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14. ABSTRACT
Our laboratory's main activity in connection with this grant has been to develop and implement NMR-based analytical tooks to characterize water, methanol, and charge transport in PEM membrane materials provided by research collaborators at other universities and research centers, including AFRL.NMR spectroscopy provides information on different structural environments of muticomponent PEM films, for example those containing phosphoric acid and ionic liquids. Dynamical processes are probed at the short range by spin-lattice relaxation measurements while pulsed field gradient techniques are used to obtain self-diffusion coefficients of water and methanol. Among the systems investigated were high phosphoric acid content polybenzimidazole (PBI) films, sulfonated polyarylene thioether sulfones, NAFION nanocomposites, and sufonated polyetherether ketone (SPEEK) nanocomposites. A new high throughput measurement scheme based on one-dimensional magnetic resonance imaging was developed that facilitates rapid screening of multiple samples.

15. SUBJECT TERMS
PEM Fuel Cell Membranes, nuclear magnetic resonance (NMR), slef-diffusion, transport properties

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Abstract

Our laboratory's main activity in connection with this grant has been to develop and implement NMR-based analytical tooks to characterize water, methanol, and charge transport in PEM membrane materials provided by research collaborators at other universities and research centers, including AFRL.NMR spectroscopy provides information on different structural environments of muticomponent PEM films, for example those containing phosphoric acid and ionic liquids. Dynamical processes are probed at the short range by spin-lattice relaxation measurements while pulsed field gradient techniques are used to obtain self-diffusion coefficients of water and methanol. Among the systems investigated were high phosphoric acid content polybenzimidazole (PBI) films, sulfonated polyarylene thioether sulfones, NAFION nanocomposites, and sufonated polyetherether ketone (SPEEK) nanocomposites. A new high throughput measurement scheme based on one-dimensional magnetic resonance imaging was developed that facilitates rapid screening of multiple samples.

Accomplishments:

Our research methodology of characterizing charge and mass (the latter for water and methanol) transport in fuel cell membranes by pulse field gradient NMR and NMR relaxation has been extended to new materials in collaboration with Thuy Dang at AFRL and Brian Benicewicz at RPI. Both projects were aimed at extending the high temperature limit of conventional PEM materials. The sulfonated polyarylenethioether sulfones prepared by AFRL proved to be stable to 130°C and more selective than NAFION for possible application in direct methanol fuel cells – that is, higher water to methanol diffusivity ratio. The PBI/PA PEM materials prepared at RPI are nominally anhydrous, and thus can work at 180°C. NMR measurements confirmed the presence of phosphoric acid with only a small amount of condensed phase (the dimer), and proton transport approaching that of "free" phosphoric acid with negligible phosphate ion transport. The importance of these kinds of systems prompted a fundamental investigation of transport in the water/phosphoric acid. Using high pressure NMR methods, it was confirmed that phosphate ionic mobility is governed by a different mechanism than proton mobility.

Our research methodology of characterizing charge and mass (the latter for water and methanol) transport in fuel cell membranes by pulse field gradient NMR and NMR relaxation has been extended to new materials in collaboration with Thuy Dang at AFRL. This project was aimed at extending the high temperature limit of conventional PEM materials. The sulfonated

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polyarylenethioether sulfones prepared by AFRL proved to be stable to 130°C and more selective than NAFION for possible application in direct methanol fuel cells – that is, higher water to methanol diffusivity ratio, but a fluorinated analogue was shown to have inferior water retention properties. Composite membranes formed by incorporating nanoscopic oxide particles into sulfonated polymers such as SPEEK and Nafion were also studied and the main conclusions are that the particles affect water uptake and retention mainly by modifying the pore structure of the membrane. However in cases where the nanoparticles are functionalized, hopping proton transport has been inferred by noting a lack of correlation between water diffusivity and proton conductivity in the nanocomposites Transport properties of several ionic liquids (IL's) and membranes incorporating IL's were investigated. One such membrane incorporating phosphoric acid and the amphoteric anion $H_2PO_4^-$ from the IL forms a three dimensional H-bonded network that facilitates proton hopping. Finally, a new high-throughput membrane characterization method has been developed that allows evaluation of up to five samples in a single measurement. The method is based on simple one-dimensional NMR imaging combined with standard diffusion measurements.

Archival publications (published) during reporting period:

Some of the publications listed below were associated with other projects or submitted prior to the start date of this grant. The work described above corresponds mostly to #'s 3, 6, 8, 11, 12, 14, 21, 22, 24.

