Chapter 19

Molecular Relaxations and Morphology of Perfluorosulfonate Ionomers for Fuel Cell Applications

Kirt Page, National Institute of Standards and Technology

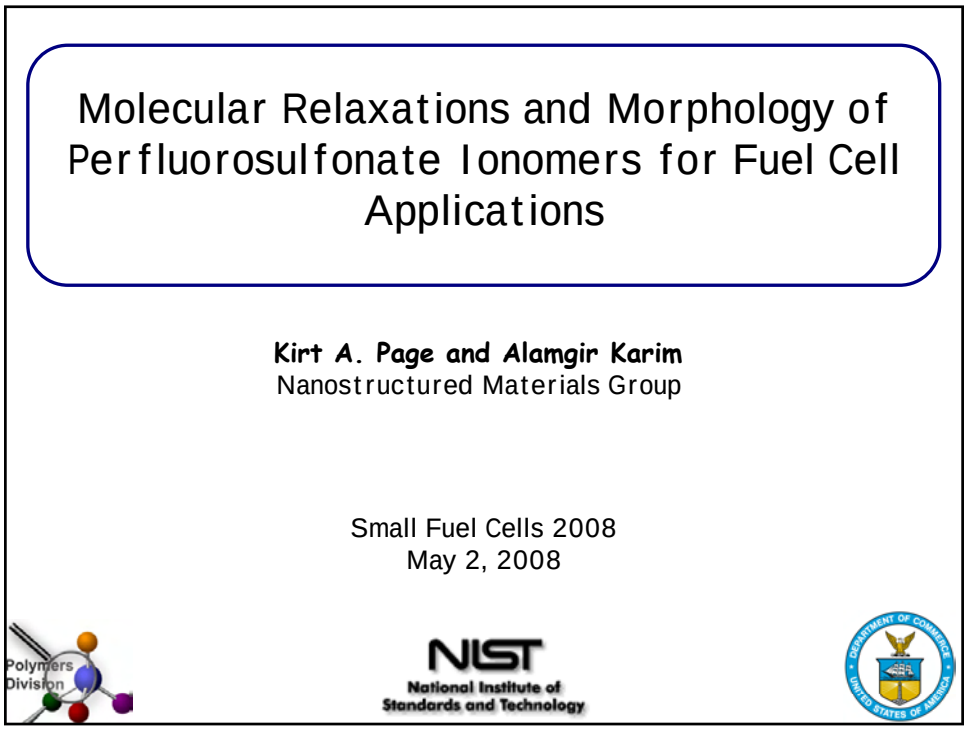


Figure 1. Title Slide

First, I'd like to thank Serge Pan and the Knowledge Foundation for inviting me to speak. While most of the talks so far have focused on advances in product development, I'm going to discuss some of the fundamental science regarding the membrane itself. I hope that I can clearly convey to you how the measurements we are doing will help to guide membrane technology development by understanding of structure and transport properties in these materials (**Figure 1**).

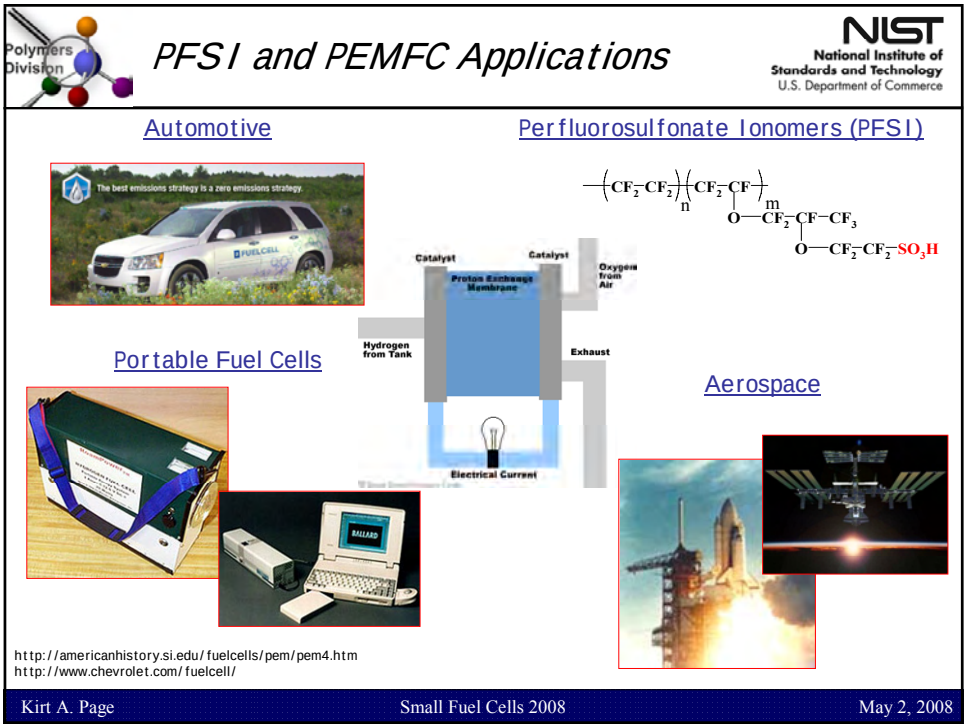


Figure 2. PFSI and PEMFC Applications

Everyone here is aware of the potential impact that fuel cell technology can, and will, have on our economy and lifestyle (**Figure 2**). This technology has a wide range of applications including transportation, portable electronic devices, and aerospace technology. While there are many types of materials used in fuel cells, today I am going to focus on the perfluorosulfonate ionomer, Nafion. A majority of my Ph.D. work was dedicated to understanding the structure and dynamics of this class of materials, and it is also part of my current work, although not exclusively.

I would like to share some information regarding my background and about what I do (**Figure 3**). Essentially, I am a polymer physicist. I am a staff scientist in the Nanostructured Materials Group within the Polymers Division at the National Institute of Standards and Technology (NIST). I use a variety of measurement techniques to study the structure and dynamics of polymeric materials, usually nanostructured materials. In my work I employ thermo-mechanical analysis—such as dynamic mechanical analysis and differential scanning calorimetry; spectroscopic techniques—such as dielectric relaxation spectroscopy, nuclear magnetic resonance spectroscopy (NMR), and neutron spectroscopy; and scattering (laser light, x-ray, and neutron) to get a picture of the morphology, physical properties, and transport properties of materials. Specifically, I have used these techniques to investigate fuel cell membrane materials. If you're going to develop a high-performance, polymeric membrane, then you should have an understanding of these things because the structure-property relationships make the membrane what it is.

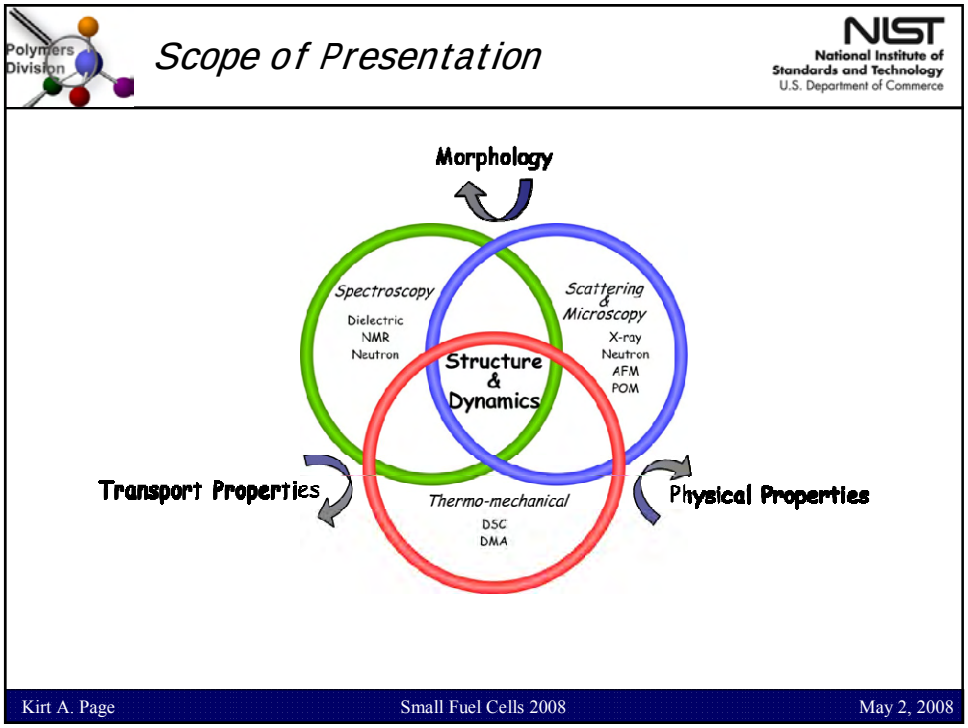


Figure 3. Scope of Presentation

Perfluorosulfonate ionomers (PFSI) has a high chemical stability, mechanical strength and high proton conductivity (**Figure 4).** As a polymer physicist and a scattering expert, I have been very interested in this material, because of its interesting chain dynamics and its nanostructure. Most of the researchers working with this material are aware that it forms nanoscopic water channels due to aggregation of the ionic functionalities and that it also has a semi-crystalline component, which provides mechanical integrity. There is considerable misunderstanding with respect to the morphology of PFSIs.

Even in current literature people are still drawing pictures of inverted micelles as the structure of this material. But if you look at the recent literature – over the last 5 years – there's been an enormous amount of work in actually determining the structure of this material, through advancements in scattering metrology, and interpretation of scattering data. Because of the hydrophobic nature of the backbone, and the hydrophilic nature of the side chain, you get more rod-like structures than you do inverse micelles, and they can aggregate to form more or less water channels, and then they overlap a contiguous phase throughout the membrane that results in its high proton conductivity. I've used solid-state nuclear magnetic resonance spectroscopy – Fluorine-19 – to look at the dynamics of this material.

More importantly, and more accessible, is small angle X-ray scattering (SAXS) to determine the structure, so I've done a lot of studies looking at the variable temperature scattering behavior of this material, both in regards to the crystalline peak, and in the ionomer peak. The ionomer peak is actually due to the inter-aggregate distance, if you will (**Figure 5).**

