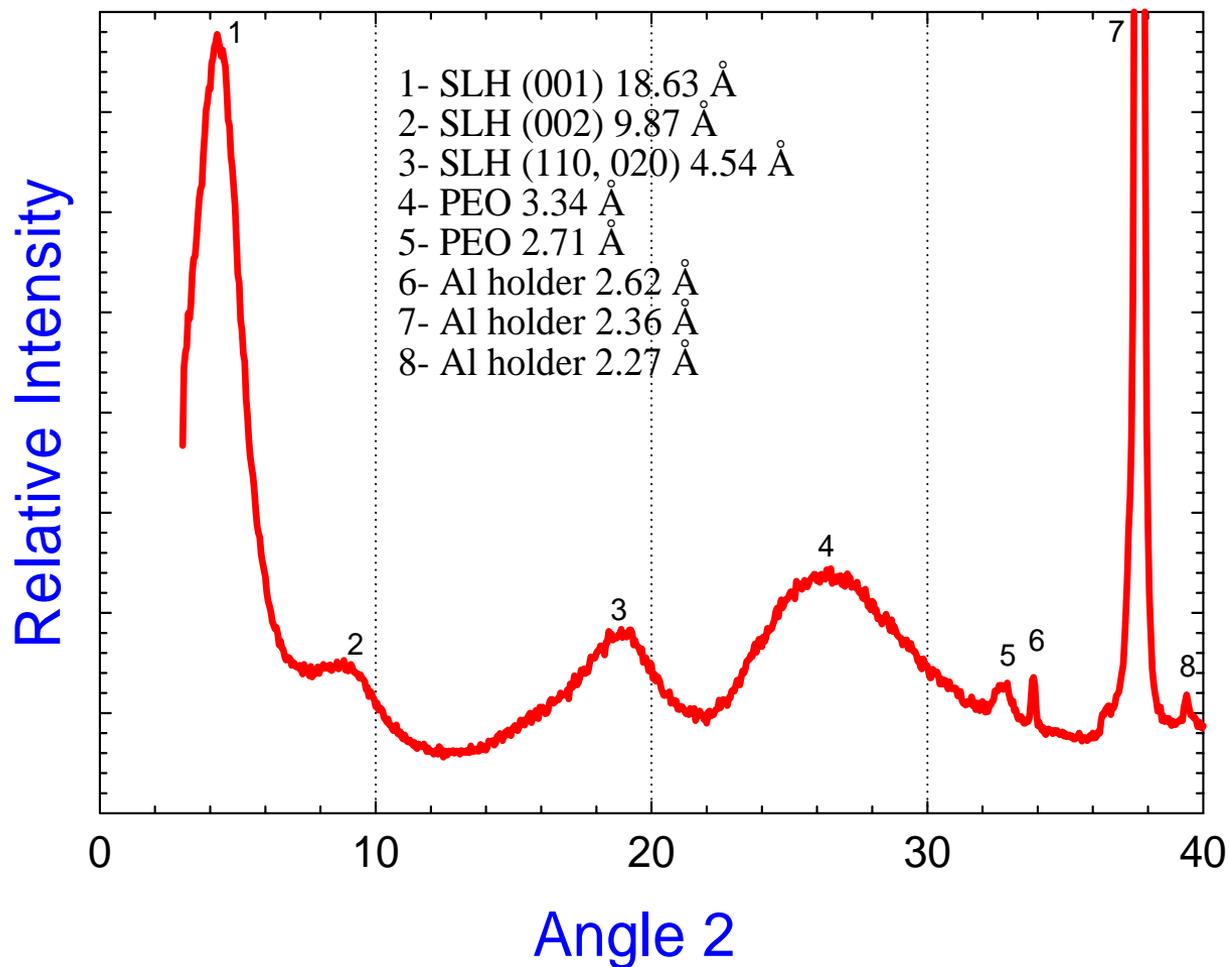
Internal PEO has activation energies lower than bulk PEO but similar to those observed for PEO lithium salt composites.

XRD Characterization



XRD of SLH

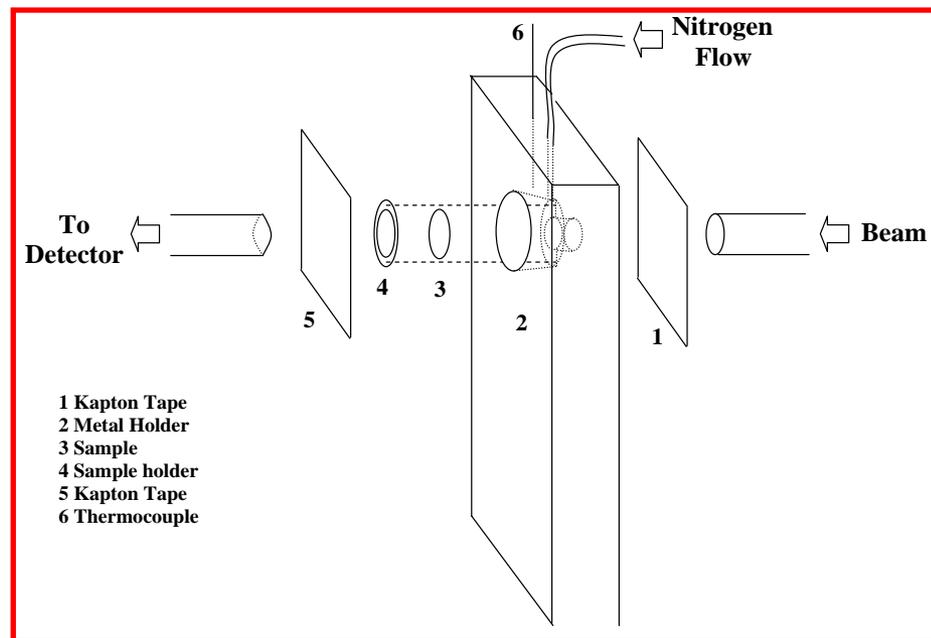
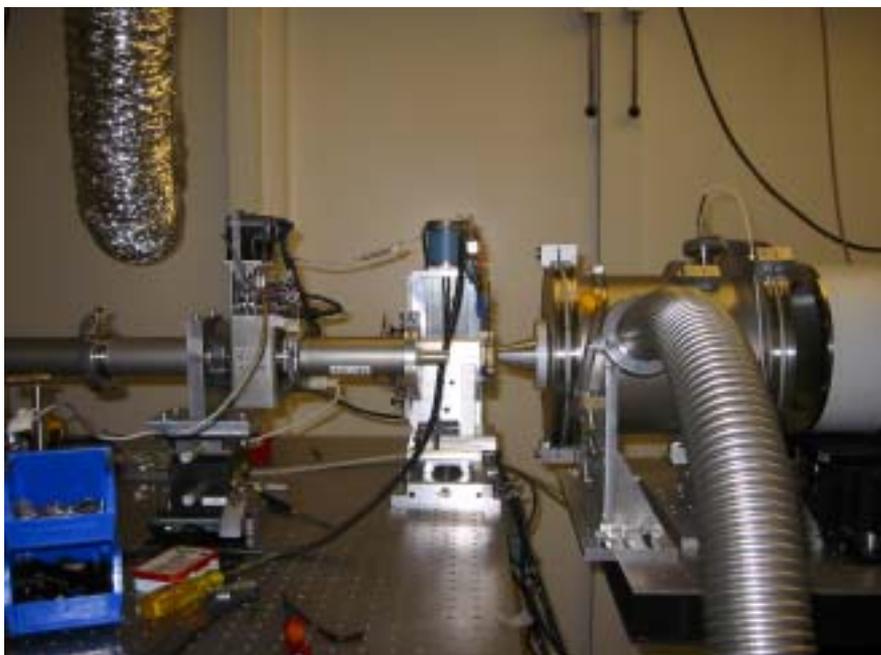
XRD Characterization



