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14. ABSTRACT The objectives of this project were to (1) develop a fundamental understanding for selectivity criteria in selective membranes and to (2) develop new highly selective membranes. The first objective focused on investigating multicomponent transport phenomena in ionic polymer membranes on a molecular scale using time-resolved Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectroscopy. The outcomes of this research project provided a fundamental understanding of multicomponent transport mechanisms and provided a new body					
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Report Title

Highly Selective Ionic Block Copolymer Membranes

ABSTRACT

The objectives of this project were to (1) develop a fundamental understanding for selectivity criteria in selective membranes and to (2) develop new highly selective membranes. The first objective focused on investigating multicomponent transport phenomena in ionic polymer membranes on a molecular scale using time-resolved Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectroscopy. The outcomes of this research project provided a fundamental understanding of multicomponent transport mechanisms and provided a new body of knowledge in selective barrier materials. The second objective focused on developing new membranes based on ionic block copolymers with improved selectivity. We were successful in accomplishing these goals and the attached report highlight the key results from this project.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Hallinan, D.T., Jr.; Elabd, Y.A. Diffusion and Sorption of Methanol and Water in Nafion using Time-Resolved FTIR-ATR Spectroscopy. J. Phys. Chem. B 2007 111 (46), 13221-13230.

Hallinan, D.T., Jr.; Elabd, Y.A. Diffusion of Water in Nafion using Time-Resolved FTIR-ATR Spectroscopy. J. Phys. Chem. B 2009, 113 (13), 4257-4266.

Chen, L.; Hallinan, D.T. Jr.; Elabd, Y.A.; Hillmyer, M.A. Highly Selective Polymer Electrolyte Membranes From Reactive Block Polymers. Macromolecules, 2009, 42, 6075-6085.

Hallinan, D.T., Jr.; De Angelis, M.G.; Baschetti, M.G.; Jr.; Sarti, G.C.; Elabd, Y.A. Non-Fickian Diffusion of Water in Nafion. Macromolecules 2010, 43, 4667-4678.

Number of Papers published in peer-reviewed journals: 4.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

Hallinan, D.T., Jr.; De Angelis, M.G.; Baschetti, M.G.; Jr.; Sarti, G.C.; Elabd, Y.A. Water Transport in Proton Exchange Membranes: Insights from Time-Resolved Infrared Spectroscopy. 218th Electrochemical Society Meeting, Las Vegas, NV, October 2010. Invited Speaker	
Hallinan, D.T., Jr.; Elabd, Y.A. Real-Time Molecular Measurements of Water Dynamics in Nafion using Fourier-Transform Infrared, Attenuated Total Reflectance Spectroscopy. Spring National Meeting of the American Chemical Society, San Francisco, CA, March 2010. Invited Speaker	
Hallinan, D.T., Jr.; De Angelis, M.G.; Baschetti, M.G.; Jr.; Sarti, G.C.; Elabd, Y.A. Understanding Mechanisms of Non-Fickian Water Diffusion in Polymer Electrolyte Membranes. Annual Meeting of the American Institute of Chemical Engineers, Nashville, TN, November 2009.	
Hallinan, D.T., Jr.; De Angelis, M.G.; Giacinti Baschetti, M.; Sarti, G.C.; Elabd, Y.A. Non-Fickian Diffusion of Water in Nafion. Annual Meeting of the American Institute of Chemical Engineers, Philadelphia, PA, November 2008.	
Hallinan, D.T., Jr.; Elabd, Y.A. Water Transport in Nafion? Using Time-Resolved FTIR-ATR Spectroscopy. Annual Meeting of the American Institute of Chemical Engineers, Salt Lake City, UT, November 2007.	
Hallinan, D.T., Jr.; Elabd, Y.A. Transport of Water in Nafion® using Time-Resolved FTIR-ATR Spectroscopy. Annual Meeting of the North American Membrane Society, Orlando, FL, May 2007.	
Hallinan, D.T., Jr.; De Angelis, M.G.; Giacinti Baschetti, M.; Elabd, Y.A. Non-Fickian Diffusion of Water in Nafion. Gordon Research Conference – Polymer Physics, Newport, RI, July 2008.	
Number of Presentations:	7.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):	
Hallinan, D.T., Jr.; De Angelis, M.G.; Baschetti, M.G.; Jr.; Sarti, G.C.; Elabd, Y.A. Water Transport in Proton Exchange Membranes: Insights from Time-Resolved Infrared Spectroscopy. Electrochemical Society Transactions 2010, 33(1), 1029-1033.	
Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):	1

