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Eugene S. Smotkin

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7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
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14. ABSTRACT
The ionomer/electrode interface governs the electrode kinetics of polymer electrolyte batteries and fuel cells. A fundamental understanding of such interfaces is required if step improvements in electrode kinetics are to be realized. Density functional theory (DFT) was used to correlate attenuated total reflectance spectra of ionomer membranes with polarization modulated infrared reflection absorption spectra (PM-IRRAS) of ionomer-electrode interfaces. Neutron reflectivity studies were initiated to characterize the structure of interfacial water. The programmatic innovations include (1) use of DFT calculated normal mode internal coordinate animations for

15. SUBJECT TERMS
Aquivion, Band broadening, Cross-linking, Density functional theory (DFT), Fuel cell, Infrared spectroscopy, Ionomer, Lithiated, Local symmetry, molecular modeling, Nafion, non-PGM , catalyst, Operando infrared spectroscopy, Operando spectroscopy,

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Eugene Smotkin
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Report Title

Final Report: Elucidation of Ionomer-Metal Interfacial Structure by Infrared Spectroscopy, Neutron Reflectivity and Density Functional Theory

ABSTRACT

The ionomer/electrode interface governs the electrode kinetics of polymer electrolyte batteries and fuel cells. A fundamental understanding of such interfaces is required if step improvements in electrode kinetics are to be realized. Density functional theory (DFT) was used to correlate attenuated total reflectance spectra of ionomer membranes with polarization modulated infrared reflection absorption spectra (PM-IRRAS) of ionomer-electrode interfaces. Neutron reflectivity studies were initiated to characterize the structure of interfacial water. The programmatic innovations include (1) use of DFT calculated normal-mode internal-coordinate animations for assignment of mechanically coupled functional group vibrational modes; (2) polarization modulated infrared reflection absorption spectroscopy to identify surface enhanced modes; (3) molecular dynamics calculations simulating aquated Nafion versus lambda and (4) operando Raman spectroscopy of the cathode of hydrogen air fuel cells. Vibrational band assignments based on the local symmetry of the ionomer exchange site were used to interpret operando spectroscopy of fuel cells.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

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

Received		Paper
01/22/2016	3	Jonathan Doan, Erin Kingston, Ian Kendrick, Kierstyn Anderson, Nicholas Dimakis, Philippe Knauth, Maria Luisa Di Vona, Eugene S. Smotkin. Theoretical and experimental infrared spectra of hydrated and dehydrated sulfonated poly(ether ether ketone), Polymer, (09 2014): 4671. doi: 10.1016/j.polymer.2014.07.011 382,779.00
01/22/2016	5	Nestor E. Navarro, Dunesh Kumari, Kierstyn Anderson, Erin Kingston, Cassandra Johnson, Andy Vong, Nicholas Dimakis, Eugene S. Smotkin, Jonathan Doan. Symmetry-based IR group modes as dynamic probes of Nafion ion exchange site structure, Polymer, (09 2015): 34. doi: 10.1016/j.polymer.2015.07.017 382,781.00
01/22/2016	4	Ian Kendrick, Jennifer Fore, Jonathan Doan, Neili Loupe, Andy Vong, Nicholas Dimakis, Max Diem, Eugene S. Smotkin. Operando Raman Micro-Spectroscopy of Polymer Electrolyte Fuel Cells, Journal of the Electrochemical Society, (01 2016): 3152. doi: 10.1149/2.0211604jes 382,780.00
04/17/2017	6	Kierstyn Anderson, Erin Kingston, Joseph Romeo, Jonathan Doan, Neili Loupe, Nicholas Dimakis, Eugene S. Smotkin. Infrared spectroscopy of ion-induced crosslinked sulfonated poly(ether ether ketone), Polymer, (01 2016): 0. doi: 382,782.00
04/17/2017	10	Neili Loupe, Nilufar Nasirova, Jonathan Doan, Danielle Valdez, Maurizio Furlani, Nicholas Dimakis, Eugene S. Smotkin. DFT - experimental IR spectroscopy of lithiated single ion conducting perfluorinated sulfonated ionomers: Ion induced polarization band broadening, Journal of Electroanalytical Chemistry, ( ): . doi: 1,039,230.00
04/17/2017	7	Neili Loupe, Jonathan Doan, Eugene S. Smotkin. Twenty Years of Operando FTIR, XAS and Raman Fuel Cell Spectroscopy, Catalysis Today, (11 2015): 0. doi: 382,783.00
10/16/2013	1	Ian Kendrick, Adam Yakaboski, Erin Kingston, Jonathan Doan, Nicholas Dimakis, Eugene S. Smotkin. Theoretical and experimental infrared spectra of hydrated and dehydrated Nafion, Journal of Polymer Science Part B: Polymer Physics, (09 2013): 0. doi: 10.1002/polb.23348 308,402.00
10/16/2013	2	Ian Kendrick, Eugene S. Smotkin. Operando infrared spectroscopy of the fuel cell membrane electrode assembly Nafion–platinum interface, International Journal of Hydrogen Energy, (8 2013): 0. doi: 10.1016/j.ijhydene.2013.07.117 308,403.00
TOTAL:	**8**	