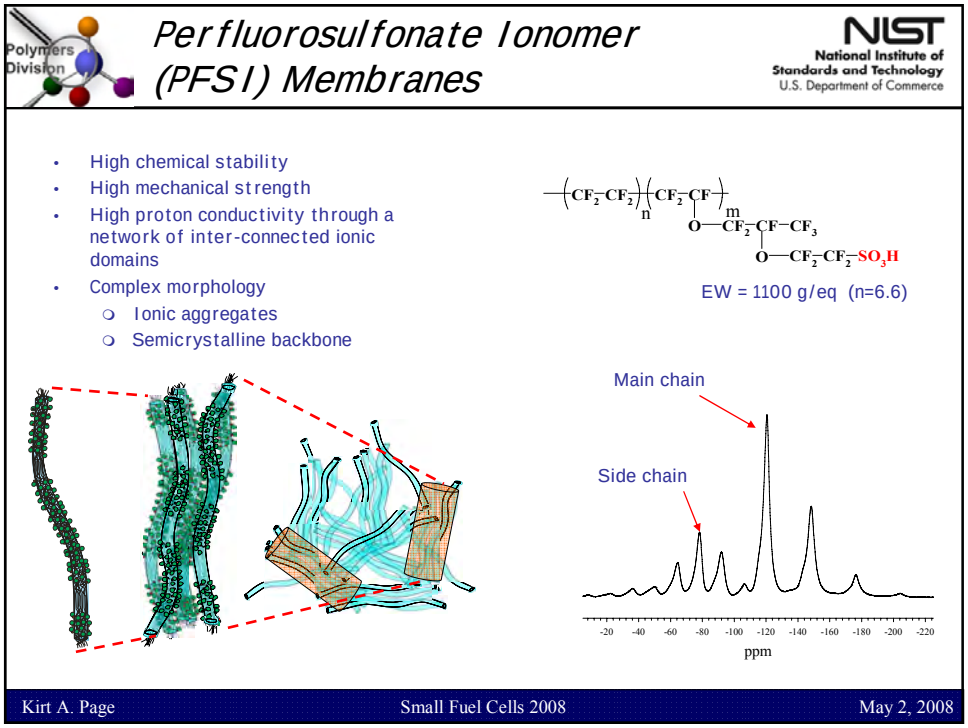


Figure 4. Perfluorosulfonate Ionomer Membranes

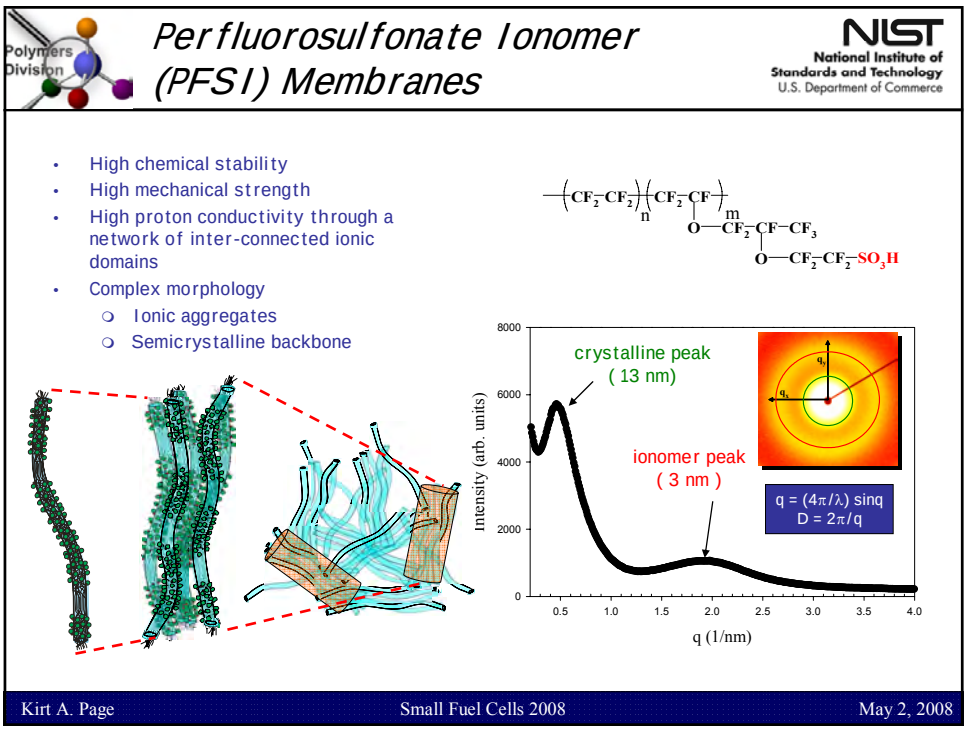


Figure 5. Perfluorosulfonate Ionomer Membranes

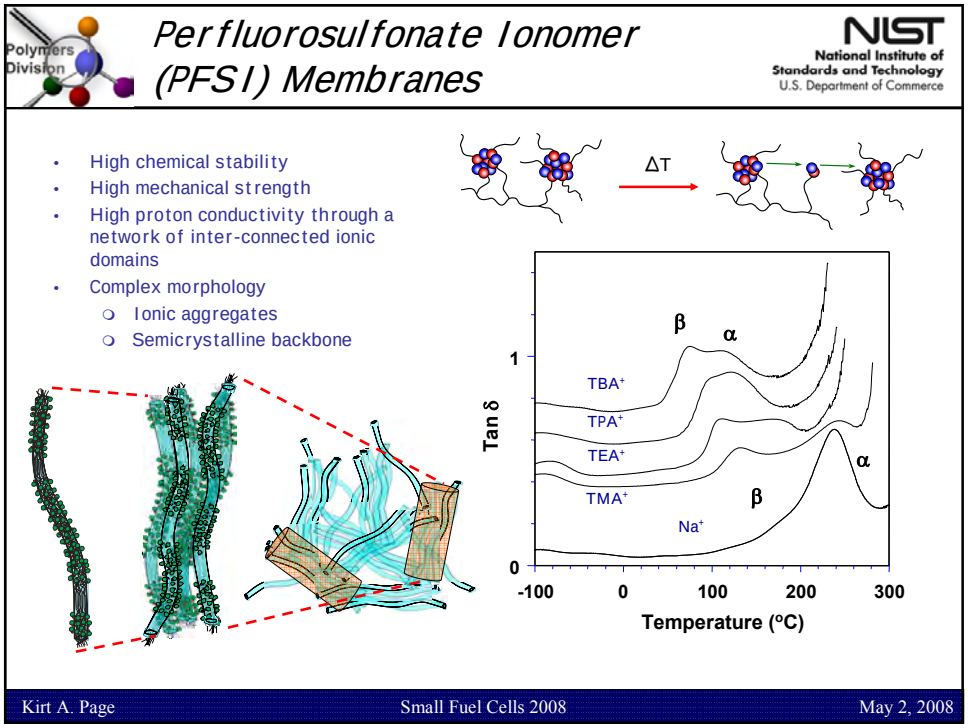


Figure 6. Perfluorosulfonate Ionomer Membranes

We've also done a lot of studies looking at the mechanical properties of this material (**Figure 6).** As a Ph.D. student, I did a very fundamental study on how the strength of the electrostatic interactions—determined by the choice of counterion—can impact the chain dynamics. This isn't directly related to fuel cell applications, but I'm learning more and more that the knowledge that I gained from these studies actually has large implications for use of this material as a fuel cell membrane. In particular, the ion hopping mechanism that facilitates long-range chain diffusion in these materials is very important in membrane creep. And then, of course, more recently we have been using neutron spectroscopy techniques to look at counterion dynamics.

Neutron spectroscopy combines the power of static scattering—allowing one to probe different size scales—with the ability to measure the energy exchange of the neutron with the material, yielding information about the dynamics (**Figure 7).** Today I will talk about counterion dynamics, but more recently I have been using this technique to study water dynamics in hydrated membranes.

One of the first studies in the Moore Research Group focused on looking at the effect of the counterion on the mechanical properties. So by changing from a sodium ion, say, to a tetramethylammonium (TMA), all the way up to a tetrabutylammonium (TBA) counterion, you can drastically change the mechanical properties of this material (**Figure 8).**

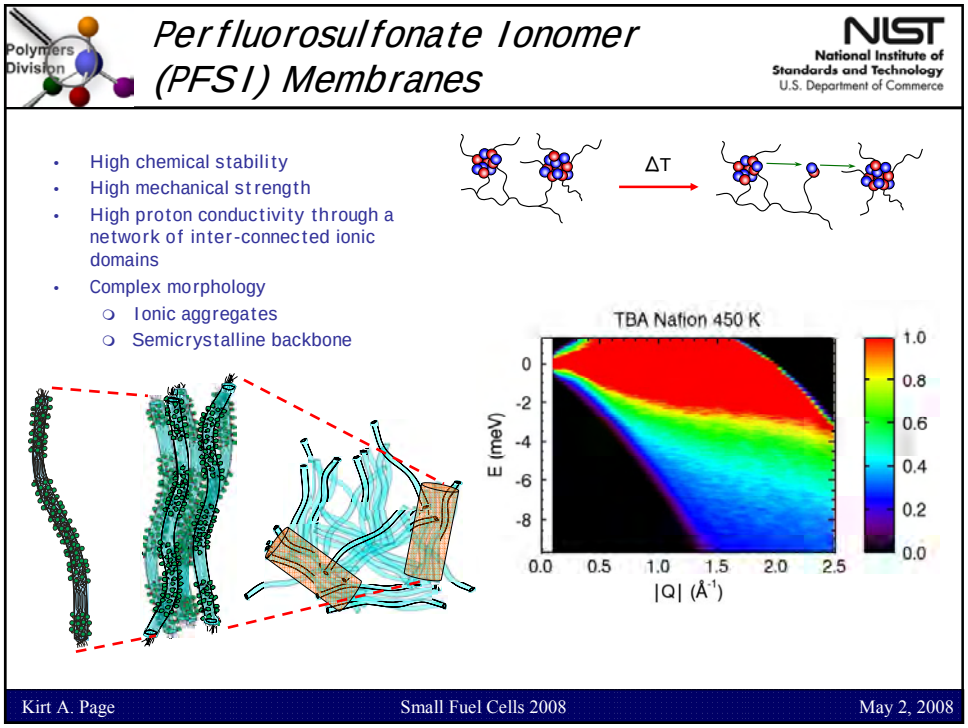


Figure 7. Perfluorosulfonate Ionomer Membranes

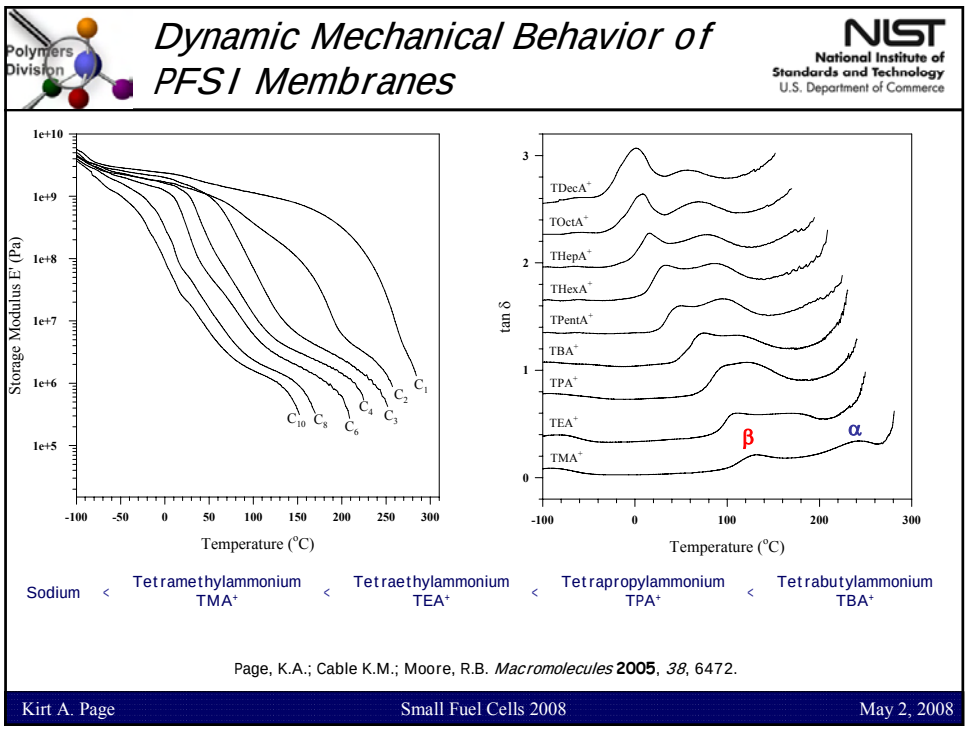


Figure 8. Dynamic Mechanical Behavior of PFSI Membranes

In particular, you can drastically change the alpha relaxation temperature, and the beta relaxation temperature. I will go into more detail later about the molecular origins of these relaxations. Important to note is the mechanical behavior of the TBA form PFSI. The nice thing about the TBA form is that it has a very similar relaxation behavior as hydrated, acid-formed Nafion. However, you don't have to worry about it drying out, so you can perform studies with it and infer information about the dynamics and the structure in a comparative way to a hydrated membrane without the disadvantage of drying out the membrane.

Based on this study and the literature for at least three decades, this alpha and beta relaxation processes were described by a paradigm used for ionomers like polystyrene sulfonate and ethylene-based ionomers, like Surlyn. The alpha relaxation was attributed to the relaxation of the ionic domains, the glass transition of the ionic phase, and the beta relaxation was assigned to the glass transition temperature of the fluorocarbon matrix **(Figure 9, 10).** Part of my Ph.D. thesis was to determine if this description of the dynamics was a valid description, or not. And if we really understand the molecular origins of these relaxations, can we learn something new about the material, or can we use that to our advantage in processing the material to get specific properties? I have used small angle X-ray and neutron scattering (SAXS), mechanical analysis, quasi-elastic neutron scattering, and ^{19}F NMR to piece together different fundamental aspects of the puzzle that is this class of materials **(Figure 11).**

Keep in mind that all of the measurement techniques that I will discuss today can be used to study any membrane. I encourage people who are developing new membranes, or have new ideas about membranes to bring any measurement challenges you are facing to NIST.

The first thing I would like to talk about was a study we published in 2005 **(Figure 12).** This work has actually been quite popular in the literature of late. In this study, we were able to change the counterion associated with the sulfonic acid group in this materials and then observe the ionomer structure as a function of temperature using variable temperature SAXS. What we were able to determine from these scattering profiles as a function of temperature was that at certain temperatures, depending on the counterion, the ionomer structure would undergo a static to dynamic transition—indicated by a sudden decrease in scattering intensity of the ionomer peak.