Peer-Reviewed Conference Proceeding publications (other than abstracts):	
Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):	0

(d) Manuscripts	
Number of Manuscripts:	0.00

Patents Submitted	

Patents Awarded	

Awards	
Elabd (PI) - NSF CAREER Award, 2007	
Hallinan (PhD Student) - George Hill Jr. Fellow, DoEd-GAANN Fellow, University Graduate Student Research Excellence Award, NSF-IGERT Fellow, Schering-Plough Research Institute Travel Award, North American Membrane Society Poster Award and Annual Meeting Student Travel Award, University Teaching Assistance Excellence Award, AIChE Poster Award (2nd Place) in the Materials Science and Engineering Section, 2008	

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Daniel Hallinan	1.00
FTE Equivalent:	1.00
Total Number:	1

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Yossef A. Elabd	0.04	No
FTE Equivalent:	0.04	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PhDs

NAME

Daniel Hallinan

Total Number:

1

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

W911NF-07-1-0149
Final Report 2010

Highly Selective Ionic Block copolymer Membranes
PI: Y.A. Elabd

The objectives of this project were to (1) develop a fundamental understanding for selectivity criteria in selective membranes and to (2) develop new highly selective membranes. The first objective focused on investigating multicomponent transport phenomena in ionic polymer membranes on a *molecular scale* using time-resolved Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectroscopy. The outcomes of this research project provided a fundamental understanding of multicomponent transport mechanisms and provided a new body of knowledge in selective barrier materials. The second objective focused on developing new membranes based on ionic block copolymers with improved selectivity. We were successful in accomplishing these goals and the projects below highlight the key results from this project.

Publications from this project

- Hallinan, D.T., Jr.; Elabd, Y.A. Diffusion and Sorption of Methanol and Water in Nafion using Time-Resolved FTIR-ATR Spectroscopy. *J. Phys. Chem. B* **2007** *111* (46), 13221-13230.
- Hallinan, D.T., Jr.; Elabd, Y.A. Diffusion of Water in Nafion using Time-Resolved FTIR-ATR Spectroscopy. *J. Phys. Chem. B* **2009**, *113* (13), 4257-4266.
- Chen, L.; Hallinan, D.T. Jr.; Elabd, Y.A.; Hillmyer, M.A. Highly Selective Polymer Electrolyte Membranes From Reactive Block Polymers. *Macromolecules*, **2009**, *42*, 6075-6085.
- Hallinan, D.T., Jr.; De Angelis, M.G.; Baschetti, M.G.; Jr.; Sarti, G.C.; Elabd, Y.A. Non-Fickian Diffusion of Water in Nafion. *Macromolecules* **2010**, *43*, 4667-4678.
- Hallinan, D.T., Jr.; Elabd, Y.A. Equilibrium States of Water in Nafion. In preparation.
- Hallinan, D.T., Jr.; Elabd, Y.A. Dynamic States of Water in Nafion. In preparation.

