Solvation and Gelation Process of Nafion®

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The Nafion[®] polymers were first introduced in the form of melt-processed membranes or aqueous dispersions by the E. I. DuPont Company in the mid-1980s and used as the industrial standard materials for polymer electrolyte fuel cells.¹ Although Nafion[®] and its sister perfluorosulfonic acid polymers have been synthesized and studied under the heading "ion conducting polymers", the nano-scale structures of Nafion® and/or Nafion® dispersion are still largely unexplored, as those groups in the scientific community focusing on their polymeric character are trying to treat them primarily like other polymers. Recently, Los Alamos National Laboratory fuel cell team successfully prepared various Nafion[®] dispersions using non-aqueous solvents, which allowed systematic approach to investigate Nafion® morphology in a wide range.² In this talk, we will discuss the nanoscale structure of Nafion[®] and its impact on dispersion and membrane properties based on our recent findings.

Nafion[®] Particle Morphology in Liquid Media Pioneering works by Aldebert and others suggested that Nafion[®] in polar solvents formed cylindrical particles.³ However, our small angle neutron scattering (SANS) experiments revealed that Nafion[®] in liquid media have wider morphological features than as reported: i) a welldefined cylindrical dispersion in glycerol and in ethylene glycol with different degrees of solvent penetration; ii) a less-defined, highly solvated large particle (> 200 nm) in water/isopropanol mixtures; and iii) a random-coil conformation (true solution behavior) in Nmethylpyrrolidone (NMP).⁴ The morphological difference of Nafion[®] particulates in liquid media was also evidenced by the difference of main and side chain mobility. Detail structural analysis of SANS and supporting data with ¹⁹F NMR will be presented.

Solubility Parameter and Thermodynamic Consideration In 1980, Yeo found that Nafion® membranes exhibited dual cohesive energy densities and suggested dual solubility parameters for Nafion®, which have been used until now.⁵ However, our SANS results indicate that only few aprotic solvents truly can solvate Nafion[®], yet most other liquid media only can disperse Nafion[®] to form a particle aggregates. Based on these facts, we have calculated single Hansen solubility parameter of Nafion[®] (i.e. $\delta_{\text{non-polar}} = 17.4 \text{ MPa}^{1/2}$, $\delta_{\text{polar}} = 12.5 \text{ MPa}^{1/2}$, $\delta_{\text{hydrogen}} = 9.6 \text{ MPa}^{1/2}$). Other thermodynamic properties such as reflective index, surface tension and Flory-Huggins interaction parameters are estimated from the solubility parameter and compared with measured values. For Nafion[®] dispersions, non-equilibrium[®] thermodynamic parameters was introduced to correlate the dispersing temperature (Figure 1) and other time-dependent relaxation behaviors. In this presentation, we will report low critical solution temperature (LCST) phase behavior of Nafion[®] dispersions for the first time which gives further insight into the dispersion process of Nafion®

Thermal Reversible and Irreversible Gelation Behavior During solvent evaporation process, Nafion[®] dispersions undergo gelation. We found that there are two types of gelation process, depending on whether the Nafion[®] in liquid media is solution or dispersion: Nafion[®] solutions from aprotic solvent systems undergo thermal reversible gelation (thermodynamic equilibrium process) while Nafion[®] dispersions from alcohols or aqueous solvent systems exhibited the irreversible gelation (thermodynamic non-equilibrium process). The critical gelation point (CGC) of each gelation process was measured. We will demonstrate how the CGC value will correlate the mechanical properties of solution-cast Nafion[®] membranes.



Figure 1. Dispersing temperature of Nafion in various alcohols. γ_s = surface tension of solvent; α = adsorption coefficient.

Acknowledgment

We thank the U.S. Department of Energy Fuel Cell Technologies Program (Technology Development Manager: Dr. Nancy Garland) for funding this work. SANS experiments were conducted at the Low-Q Diffractometer beamline of Los Alamos Neutron Science Center and NG-3 beamline of the NIST center for Neutron Research (U.S. Department of Commerce)

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