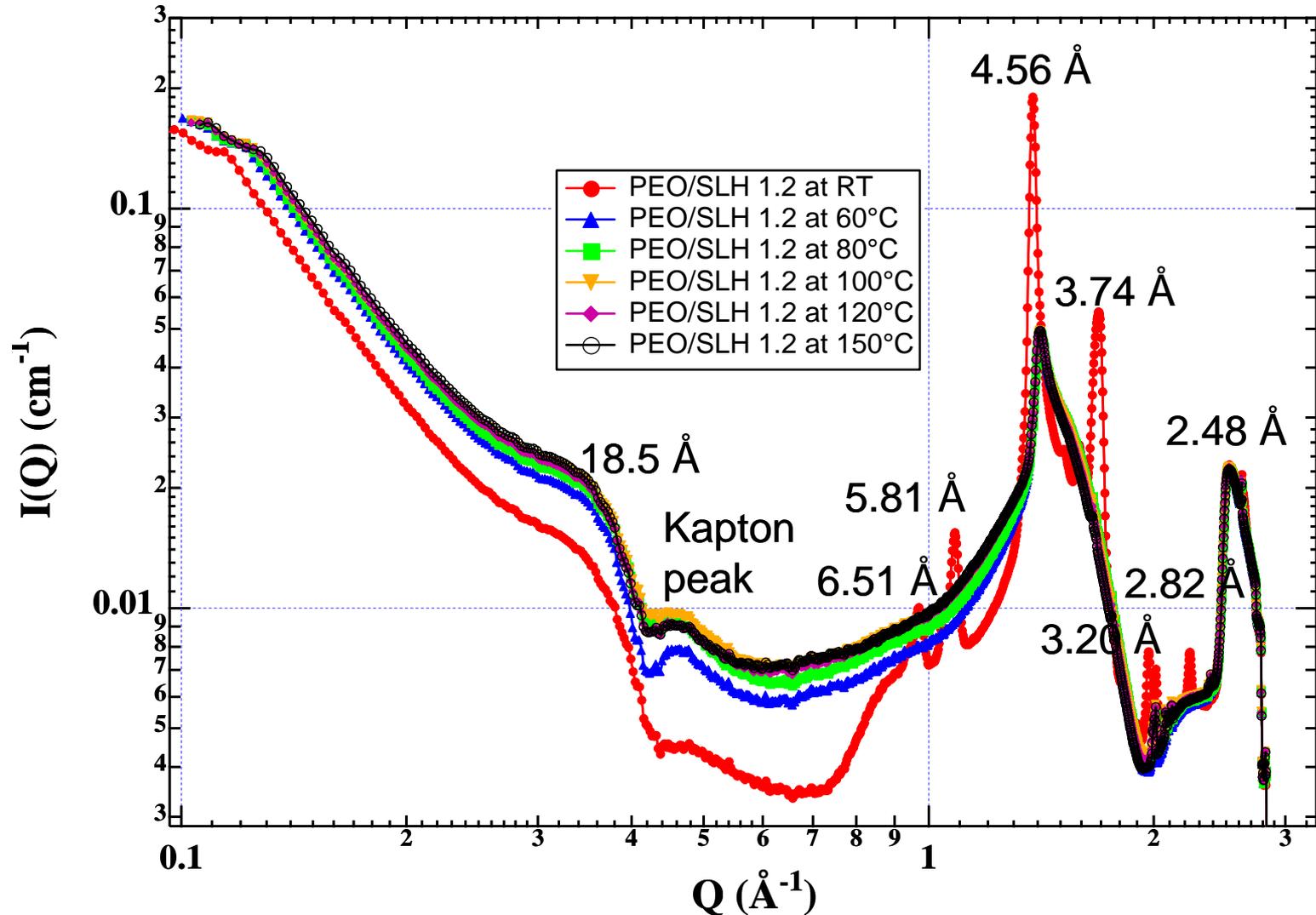
XRD of a PEO:SLH 1:1 ratio film

Small Angle X-Ray Scattering

For these studies, a specially designed sample holder was used to heat up the sample and collect SAXS data at the same time.



In Situ SAXS Data of a SLH:PEO 1.2:1 Ratio Film



Small Angle X-Ray Scattering

- At any PEO/SLH ratio, upon increasing the temperature, the polymer relaxes and the crystalline phase becomes amorphous, as indicated by the broadening of the peaks or the absence of them.
- In the higher ratios of PEO, the structural changes happen between 60 and 80°C and those changes are irreversible.