The location of this transition temperature was highly dependent upon the counterion, and when we compared the transition temperatures measured from SAXS with the alpha relaxation temperatures from the mechanical analysis, we saw a very strong correlation of the transition temperature with the relaxation behavior. What we were able to show with this study, or partially show with this study, is that the structure of the membrane, and the strength of the electrostatic interactions are intimately combined. Also, whatever was giving rise molecularly to this mechanical relaxation is linked to the ionic aggregation in the system.

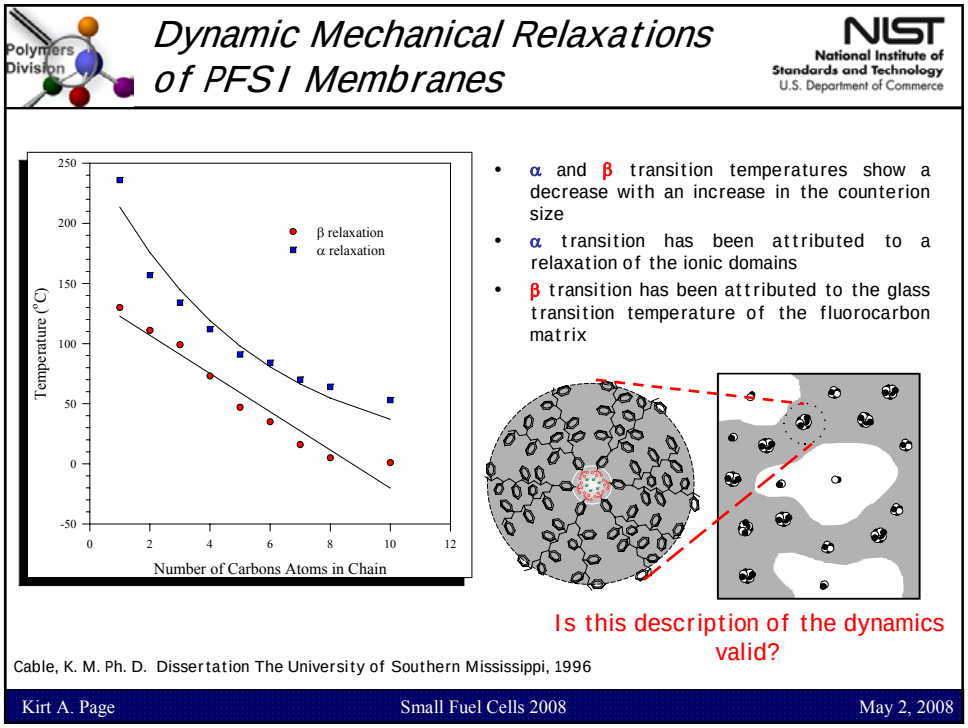


Figure 9. Dynamic Mechanical Relaxations of PFSI Membranes

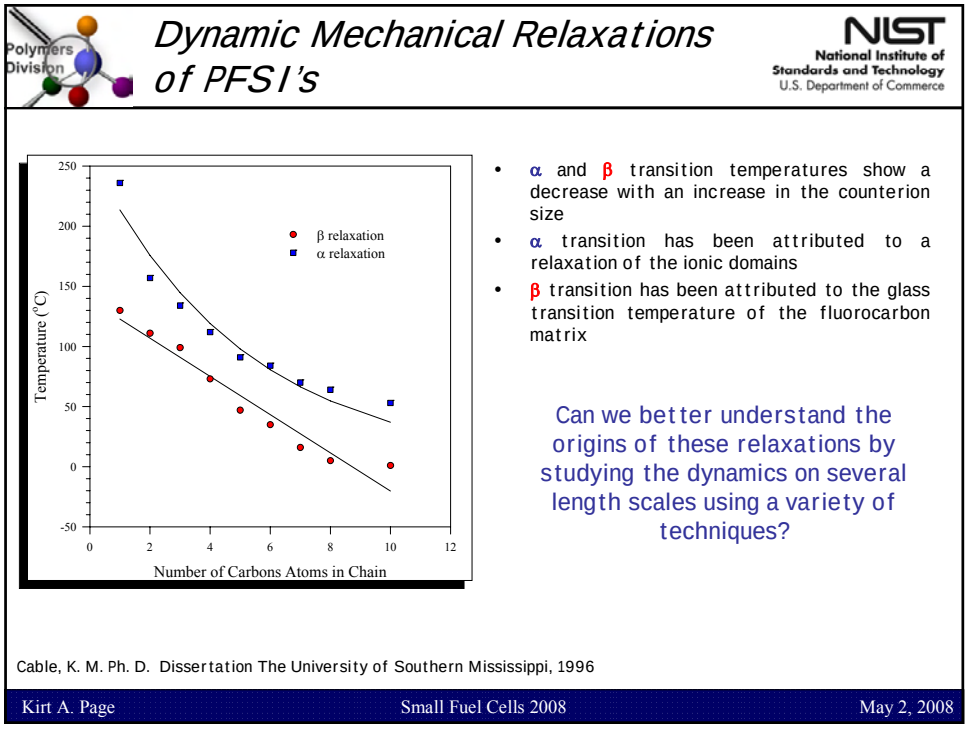


Figure 10. Dynamic Mechanical Relaxations of PFSI Membranes

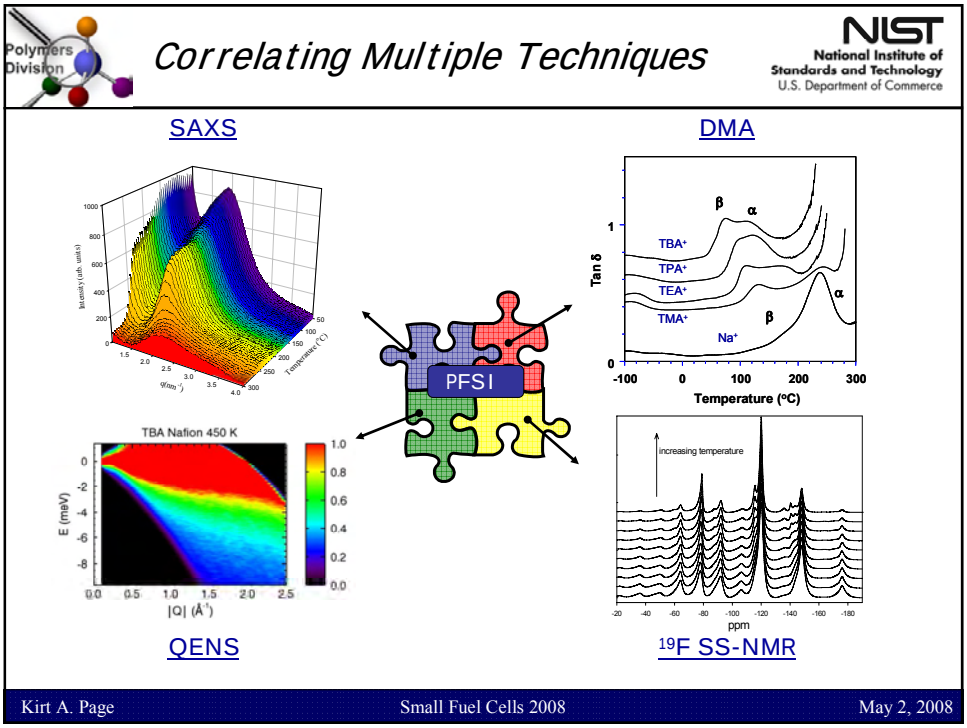
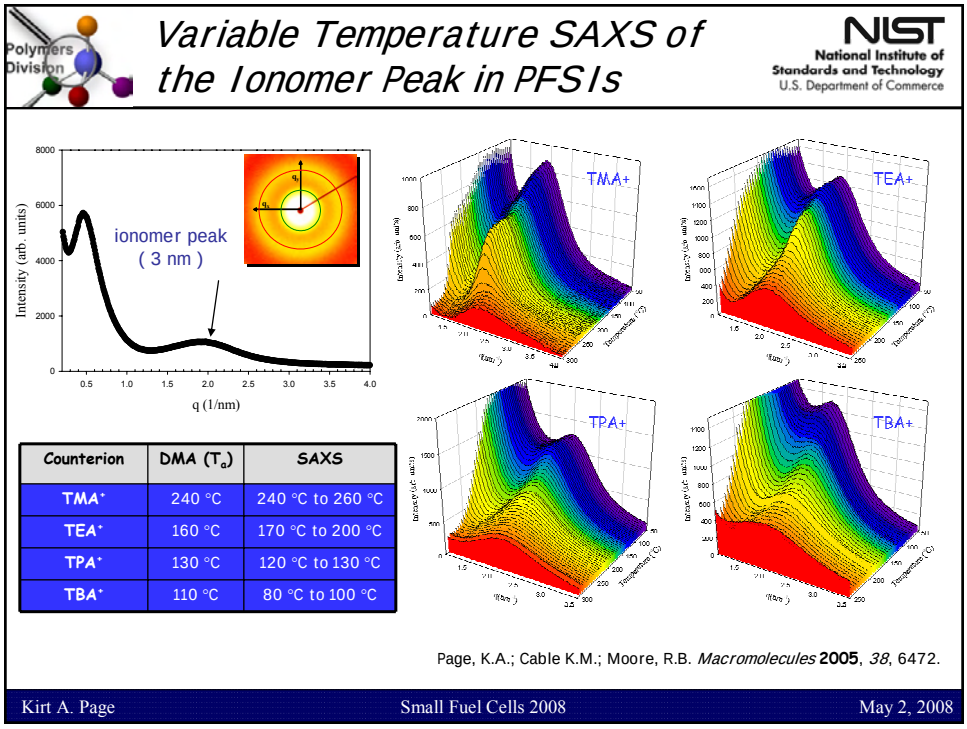


Figure 11. Correlating Multiple Techniques



Counterion	DMA (T_α)	SAXS
TMA^+	240 °C	240 °C to 260 °C
TEA^+	160 °C	170 °C to 200 °C
TPA^+	130 °C	120 °C to 130 °C
TBA^+	110 °C	80 °C to 100 °C

Figure 12. Variable Temperature SAXS of the Ionomer Peak in PFSIs

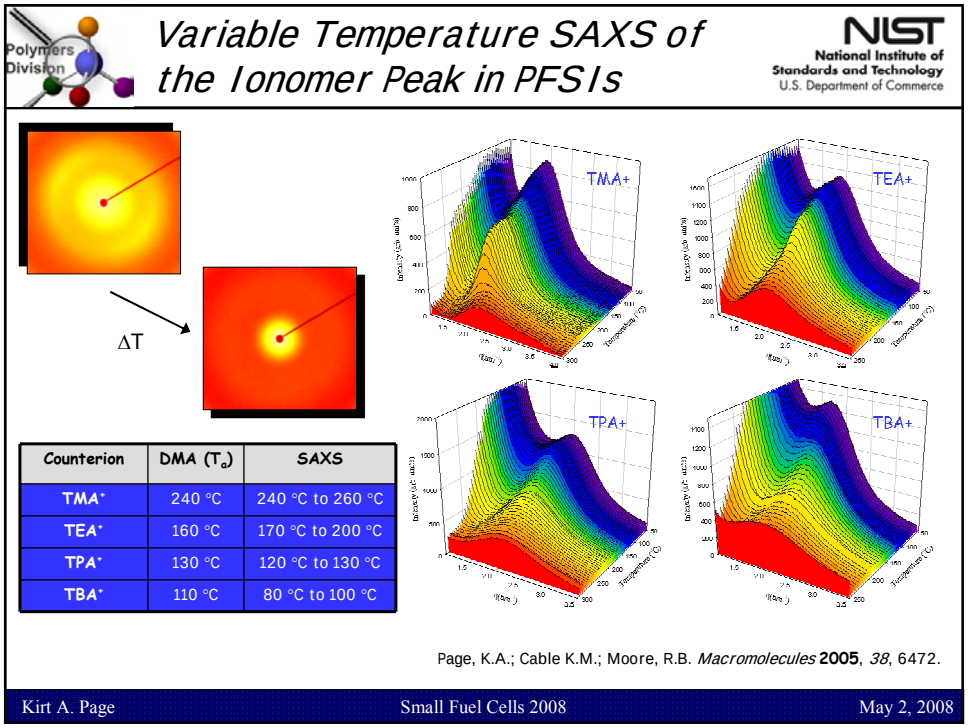


Figure 13. Variable Temperature SAXS of the Ionomer Peak in PFSIs

And so you can see here that the ionomer peak shows up as this nice bright ring in the X-ray pattern, but as you go up in temperature it disappears **(Figure 13).** It doesn't actually disappear completely, though. It's still there, which is very important, because it means that there's still a network, a structure, but it's now a dynamic network. So, how does this relate to a fuel cell? Let's say the fuel cell is operating at 80 °C under some level of humidity, the ionomer structure that is responsible for transport is now something that is dynamic and could be changing over time.