Number of Papers published in peer-reviewed journals:

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

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper
04/18/2017	13 N Loupe, J Doan, R Cruse, N Dimakis, K Abu-Hakmeh, SS Jang, WA Goddard III, ES Smotkin. Operando IR and Raman Spectroscopy of the Catalyst Ionomer Interface, DOE Catalysis Working Group Meeting. 26-JUL-16, Argonne National Laboratory, IL. : ,
04/18/2017	14 Eugene S Smotkin. Operando Spectroscopy of Ionomer Metal Interfaces, 5th International Congress on Operando Spectroscopy. 17-MAY-15, Deauville, France. : ,
04/18/2017	15 Eugene Smotkin, Jonathan Doan, Erin Kingston, Ian Kendrick, Kierstyn Anderson, Nicholas Dimakis, Philippe Knauth, Maria Luisa Di Vona. Theoretical and experimental infrared spectra of hydrated and dehydrated Sulfonated Poly(Ether Ether Ketone), International Materials Research Congress, 23rd. 19-AUG-14, Cancun, Mexico. : ,
04/18/2017	17 J Doan, J Dura, ES Smotkin. Infrared and neutron reflectometry of sulfonated poly(ether ether ketone) interfaces with Pt and SiO2, 249th ACS National Meeting & Exposition. 22-MAR-15, Denver, CO. : ,
04/18/2017	16 ES Smotkin, J Doan, E Kingston, K Anderson, A Vong. Theoretical and experimental vibrational spectroscopy of ionomers, 249th ACS National Meeting & Exposition. 22-MAR-15, Denver, CO. : ,
04/18/2017	12 N Loupe, R Cruse, J Doan, N Dimakis, K Abu-Hakmeh, SS Jang, WA Goddard III, D Brandell, ES Smotkin. A local symmetry analysis of the PFSI exchange site environments vs. state-of-hydration, International Symposium on Polymer Electrolytes-XV9. 15-AUG-16, Uppsala, Sweden. : ,
04/18/2017	18 J Doan, T Mion, I Kendrick, A Vong, N Dimakis, ES Smotkin. Mechanically coupled internal coordinates: Adding color to infrared spectroscopy, 250th ACS National Meeting & Exposition. 16-AUG-16, Boston, MA. : ,
04/18/2017	19 E S Smotkin. Color coded infrared spectra of polymer electrolytes, Electrochemistry Gordon Conference Five Decades of Impact and Sustained Growth. 10-NOV-14, Ventura, CA. : ,
04/18/2017	20 Eugene S. Smotkin. Theoretical and Experimental Infrared Spectra of Hydrated and Dehydrated Ion Exchange Membranes in Fuel Cells, Department of Chemical Engineering, Goddard Hall, Worcester Polytechnic Institute. 12-NOV-14, Worcester, MA. : ,
04/18/2017	21 E. S. Smotkin. Theoretical and Experimental Infrared Spectra of Hydrated and Dehydrated Ion Exchange Membranes in Fuel Cells, Fuel Cells Gordon Conference Technological Progress and New Scientific Insights. 03-AUG-14, Bryant University, Smithfield, RI. : ,
TOTAL:	**10**