Personnel in this project

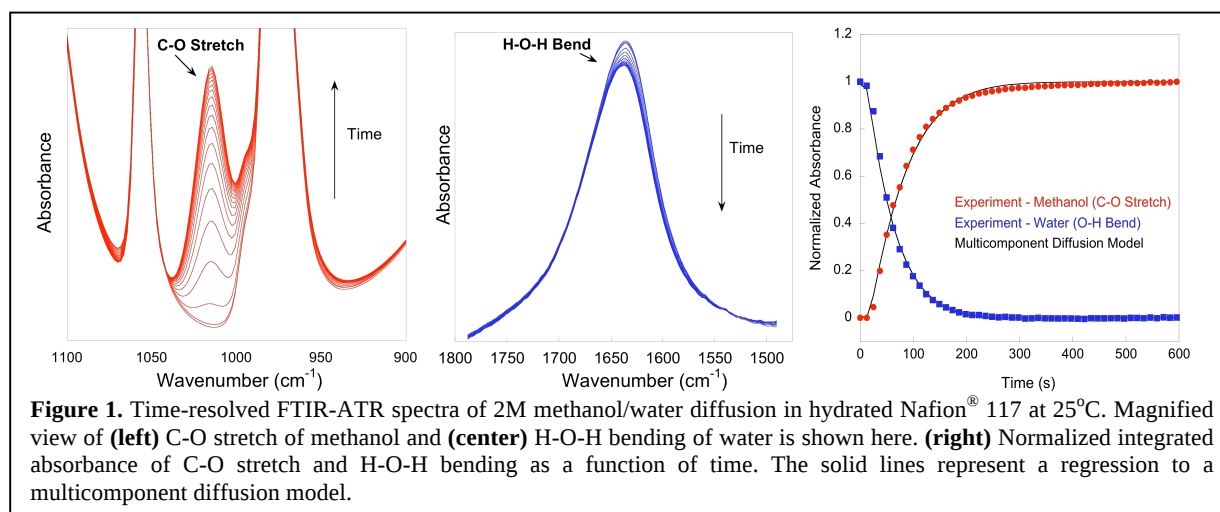
This work supported one PhD student, Dan Hallinan. Dan graduated with his PhD and is now currently a postdoc at University of California, Berkeley. Dan's work resulted in four publications and two more manuscripts in preparation. During this time, Dan also mentored four undergraduate students (3 female). In addition, we began a new collaboration with Marc Hillmyer at the University of Minnesota. Dan was instrumental in this collaboration and interacting with Marc's PhD student Liang Chen on this project.

Key Results from this Project

Multicomponent Diffusion and Sorption in an Ionic Polymer Membrane

We recently measured the diffusion and sorption of methanol/water mixtures in Nafion (most commonly used ionic polymer membrane in fuel cells) as a function of methanol solution concentration using time-resolved FTIR-ATR spectroscopy. This study applies to the methanol fuel cell, which is a promising alternative to lithium-ion batteries in portable electronic devices, however their performance diminishes significantly because of high methanol crossover (flux) in

the ionic polymer membrane at the desired stoichiometric methanol feed concentration (17 M). **Figure 1** shows one experiment where hydrated Nafion was exposed to a 2 M methanol/water liquid mixture resulting in methanol diffusing in and water diffusing out (counter-current multicomponent diffusion) of the polymer simultaneously. The results from this technique are unique because of the ability to measure multicomponent diffusion and sorption within a polymer on a molecular level in real time. Both the effective mutual diffusion coefficients (obtained from a regression of the dynamic absorbances to a diffusion model) and multicomponent concentrations (obtained from the equilibrium absorbances calibrated to total gravimetric sorption) of methanol and water in Nafion were determined as a function of methanol solution concentration.



A methanol flux was determined from this FTIR-ATR data (from the methanol diffusion coefficient and methanol concentration in Nafion) and this flux matched the flux obtained from a conventional permeation cell technique (from the methanol permeability coefficient and methanol solution concentration) at all methanol solution concentrations studied. An increase in methanol flux by nearly three orders of magnitude over the methanol solution concentration range of 0.1-16 M was observed. A key finding in this study is that the main contributing factor to the increase in methanol flux (crossover) was from methanol sorption in Nafion and not methanol diffusion, clarifying a common misconception in this field of study. These results suggest that methanol fuel cell performance and efficiency can be improved by developing new ionic polymers that sorb less methanol, while maintaining a high proton conductivity.