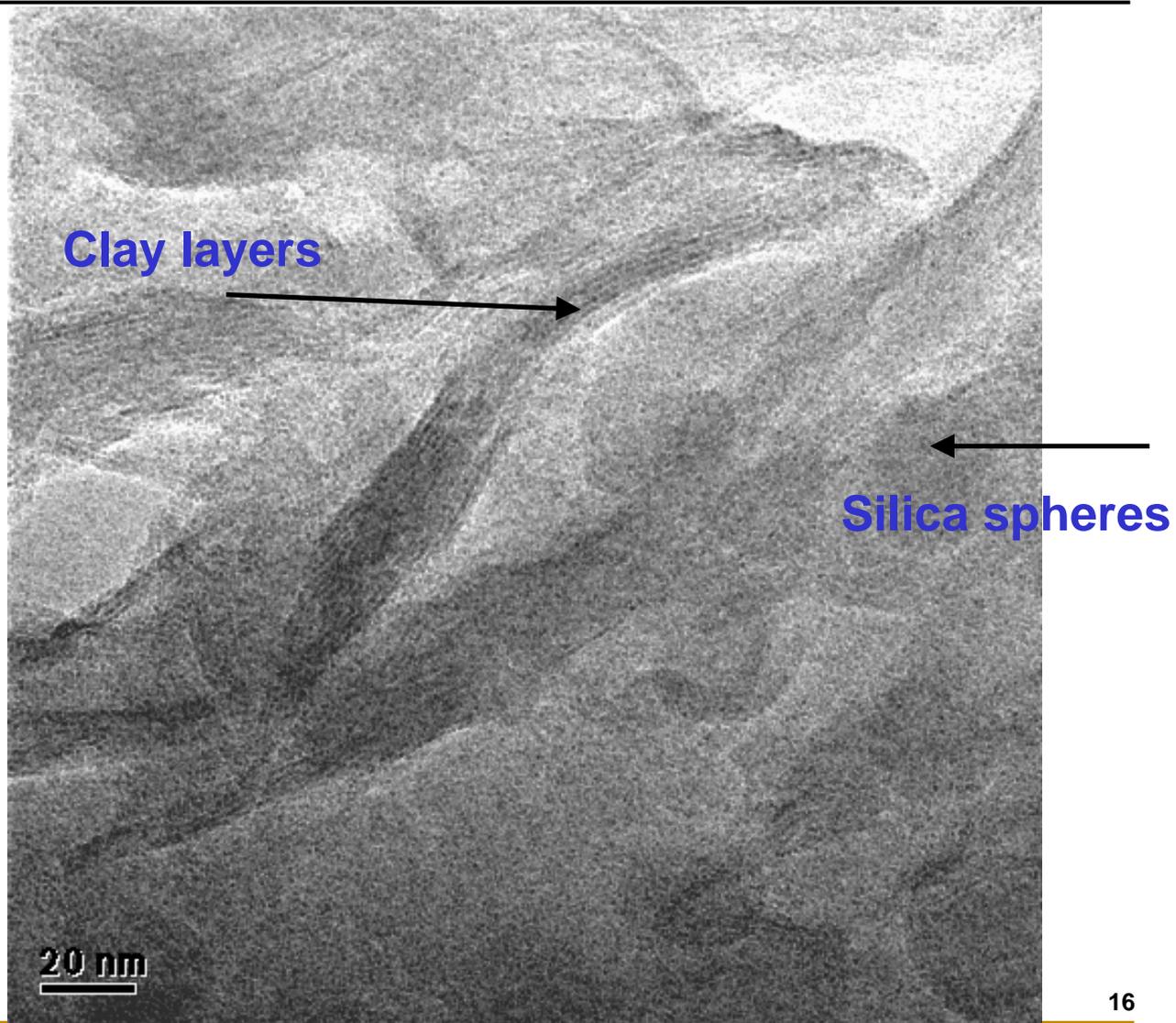
High Resolution TEM of a Film Made of SLH:PEO 1:1 Ratio

What is the nature of the spheres shown on the background?

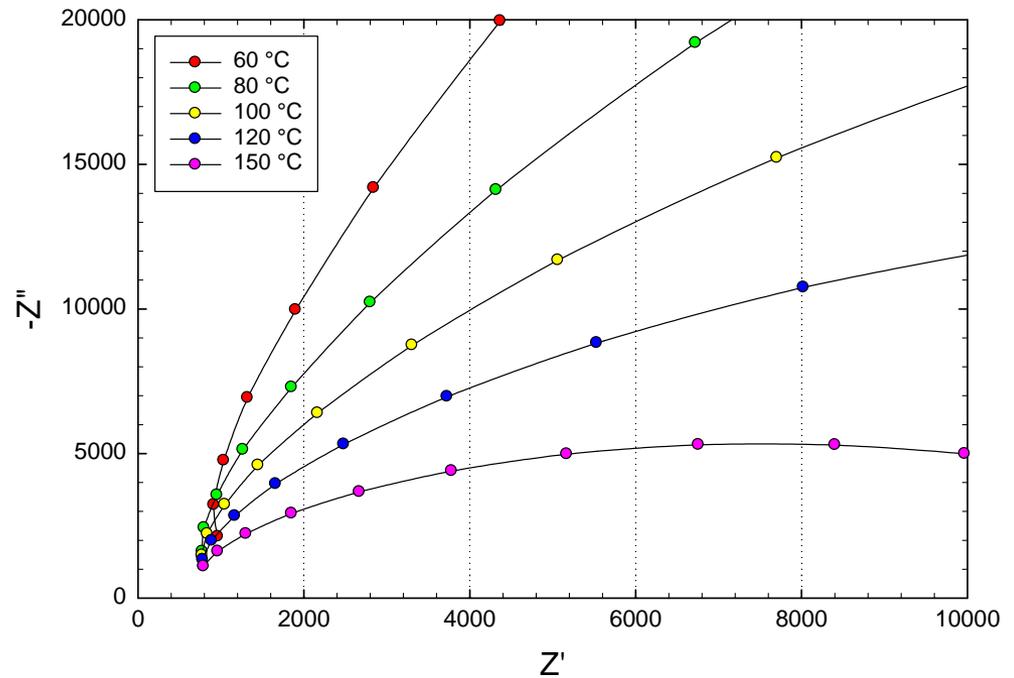
SiO₂

Where is the SiO₂ coming from?

