Water Diffusion in Polymer Electrolytes for Lithium Air Batteries

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Li-Air Battery with Polymer Electrolyte

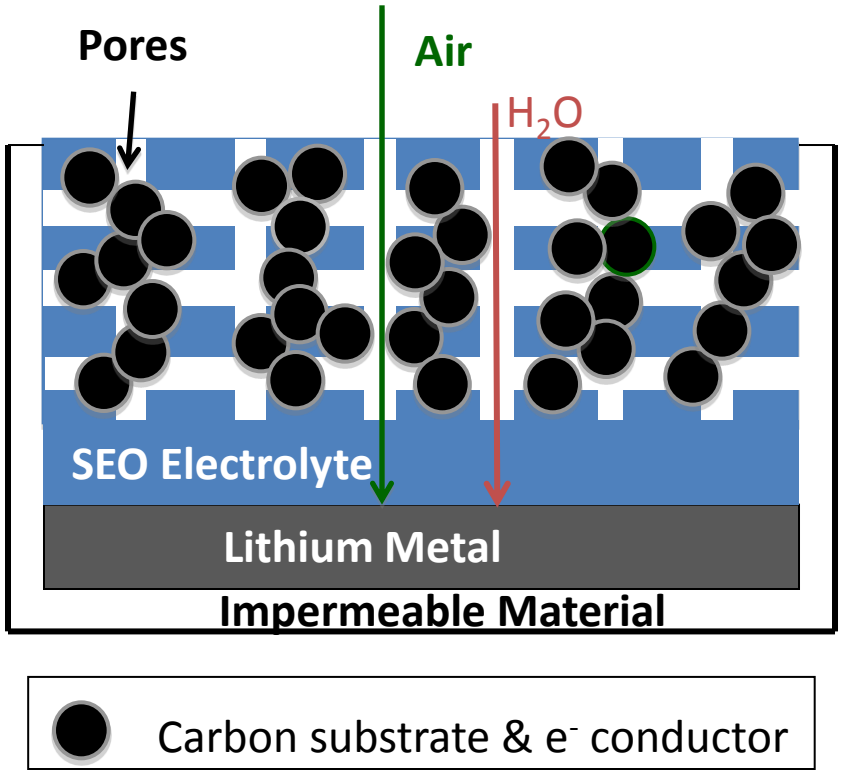
Irreversible reactions consuming Li

$2Li + O_2 \longrightarrow Li_2O_2$

$3Li + ½N_2 \longrightarrow Li_3N$

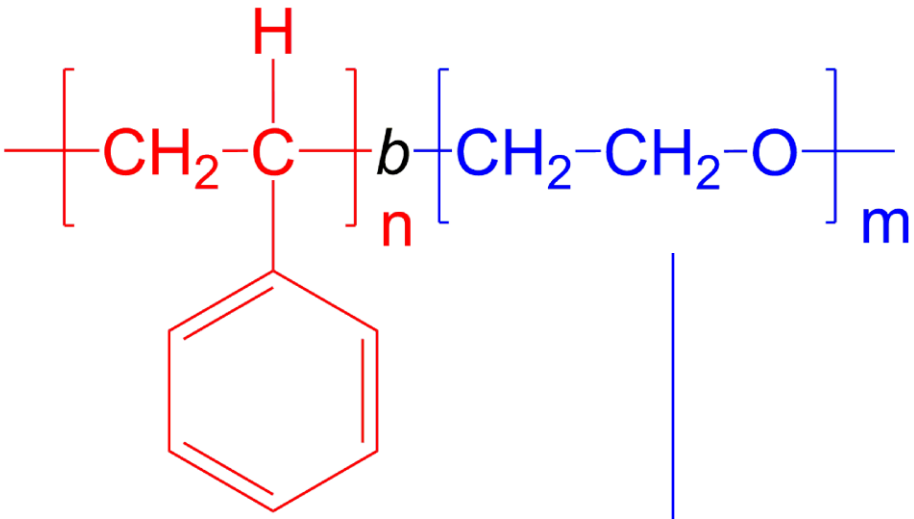
$2Li_2O_2 + 2CO_2 \longrightarrow 2Li_2CO_3 + O_2$

$2Li + 2H_2O \longrightarrow 2LiOH + H_2$



- Low water diffusion in SEO electrolyte is important.