1. "Anhydrous Proton Conducting Polymeric Electrolytes for Fuel Cells", with S. R. Narayanan, Shiao-Pin Yen, and L. Liu, *Journal of Physical Chemistry B*, 110, 3942 (2006).

2. "Characterization of Single Walled Carbon Nanotube –Polyvinylene Difluoride Composites" with J.R.P. Jayakody and F.J. Owens, *Composites Science and Technology*, 66, 1280-1284 (2006).

3. "NMR investigation of water and methanol transport in sulfonated polyareylenethioethersulfones for fuel cell applications, with J.R.P. Jayakody, A. Khalfan, E.S. Mananga, T.D. Dang and R. Mantz, *Journal of Power Sources*, 156, 195-199 (2006).

4. "Pyrite-induced hydroxyl radical formation and its effect on nucleic acids" with Corey A Cohn, Steffen Mueller, Eckard Wimmer, Nicole Leifer, Daniel R Strongin, and Martin AA Schoonen. *Geochemical Transactions* 7, 3 (2006).

5. "Polymeric δ-$MgCl_2$ nanoribbons", with Michele Vittadello, Philip E. Stallworth, Faisal M. Alamgir, Sophia Suarez, Sabina Abbrent, Charles M. Drain, and Vito Di Noto, *Inorganica Chimica Acta*, *Inorganica Chimica Acta*, 359, 2513 (2006).

6. "Ormosil/SPEEK Based Hybrid Composite Proton Conducting Membranes", with Silvia Licoccia, M. Luisa Di Vona, Alessandra D'Epifanio, Debora Marani, Michele Vittadello, and Jayakody R. P. Jayakody, *Journal of the Electrochemical Society*, 153 A1226-A1231 (2006).

7. "Investigation Of Fundamental Transport Properties And Thermodynamics In Diglyme-Salt Solutions", with M. Petrowsky, R. Frech, S. Suarez, and J.R.P. Jayakody, *Journal of Physical Chemistry B*, 110, 23012 -23021, (2006).

8. "Multinuclear NMR Studies Of Mass Transport Of Phosphoric Acid In Water" with J. R. P. Jayakody[1], E. S. Mananga[2], A. Khalfan[2], S. H. Chung[3], and R. Lopato, proceedings of the 10th Asian Conference on Solid State Ionics (World Scientific Publishers, Singapore), 2006, pp 19-28.

9. "Morphology of PI-PEO Block Copolymers for Lithium Batteries", Chenchen Xue, Mary Ann B. Meador, Valerie A. Cubon, Lei Zhu, Jason J. Ge, Stephen Z. D. Cheng, R. K. Eby, Ameesh Khalfan, George D. Bennett, and Steve G. Greenbaum, *Polymer*, 47, 6149 (2006).

10. "Solid State NMR Characterization of Electrolyte Breakdown Products in Nonaqueous Asymmetric Hybrid Supercapacitors" with I. Nicotera, G. D. McLachlan, G. D. Bennett, I. Plitz, F. Badway, and G. G. Amatucci, *Electrochemical and Solid State Letters*, 10, A5 (2007).

11. "NMR Studies Of Mass Transport In High Acid Content Fuel Cell Membranes Based On Phosphoric Acid and Polybenzimidazole, with J.R.P. Jayakody, S.H. Chung, Lisa Durantino, H. Zhang, L. Xiao, and B. Benicewicz, *Journal of the Electrochemical Society*, 154, B242 (2007).

12. "NMR Characterization of Composite Polymer Membranes for Low Humidity PEM Fuel Cells", with Isabella Nicotera, Tao Zhang, and Andrew Bocarsly, *Journal of the Electrochemical Society*, 154, B466 (2007).

13. "Nuclear Magnetic Resonance and X-Ray Absorption Spectroscopic Studies of Lithium Insertion in Silver Vanadium Oxide Cathodes", with N.D. Leifer, F.M. Alamgir, A. Colon, K. Martocci, and S.G. Greenbaum, T.B. Reddy, *Journal of the Electrochemical Society*, 154, A500 – 506 (2007).

14. "A Nuclear Magnetic Resonance Study of Room Temperature Ionic Liquids with $-CH_2Si(CH_3)_3$ vs $-CH_2C(CH_3)_3$ Substitutions on the Imidazolium Cations,", with Song H. Chung, Richard Lopato, Hieaki Shirota, Edward W. Castner, Jr., and James F. Wishart, *Journal of Physical Chemistry B*, . 2007, 111, 4885-4893.