It is coming from the Si precursor (clay synthesis)



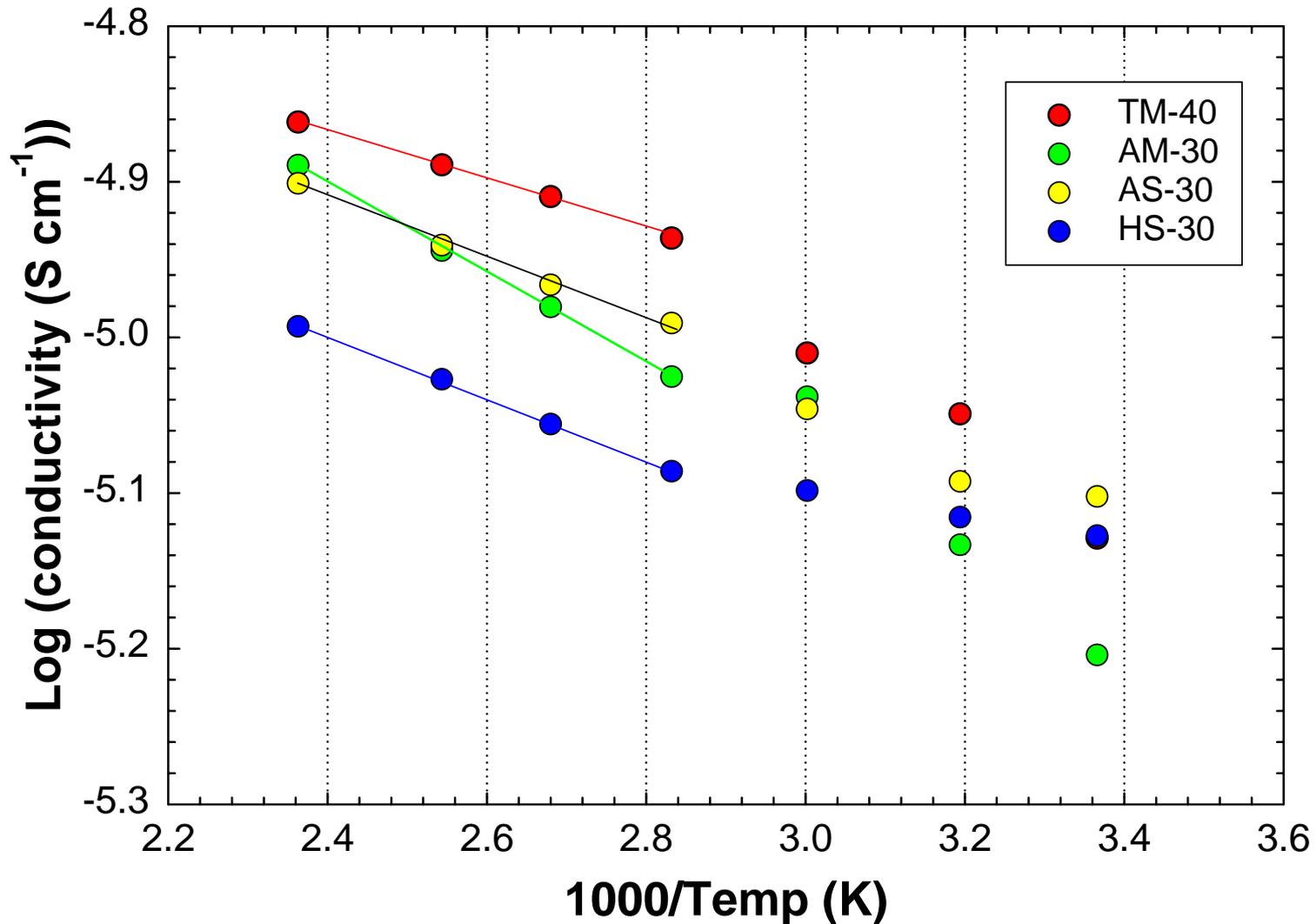
Experimental Setup for Conductivity Measurements