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

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

Received Paper

TOTAL:

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

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received	Book Chapter

04/18/2017	9.00	Neili Loupe, Jonathan Doan, Bogdan Gurau, Eugene S. Smotkin. Electrochemical Energy Storage: Current and Emerging Technologies, : Springer US, (2017)
04/18/2017	11.00	Ian Kendrick, Jonathan Doan, Eugene S. Smotkin. Vibrational Spectroscopy of the Ionomer-Catalyst Interface, : John Wiley and Son INC, (2013)

TOTAL: **2**

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	DISCIPLINE
Ian Kendrick	16	Chemistry
Adam Yakaboski	7	Chemistry
Jonathan Doan	38	Chemistry
Sara Evarts	21	Chemistry
FTE Equivalent:	**0.82**	
Total Number:	**4**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Eugene S Smotkin	0.01	
FTE Equivalent:	**0.01**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	DISCIPLINE
Andy Vong	6	Chemistry
FTE Equivalent:	**0.06**	
Total Number:	**1**	

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:	5.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:	5.00
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:	5.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	5.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	1.00
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:	1.00

Names of Personnel receiving masters degrees

NAME	
Sara Evarts	
Total Number:	**1**

Names of personnel receiving PHDs

NAME	
Ian Kendrick	
Jonathan Doan	
Total Number:	**2**

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

5 **Operando Raman Fuel Cell**

Patent Filed in US? (5d-1) N

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: Ian Kendrick and Eugene S. Smotkin

5f-1a: Northeastern University

5f-c: 360 Huntington Ave

Boston MA 02134

Scientific Progress

See Attachment

Technology Transfer

"See Attachment"

Table of Contents

(1) Foreword

Project Summary - Grant # 60380CH
(Reporting Period: 2013 – 2016)

Elucidation of Ionomer-Metal Interfacial Structure by Infrared Spectroscopy, Neutron Reflectivity and Density Functional Theory

Eugene S. Smotkin
Chemistry and Chemical Biology Department
Northeastern University, Boston, MA 02115

(2) List of Appendixes, Illustrations and Tables

Table 1: Group mode assignments, DFT calculated normal modes and transmission IR bands for Aquivion and Nafion membranes, triflate, triflate-Li aggregate and triflic acid. **(Papers 1 and 4)**

Figure 1. Left: Transmission spectra of fully-hydrated, ion-exchanged Nafion. Right: Transmission spectra of dehydrated ion-exchanged Nafion with $-\Delta H_{hyd}$. **(Paper 4)**

Figure 2. Left: Transmission spectra of Aquivion-Li, fully hydrated (dashed red) to totally dehydrated (dash dotted blue). Right: Aquivion-H (solid), fully hydrated (top red) to totally dehydrated (bottom blue). **(Paper 1)**

Figure 3. Model of SPEEK-M with sulfonic acid groups and a metal ion cross-link. Carbon (gray), Oxygen (red), Sulfur (purple), Metal ion (blue). **(Paper 3)**

Figure 4. Kendrick Raman cell. (a) Schematic of MEA installed in the operando spectroscopy fuel cell. (b) Confocal Raman microscope depth profiling spectra of Fe-N_x/C cathode with O_2 flow. **(Paper 5)**

Figure 5. Left: Nafion MD simulations at various λ_{avg} values. Right: Nafion transmission IR spectra under membrane dehydration. Red lines correspond to C_{3V} modes and blue lines correspond to C_1 modes.

(3) Statement of the problem studied

Objective

The proposed research aims to elucidate the relationship between the ion-exchange membrane state-of-hydration, and the exchange site environment, for both protonated and alkali metal (e.g., Li^+, K^+, Na^+) exchanged membranes. The scientific questions are: How are overall ratios of water/exchange site (λ) expressed as distributions of λ_{local} throughout the membrane? How can vibrational spectroscopy be coupled molecular dynamics to probe λ_{local} distributions? What is the relationship between an exchange site λ_{local} and its local symmetry? How is exchange site local symmetry a direct probe of structure versus state-of-hydration?