Block Copolymer, PS – *b* – PEO

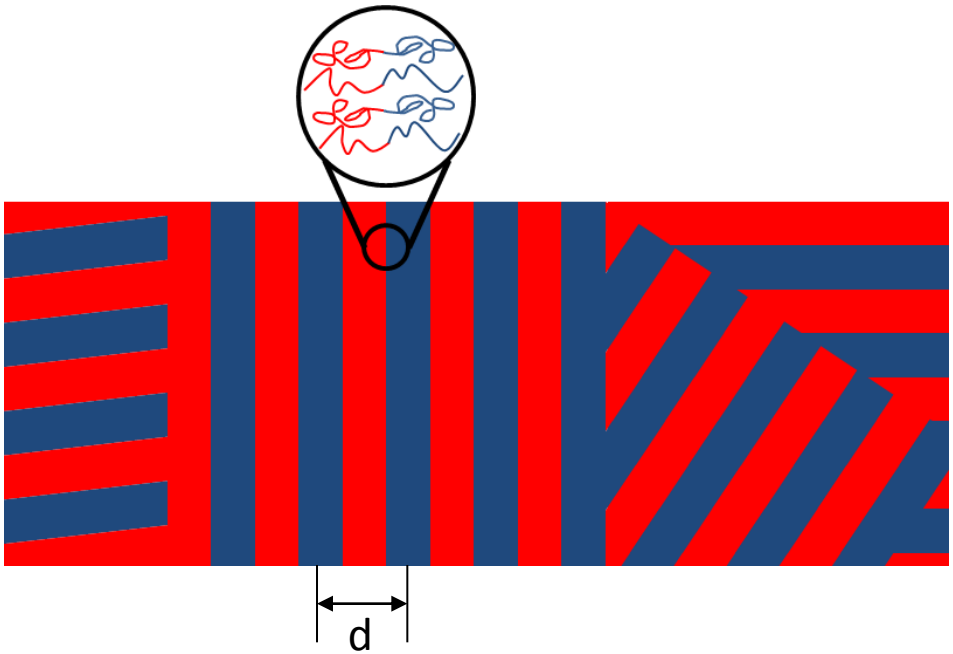


Polystyrene blocks

Provides mechanical strength

PEO blocks

Provides ion conductivity medium

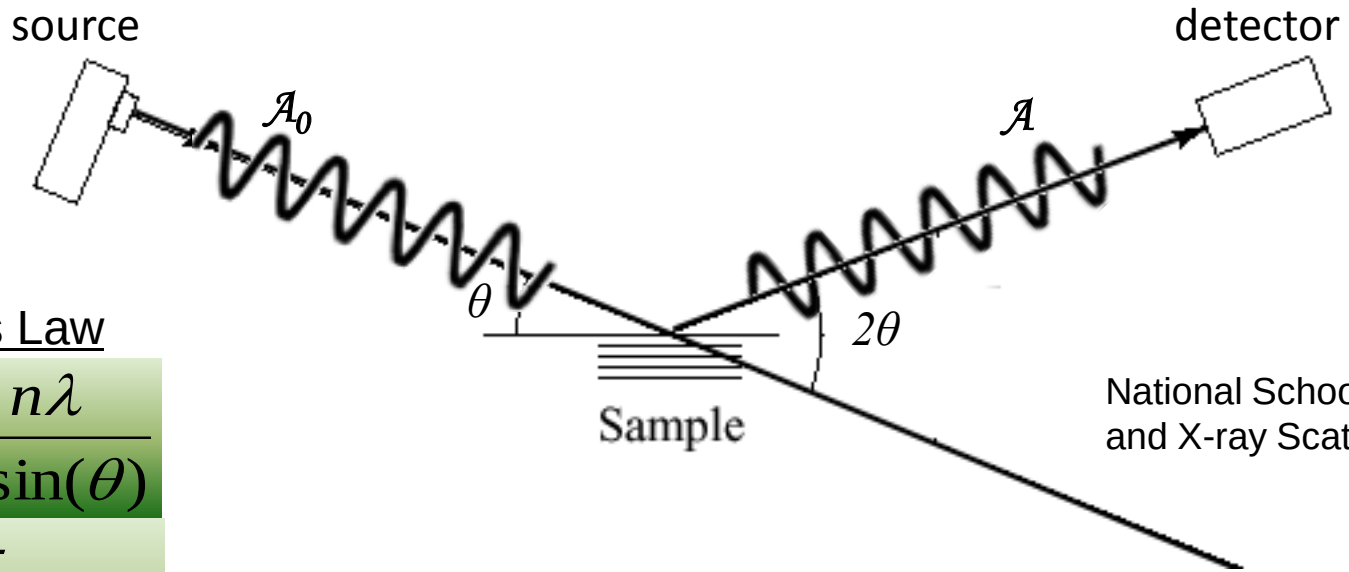


Lamellar Morphology

Mn (kg/mol): 140-*b*-141

- Equimolar ratio of PS and PEO blocks.

Small Angle X-ray Scattering (SAXS)