This type of information can be very important for understanding fuel cell performance and establishing design rules for more efficient, high performance materials that maintain structure over a range of operating conditions.

Further studies were aimed at focusing our understanding of the dynamics on a molecular level. This was achieved through the use of various ^{19}F solid-state NMR techniques. The first of these studies used something called spin diffusion, and I'll just briefly talk about what spin diffusion is **(Figure 14).** Spin diffusion is an experiment where you can tune the resonance of the signal to match the resonance of one of the nuclei in the material.

In this case, we chose the fluorines on the side chain. The 180° pulse (tuned to the correct resonance) is used to flip the spin of those particular nuclei. One can then observe the transfer of spin back to the fluorines in the backbone. Eventually they reach an equilibrium spin temperature, and that's called the spin diffusion time. From this measurement, one can get an idea about the relative motions of these two entities within the material. Others have also used this technique to look at the size of the ionic domains. However, in our case we use this as a measure of the mobility of the side chain, relative to that of the main chain. What one can see here is that, depending on the counterion, you get very distinct differences in the relaxation behavior.

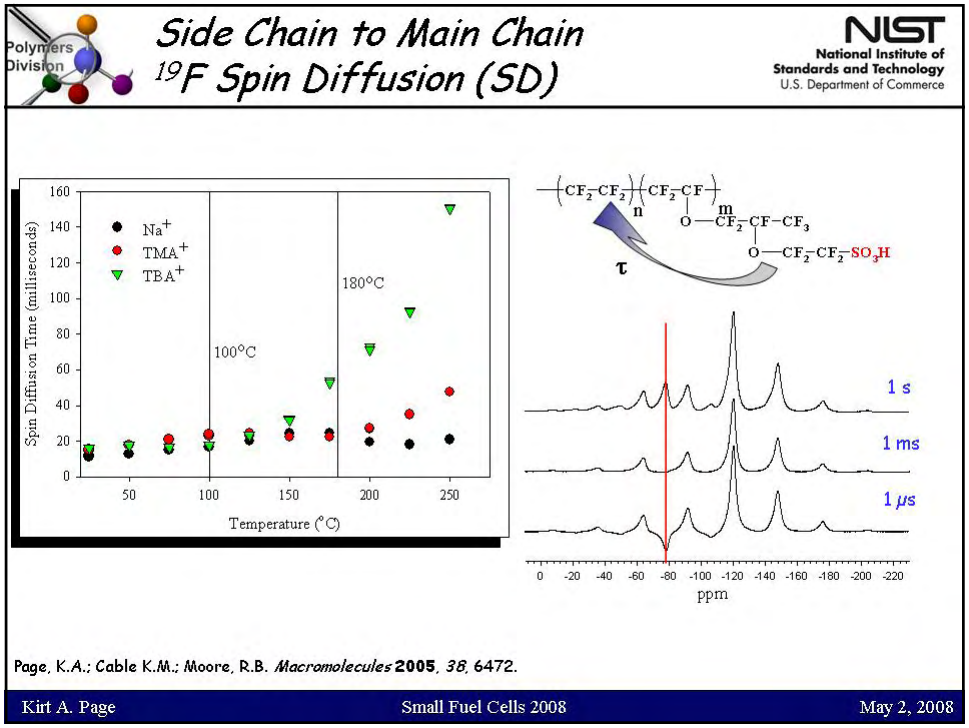


Figure 14. Side Chain to Main Chain ^{19}F Spin Diffusion (SD)

We were able to correlate this directly with the mechanical data **(Figure 15).** We observed that the onset of mobility of the side chain and the main chain—indicated by a rise in the spin diffusion time—coincides with the onset of the alpha relaxation. We were also able to carry out studies using sideband analysis **(Figure 16).** In the solid-state ^{19}F pattern, one can get 'extra' peaks known as side bands.

These side bands are part of chemical shift anisotropy due to the dipolar coupling between nuclei. In these experiments, we observed the change in the side band intensity, relative to the main isotropic resonance peak, as a function of temperature. Changes in the relative intensity as a function of temperature can yield information regarding the dynamics in the material. Transitions in side band intensity were compared to transitions determined by mechanical and scattering methods **(Figure 17, 18).** We found that the onset of motion of the main chain was more closely related to the beta relaxation while the onset of mobility of the side chain was more closely related to the alpha relaxation.

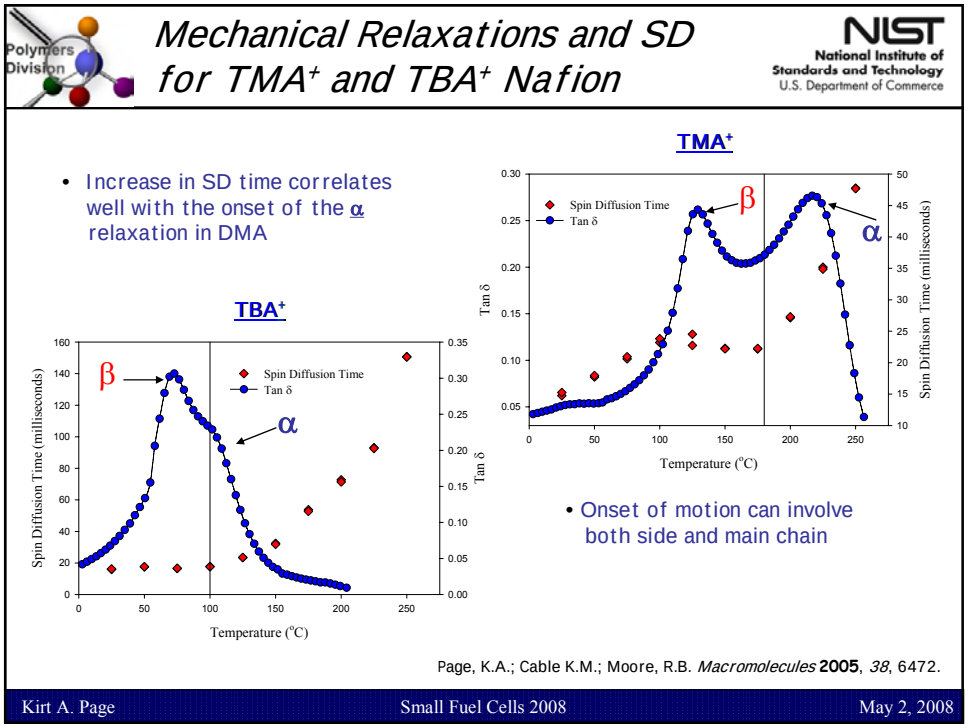


Figure 15. Mechanical Relaxations and SD for TMA$^+$ and TBA$^+$ Nafion

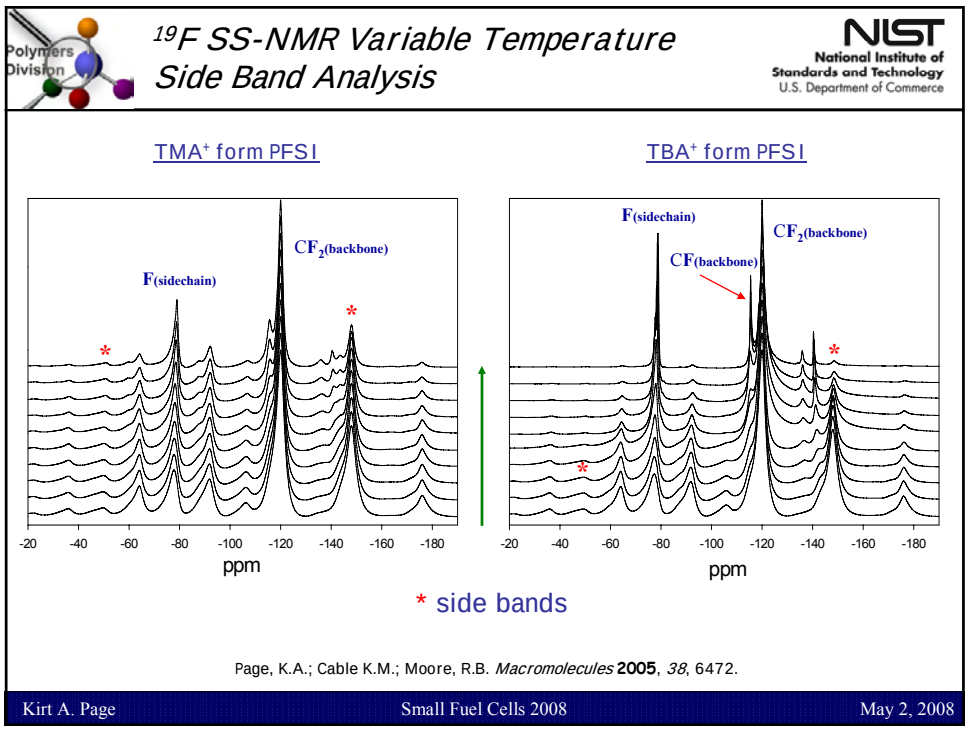
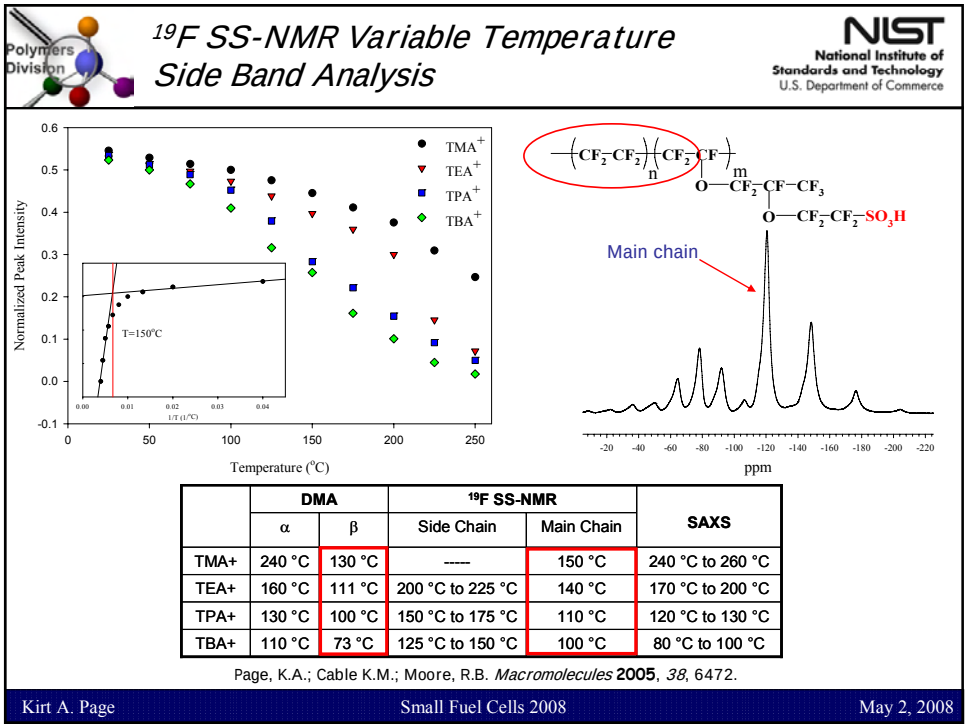