Approach

- Bruker FTIR instruments were housed in controlled atmosphere chambers for acquisition of spectra versus state-of-hydration.
- Density functional theory calculated normal mode analysis yielded eigenvector animations that enabled visualization of vibrational modes and band assignments in terms of the exchange site local symmetry.
- Molecular dynamics of Nafion at various λ enables direct visualization of λ_{local} values. We working to develop Python algorithms (a code that works with atom coordinates resulting from MD calculations) to determine λ_{local} values within the hydrophobic and interphasial domains of membranes versus state-of-hydration using MD results from the Georgia Tech/Cal Tech team.

Relevance to Army

Polymer electrolytes are relevant to fuel cells, batteries, flow batteries, electrolyzers and electro-organic flow reactors. Organic electrochemistry is experiencing a major resurgence as evidenced by the Scripps Research Institute (Phil S. Baran), University of Wisconsin (Shannon S. Stahl), GlaxoSmithKline, Abbott Labs, Pfizer and within organic flow batteries (Mike Aziz, MIT). In all afore mentioned applications, an understanding of how the extent of sorption (aqueous or non-aqueous) impacts transport is critical to the advancement of polymer electrolytes. This proposal

is the first atomistic approach to λ (i.e. λ_{local}) that correlates it to the state-of-sorbtion, vibrational spectra and structure & symmetry of the exchange site.

Scientific Challenges:

Humidity control during acquisition of spectra
Obtaining ionomer operando spectroscopy
Fitting neutron scattering data

(4) Summary of the most important results

Major Accomplishments:

Acquired first operando Raman spectroscopy of fuel cell ionomer catalyst interfaces.
Developed and applied exchange site local symmetry based IR band assignments for ionomer catalyst environments.
Developed collaborative team and initial results towards MD analysis of hydration dependent spectroscopy.

Personnel: 1 faculty; 6 undergraduate, 5 graduate students (see publication list)

Accomplishments for Reporting Period

1. The categorization of ionomer side-chain IR group modes by exchange site local symmetry enables correlation of exchange site structure to state-of-hydration and ion exchange. (**Papers 1 – 5**)
2. In Nafion, metal ions with low hydration enthalpy (ΔH_{hyd} < 550 kJ/mol) alter the exchange site at all states-of-hydration. They bind with C_{3V} symmetry and exhibit high orbital overlap with the sulfonate sulfur and oxygen atoms. Hydration waters of ions with ΔH_{hyd} > 1800 kJ/mol cannot be displaced by sulfonate oxygens. (**Paper 4**)
3. Analysis of both Nafion and its similar ionomer counterpart Aquivion reveals cation binding, at low states of dehydration, in an aggregate structure maintaining C_{3V} symmetry (3-fold axis of symmetry). (**Paper 1**)
4. In SPEEK, divalent cation hydration waters preclude interaction of ions with exchange site at high states of hydration. At full dehydration, divalent binding to exchange sites induce polymer cross-linking. The extent of crosslinking is inversely correlated to the cation hydration enthalpy. (**Paper 3**)
5. Coarse depth-profiling of a fuel cell by confocal Raman micro-spectroscopy enabled appropriate positioning of the laser focal point for study of the MEA catalytic layer. The gradual transition of the MEA spectra from C_1 to C_{3V} modes, from the fuel cell open circuit voltage to the short circuit current, respectively, show the initiation of oxygen reduction to water at the catalyst/ionomer interface. (**Paper 5**)
6. Molecular dynamic (MD) simulations of Nafion are used to correlate a distribution of λ_{local} to state of hydration ($\lambda_{overall}$ = 1, 3, 10, 15, 20). Density functional theory calculations of small scale MD λ_{local} subsets yield IR spectra of λ_{local}. The λ_{local} IR spectra linearly combine with

proportions from λ_{local} distributions. This juxposition of IR spectra from DFT can be matched to experimental spectra.