National School on Neutron and X-ray Scattering, 2014

Bragg's Law

$$d = \frac{n\lambda}{2\sin(\theta)}$$

$$d = \frac{2\pi}{q^*}$$

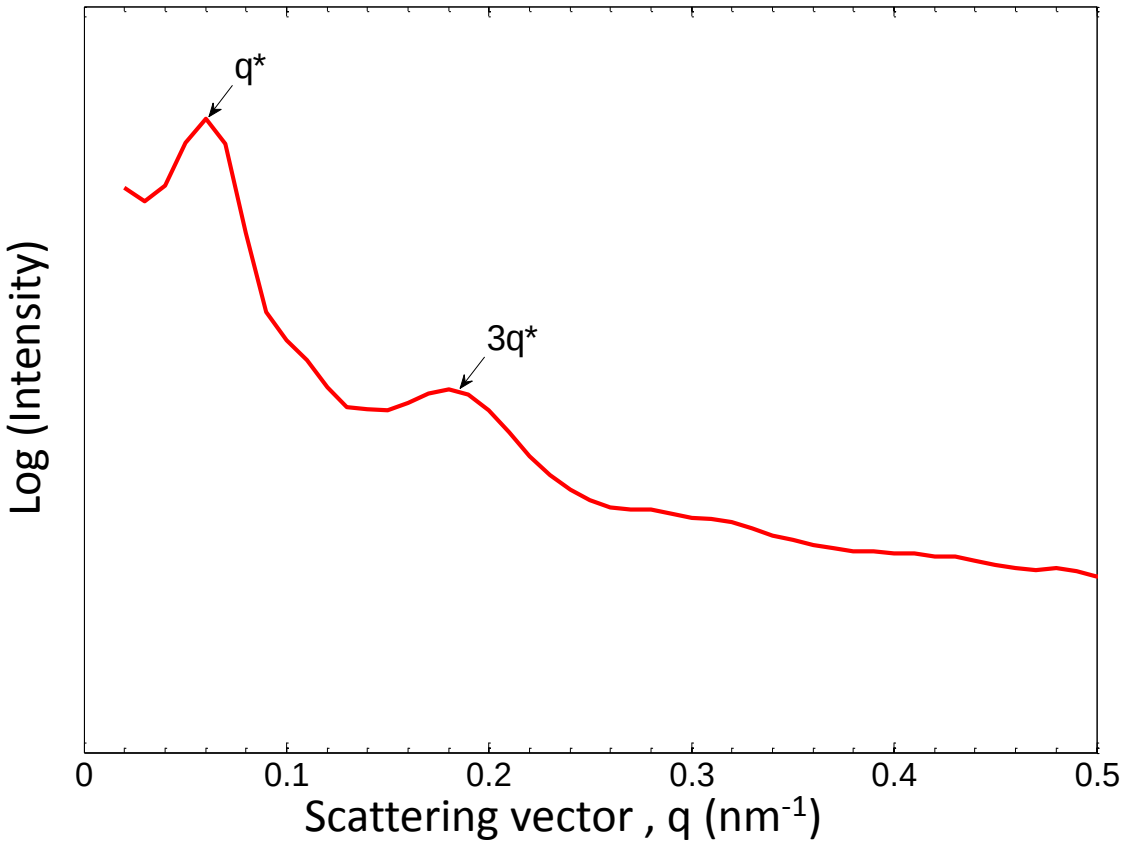
Material structural information , d

$$q^* = \frac{4\pi}{\lambda}\sin\theta$$

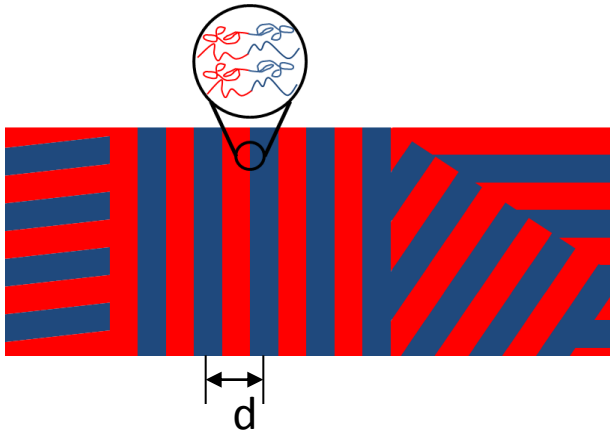
Scattering Vector, q*

- Lamellar morphology has characteristic q – spacing: q*, 2q*, 3q*, …… nq*

SAXS Profile of PS-*b*-PEO



$$d = \frac{2\pi}{q^*}$$



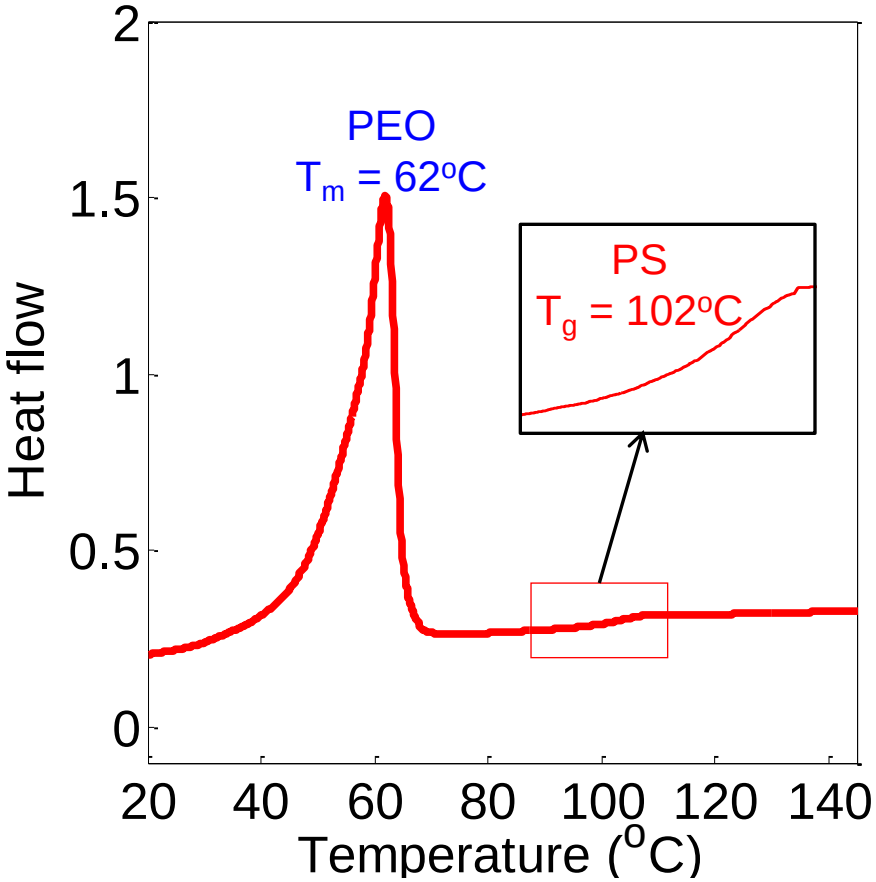