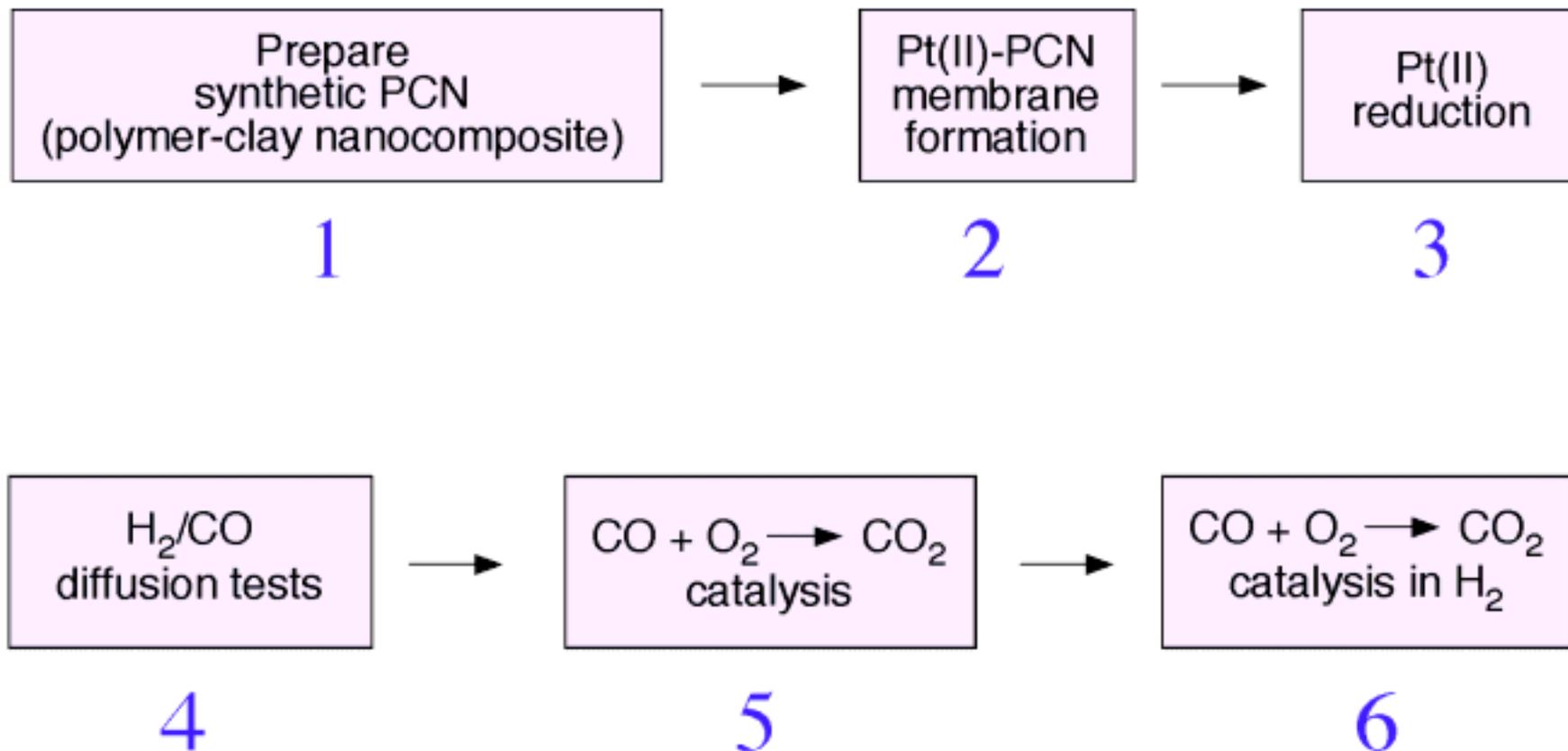
Impedance data: High Frequency end



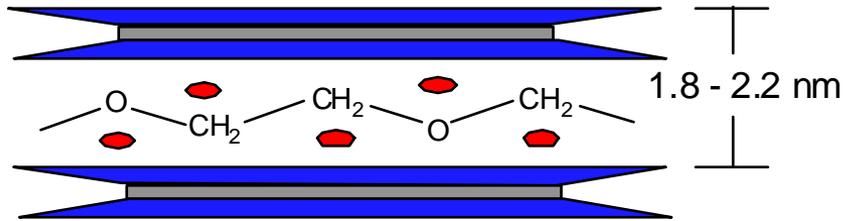
Arrhenius Conductivity Plots Derived from Nanocomposite Films of PEO:Clay:1.2:1 Ratio



Membranes for Catalytic and Separation Applications

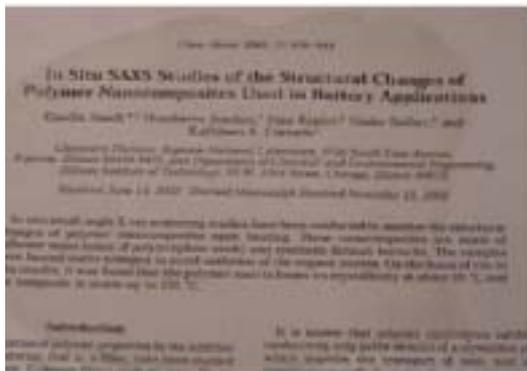


PEO-PCNs for Catalytic Membranes

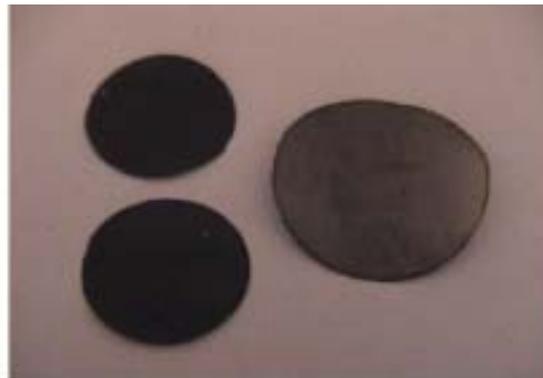


● = 2.4 wt% Pt(II)
reduced to Pt(0)
(200°C under H₂)

polymer added during or after synthesis
1:1 PEO-clay ratio
e.g. polyethylene oxide (PEO)



