

²³Na NMR mobility studies on new electrolytes for sodium-ion batteries.

Marc B. Berman, Xavier Bogle, Steve G. Greenbaum
Hunter College, City University of New York
695 Park Avenue, New York, New York 10065

²³Na and ¹⁹F Nuclear Magnetic Resonance (NMR) measurements were conducted on a variety of polymer electrolytes designed for use in sodium ion or sodium air batteries. In a collaboration with University of Rome La Sapienza (J. Serra Moreno, S. Panero, B. Scrosati), we have examined the effect of nanometric SiO₂ filler addition on the transport properties of poly(ethylene oxide) (PEO) sodium (bis)trifluoromethanesulfonate imide salt (NaTFSI) solid electrolyte membranes. We have also investigated ionic mobility in NaTFSI or NaCF₃SO₃ (triflate) dissolved in either PEG500 or PYR₁₄TFSI ionic liquid (IL), in collaboration with Tel Aviv University (E. Peled, D. Golodnitsky).

Pulsed Field Gradient Nuclear Magnetic Resonance (PFGNMR) measurements on the ¹⁹F nucleus have determined that the anion diffusion coefficient decreases with the addition of filler which may have a positive effect on the cation transference number. PFGNMR on the anion was not possible as a result of the extremely short spin-lattice relaxation characteristic of the quadrupolar ²³Na nucleus in a dynamic environment of lower than cubic symmetry. NMR linewidth measurements were conducted on both the ²³Na and ¹⁹F. The ¹⁹F linewidth exhibits only weak temperature dependence and the effect of the filler is consistent with what was observed for the diffusion measurements. On the other hand, the ²³Na linewidth increases with increasing temperature. This behavior has been reported for other Na polymer electrolytes, whereby initial motional narrowing is followed by motional broadening resulting from the very short spin-lattice relaxation times at higher temperature^{1,2} The figure below shows an Arrhenius plot of the linewidth measurements in the PEO based samples with and without the silica added for both ¹⁹F and ²³Na.

The liquid electrolytes (either PEG500 or PYR₁₄TFSI) had nanoscopic Al₂O₃ added to them as filler. ²³Na linewidth and spin-lattice relaxation measurements were performed on the electrolyte samples to assess the relative degrees of translational motion of the cations and anions as well as ¹⁹F NMRPFG on the cation (again because of the short spin-lattice relaxation, self diffusion is not possible for ²³Na). In contrast to the PEO complexes, the PFG measurements on the liquid electrolytes showed that the effect of the filler was negligible. There is also a clear separation in mobility of the anion between the IL- and PEG-based liquid electrolytes, with the PEG-based showing much higher values for the anion self-diffusion coefficient than the IL. Of these, the triflate anions are more mobile than the TFSI anions.

From the measurements in the ²³Na linewidth and the spin-lattice relaxation the following becomes apparent: (i) the addition of filler has little observable effect; (ii) the choice of anion (TFSI or Triflate) in the PEG solutions also has little effect; (iii) the simultaneous presence of a broad T₁ minimum and a linewidth maximum in the IL Na salt mixture at around 65°C is absent in the PEG solution, which most likely occurs at a lower temperature in the latter. Linewidth maxima have been observed in ²³Na and other half-integer quadrupolar nuclei undergoing large changes in local correlation time³. Taken together, this is consistent with higher Na⁺ mobility in the PEG solutions than in the IL solutions.

References:

- [1] Y.S. Pak, K.J. Adamic, S.G. Greenbaum, J.J. Fontanella, M.C. Wintersgill, *Solid State Ionics* 45 (1991) 277-284
- [2] Y.S. Pak, K.J. Adamic, M.C. Wintersgill, J.J. Fontanella, S.G. Greenbaum, "NMR Studies of Polymer Electrolytes" Materials Research Society Symposium Proceedings 210 (Solid State Ionics II), 1991, p.237
- [3] Y.S. Pak, K.J. Adamic, S.G. Greenbaum, J.J. Fontanella and M.C. Wintersgill, "Complex Impedance and Multifrequency ²³Na NMR Study of Poly(propylene oxide) Complexed with NaB(Ph)₄", *Solid State Ionics*, **45**, 277 (1991).

The work was supported by Grant # DE-SC0005029 from the Basic Energy Sciences Division of the U.S. Department of Energy.