- Lamellar domain spacing, d = 105nm

SAXS experiment carried in Argonne Nat. Lab, Beamline 12-ID-B

- SEO membrane has a lamellar morphology

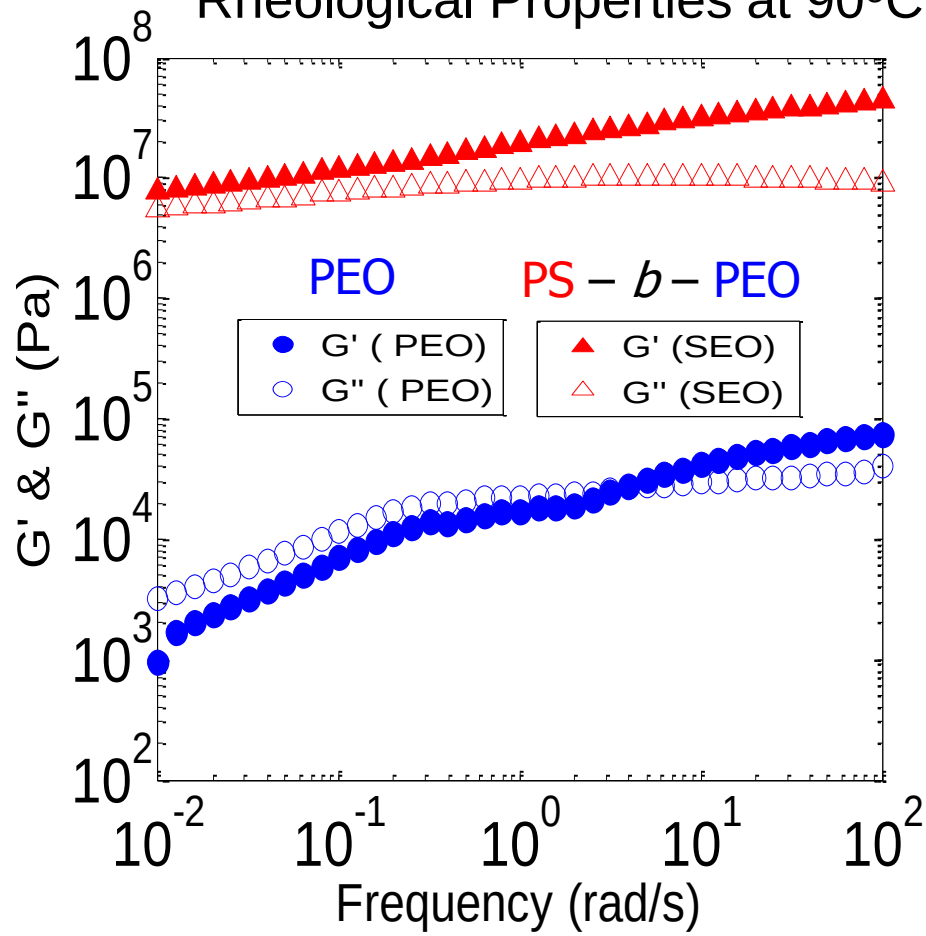
Physical Properties of PS – *b* – PEO

Thermal Properties



DSC experimental result of PS – *b* – PEO

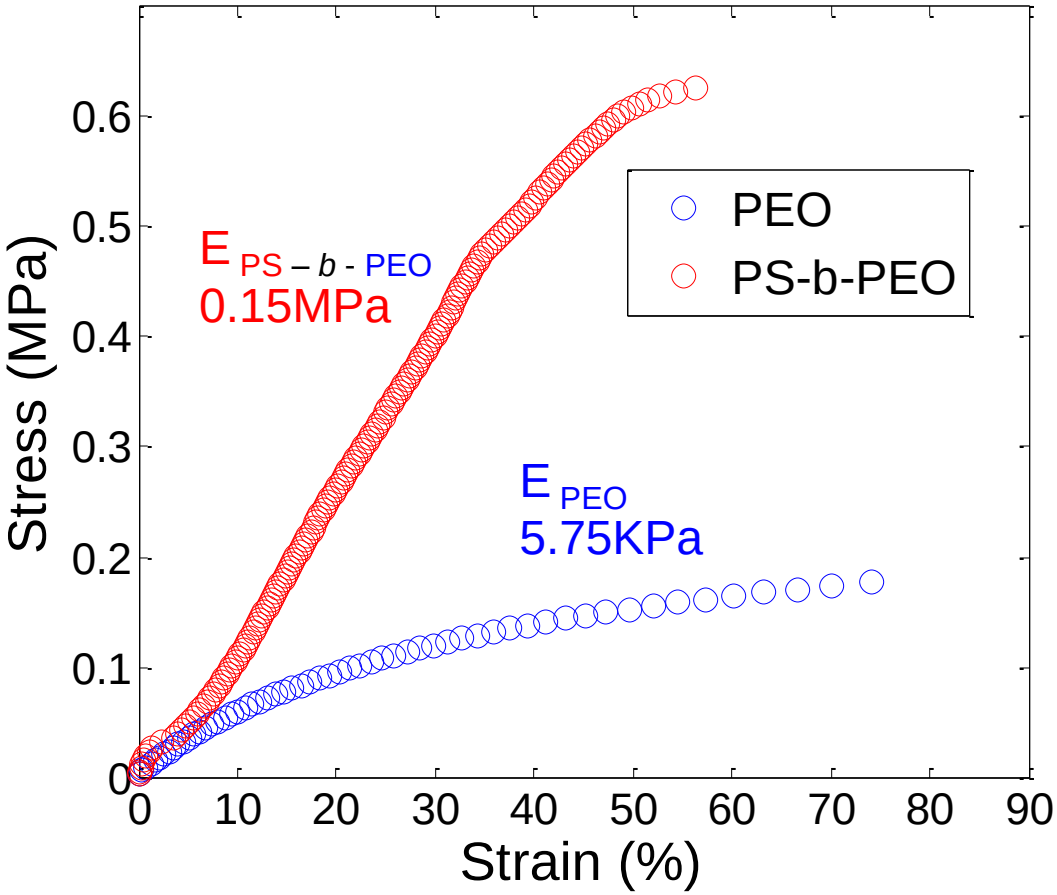
Rheological Properties at 90°C



Storage and Loss moduli of PS – *b* – PEO

- PS – *b* – PEO membrane also has both storage and loss moduli "1 x 10^4" times higher than PEO

