Insight into the structural construction of a perfluorosulfonic acid membrane derived from a polymeric dispersion
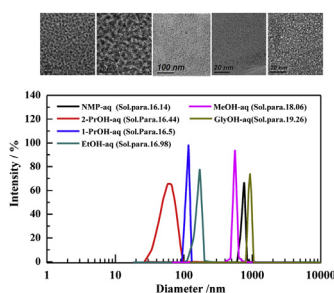
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HIGHLIGHTS

- Performance and microstructure of perfluorosulfonic membrane is depended on the solvents.
- Nafion aggregation decrease with the increase of the dielectric constant.
- Nafion aggregation decrease with the decrease of solubility parameters gap.

GRAPHICAL ABSTRACT

ABSTRACT

The effects of the nature of the solvent on the morphology of perfluorosulfonate ionomers in dispersions and the microstructures of the corresponding formed membranes are investigated. The subsequent electrochemical performances of the formed proton exchange membranes are also studied in detail. It is found that the diameters of the Nafion molecular aggregates in variable solutions decrease with an increase in the solvent dielectric constant (ε) and a decrease in the gap of the solubility parameters (δ) between the resin and the solvent. The micromorphology of Nafion is further examined by means of transmission electron microscopy, small-angle X-ray scattering, and X-ray diffraction. It is found that the membrane cast from a Nafion-2-propanol/water dispersion with ε value of 42.38 and a δ gap of 0.01 (cal cm^{-3})$^{1/2}$ has a better ion cluster arrangement, smaller ion cluster size (approximately 13 Å), and higher crystallinity (16.7%) than the other samples. The electrochemical properties of the formed membranes are further investigated as a function of temperature, relative humidity, and the solubility parameter of the applied solvents. The results demonstrate that the electrochemical performance is strongly influenced by the solvent-induced microstructure of the backbone and the ionic clusters in the perfluorosulfonic acid membrane.

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1. Introduction

Perfluorosulfonic acid (PFSA) ionomers such as Nafion have been extensively used in proton exchange membrane fuel cells as a polymer electrolyte and separator between the cathode and the anode because of their high structural stability and superior electrochemical properties in the hydrated state [1,2]. Generally, the technique for preparing a Nafion membrane is the solution-cast method, with which Nafion solutions are added to a desired container and then the solvent is allowed to evaporate to form the membrane through a particular thermal process [3]. Therefore, detailed information about the Nafion ionomer dispersion is crucial and helpful for achieving a better understanding of the nature and microstructure of the membrane that forms [4,5].

Nafion is a copolymer with comb-like structure that contains a hydrophobic poly(tetrafluoroethylene) (PTFE) backbone and

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perfluorovinyl ether side chains terminated with hydrophilic sulfonate groups. It is, therefore, not surprising that a degree of phase separation occurs in the hydrated Nafion membrane, which leads to the formation of interconnected, hydrated ionic clusters inside the membrane that determine the electrochemical properties of the membrane. The mechanical strength of the Nafion membranes is also improved through the crosslinking of the perfluorinated backbones induced by thermal treatment during the membrane formation process [6]. In the 1970s, the cohesive energy density of Nafion was determined experimentally from swelling measurements using the method developed by Britow and Watson [7]. The results showed that there are two distinct swelling envelopes corresponding to dual cohesive energy densities: one is ascribed to the organic part of the membrane, whereas the other is tentatively attributed to the ion clusters within the material. It was reported that the conformation of the Nafion molecules in solution depends strongly on the dielectric constant and the solubility parameter of the solvent that was used [8]. Ubbelohde viscosity measurements showed that dilute solutions of the perfluorosulfonated ionomer in various solvents exhibited quite different dielectric constants. For alcoholic and aqueous solutions of Nafion, an enhanced "polyelectrolyte effect" was observed with an increase in the dielectric constant of the solvent; however, this polyelectrolyte effect was not significant for other highly polar solvents [9]. It was also observed that the zeta potential of the Nafion dispersion, which reflects the aggregation status of the ionomer molecules, strongly depends on the concentration of the molecules. When the concentration of Nafion was varied from 0.5 to 1 wt%, the zeta potential increased significantly from approximately 0—12 mV, which corresponds to a change in the structure of the Nafion molecules from a true solution to a dispersion [10]. In addition, the conformation and the structure of the perfluorosulfonated ionomer in polar solvents such as alcohols, amides, and water have also been investigated using small-angle neutron scattering (SANS) and small-angle X-ray scattering (SAXS) [11—16]. In general, two Nafion molecular aggregation processes in alcoholic or aqueous solutions have been proposed based on the scattering data [17]. The primary aggregation induced by the hydrophobic interaction of the perfluorocarbon backbone can lead to the formation of rod-like aggregated particles with sizes of several hundred nanometers. It is worth noting that the primary aggregated particles can be dissociated into single molecular chains by further diluting the dispersion. The secondary aggregation process is attributed to the ionic aggregation of primary aggregated particles induced by the electrostatic attraction of the Nafion side chain $-SO_3^-$ ion pairs, which leads to the formation of large aggregated particles with sizes of approximately 10^4 nm. Thus, a cylinder-like conformation of Nafion is expected in solution, where the aggregated perfluorocarbon backbones form the compact cylinders and the sulfonated vinylether side chains are located at the polymer/solvent interface. Moreover, the dispersion properties could affect the microstructure of the membrane that forms. Accordingly, the conductivities and transport selectivities of the membranes that form, which are related to the membrane electrode assembly performance, are also dependent on the dispersion properties of Nafion. Therefore, it is of great importance to understand the dispersion properties of the Nafion ionomer used in PEMs.