(5) Collaborations and Technology Transfer

- Collaborative effort with GlaxoSmithKline in operando spectroscopy of organic electro-reduction processes in polymer electrolyte based flow reactors.
- Commercialization of operando cells by NuVant Systems Inc.
- Invited presentation at Argonne National Laboratory Catalyst Working Group Meeting: https://energy.gov/eere/fuelcells/downloads/operando-raman-and-theoretical-vibration-spectroscopy-non-pgm-catalysts. This was an invited presentation of our operando spectroscopy work published in reference 5 below.
- Development of collaborative efforts in MD calculations of hydrated membranes with Khaldoon Abu-Hakmeh*, William A. Goddard III#, Seung Soon Jang*

*Institute for Electronics and Nanotechnology, Georgia Institute of Technology, Atlanta, GA 30332

#Materials and Process Simulation Center, California Institute of Technology, Pasadena, CA 91125

- Solvay collaborative effort. In response to our most recent paper published (Paper 1) Solvay contacted us to establish a collaboration on work related to Aquivion. Claudio Oldani (Solvay) has offered the following:

1- Supply our lab with commercially available Aquivion grades.
2- Supply our lab with cast membranes obtained from commercial Aquivion dispersions having lower EW than commercial membranes (790 and 720 g/mol vs. 870 and 980 g/mol)
3- Supply our lab with developmental Aquivion grades (EW lower than 720 g/mol). This is pending likely approval from upper management.
4- Deliver a letter of intent declaring a commitment to send the above material and their availability to exchange non-confidential information.

The overall Solvay/Northeastern goal is to draw the structure-activity relationship by changing the composition of the single-ion conductor.

(6) Bibliography (Programmatic publications)

1. N. Loupe, N. Nasirova, J. Doan, D. Valdez, M. Furlani, N. Dimakis and E. S. Smotkin. "DFT - experimental IR spectroscopy of lithiated single ion conducting perfluorinated sulfonated ionomers: Ion induced polarization band broadening." Journal of Electroanalytical Chemistry, In Press. 2017. Work completed and submitted in 2016

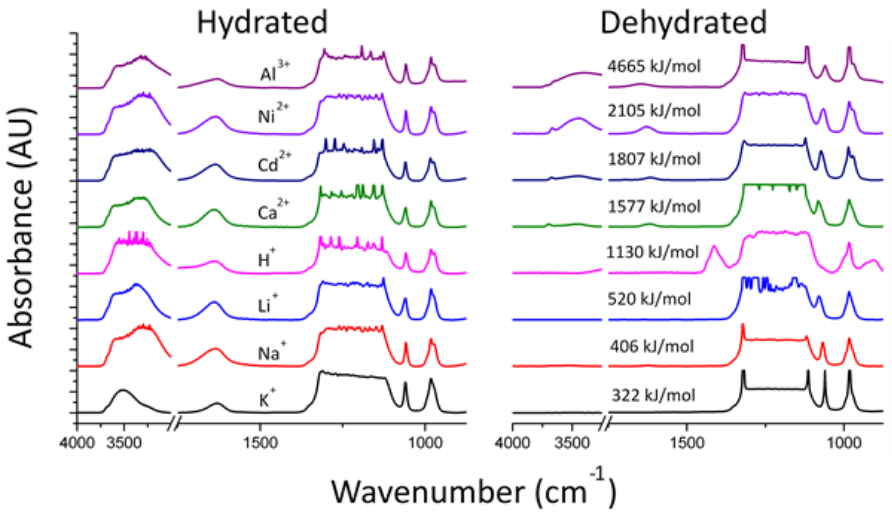
2. N. Loupe, J. Doan and E. S. Smotkin. Twenty years of operando IR, X-ray absorption, and Raman spectroscopy: Direct methanol and hydrogen fuel cells. Catalysis Today, 283, pp.11-26. 2017. Work completed and submitted in 2016
3. K. Anderson, E. Kingston, J. Romeo, J. Doan, N. Loupe, N. Dimakis and E. S. Smotkin. "Infrared spectroscopy of ion-induced cross-linked sulfonated poly (ether ether ketone)." Polymer, 93, pp.65-71. 2016.
4. J. Doan, N. E. Navarro, D. Kumari, K. Anderson, E. Kingston, C. Johnson, A. Vong, N. Dimakis and E. S. Smotkin. "Symmetry-based IR group modes as dynamic probes of Nafion ion exchange site structure." Polymer, 73, pp.34-41. 2015.
5. I. Kendrick, J. Fore, J. Doan, N. Loupe, A. Vong, N. Dimakis, M. Diem and E. S. Smotkin. "Operando Raman Micro-Spectroscopy of Polymer Electrolyte Fuel Cells." Journal of The Electrochemical Society, 163(4), pp.H3152-H3159. 2016.