Mechanical Properties (Elastic Moduli) at 90°C



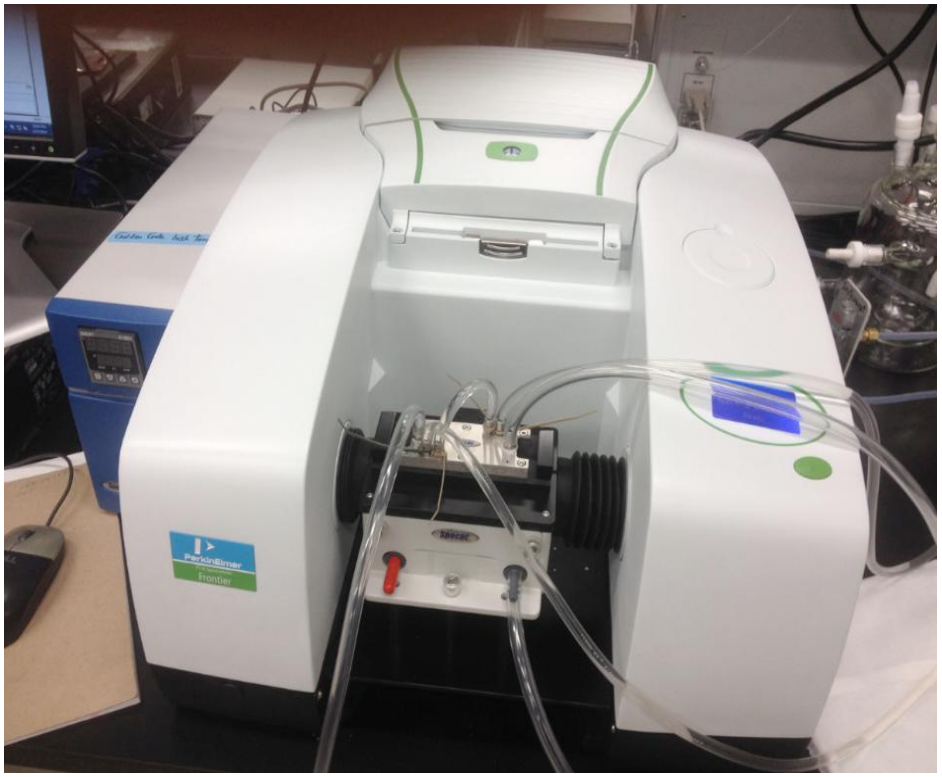
Elastic Modulus

= slope of stress - strain plot within linear region of curve

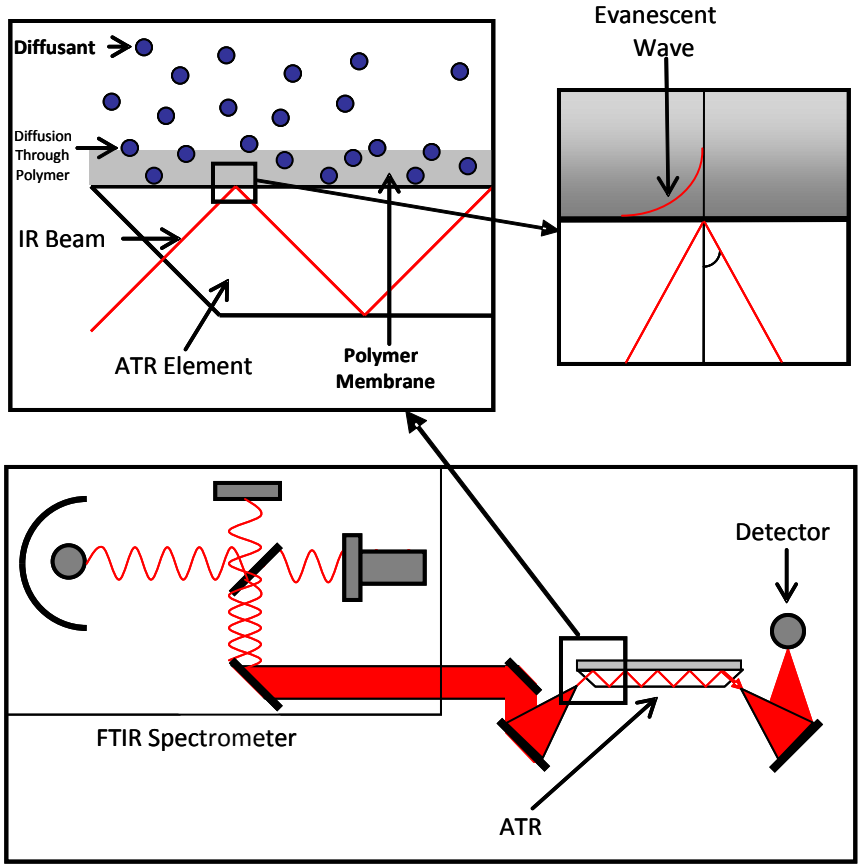
Stress – strain relationship data collected using Dynamic Mechanical Analysis

- Elastic moduli shows that PS – *b* - PEO membrane has better mechanical properties than PEO at 90°C.