In addition to measuring the diffusion of hydrogen-bound methanol and water clusters, the infrared spectra also provides evidence of protonated methanol and protonated water species, when the polymer is exposed to methanol/water mixtures in the vapor state. Quantification of the equilibrium and dynamic states of these species are currently underway along with the development of new multicomponent diffusion models that account for diffusant-diffusant and diffusant-polymer interactions. The multicomponent models that are currently being developed in conjunction with the new multicomponent data will aid in determining the true multicomponent diffusion effects in this system.

Key Results

- (1) Both multicomponent diffusion and sorption were measured within an ionic polymer membrane on a molecular level in real time as function of concentration. This has not been demonstrated before for mixtures in an ionic polymer.
- (2) The main contribution to the increase in methanol flux was due to methanol sorption in the membrane and not diffusion. The typical assumption in ionic polymer development for the methanol fuel cell is that the diffusion coefficient is the main contribution to the increase in flux (crossover). These results provide new insights for the future development of ionic polymers for the methanol fuel cell.
- (3) These findings illustrate not only the ability to measure multicomponent diffusion and sorption, but also the ability to measure complex molecular diffusing species, such as protonated or ionic methanol and water.

New Ionic Polymer Membranes Based on our Multicomponent Transport Results (collaboration with the University of Minnesota – Marc Hillmyer)

Based on our multicomponent transport results (detailed in the section above), new ionic polymer membranes that sorb less methanol, while maintaining high proton conductivity was the new future design goal. With this new approach in mind, the synthesis of a reactive (crosslinkable) ionic block copolymer containing a norbornene-functional block for ultimate metathesis crosslinking, and a polystyrenesulfonate ester block as the precursor to a proton-conducting phase was explored (**Figure 2**). In this strategy, we envisioned a micro-phase segregated polymer, where one block could act to minimize methanol sorption (via crosslinking), while the other block could rapidly transports protons (via sulfonic acid).

A series of reactive poly(norbornenylethylstyrene-*s*-styrene)-poly(*n*-propyl-*p*-styrenesulfonate) (PNS-PSSP) block polymers were prepared by atom transfer radical polymerization (synthesized in Marc Hillmyer's laboratory at the University of Minnesota). Solutions containing PNS-PSSP, cyclic olefin dicyclopentadiene, and the 2nd generation Grubbs metathesis catalyst were prepared, cast as thin films, and allowed to cure at room temperature by a ring-opening metathesis polymerization (ROMP) mechanism. The PSSP phase in these films were converted into the sulfonic acid form by hydrolysis of the propyl sulfonate ester. This last step is different than the traditional approach, where ionic polymers containing styrenesulfonic acid are typically produced by sulfonation of the styrene or by radical polymerization of sodium styrenesulfonate. In these examples, the processabilities of the resultant polymers can be

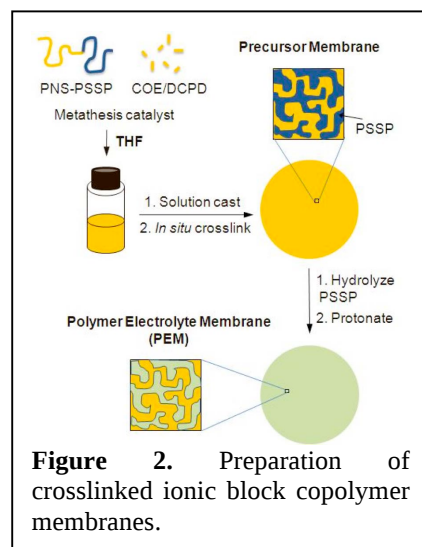
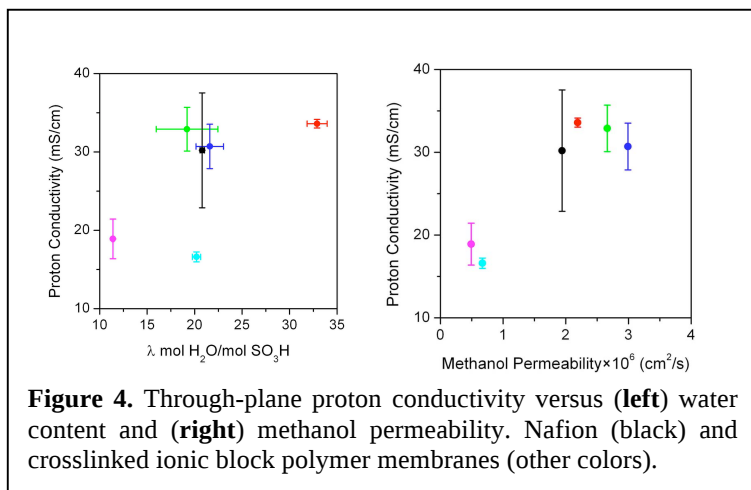
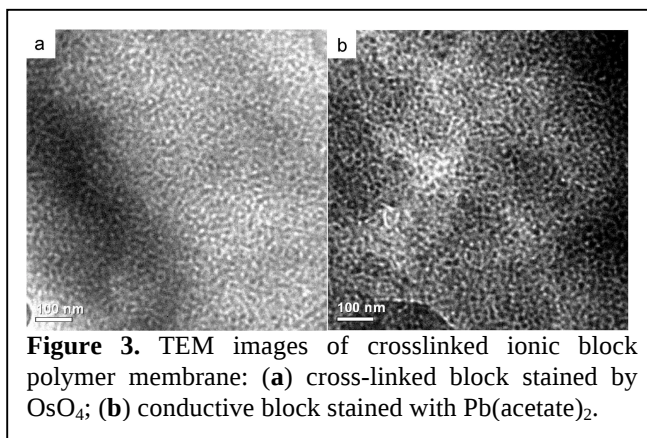