The unique construction and properties of Nafion membranes are believed to be closely related to the microscopic phase separation of the ionic parts ($-SO_3H$ groups) from the fluorocarbon matrix. Although the conformation of Nafion has been well studied with respect to its cation form, equivalent weight, and water content [18—24], the effect of the applied solvent on the conformation of the Nafion molecules and the microstructure of the subsequently formed membrane have not been reported. In this paper, we

evaluated the structures of the perfluorosulfonic acid membranes formed by casting Nafion resin from different solvents, including methanol, ethanol, 2-propanol, 1-propanol, glycerol, and *N*-Methyl pyrrolidone. The influence of the solvent's properties, e.g., the polarity and the solubility parameter, on the dispersive behavior of the perfluorosulfonate ionomers, the ionic aggregate size, and the crystallinity is the main focus of this work. In addition, the relationship between the dispersive behavior of the Nafion sol and the proton conductivity of the membrane formed under various conditions, the activation energy of the proton transportation, and the stability of the physical structure of the formed membranes are also discussed in this study.

2. Experimental section

2.1. Preparation and characterization of the Nafion solutions

Nafion dispersion (EW1000), which contains 5 wt% of perfluorosulfonate resin (H^+ form) and 95 wt% of an isopropanol/water mixture (10:9 weight ratio), was purchased from DuPont Ind. Co. The Nafion solutions used in this study were prepared by the following procedure. To 500 mL of the commercial Nafion dispersion, 500 mL of deionized water was added. The mixture was concentrated to approximately 250 mL by evaporation of the solvent at 60 °C using a hot plate. To the resulting solution, 500 mL of deionized water was added, and solvent evaporation was carried out again. This process was repeated 3 more times to make sure that the isopropanol was removed from the Nafion solution. The final Nafion concentration in the aqueous solution was 10.63 wt%, which was checked by casting 100 mL of the Nafion aqueous solution to form a membrane and then titrating the EW value. The resultant Nafion aqueous solution was then diluted with the desired solvent, and that solution was then used for the preparation of the membranes. Six prepared Nafion solutions with different mixtures of solvents and the properties of those applied solvents, including the solubility parameters (δ) and dielectric constants (ε), are shown in Table 1. For comparison, the δ and ε of the single solvents and the Nafion resin are presented in Table 2. The final prepared solutions, which contained new solvents for the preparation of the membranes, had a Nafion concentration of 3 wt%.

Samples for transmission electron microscopy (TEM) were prepared according to the following method: to make a relatively thin film for TEM examination, carbon-coated grids were soaked in 1 wt% Nafion solutions, and the liquid was removed after 30 s using filter paper. A thin layer remained, which was then quickly dried to form a Nafion film with an estimated thickness of 30—50 nm. After that, the carbon-coated grids with thin Nafion membranes on the surface were stained by soaking them in 0.1 mol L^{-1} mercury nitrate solutions for 15 min and then washing them with deionized water. The images were obtained using a Hitachi H7600 microscope with an acceleration voltage of 80 kV. Image J software was used for the analysis of the obtained micrographs.

Dynamic light scattering (DSL) measurements were carried out with a Malvern HPPS Laser Particle Size Analyzer (Malvern, UK)

Table 1
Mixed solvents used for preparation of Nafion solutions in this study and their solubility parameters and dielectric constants.

Mixed solvent (6/4, v/v)	Abbreviation	$\delta/(\text{cal cm}^{-3})^{1/2}$	ε
N-Methyl-2-pyrrolidone/water	NMP-aq	16.14	50.6
2-Propanol/water	2-PrOH-aq	16.44	42.38
1-Propanol/water	1-PrOH-aq	16.5	44.72
Ethanol/water	EtOH-aq	16.98	46.82
Methanol/water	MeOH-aq	18.06	50
Glycerol/water	GlyOH-aq	19.26	65