FTIR – ATR SPECTROSCOPY



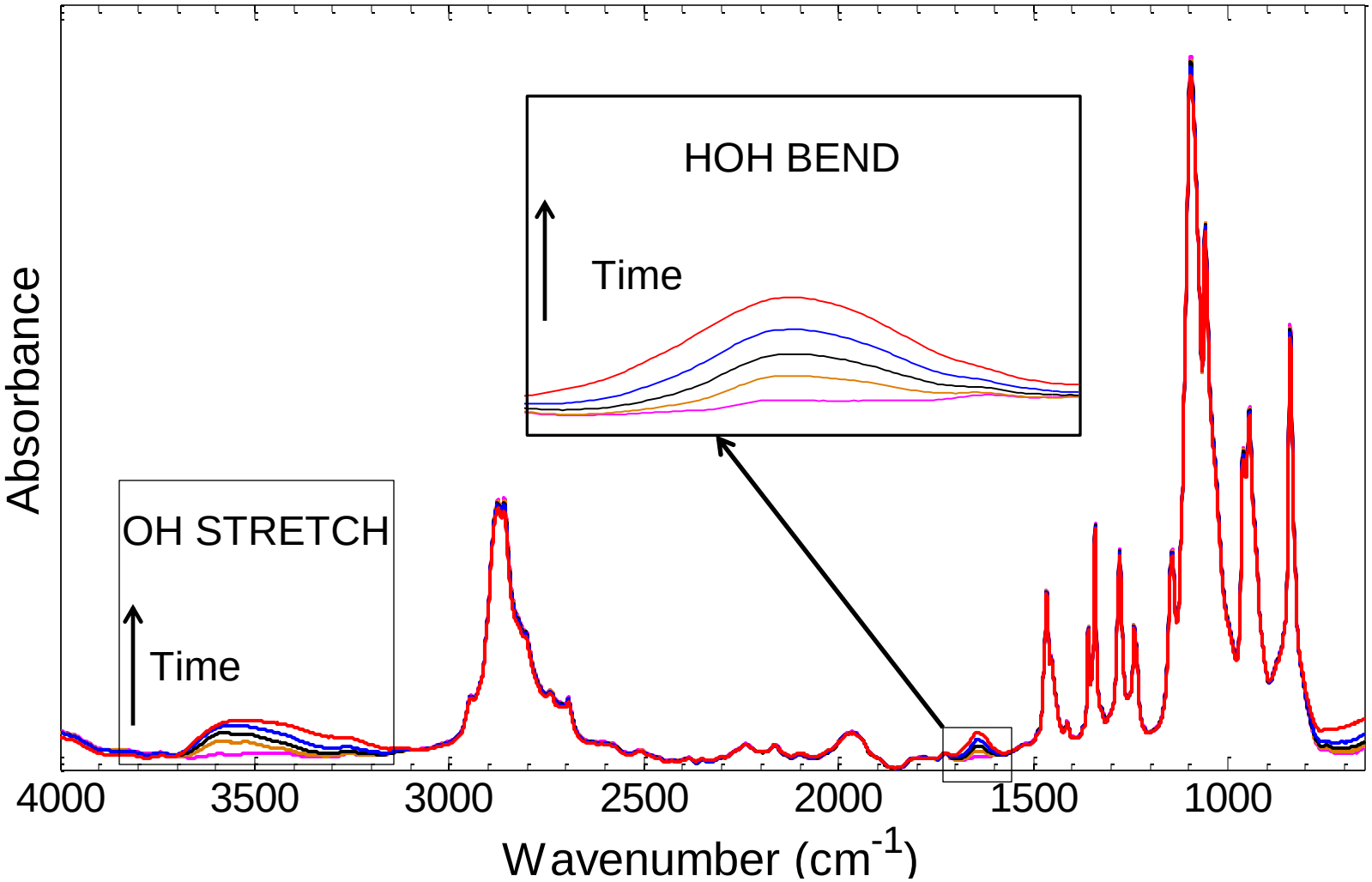
FTIR-ATR experimental set-up



Schematic of FTIR-ATR apparatus
[Hallinan, Elabd, *J. Phys. Chem. B* **(2007)]**

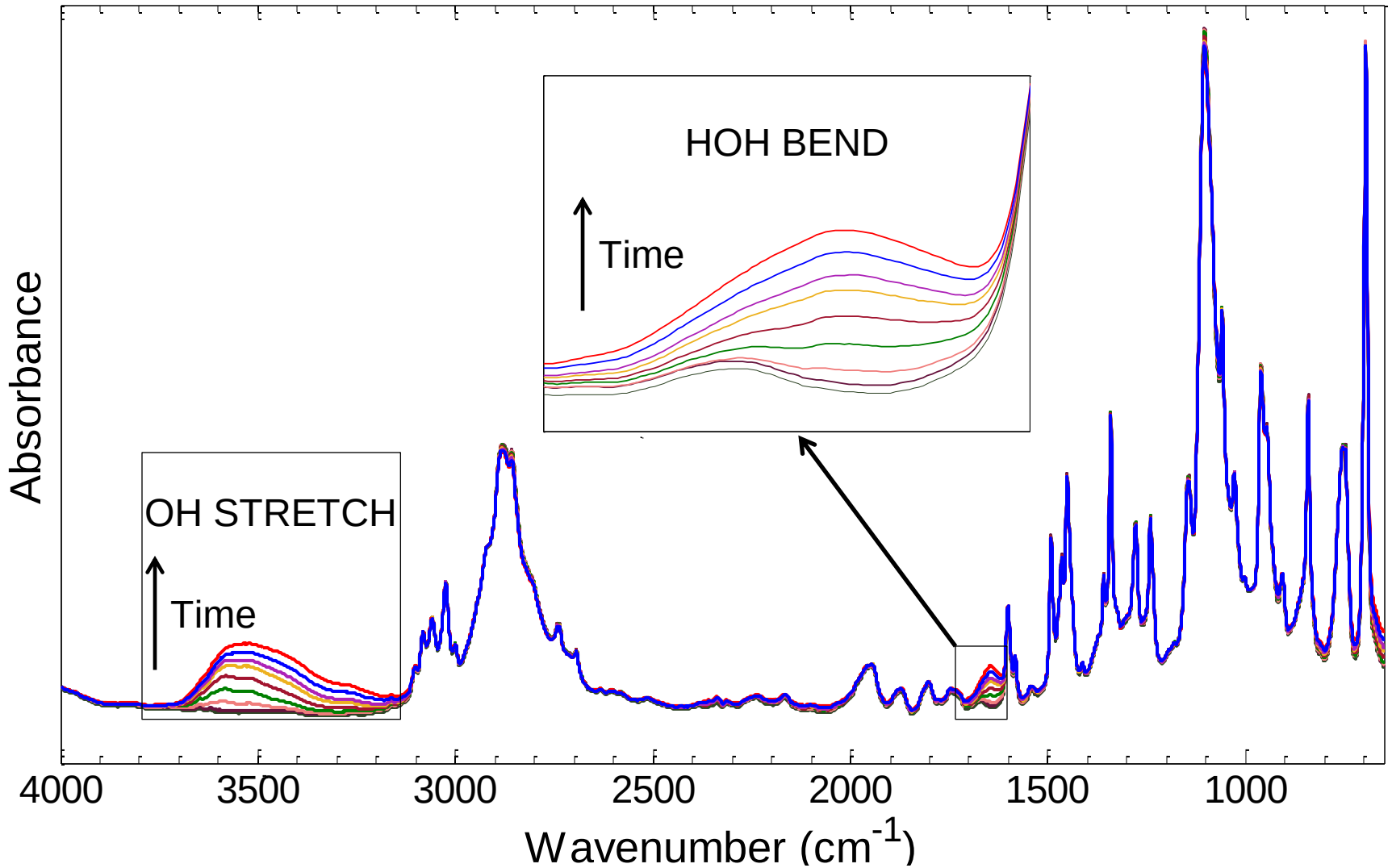
- ❑ Molecular resolution.
- ❑ Time resolved study of water diffusion in polymer membrane.

Water Diffusion in PEO Membrane



- Water diffusion in PEO membrane at 30° C and 75%RH.
- Membrane thickness = 100 µm.

Water Diffusion in PS – *b* - PEO Membrane



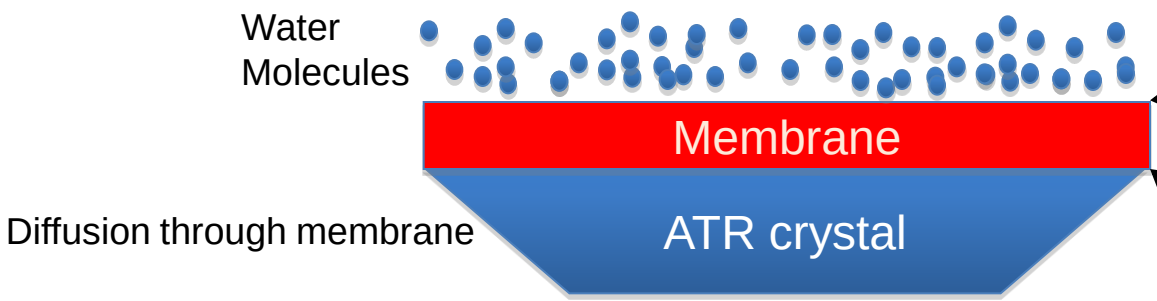
- Water diffusion in PS – *b* – PEO membrane at 30° C and 75%RH.
- Membrane thickness = 100 µm.