Figure 2. Preparation of crosslinked ionic block copolymer membranes.

compromised by their ionic character. The polymerization of styrenesulfonate esters, on the other hand, allows for the synthesis of copolymers with tailored levels of sulfonation using controlled free radical polymerization followed by base hydrolysis.

Figure 3 demonstrates that the synthesized crosslinked ionic block copolymer membranes resulted in a bicontinuous morphology with continuous domains of the sulfonic acid phase supported by a continuous and mechanically robust poly(dicyclopentadiene) phase. The molecular weight of the PNS-PSSP block polymer controlled the domain sizes, and the mechanical properties of the membranes could be tuned through the choice of cyclic olefins used. The ionic polymer membranes exhibited pronounced mechanical and thermal robustness. This reactive block polymer strategy for the preparation of ionic polymers is attractive due the ready formation of bicontinuous structures, the facile control of domain size, and the ability to independently control mechanical and swelling properties of the matrix material.

Preliminary transport property measurements on these crosslinked ionic block copolymer membranes revealed several surprising results. Contrary to what has been observed in most ionic polymer membranes (e.g., Nafion), the proton conductivities in these materials were relatively independent of water content (**Figure 4**). Furthermore, proton conductivities in these membranes were similar to those observed in Nafion at high humidity. Also, we noted that proton conductivity appears to increase with decreasing domain size in these materials. A key result as it applies to the methanol fuel cell is that select membranes showed significantly lower methanol crossover (flux) than Nafion while maintaining high saturated proton conductivities (Figure 4).