Non-reduced membrane



30 min

1 hr

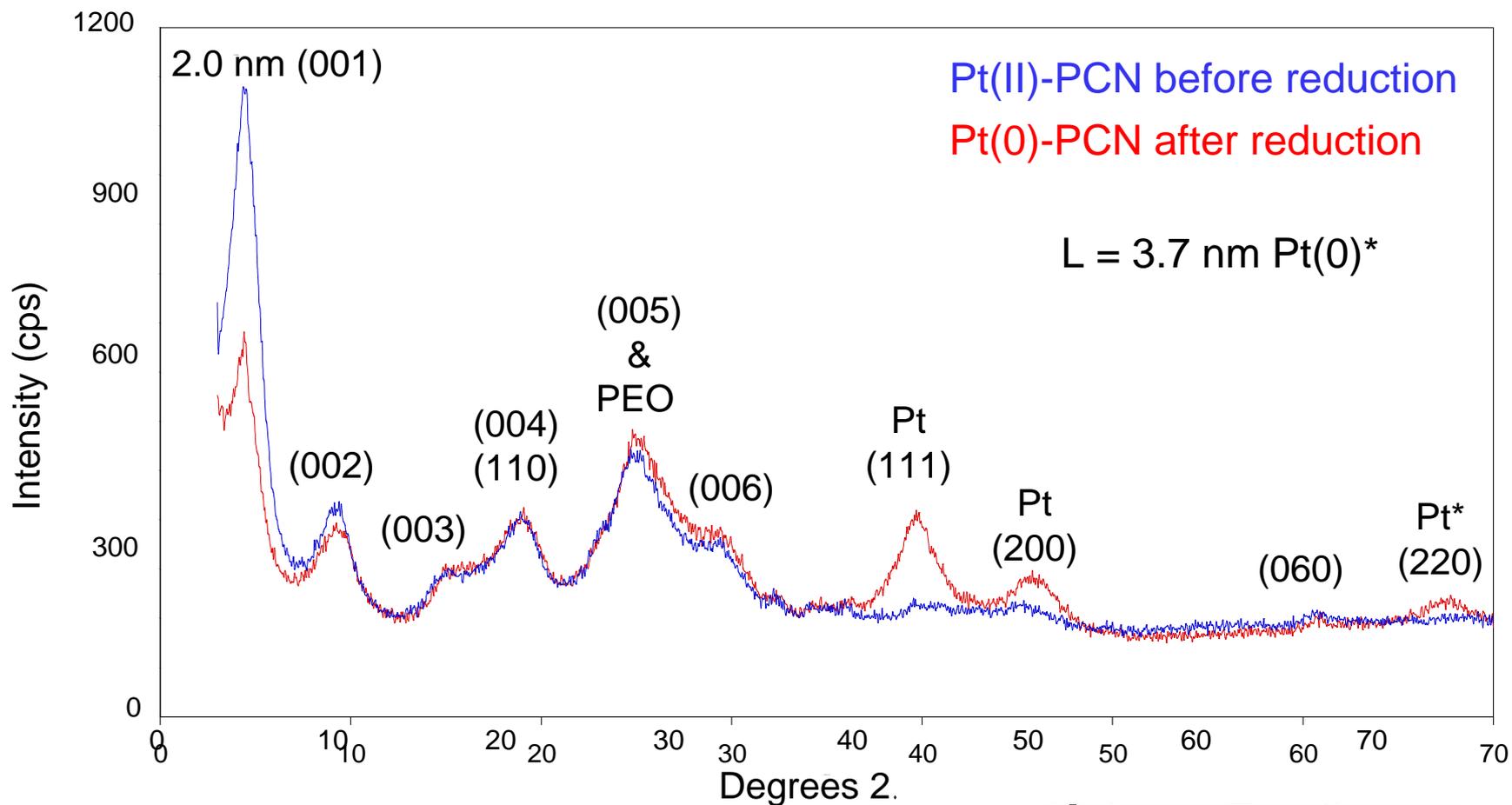


1.5 hr

2 hr



XRD of Pt-PCN Membranes

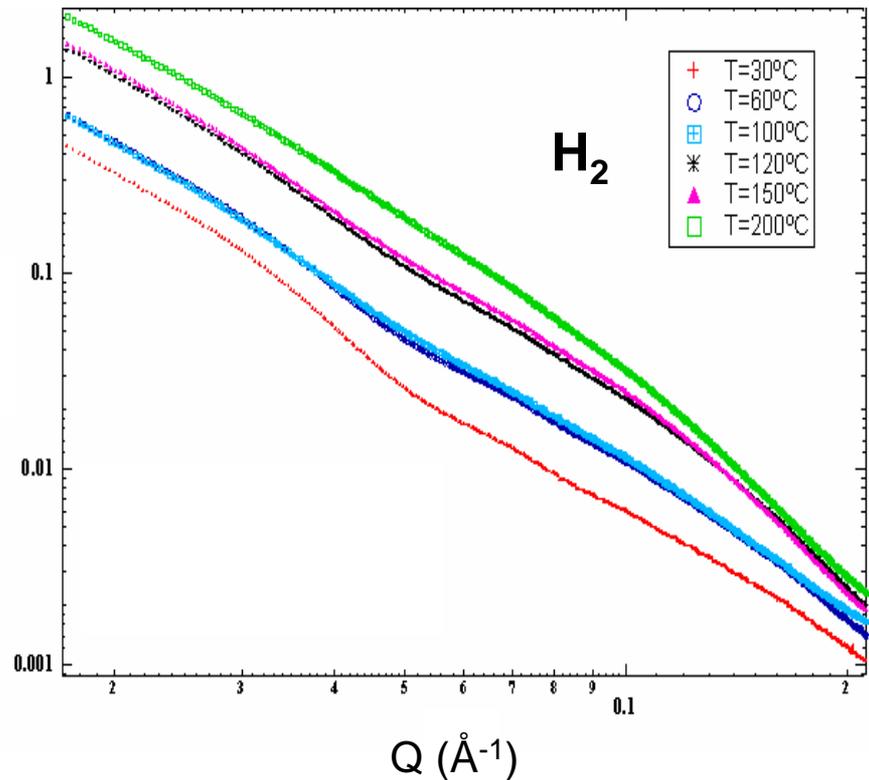
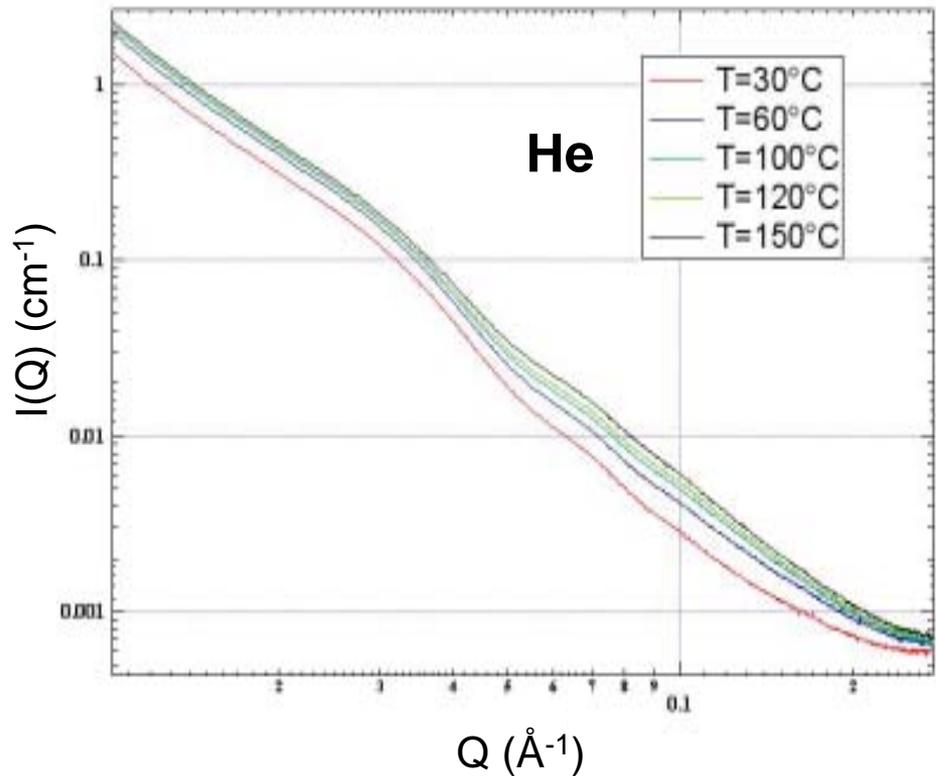


*Scherrer Equation:

$$L = 0.9 \lambda / B_{2\theta} \cos \theta_{\max}$$

(J. Catal. 1995, 154, 98)