Model Description

Concentration, C = Absorbance, A

$$\frac{\P C}{\P t} = D_{eff}\frac{\P^2 C}{\P z^2}$$

Boundary conditions



$$z = l; \quad C = C_{eq}$$

$$z = 0; \quad \frac{\partial C}{\partial z} = 0$$

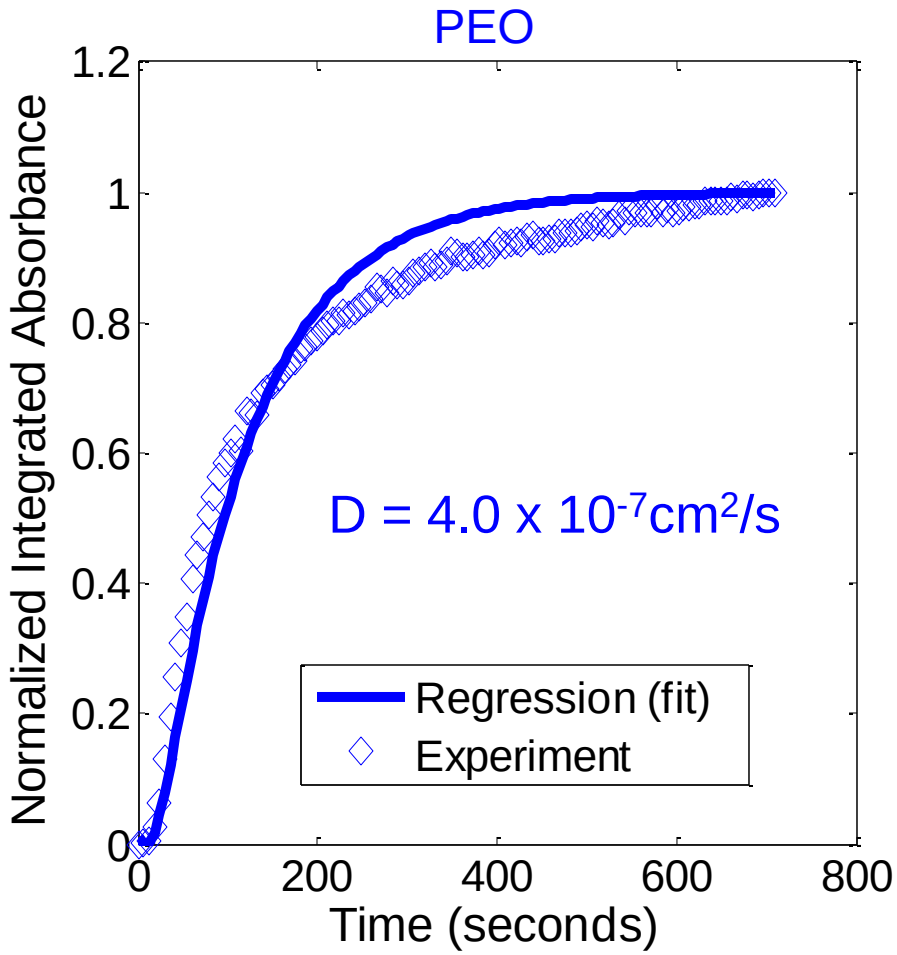
Initial condition : $C = C_0 \; @ \; 0 < z < l$

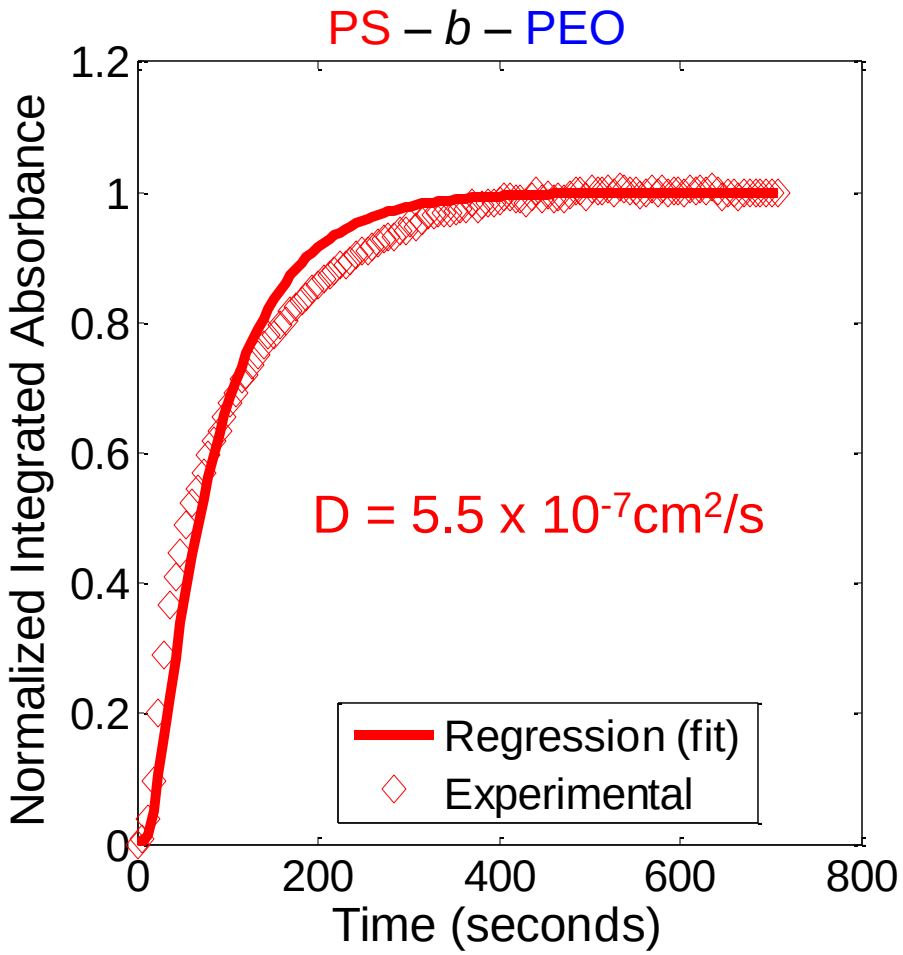
Analytical solution

$$\frac{C - C_0}{C_{eq} - C_0} = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\exp\left(-D_{eff} f^2 t\right)\cos(fz)$$