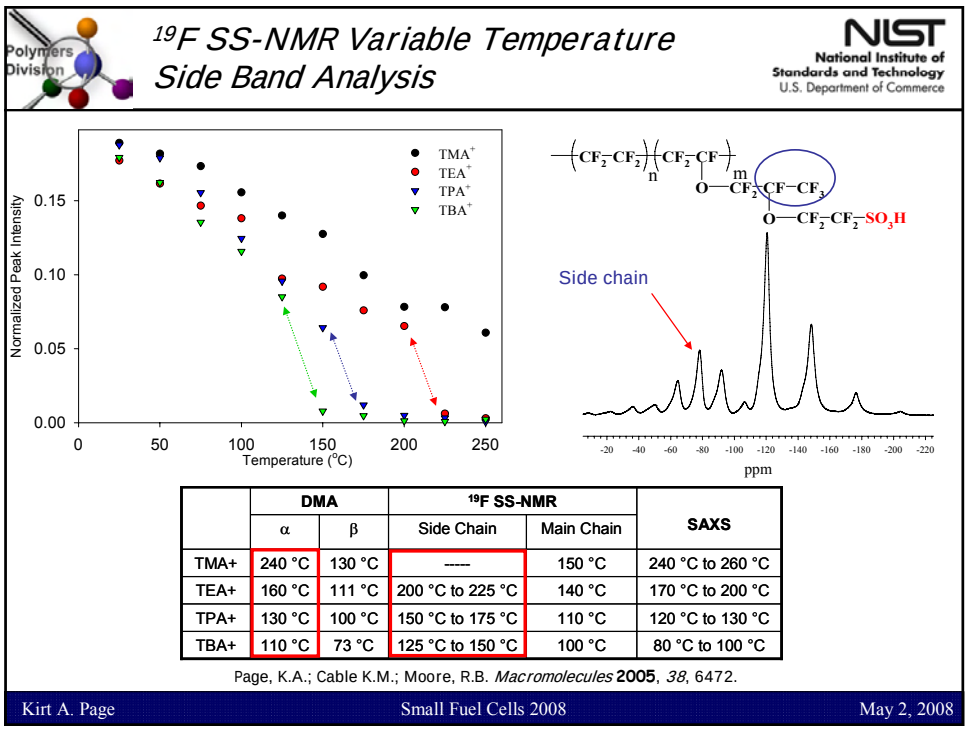
Figure 16. ^{19}F SS-NMR Variable Temperature Side Band Analysis



	DMA		19F SS-NMR		SAXS
	α	β	Side Chain	Main Chain	
TMA+	240 °C	130 °C	-----	150 °C	240 °C to 260 °C
TEA+	160 °C	111 °C	200 °C to 225 °C	140 °C	170 °C to 200 °C
TPA+	130 °C	100 °C	150 °C to 175 °C	110 °C	120 °C to 130 °C
TBA+	110 °C	73 °C	125 °C to 150 °C	100 °C	80 °C to 100 °C

Page, K.A.; Cable K.M.; Moore, R.B. *Macromolecules* **2005**, *38*, 6472.

Figure 17. ^{19}F SS-NMR Variable Temperature Side Band Analysis



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TPA+	130 °C	100 °C	150 °C to 175 °C	110 °C	120 °C to 130 °C
TBA+	110 °C	73 °C	125 °C to 150 °C	100 °C	80 °C to 100 °C

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Figure 18. ^{19}F SS-NMR Variable Temperature Side Band Analysis

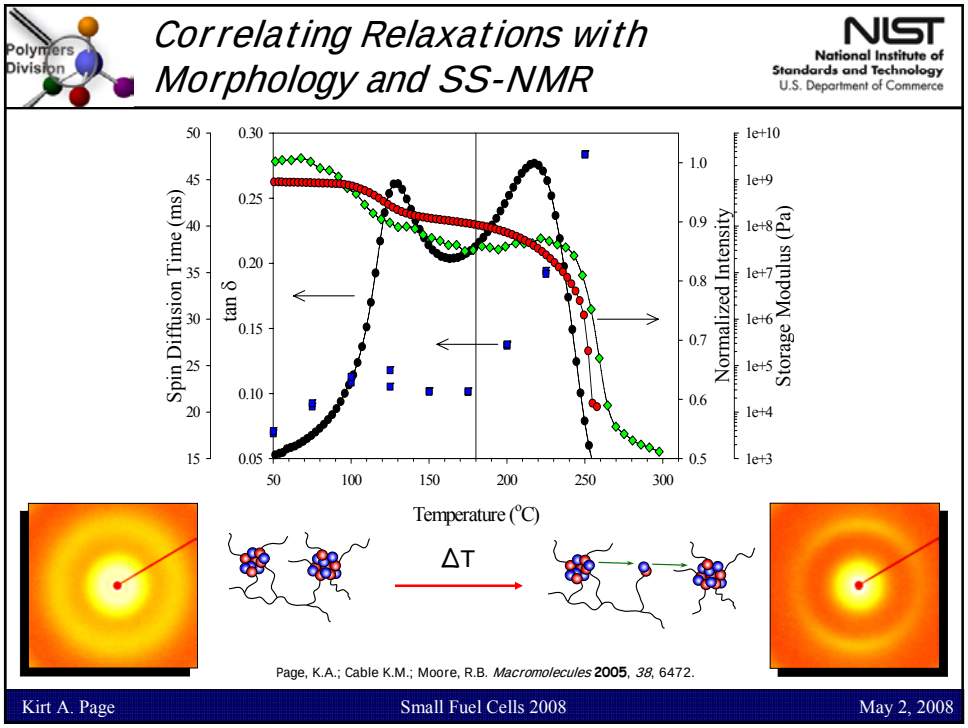


Figure 19. Correlating Relaxations with Morphology and SS– NMR

Ultimately we were able to compare the relaxation behavior measured using these different techniques to develop a complete picture of the dynamics of this material **(Figure 19).** The graph here shows how closely the relaxation phenomena from mechanical analysis match with the structural changes in the membrane as a function of temperature from scattering. It is also shown from the NMR data that, molecularly, the beta relaxation is more due to main chain motions with some side chain contributions, but also that the alpha relaxation shows this drastic onset of side motions, while the main chain is still moving. This is what led us to this picture of a static-to-dynamic network transition. Although this description of the dynamics has existed for many years in the field of ionomers, it has never been demonstrated so explicitly for this material.

In order to demonstrate how these molecular relaxation processes manifest themselves in the bulk relaxation behavior, we have also studied the relaxation of anisotropic membranes as a function of temperature **(Figure 20).** While there are several reasons why you would want to orient a fuel cell membrane, I won't go into detail here.

In general, we have simply used orientation to probe the structure and relaxation behavior of these materials. The scattering pattern for an oriented membrane can be seen here. By integrating the intensity in the azimuthal direction and employing the Hermans orientation function, we were able to characterize the degree of order of the ionic aggregates. Using this analysis technique, we were able to observe the azimuthal scattering profile as a function of temperature for several counterions **(Figure 21).**

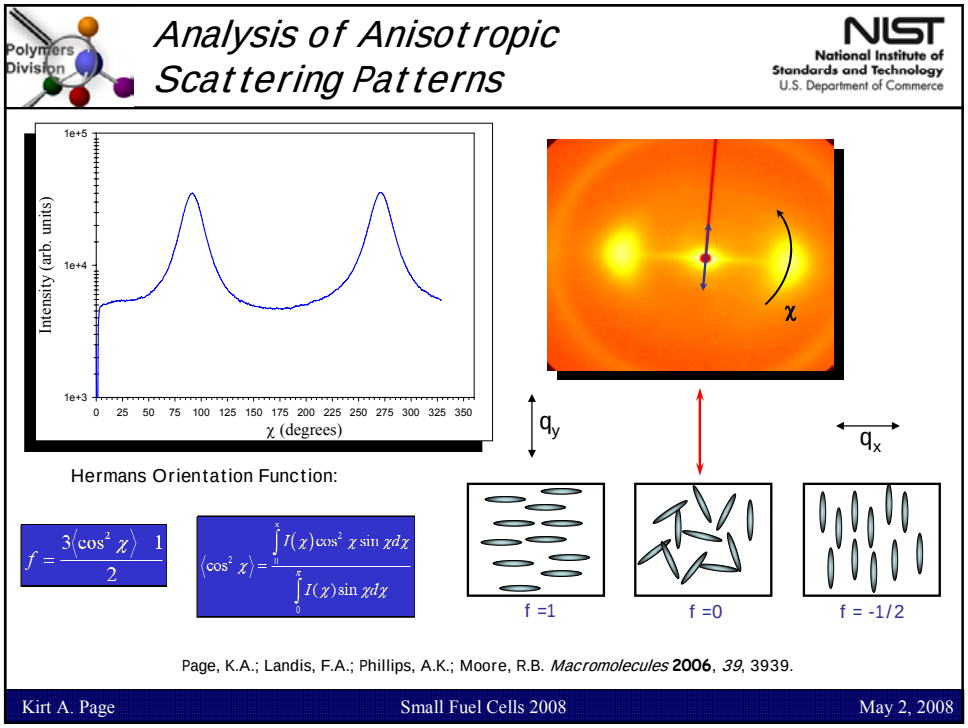
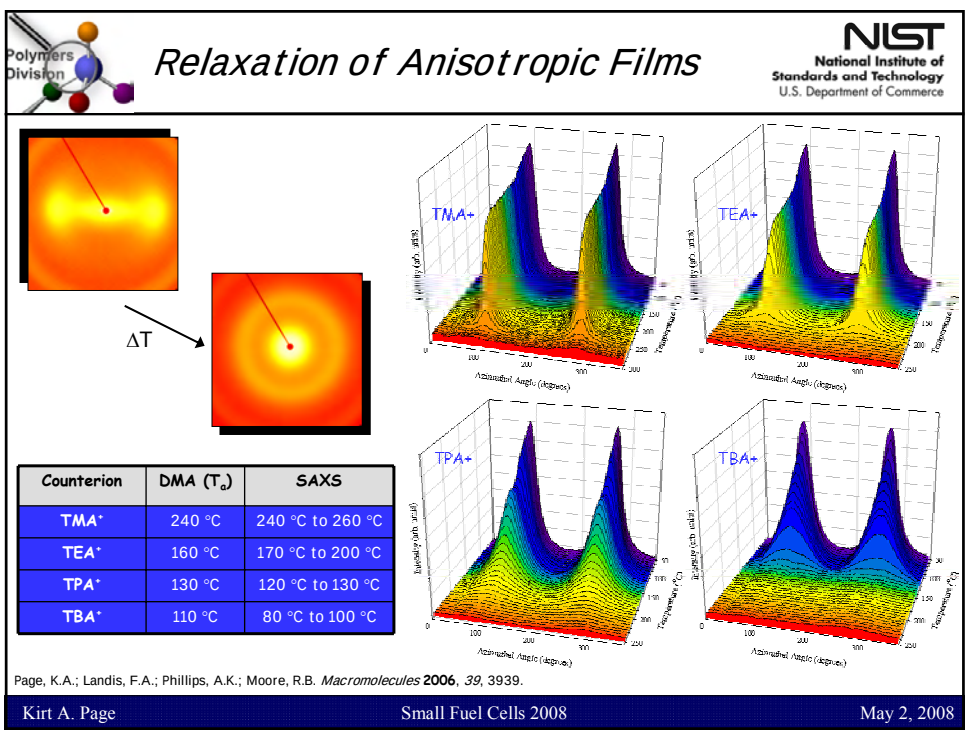


Figure 20. Analysis of Anisotropic Scattering Patterns



Counterion	DMA (T_α)	SAXS
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TEA^+	160 °C	170 °C to 200 °C
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TBA^+	110 °C	80 °C to 100 °C

Figure 21. Relaxation of Anisotropic Films

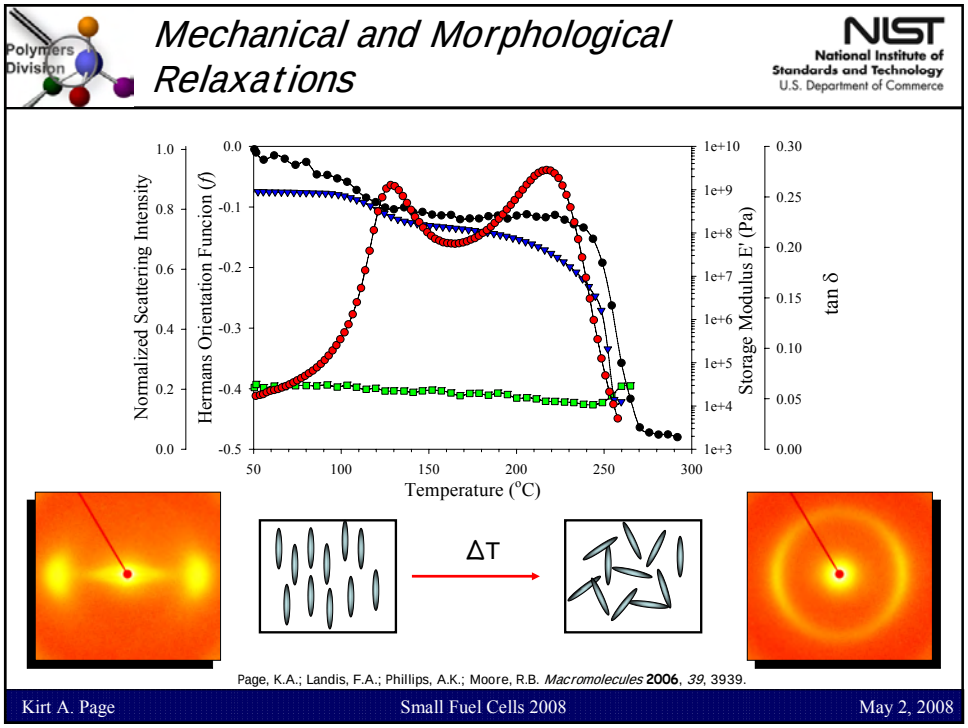

Figure 22. Mechanical and Morphological Relaxations

Again, we saw excellent agreement between the temperature at which the anisotropic scattering transitions to an isotropic one and the alpha relaxation temperature measured by mechanical analysis **(Figure 22).**

In addition, we were able to study the scattering due to crystallinity in this material as a function of temperature **(Figure 23).** We observed that the peak due to crystallinity (ca. $q = 0.5\ nm^{-1}$) undergoes an increase in intensity with increasing temperature before the crystallites begin to melt, which then results in a decrease in the scattering intensity. This initial increase was a bit surprising until we discovered literature from the 1960's which showed how this behavior could be used to determine the glass transition (T_g) of a material. As the material is heated, the contrast between the crystalline phase and amorphous phase increases, due to the difference in the coefficient of thermal expansion (CTE).