In Situ SAXS of Pt-PEO-PCN Membrane Reduction



25-100°C at 1°C/min; 100-200°C at 0.5°C/min



SAXS Analysis: General Unified Fit

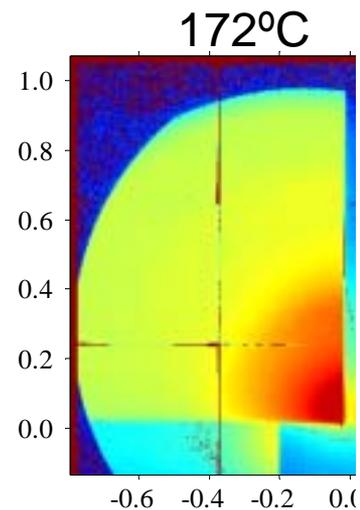
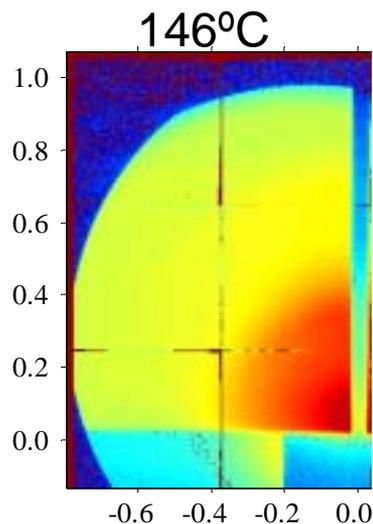
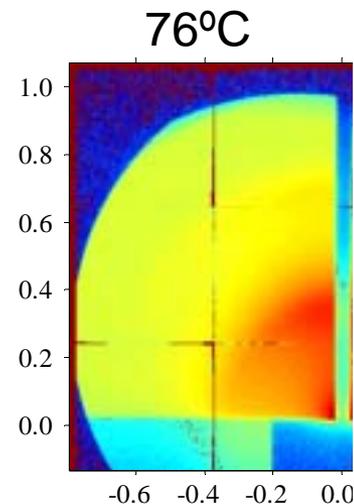
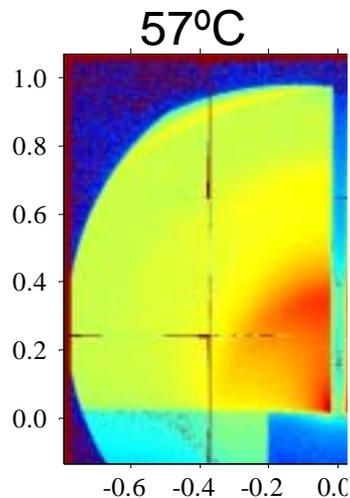
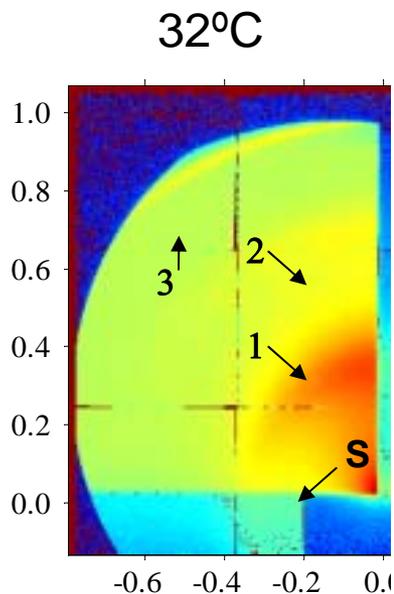
T (°C)	R _g (Å)			D, nm
	He	H ₂		
	Layer 1	Layer 1	Layer 2	
30	81.3	80.0	-	
60	79.2	81.9	-	
100	79.7	84.2	-	
120	81.7	88.1	18.6	4.8
150	82.0	90.5	19.0	4.9
200	89.8	104.7	19.8	5.1

$$I(q) = G \exp(-q^2 R_g^2/3) + B[\text{erf}(qR_g/6^{1/2})]^3/q^P$$

(Beaucage 1994, *J. Non-Cryst. Solids*, 797)

for a sphere, $R = (5/3)^{1/2} R_g = 1.29 R_g$; $D = 2R$

GISAXS of a Catalytic Membrane (1:1 SLH:PEO and Pt²⁺)



S : SAXS (Pt clusters + PEO + SLH)

1 : (001) of SLH, $d=18.5\text{\AA}$

2 : (002) of SLH, $d=9.2\text{\AA}$

3 : PEO, $d=6.4\text{\AA}$

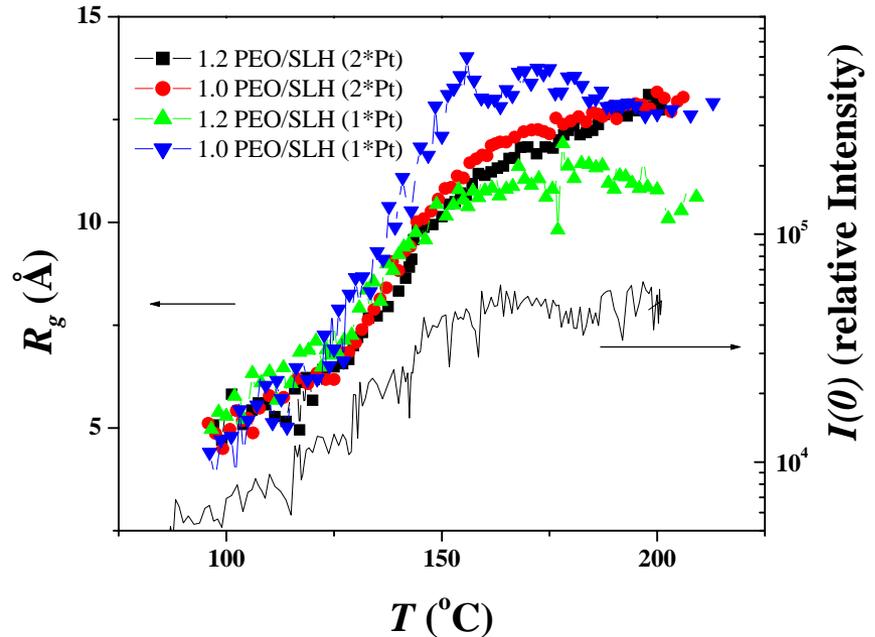
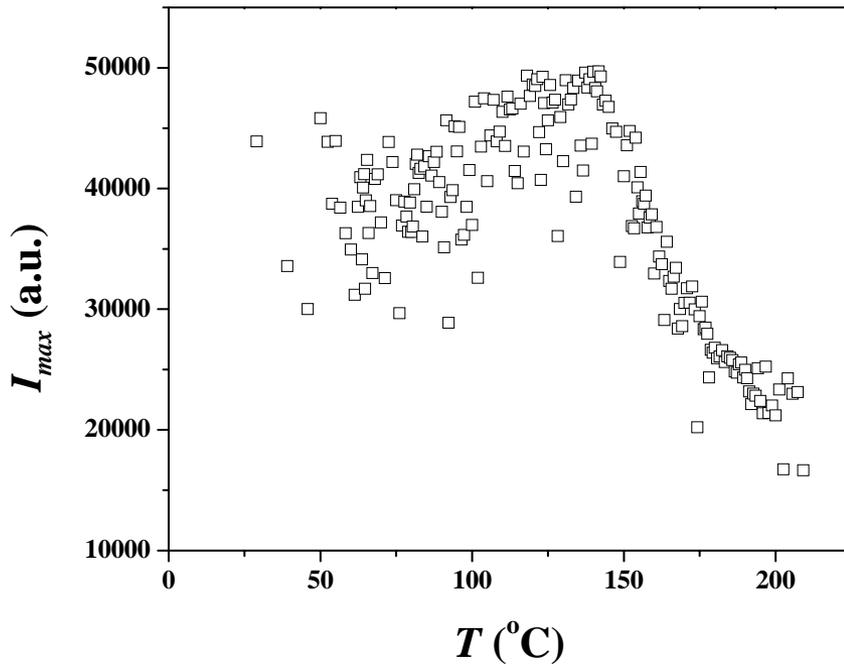
Experimental Conditions and Analysis