Key Results

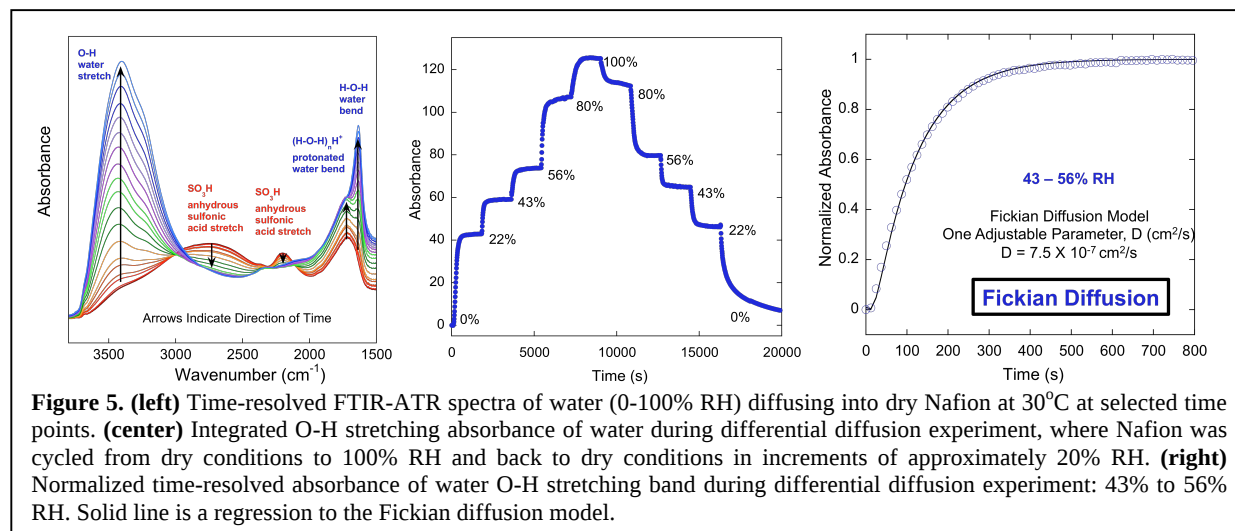
(1) Developed a new strategy for ionic polymers (crosslinked ionic block copolymers) which is attractive due the ready formation of bicontinuous structures, the facile control of domain size, and the ability to independently control mechanical and swelling properties of the matrix material.

(2) Transport results in these materials confirmed our multicomponent transport findings (detailed in previous section), where crosslinking resulted in reduced methanol flux (due to sorption) while maintaining high saturated proton conductivity. Additionally, the morphology was closely tied to transport (conductivity-domain size relationship).

Non-Fickian Dynamics in Ionic Polymer Membranes

We have also recently measured the sorption and desorption dynamics of water vapor in Nafion as a function of water vapor activity and water flow rate using time-resolved FTIR-ATR spectroscopy (**Figure 5**). The application is the hydrogen fuel cell, which is an attractive alternative power sources for applications, such as transportation; however, fuel cell performance is a strong function of water equilibrium content and water sorption and desorption kinetics in ionic polymer membranes (e.g., Nafion). Although similar water sorption isotherms for Nafion have been reproduced in many laboratories, reported diffusion coefficients of water in Nafion vary by up to four orders of magnitude. Both integral and differential experiments were performed in this study, where integral experiments consisted of increasing the vapor activity from 0% RH to one of five values (22%, 43%, 56%, 80%, or 100% RH), while in differential experiments, the activity was sequentially increased in smaller steps from 0% to 22% to 43% to 56% to 80% to 100% RH.

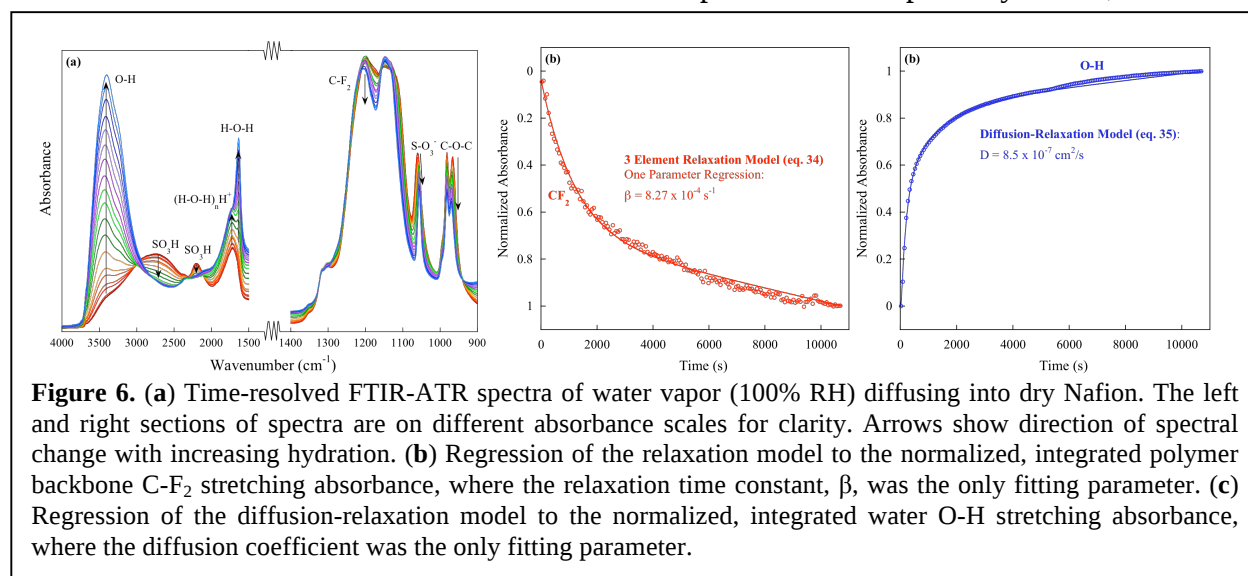
Sorption kinetics was found to be a function of flow rate, where mass transfer resistance at the vapor/polymer interface was significant at low flow rates, but was insignificant at high flow rates. Accurate sorption and desorption diffusion coefficients were calculated in this study (measured at high flow rates with no mass transfer resistance) and did not vary significantly over the entire water vapor activity range ($\sim 10^{-7} \text{ cm}^2/\text{s}$).