(7) Appendixes

Figures

		Local symmetry	Group Mode Assignment	DFT (cm^{-1})*	Transmission (cm^{-1})
Aquivion-H	Hydrated	**$C_{3v, LF}$**	SO_3^{-1} ν_s, COC ν_{as}	**923**	**970**
		$C_{3v, HF}$	COC ν_{as}, SO_3^{-1} ν_s	**1051**	**1057**
	Dehydrated	**$C_{1, LF}$**	SO_3H ν_s, COC ν_s	**777**	**905**
		$C_{1, HF}$	SO_3H ν_{as}, COC ν_{as}	**1396**	**1414**
Aquivion-Li	Hydrated	**$C_{3v, LF}$**			**973**
		$C_{3v, HF}$			**1064**
	Dehydrated	**$C_{3v, LF}$**			**974**
		$C_{3v, HF}$			**1077**
Nafion-H	Hydrated	**$C_{3v, LF}$**	SO_3^{-1} ν_s, COC-A ν_{as}	**983**	**969**
		$C_{3v, HF}$	COC-A ν_{as}, SO_3^{-1} ν_s	**1059**	**1061**
	Dehydrated	**$C_{1, LF}$**	SO_3H ν_s, COC-A ν_s	**786**	**910**
		$C_{1, HF}$	SO_3H ν_{as}, COC-A ν_{as}	**1405**	**1414**
Nafion-Li	Hydrated	**$C_{3v, LF}$**			**969 (shoulder)**
		$C_{3v, HF}$			**1061**
	Dehydrated	**$C_{3v, LF}$**	SO_3Li ν_s, COC-A ν_{as}	**940**	
		$C_{3v, HF}$	COC-A ν_s, SO_3Li ν_s,	**1037**	**1080**
			SO_3Li ν_{as}, COC-A ν_{as}, COC-A ν_{as}	**1162**	
			SO_3Li ν_{as}, COC-A ν_{as}, COC-A ν_{as}	**1197**	
Pure Mode Models					
Triflate		**$C_{3V, LF}$**	SO_3^{-1} ν_s	**613**	
		$C_{3V, HF}$	SO_3^{-1} ν_s	**981**	
Triflate-Li Aggregate		**$C_{3V, LF}$**	SO_3^{-1} ν_s	**774**	
		$C_{3V, HF}$	SO_3^{-1} ν_s	**1014**	
Triflic acid		**$C_{1, LF}$**	SO_3H ν_s	**795**	
		$C_{1, HF}$	SO_3H ν_{as}	**1398**	

Table 1: Group mode assignments, DFT calculated normal modes and transmission IR bands for Aquivion and Nafion membranes, triflate, triflate-Li aggregate and triflic acid. **(Papers 1 and 4)**