- **Detector : Gold CCD [9 mosaic CCD cells]**
- **X-ray Energy : 12keV**
- **Incidence angle : 0.15deg.**
- **SDD : 760.5mm**

- **No reflection effects observed due to sample thickness. Data were analyzed with the kinematic theory.**
 - **Cluster size** : Guinier analysis is performed for horizontal cuts after subtracting a background [RT pattern is assumed as a background for SAXS]



GISAXS Analysis



SLH peak intensities at $q_z = 0.34\text{\AA}^{-1}$
Increment until about 125°C is caused
by the increase of background [SAXS]

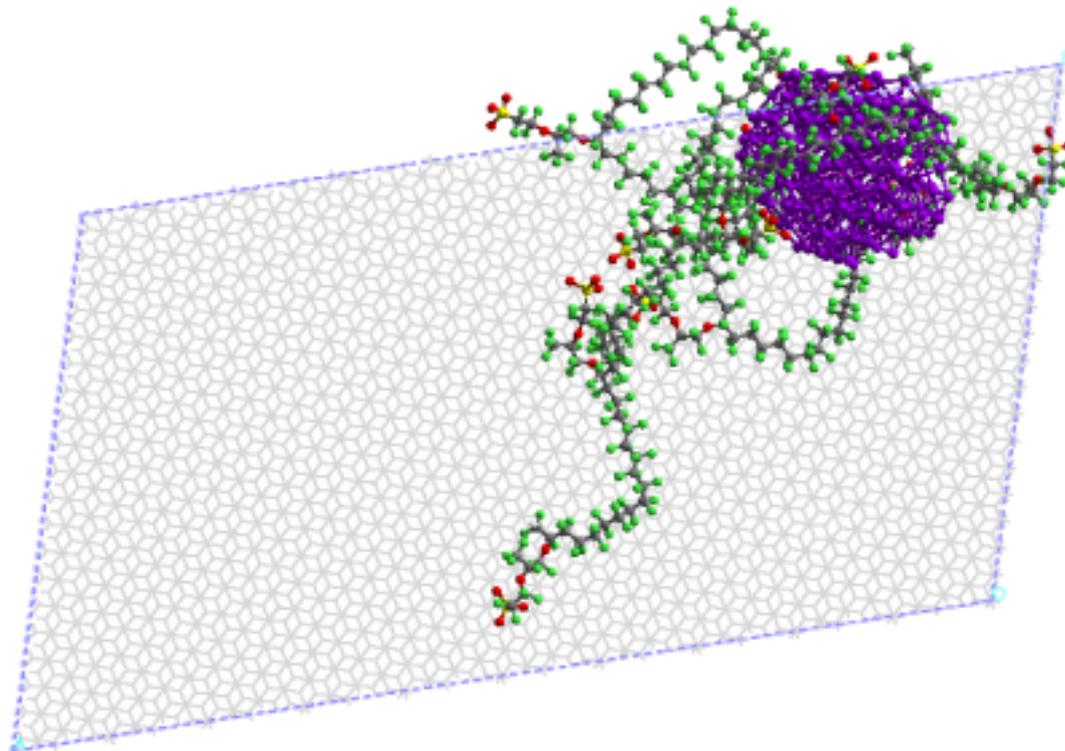
R_g and $I(0)$ for Pt clusters

All 4 samples show the same
tendency.

Low concentration samples reach the
maximum size and maintains the size.

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Molecular Modeling w/ P. Balbuena (TAM)



Polymer solvation?

**MD simulations of 256-atom Pt on graphite with
Nafion polymer (10 units)**

Conclusions

- The motion of the lithium cation appears to be correlated to the PEO conformational dynamics. The activation energies of the mobile lithium cations is similar to those observed for PEO intercalated in the clay. The lithium cation activation energies are similar to those observed in other solid polymer electrolytes.
- Not all of the lithium appears to be mobile even at high temperatures. Lithium may be trapped along the interface of the PEO and clay; bound by hydroxyl groups at the surface.
- At 60°C, PEO loses its crystallinity and it is at this point where the films become more conductive, as also indicated by the high conductivity and the almost unity transference number (0.95).



Conclusions

- A Pt-PEO-PCN catalytic membrane is reduced successfully under H₂ flow at 200°C (SAXS/TGA show PEO is stable).
- SAXS, TEM, XRD yield Pt(0) size (from 4-5 nm up to 16 nm); Pt(0) size and dispersions are being optimized.
- The PEO-PCN membranes can go to 200°C, but CO oxidation occurs at higher temps. Therefore, more thermally stable polymers will be tested.
- Pure clay can be used, but the speculation is that the polymer helps to solvate the metal clusters and keep them from aggregating.



Acknowledgments

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Kathleen Carrado, CHM (ANL)

Riza Kizilel, and Humberto Joachin, Department of Chemical and Env. Eng., IIT

Sönke Seifert, APS (ANL)

Byeongdu Lee, APS (ANL)

Randall Winans, CHM (ANL)

Christopher Marshall, CMT (ANL)