$$f = \frac{(2n+1)\pi}{2l}$$

Transport Properties of Membranes





- PEO and PS – *b* – PEO have similar water diffusion coefficient

Modeling Lithium Consumption in Li-air Battery

$$2Li + 2H_2O \longrightarrow 2LiOH + H_2$$

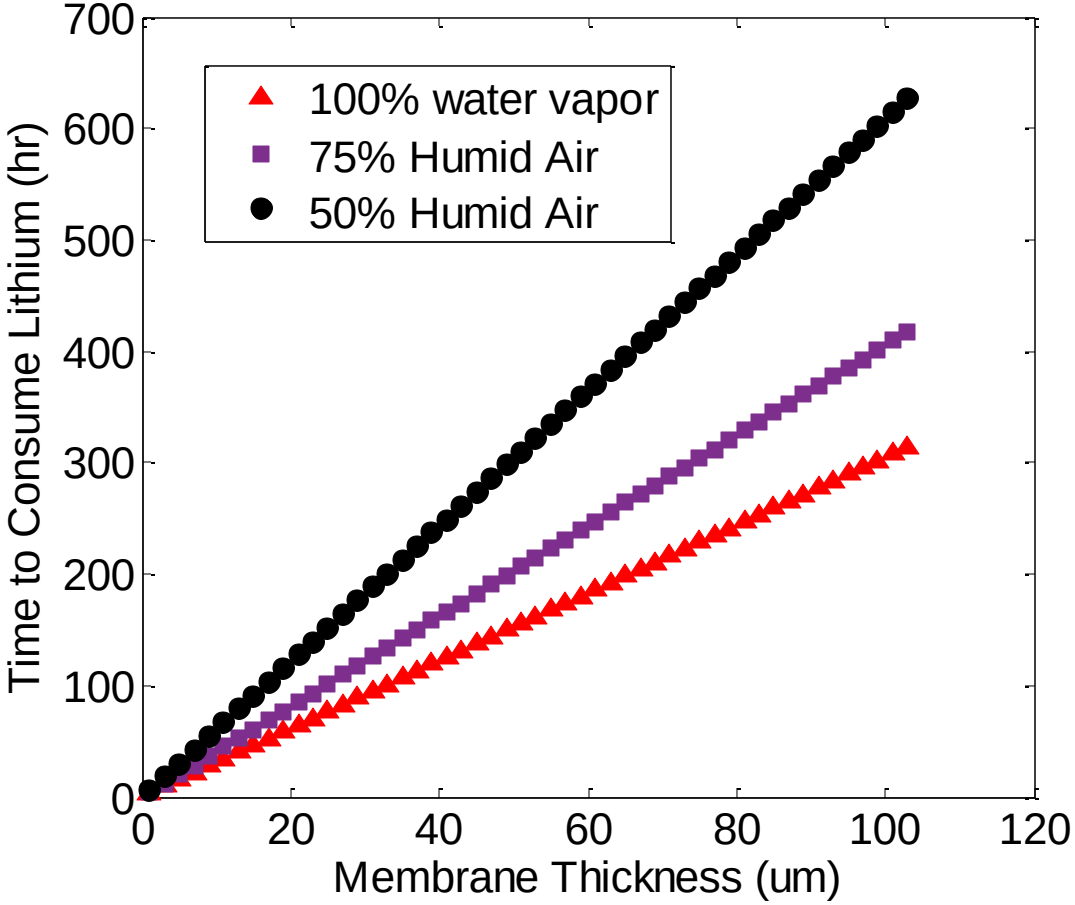
<u>*Lithium Consumption Time(Hours)*</u>

$$= \frac{Amount\ of\ Li\ (mol/cm^2)}{\left(stoichiometric\ constant * \left(\frac{Permeation}{Thickness\ of\ electrolyte}\right) * \Delta P\right)}$$

<u>*H_2O Flux (mol/hr)*</u>

$$= \left(\left(\frac{Permeation}{Thickness\ of\ electrolyte}\right) * \Delta P * cross\ -sectional\ area\ of\ electrolyte\right)$$

Modeling Lithium Consumption in Li-air Battery



- Environmental factor affects the used-up of Lithium air battery consumption

Conclusions

- PS – *b* - PEO copolymer (lamellar) has promising engineering properties.
- FTIR-ATR spectroscopy is a good technique to track molecular diffusion.
- PS – *b* - PEO copolymer (lamellar) has low diffusion coefficient similar to PEO.
- Low diffusion coefficient increases the time of Lithium (Anode) consumption

Acknowledgements

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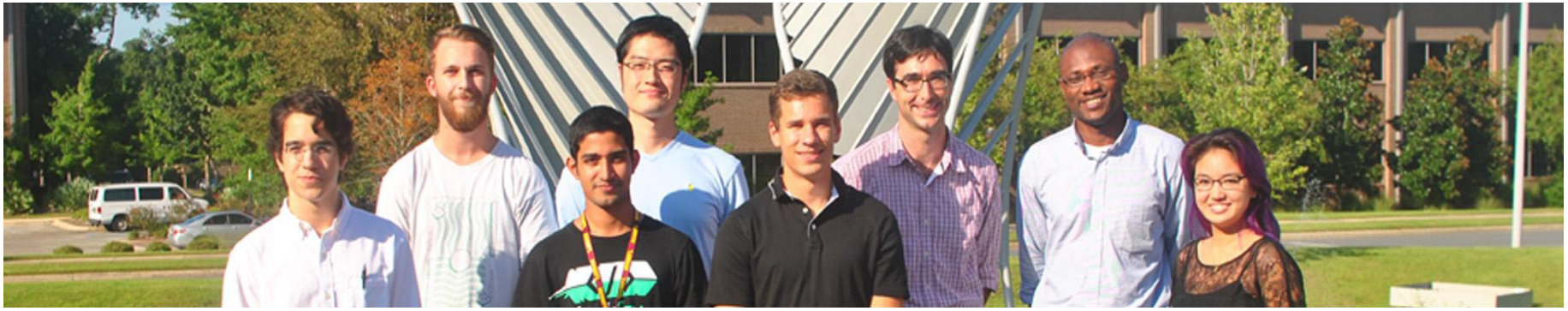

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