For differential experiments, Fickian behavior was observed at all vapor activities except at low vapor activities (0% to 22% RH). For integral experiments, Fickian behavior was only observed at moderate vapor activities, while non-Fickian behavior was observed at both low and high vapor activities (0% to 100% RH). At low humidities, an extended initial time lag resulted in non-Fickian behavior, where dynamic infrared data provided evidence for an interaction or reaction between water and sulfonic acid. A diffusion-reaction model was developed and described this anomalous behavior, where the time lag was a function of water content. At high humidities, a slow approach to steady state resulted in non-Fickian behavior, where dynamic infrared data provided evidence of water-induced relaxation in the polymer backbone. A diffusion-relaxation model was developed that was consistent with the polymer relaxation (three

element viscoelastic model) and water diffusion data, where only one fitting parameter (where up to six parameters have been used previously for dynamic gravimetric data) was used for each data set to determine both a relaxation time constant and diffusion coefficient (**Figure 6**). Not only do the diffusion coefficients from these two models compare well with Fickian diffusion coefficients from experiments at small water concentration gradients, but also the results in this study provide physical insight into the transport mechanisms of water and relaxation phenomena in ionic polymer membranes.

In addition to observing non-Fickian dynamics, where both acid dissociation and polymer relaxation can be measured in addition to water sorption and desorption dynamics, the FTIR-



ATR spectra also provides molecular information on the dynamics on the different states of water and also ionic water (protonated water). We have recently deconvoluted this data and observed interesting new findings as it pertains to understanding conductivity-states of water relationships. Currently, more complex transport models are under development that incorporates different states of water. This data is the first to our knowledge that quantitatively measures the dynamic states of water (including protonated water) in an ionic polymer.

Key Results

(1) Time-resolved FTIR-ATR spectroscopy experiments allow for the determination of accurate mutual diffusion coefficients of water in Nafion with molecular-scale resolution when mass transfer resistance is accurately considered. This is a critical finding since the literature reports diffusion coefficients of water in Nafion that vary by as much as four orders of magnitude. Knowing the accuracy of water transport in Nafion is important because fuel cell performance is such a strong function of water equilibrium content and water sorption and desorption kinetics in Nafion.

(2) This study also identified two different non-Fickian regimes under low humidity sorption and high humidity sorption with a large concentration gradient. In addition, the time-resolved FTIR-ATR spectra provides real-time molecular information regarding the acid dissociation reaction and polymer relaxation, which not only provides new insights into the fundamental transport mechanisms of water in Nafion, but this data was used in conjunction with more complex models

that accurately capture diffusion-reaction and diffusion-relaxation phenomena with minimal fitting parameters required.

(3) The dynamic behavior of different states of water including protonated water in an ionic polymer was quantified.