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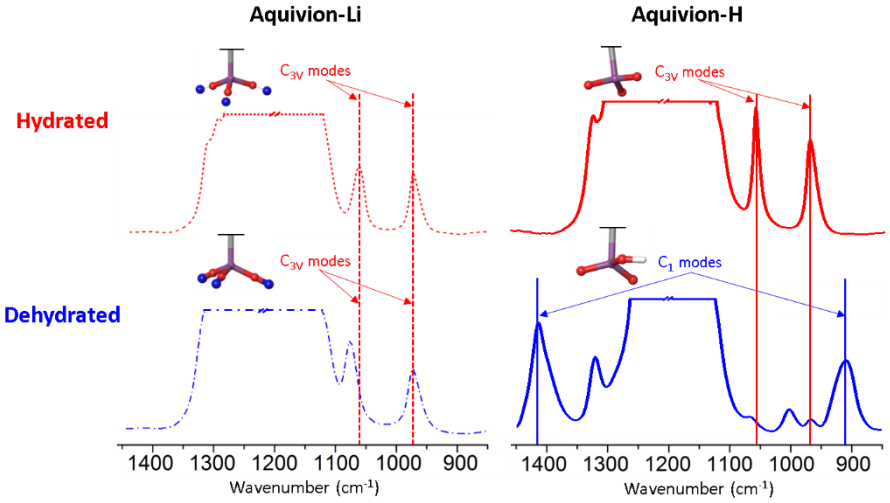
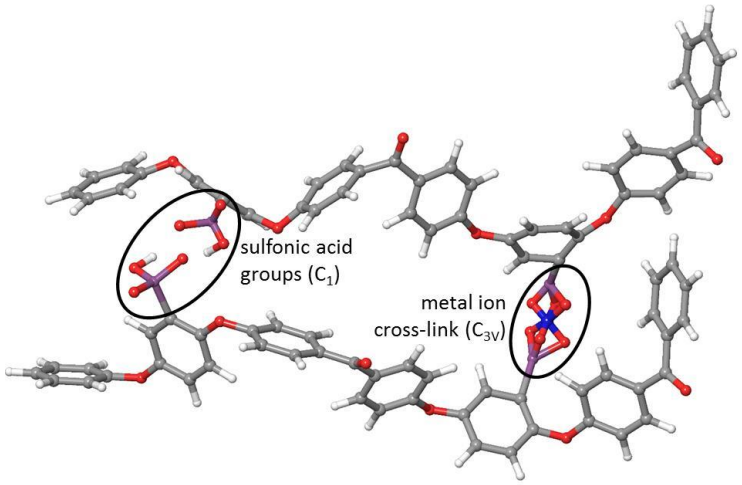


Figure 2. Left: Transmission spectra of Aquivion-Li, fully hydrated (dashed red) to totally dehydrated (dash dotted blue). Right: Aquivion-H (solid), fully hydrated (top red) to totally dehydrated (bottom blue). **(Paper 1)**



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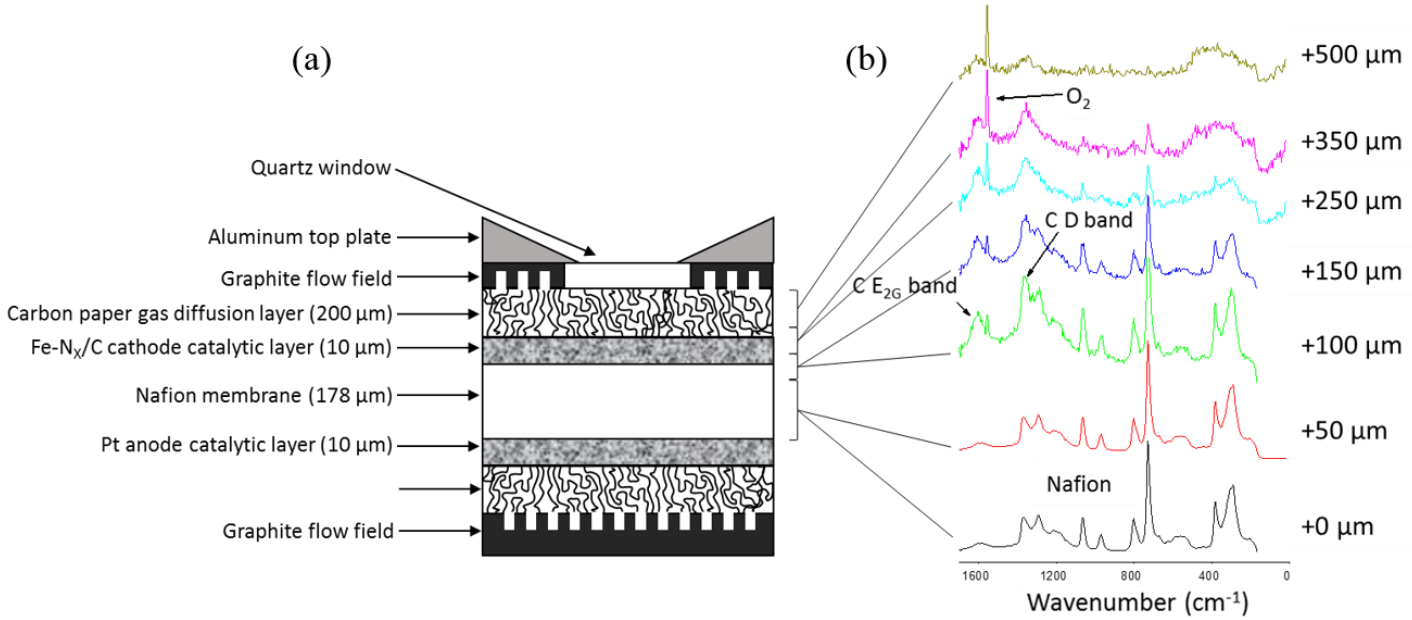