Of course, below the melting temperature, the amorphous phase can undergo a significant change in the CTE, especially as it goes through the T_g, while the crystalline phase is relatively unaffected. This manifests itself as a change in the slope of the normalized scattering intensity (as shown in the graph) as a function of temperature. One can then determine the T_g from the intersection of the two lines with differing slopes. Using this method, we were able, for the first time, to explicitly determine the glass relaxation temperature for Nafion.

During my post-doc, I had the opportunity to learn about quasielastic neutron scattering and to use some of the instrumentation at the NIST Center for Neutron Research (NCNR) to probe deeper into the counterion dynamics in fuel cell membrane materials. I would like to give a brief explanation of this technique **(Figure 24).** The High-Flux Backscattering Spectrometer (HFBS) at the NCNR relies on the incoherent inelastic scattering to investigate the dynamics of a material. Because hydrogen has such a large incoherent scattering cross section, this measurement is sensitive to hydrogenated species.

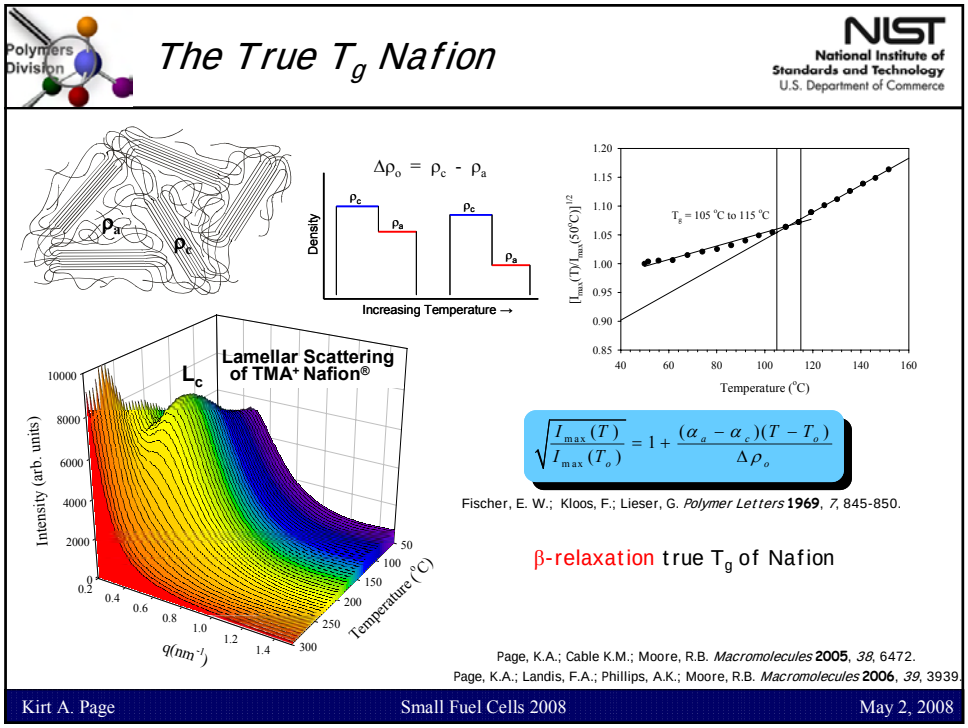

Figure 23. The True T_g Nafion

The configuration of instrument allows one to measure the change in energy of the neutron and the scattering angle simultaneously, therefore yielding information about the dynamics at different length scales. At a particular scattering angle or scattering vector, Q, one is probing a scattering volume, or cage, of a specific size. At low temperatures, one can imagine that the hydrogenated species are rattling around in that cage. In this case, the scattering (at this Q value) will be elastic. As you increase the temperature, the species can rattle out of that cage, which gives an intensity drop in the elastic scattering intensity signal because the intensity is being 'diverted' into quasielastic scattering.

Due to this phenomenon, one can learn about how fast things are moving around, and diffusing through the membrane, using this technique. We were able to show that the 'long-range' counterion motions were directly related to, again, the alpha relaxation temperature. We were also able to use modeling techniques to determine that the counterions diffuse through the membrane by a random jump diffusion mechanism and using this model we calculated the diffusion coefficient of the counterions at temperatures exceeding the ion-hopping temperature (i.e., the alpha relaxation temperature) **(Figure 25).**

Based on all the experimental evidence that I have presented today, we have been able to develop a new description for the dynamics and structure of this material **(Figure 26).**

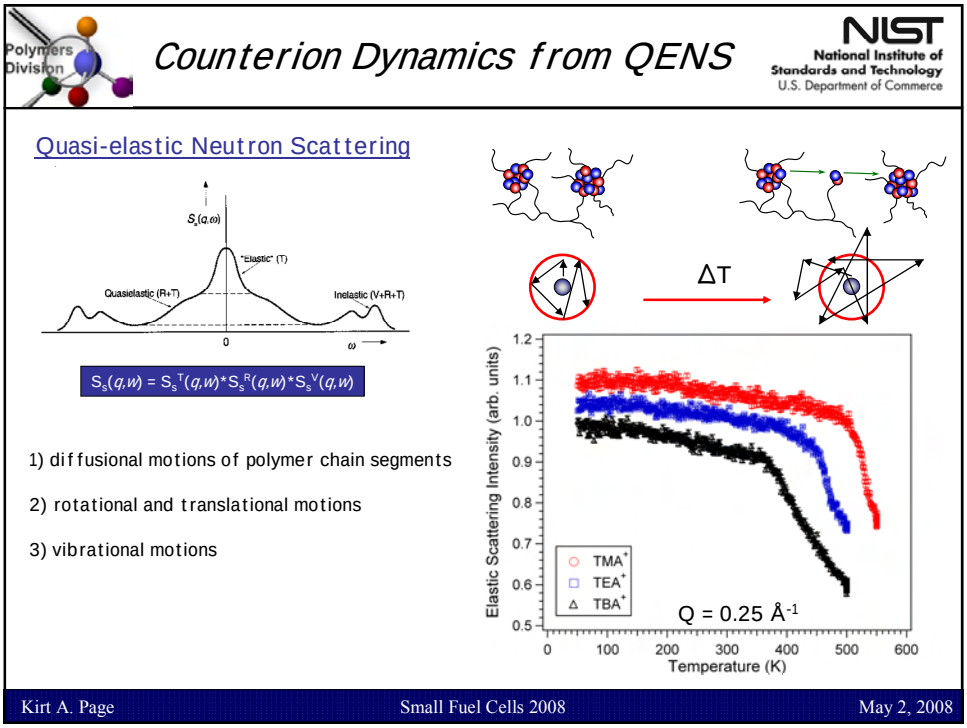

Figure 24. Counterion Dynamics From QENS

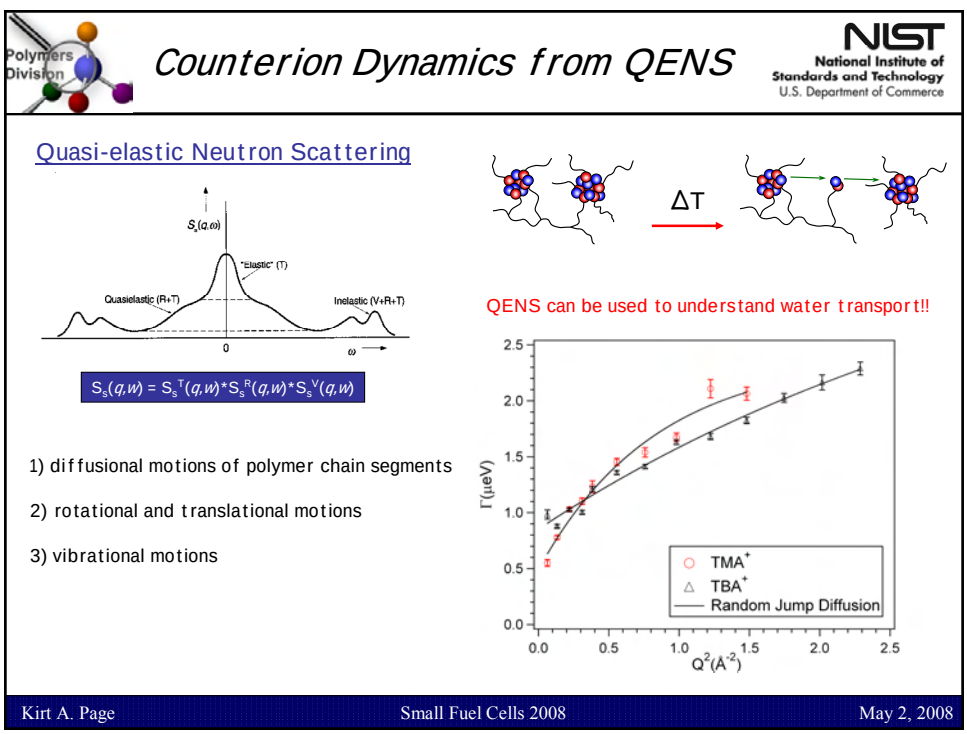

Figure 25. Counterion Dynamics From QENS

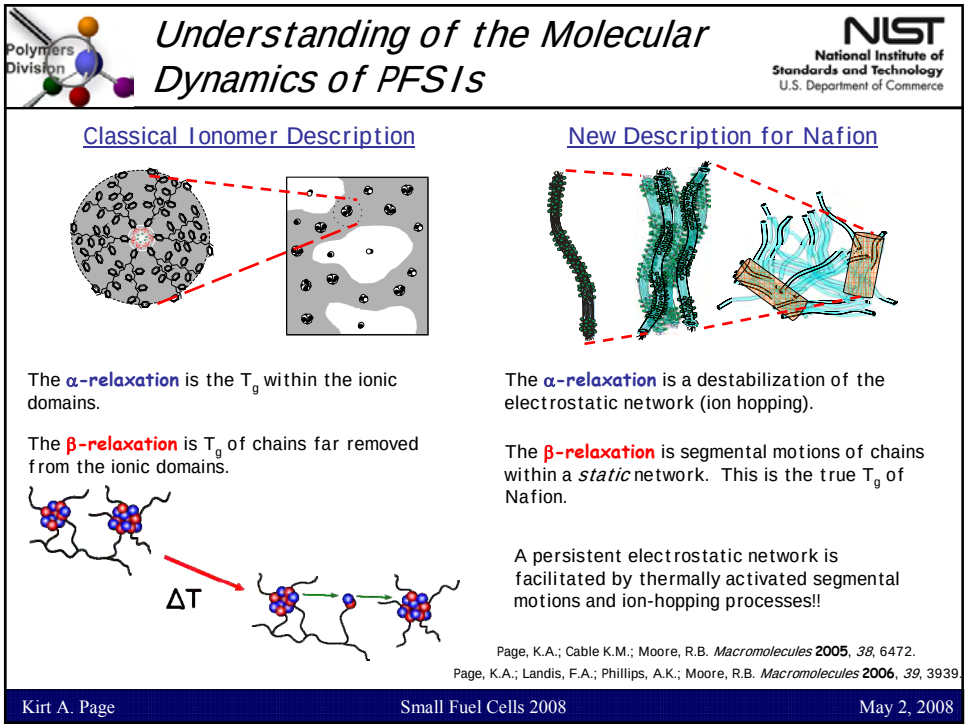

Figure 26. Understanding of the Molecular Dynamics of PFSIs

In essence, the alpha relaxation is attributed to a destabilization of the electrostatic network through an ion hopping process, and that the beta relaxation is the true T_g of Nafion. Keep in mind that is not simply the backbone T_g, but it is the T_g of a static, electrostatic network. This is a subtle, but important, difference to note. The knowledge that I have gained on the structure and dynamics of this material has been very useful. I am currently using it to investigate how the development of morphology can influence performance and durability. In addition, the characterization tools that I have learned have proved to be of great value in other projects that I have worked on.

