Continued Investigations in Carbon-Based Thin Films for Fuel Cells and Batteries

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Carbon Film Background

• Nafion has shown lamellar interface structures when grown on SiO$_2$, but not when grown on Au or Pt

• In Hydrogen Fuel Cell PEMs, Nafion grows on Carbon-black, which is too rough for reflectometry

• This is an attempt to grown thin, smooth carbon layers and characterize the Nafion interfaces that might exist in PEMs.
Specular Reflectometry

• Specular Reflectometry measures Reflected Intensity vs. grazing angle $\theta$ or $Q_z$ with $\theta_i=\theta_f$

$$Q_z = 4\pi \sin \Theta / \lambda$$

• XRR and NR Provide Depth Profile of the SLD
• SLD is related to Composition, and is proportional to the scattering lengths of the elements $Z(i)$

$$SLD(x) = \Sigma_i Z(i) n_i(x)$$

• Averages SLD in the plane perpendicular to x
• Critical Edge due to total external reflection
• Oscillations with period $2\pi / \text{layer thickness}$
• Additional layers cause additional beating patterns
Specular 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.

\[ \text{Path length difference } = 2 \cdot t \cdot \sin(\theta) \]

• Reflectometry 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.
Post Pyrolyzation Thickness vs. Concentration

\[ y = 72.97x - 146.33 \quad R^2 = 0.9971 \]

\[ y = 11.466x - 9.8437 \quad R^2 = 0.9969 \]

**Ratio of Pre-Pyrolyzation Thickness to Post-Pyrolyzation Thickness**
RMS Roughness vs. Film Thickness
Roughness decreases with decreasing thickness

\[ y = 0.0095x + 5.5998 \]

\[ R^2 = 0.9826 \]

Ideal Roughness for Nafion Study
<table>
<thead>
<tr>
<th>Sample #</th>
<th>%S1813</th>
<th>Desired Prepyrolysis Thickness (Å)</th>
<th>Measured PrePyrolysis Thickness (Ellipsometry)</th>
<th>Desired Final Thickness</th>
<th>Measured Final Thickness (X-Ray Reflectometry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>35.7</td>
<td>5000</td>
<td>2479</td>
<td>1000</td>
<td>398</td>
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<tr>
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<td>250</td>
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<td>500</td>
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<td>100</td>
<td>36.2</td>
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</tbody>
</table>
2013 Glassy Carbon Film Preparation

- Use 2012 data to determine photoresist concentrations needed to achieve 2 target film thicknesses: 30 Å and 50 Å
- Mix 2 different concentrations of S1813 Photoresist diluted in PGMEA
- Spin Coat each concentration on 2 thick and 2 thin wafers at 3500 rpm for 45sec
- Soft bake half of the samples overnight
- Pyrolyze all samples in forming gas (1000°C)
- Analyze all samples using XRR and pick most suitable for Nafion investigation
- Spin coat Nafion layer on thin carbon film
- Use XRR and NR in multiple environments to characterize the Nafion/Carbon film interface
Determining 2013 Photoresist Concentrations

By entering the target thicknesses of 30 Å and 50 Å into the best fit equation, we determine S1813 concentrations of 3.47% and 5.22%.

\[ y = 11.466x - 9.8437 \]

\[ R^2 = 0.9969 \]
Slide Preparation

- First, dilute S1813 to 10% in PGMEA (1 mL S1813 + 9 mL PGMEA = 10 mL solution)
- Adjust to final concentrations
  - 3.47% = 3.47 mL of 10% + 6.53 mL of PGMEA
  - 5.22% = 5.22 mL of 10% + 4.78 mL of PGMEA
- Spin-coat all labeled slides at 3500 rpm for 45 seconds
- Soft-bake half of all samples (1b, 2, 3, & 5) at 200° C overnight
- Have all samples pyrolyzed in forming gas at CNST.
- Because of time constraints, perform quick XRR to see which sample has ideal thickness for Nafion study. (These were only done for thick wafers; thin wafers are available for follow-up/further study)
A quick analysis indicated that this sample missed its target by too great a margin: We achieved 55 Å while aiming for 30 Å. The difference could possibly be due to impurities or unwanted absorption in the bake oven. For this reason, we avoided baked samples.
Sample #5: 5.22% S1813; Soft-Bake

Here again we see an overshoot of desired thickness (74 Å instead of 50 Å). This is outside the range of desired thickness and also probably contains unwanted impurities. We pursued analyses of the two unbaked samples: #4 and #25.
Sample #4: 3.47% S1813; No Bake

This XRR fit shows the non-baked sample fits pretty closely to the target thickness (31.6 Å, aiming for 30 Å). We proceeded with NR but were only able to take one set of scans in a D₂O wet bath environment.
Sample #4; NR in D$_2$O Liquid

The NR data show a PPR layer with a thickness around 30 Å as well, but there is also a transition layer between the SiO$_2$ and the PPR. The roughness revealed in the PPR layer is much too high.
Sample #25: 5.22% S1813; No Bake

The target thickness for the 5.22% solution was 50 Å, but this XR fit indicates a total thickness for the PPR of ~34 Å. We extended the analysis for this sample, using NR in a dry environment and in a 90% RH (D$_2$O) environment. This was the sample that we put Nafion on for additional NR measurements. (Thanks to Joe Dura for completing this data fit.)
Sample #25: NR in Dry Cell

NR data for the same sample fit to a thinner total thickness (~29.7 Å) and greater total roughness.
NR data in D$_2$O vapor reveal a bit higher total layer thickness (~35 Å). The majority of the SLD measures higher, indicating pores filled with the vapor.
Adding Nafion to Sample #25

• Spin-coat 1:16 solution of Nafion in Ethanol onto sample
• Bake for one hour at 60°C
• Collect NR data in various environments
  – Dry (Argon gas)
  – 90% RH D₂O
  – 90% RH H₂O
• Thanks to Ben Jones for data fits that follow
Dry Nafion on PPR reveals a thin layer of high sld under the bulk Nafion with a sharp interface.

\[ \chi^2 = 5.77 \]
Fit Neutron Data

Nafion/PPR in H₂O vapor, RH = 90%

χ² = 4.46

H₂O 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$_2$O vapor, RH = 90%

$\chi^2 = 6.95$

D$_2$O reveals a strong peak in sld between the Nafion and PPR layers, also corresponding to a single water-rich layer at the interface.
Conclusions

• We did not hit target roughness values with carbon films

• Variations in Nafion SLD in H\textsubscript{2}O and D\textsubscript{2}O vapor indicate either porosity within the layer or a water-rich layer at the interface with the PPR

• We do not see the lamellae seen on SiO\textsubscript{2}

• Simultaneous fitting of two data sets would provide better indicators of layer structures
Next Steps

• Investigate different photoresists or possibly combinations of photoresists to minimize roughness
• Change the pyrolyzation environment to vacuum
• Investigate Nafion on graphene
Simple Scientific Method-Finding
Meaning in the World

Observe
• Seek new environments to observe
• Observe your actions/influence on the environment you are observing

Describe
• Observations are limited by language
• Language/knowledge enhance observation

Relate
• It is not science until it is shared with others
• Participating means serving as author and audience
Scientific Method

Plan Experiments

- Create Environment
- Improve/Study Measurement
- Collect Data
- Analyze Data
- Fit to Known Models

Discuss

- Specialty Area
- Related Fields
- Aim to diversify thinking

Learn From Data

- Share Knowledge
- Apply Knowledge

Read

Write

Reflect

Edit