15. "Lithium transport properties of solid electrolytes based on PEO/CF_3SO_3Li and aluminum carboxylate" with E. Zygadło-Monikowska, Z. Florjańczyk, E. Rogalska-Jońska, A. Werbanowska, N. Langwald, D. Golodnitsky, E. Peled, R. Kovarsky, S.H. Chung, *Journal of Power Sources*, 173, 734-742 (2007).

16. "Interpreting the structural and electrochemical complexity of $0.5Li_2MnO_3 \bullet 0.5LiMO_2$ electrodes for lithium batteries ($M=Mn_{0.5-x}Ni_{0.5-x}Co_{2x}$, $0 \le x \le 0.5$)", with S.–H. Kang, P.

Kempgens, J. Kropf, K. Amine, and M. M. Thackeray, *Journal of Materials Chemistry*, 2007, 17, 2069–2077.

17. "Reversible Intercalation of Fluoride-Anion Receptor Complexes in Graphite", with William West, Jay Whitacre , Nicole Leifer, Marshall Smart , Ratnakumar Bugga , Mario Blanco , and S. Narayanan, *Journal of the Electrochemical Society*, **154** A929-A936 (2007).

18. "Spectroscopic analysis of SEI formation in Lithium-ion batteries", with N. D. Leifer, in Advanced Materials and Methods for Lithium-Ion Batteries, SS. Zhang, ed. Series on Recent Research Developments in Electrochemistry, Research Signpost. 2007.

19. "Synthesis and Characterization of New Types of Ionic Liquids", with S. Lall-Ranmarine, D. Coleman, J. Wishart, M. Thomas, A. Ipe, S. Suarez, and R. Engel in Molten Salts XIV, R.A. Mantz, P.C. Trulove, H.C. DeLong, G.R. Stafford, R. Hagiwara, and D.A. Costa, eds., p.303. The Electrochemical Society, Pennington, NJ 2007.

20. "Novel Li Ion Conducting Polymer Gel Electrolytes Based on Ionic Liquid / PVDF-HFP Blends", with Hui Ye, Jian Huang , John Xu , and Amish Khalfan, *Journal of the Electrochemical Society,* **154,** A1048-A1057 (2007).

21. "Water And Proton Transport Properties Of Hexafluorinated Sulfonated Poly (Arylenethioethersulfone) Copolymers For Applications To Proton Exchange Membrane Fuel Cells" with Amish N. Khalfan, Luz M. Sanchez, Chandana Kodiweera, Zongwu Bai and Thuy D. Dang, *Journal of Power Sources*, 173, 853 (2007).

22. "New Membranes Based on Ionic Liquids for PEM Fuel Cells at Elevated Temperatures" with H. Ye, J. Huang and J. Xu, N.A.C. Kodiweera, and J.R.P. Jayakody, *Journal of Power Sources*, 651-660 (2008).

23. "Ferromagnetic resonance studies of surface and bulk spin-wave modes in a CoFe/PtMn/CoFe multilayer film", with Cheng Wu, Amish N. Khalfan, Carl Pettiford, Nian X. Sun, and Yuhang Ren, Journal of Applied Physics, 103, 07B525 (2008).

24. "Effect of a Proton Conducting Filler on the Physico-Chemical Properties of SPEEK-based Membranes" with B.Mecheri, A.D'Epifanio, L.Pisani, F.Chen, E.Traversa, F.C.Weise, and S. Licoccia, 1st CARISMA conference, Progress MEA 2008, in Fuel Cells, Wiley-VCH, in press.

25. "High-resolution NMR characterization of a spider-silk mimetic composed of 15 tandem repeats and a CRGD motif", with Glendon D. McLachlan, Joseph Slocik, Robert Mantz, David Kaplan, Sean Cahill, and Mark Girvin, *Journal of Protein Chemistry*, in press.

Student accomplishments

Ph.D. degrees received.
Amish Khalfan 2006 – postdoc NHFML, Florida State U.
Nicole Leifer 2008 – postdoc, Bar Ilan U. (Israel)

Undergraduate degrees
Bernie Koliskor, 2006, SUNY Downstate Medical School
Luz Sanchez, 2007, U. Maryland (Ph.D. Program, Materials Science & Engineering)
Krista Martocci, 2008, U. Chicago (Ph.D. Program, Astrophysics)
Amy Colon, 2008, U. North Carolina (Ph.D. Program Astrophysics)