One of the newest things that we have been developing in the Nanostructured Materials Group on is a rotational small angle neutron scattering (SANS) technique, which is actually quite exciting **(Figure 27).** Essentially we have developed a technique that not only allows one to collect a normal scattering pattern, but by rotating the sample in the beam, allows one to collect scattering patterns at different rotational angles. In a very clever fashion, you can create a three-dimensional representation of the reciprocal space scattering of a sample. Traditional SANS techniques only yield information concerning the scattering in the plane of the sample (Q_x-Q_y), in my case a membrane.

However, rotational SANS allows one to collect information in the Q_z direction. We have been able to do some preliminary measurements applying this technique to oriented PFSI membranes. Here are two of the representative scattering patterns obtained by placing an oriented membrane in the neutron beam a rotating the sample about the axis perpendicular to the axis of orientation **(Figure 28)**.

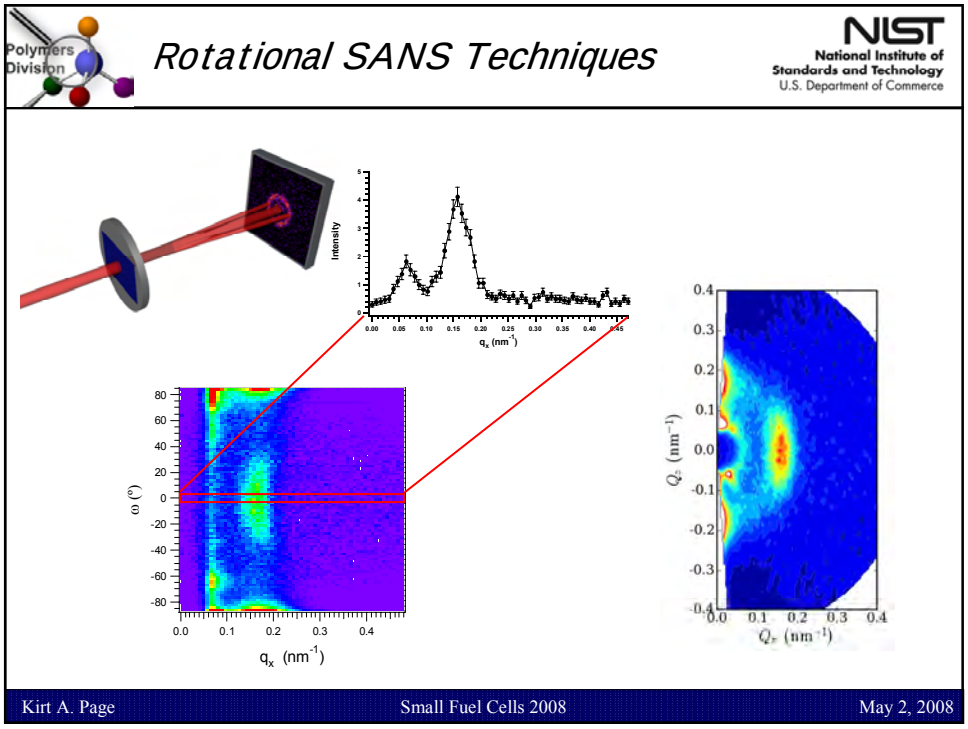

Figure 27. Rotational SANS Techniques

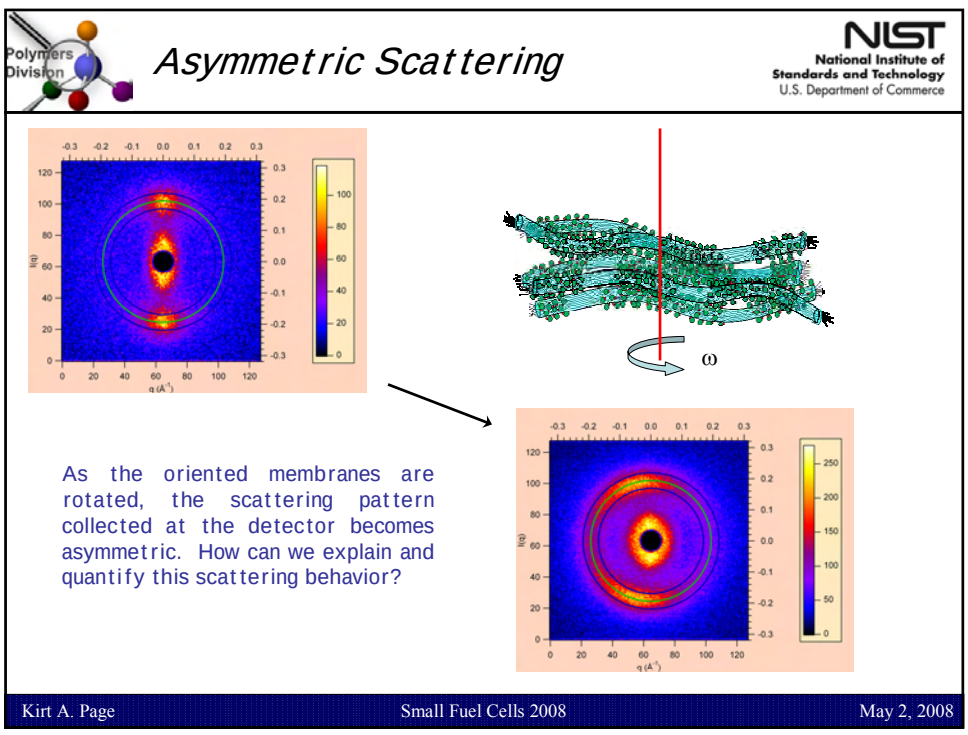

Figure 28. Asymmetric Scattering

One of the interesting, and unexpected, features is the asymmetric scattering pattern that is obtained. We have been able to explain this effect by simple geometric considerations of how the scattering 'ring' intersects the Ewald Sphere **(Figure 29).** This kind of scattering behavior has been observed once before by researchers investigating the orientation of cellulose fibrils in wood cell structures **(Figure 30).**

This early literature gave us a geometric paradigm in which we could quantitatively describe the scattering behavior that we have observed. Some of the potential benefits could allow us to determine the "true" structure of this material **(Figure 31).** This first study certainly confirmed earlier studies which claimed that, in the oriented state, there are fibular structures formed in the membrane. In addition, we may also be able to learn something about the shape of the ionic aggregates, the relative spatial distribution of the crystallites with respect to the ionic aggregates, or even the nature of the large-scale heterogeneities, which are very important for proton transport.

Because this particular project is so new, we are still at the project development stage **(Figure 32).** However, we have a very good start on building a program of research in this area. Some of the areas that we believe will be important to the state of the art include: polymer and water dynamics, ion migration, catalyst ink and catalyst layer structure. We are currently investigating the structure of catalyst ink formulations in collaboration with General Motors. The catalyst ink is a mixture of nanoparticles (carbon and platinum), polyelectrolyte, and co-solvents. We are interested in understanding the structure of that ink.

Fundamentally, how does the structure of the ink result in the structure and performance properties of the final electrode? I think that's a very important fundamental problem that can, if properly understood, lead to more efficient electrode structures. We are also working on how processing can affect the performance of a membrane. The electrostatic interactions, crystallinity, all of those things I discussed earlier have a large influence over the processing of the material. How does processing and all of these factors influence the nanostructure? Can we determine the nanostructure, and the influence of processing on the nanostructure? In addition, I am interested in learning more about the scattering behavior of regular hydrated, acid-form PFSIs. To my knowledge, there has never been a complete study on the scattering behavior of PFSIs over large range of humidity and temperature. I believe that knowing the structure of this material under a range of conditions can be an important cornerstone for the community. Especially where this information can be used in developing new metrologies for, say, determining the water profile in the transverse direction of the membrane in a working fuel cell.