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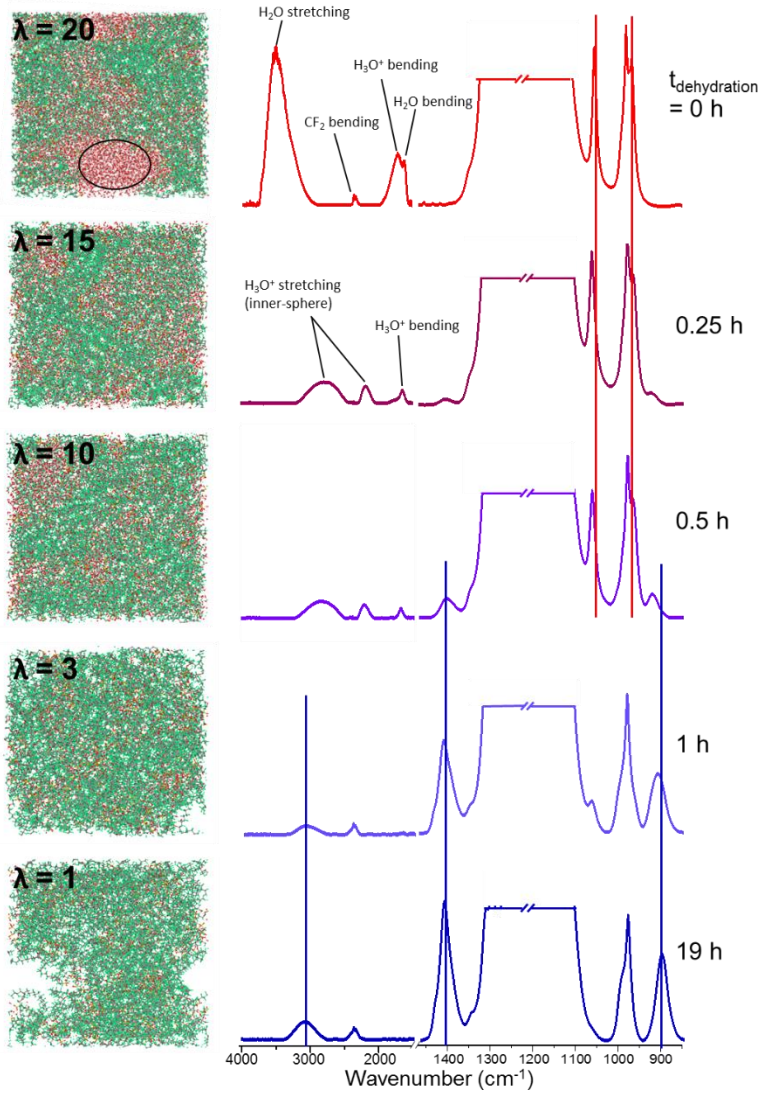

Figure 5. Left: Nafion MD simulations at various λ_{avg} values. Right: Nafion transmission IR spectra under membrane dehydration. Red lines correspond to C_{3V} modes and blue lines correspond to C_1 modes.