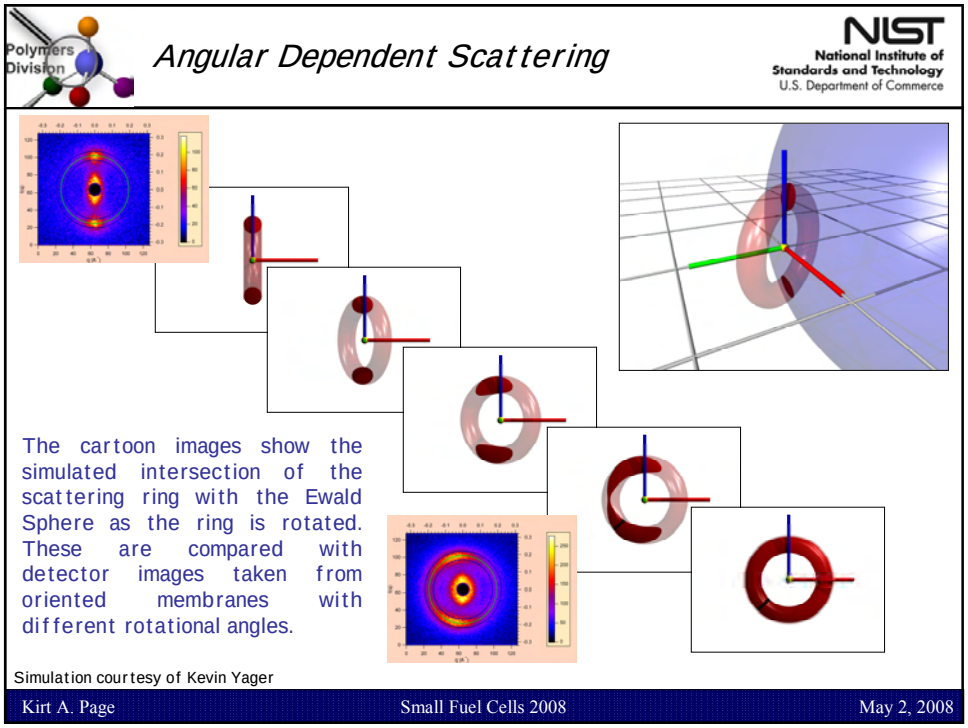

Figure 29. Angular Dependent Scattering

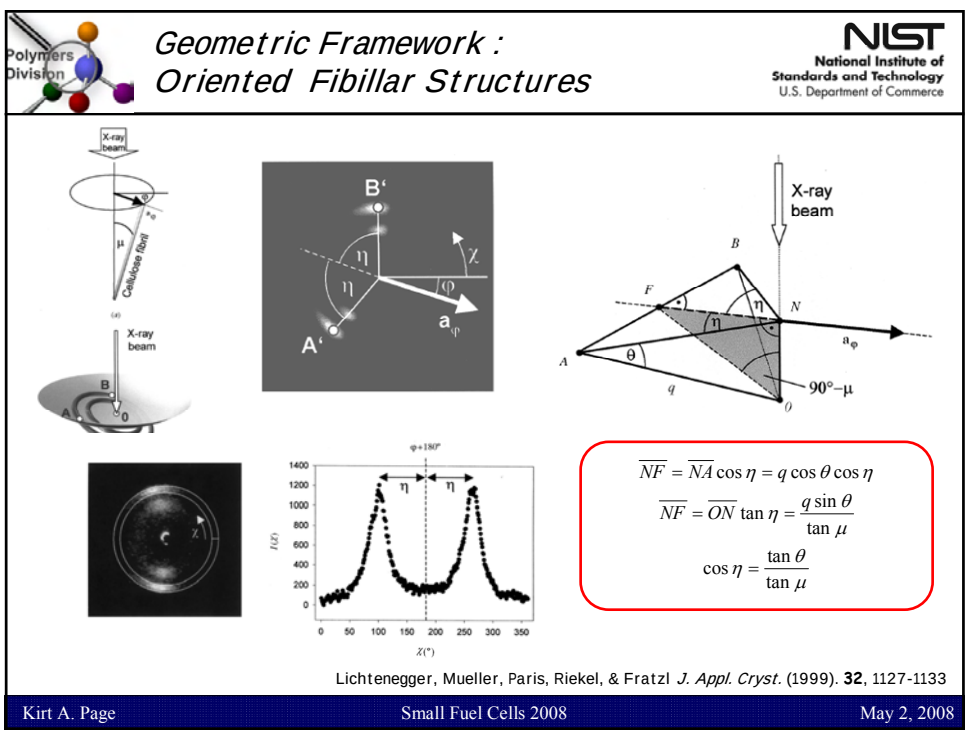

Figure 30. Geometric Framework: Oriented Fibillar Structures

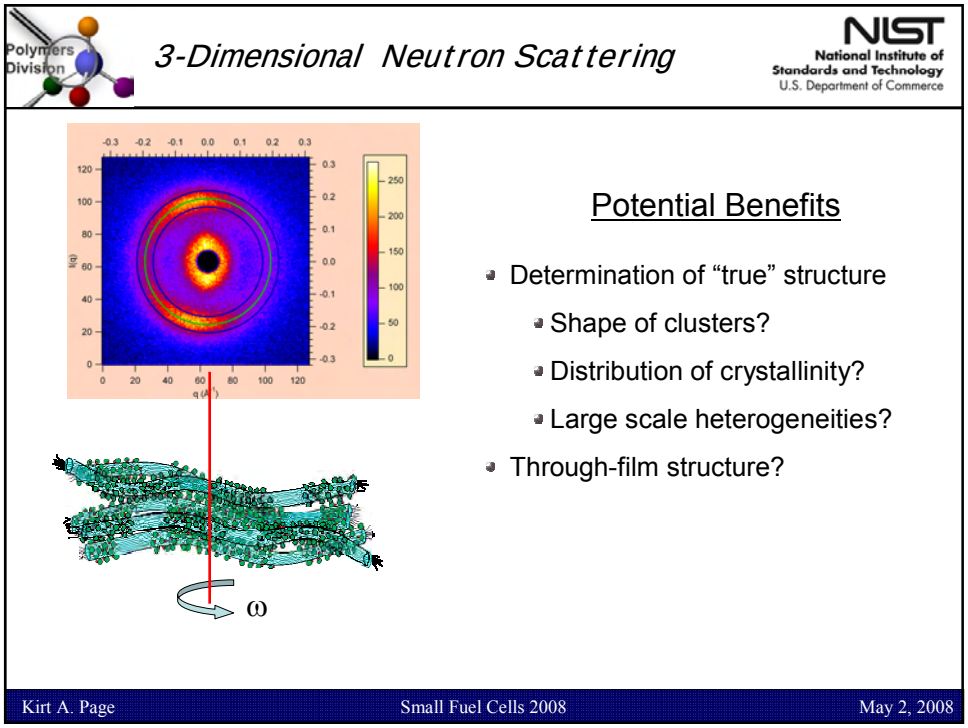

Figure 31. 3-Dimensional Neutron Scattering

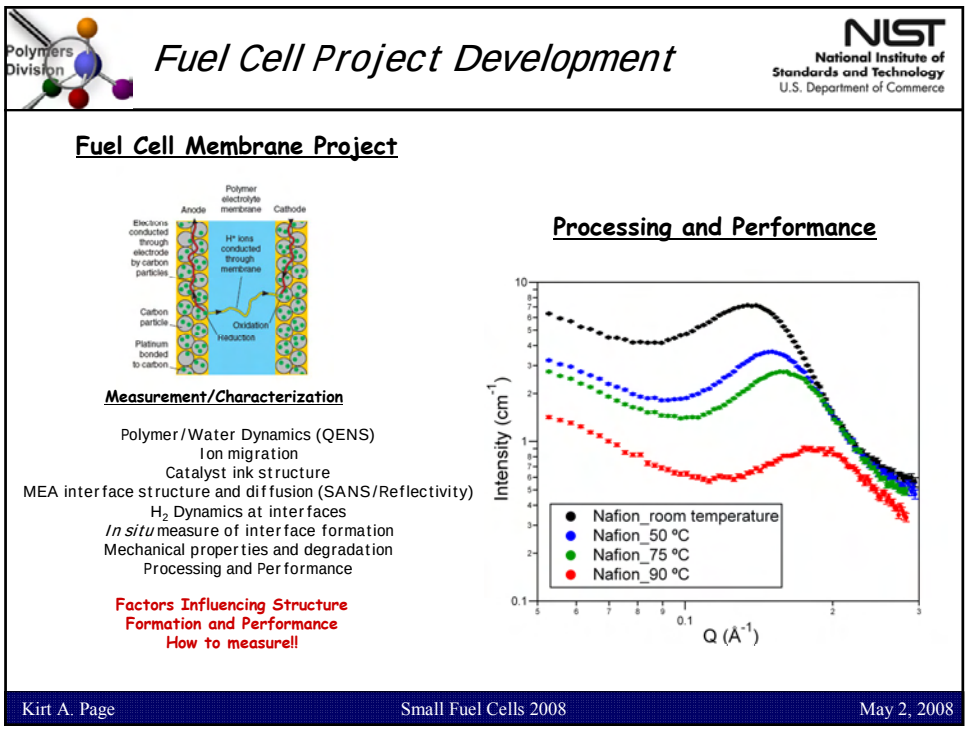

Figure 32. Fuel Cell Project Development

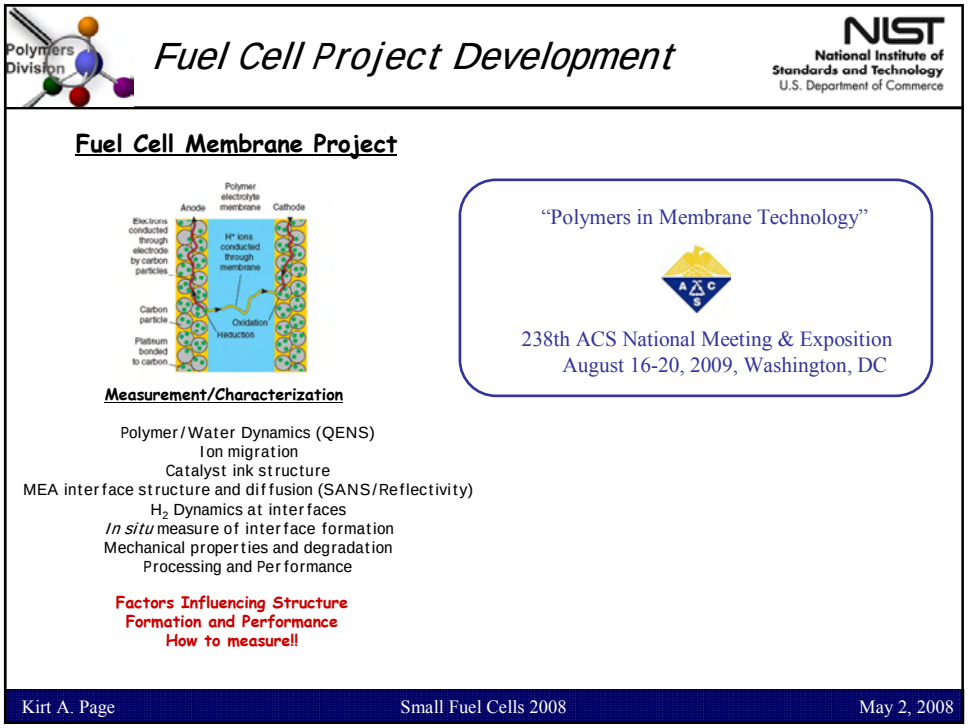

Figure 33. Fuel Cell Project Development

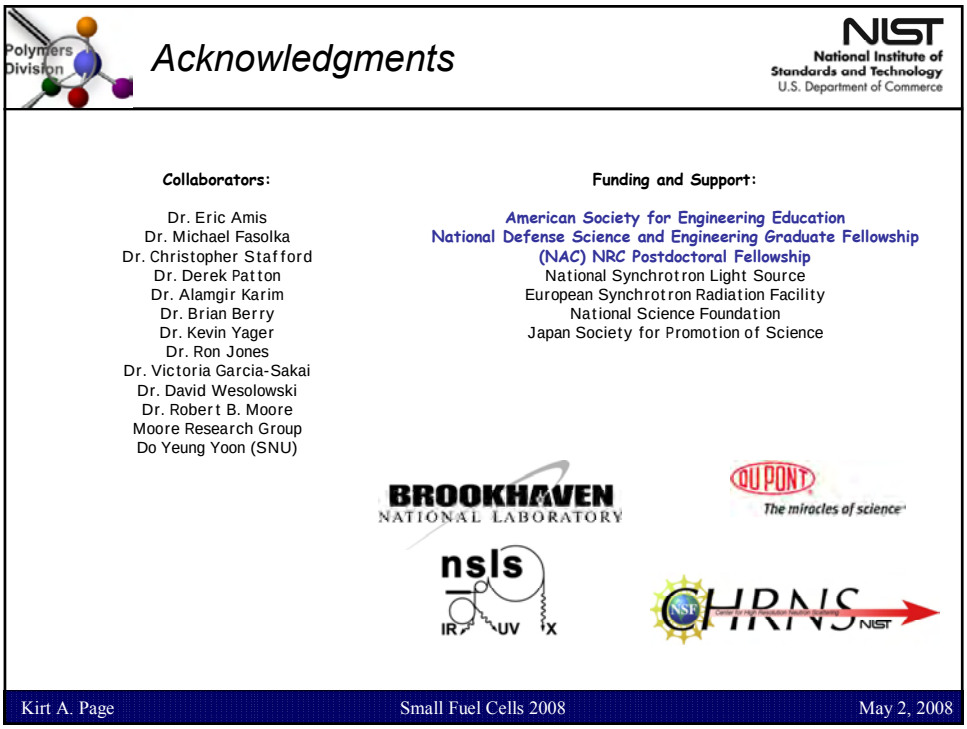

Figure 34. Acknowledgements

I would also like to mention that in the fall of 2009, I am slated to organize a symposium at the ACS on Polymers and Membrane Technology **(Figure 33).** I hope that it will be a very productive event that will spawn a network of collaborations in this field. To conclude I would like to thank again the Knowledge Foundation, all of my collaborators and funding agencies and everyone for taking time to listen to my talk. Thank you **(Figure 34).**

Question & Answer:

Audience Member: Let me understand: You guys will do this type of analysis for us?

KP: Yes. I mean, the role of NIST is to advance measurement science, and measurement techniques to help industry propel forward, so if there's a measurement challenge that you have, in terms of looking at membrane structure, and how that relates back to performance, then perhaps we can help. It's something that we're very interested in working with industry to achieve. Again, we would like to be able to publish the data, so that's the tricky part for people in this industry. We're not materials developers, but if you have materials that you would like to investigate and do not mind sharing those materials, that's good for us.

Audience Member: Are you able to take a final outcome, like maximizing ion transport, and knowing what the microstructure is, and then define what the best process is in creating that microstructure?

KP: That's my goal and one of the studies that I've proposed. It's actually still a very fundamental study, but I want to look at processing, and its effect on microstructure, and then couple that with information about proton conductivity and water dynamics using quasi-elastic neutron scattering. One of my goals is to look at this particular problem in a working fuel cell, so I would like to be able to put a working fuel cell in the neutron beam, and look at the water dynamics under those *in situ* conditions, and get that very information.

Audience Member: If you are able to do that, let's say optimize the structure based on various things, and make your film and start testing it, since Nafion isn't cross-linked, and it is a dynamic polymer, do you think you'd be able to keep that optimized structure? Wouldn't it just equilibrate over time, and end up same old, same old?

KP: Well, that's a good question. The idea would be to find out what the structure is, as processed, see what structures result in an equilibrium state, and then work backwards, right? So, tweak the beginning process to get what you would want. But this is, ultimately, still a problem because any membrane that you use is going to degrade over time, right?

Audience Member: It wouldn't necessarily be degradation. I don't know if it just changes, right?

KP: Well, right, not in the sense of degrading, falling apart, but any structure that you put in is probably going to change over time, as a result of different degradation by-products, or just the nature of cycling, itself. There can be changes in structure due to thermal hysteresis and/or swelling hysteresis.