European Polymer Journal 50 (2014) 271–278

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

The role of a metal ion within Nafion upon its physical and gas transport properties

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ARTICLE INFO

Article history:
Received 11 October 2013
Received in revised form 8 November 2013
Accepted 12 November 2013
Available online 20 November 2013

Keywords:
Nafion
Ionomer
Cation interaction
Physical properties
Gas transport

ABSTRACT

The physical and transport properties of Li^+, Na^+, K^+, and Ca^{2+} neutralized Nafion were compared to its acid form. Nafion crystallinity was disrupted with a variety of cations while average *d*-spacing remained constant. Higher thermal stability in metal ion exchanged Nafion was observed using TGA. Ionic interactions were probed by DMA and spectroscopic techniques. Divalent Ca^{2+} exhibited a distinctive influence on the chain's mobility as compared to monovalent ions. The interaction strength cation exchanged Nafion decreased in the following order: $Li^+ > Ca^{2+} > Na^+ > K^+$. Gas permeability increases were primarily attributed to gas solubility. Nafion had a higher gas activation energy E_p, but its permeability was lower than unsulfonated PTFE.

1. Introduction

The perfluorosulfonic acid ionomer Nafion® developed in the 1960s by DuPont is the benchmark material for proton exchange membrane (PEM) fuel cells [1,2]. It consists of a polytetrafluoroethylene (PTFE) backbone with perfluorovinylether side chains that terminate with sulfonate groups. Tetrafluoroethylene chain segments with sufficient length tend to organize, and accordingly lead to the formation of crystalline and amorphous domains. Thus, Nafion's morphology is very complex, but it has good ion transport and physical properties [1]. Ion aggregation within it is governed by strong Columbic attractive forces, which may also inhibit chain mobility. Nafion can be developed with a variety of tailored physical and transport properties for various applications such as gas separation or desalination [3–5].

Ionomer composition is critical to its physical properties, and it may exhibit a diversity of properties when complexed with a counter-ion type. It has been found that doping a PEM with a metal cation affects selective transport and physical properties [6–10]. The relatively bulky metal ion occupies increasing space between neighboring polymer chains and impedes their mobility. For example, K^+ neutralized Nafion has lower gas diffusivity than its acid form, but higher solubility [11]. Chowdhury et al. performed a systematic investigation of cation specie effect upon gas permeability in sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (sPPO) [12]. The CO_2/CH_4 permeance ratio for divalent cations was higher than monovalent ions. Min Lee et al. [8] studied the gas transport properties through cation-exchanged sulfonated polysulfone (SPS) membranes. The SPS films exchanged with monovalent metal ions showed higher permeability coefficients than materials exchanged with multivalent.

Our previous poly(*t*-butylstyrene-*b*-ethylene-*co*-propylene-*b*-styrene-*co*-styrenesulfonate-*b*-ethylene-*co*-propylene-*b*-*t*-butyl styrene) pentablock ionomer (PBC) pentablock (PBC) ionomer study [13] discussed how divalent metal ions interact with sulfonate groups differently than monovalent. This is due to ionic cross links that are impossible with a monovalent ion. All these factors influence the functional groups chemical environment

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http://dx.doi.org/10.1016/j.eurpolymj.2013.11.011

observed as vibration mode changes using Raman scattering. Their gas transport properties were correlated with these molecular motions. For example, smaller metal ion Li^+ exchanged PBC has lower gas permeability than Na^+ and K^+. However, divalent ion Ca^{2+} exchanged PBC ionomer has lower gas permeability than a similar ion radius Na^+ exchanged film. All these studies suggest that polyvalent ions create better ionic cross-links that inhibit polymer chain motion. Based upon current literature, there are no gas transport properties studies examining Li^+ and Ca^{2+} complexed Nafion. In this work, the structure, physical, and transport properties of various cation neutralized Nafion membranes were investigated in order to create structure–property relationships.

2. Experimental

2.1. Materials

The Li^+, Na^+, K^+, and Ca^{2+} form Nafion-1035 membranes were prepared by soaking the acid-form in 1 M solutions of the appropriate hydroxide. The neutralized films were thoroughly rinsed to remove excess salts and dried in a vacuum oven at 80 °C for 24 h. All Nafion salt form films were abbreviated as Nafion-Y with Y representing the cation species.

2.2. Elemental analysis

Nafion compositional changes were investigated by elemental analysis. PHI 595 Multiprobe System equipped with an X-ray Photoelectron Spectroscopy (XPS) was used to perform an analysis. The XPS of the Multiprobe has an aluminum/magnesium twin X-ray source with pass energy of 100 eV at the anode.

2.3. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) images were collected with a FEI Tecnai Biotwin G2 Spirit Transmission Microscope using 80 kV. All samples were treated using a $BaCl_2$ solution to enhance electron density and contrast of sulfonated domains. Membrane strips with 0.5–1.0 mm width by 5.0–10.0 mm length were embedded in epoxy. Sections were cut using a Diatome diamond knife and mounted on 400 mesh Copper–Ruthenium grid.

2.4. Thermal analysis

Thermal gravimetric analysis (TGA) was performed using a TGA Q500 (TA Instruments). Samples were pretreated to remove residual water by isothermal heating at 120 °C for 20 min. Pretreated samples were heated in an inert N_2 atmosphere from 50 °C to 700 °C using a heating rate of 10 °C/min.

2.5. Raman and infrared spectroscopy

Raman spectra were obtained from a WITec alpha 500R confocal Raman spectroscopy instrument with a Nikon 100× objective. The instrument used a laser with a wavelength of 785 cm^{-1}. Data was collected using a single spectrum mode with an integration time of 10 s.

Fourier transform infrared spectra (FTIR) was measured with a Nicolet *iS* 10 spectrophotometer with a wavenumber resolution of 4 cm^{-1}. A spectrum was collected in the attenuated total reflectance (ATR) mode using a single bounce Zinc Selenide (ZnSe) crystal and a scan rate of 16.

2.6. Dynamic mechanical analysis

Glass transition temperatures were obtained using Dynamic Mechanical Analyzer Q800 (DMA, TA Instruments). Membrane samples were analyzed in the tensile mode at a frequency of 1 Hz and a heating rate of 2 °C/min over a temperature range from −90 °C to 200 °C. The tensile strain ε_t applied was 0.01%.

2.7. Wide angle X-ray diffraction

Wide-angle X-ray diffraction (WAXD) patterns were measured using an Oxford X-ray diffractometer. The distance from the sample to the X-ray source was 65 mm and the broad scattering peak is attributed to the intersegmental distance between polymer chains (*d*-space).

2.8. Gas transport properties

Various gas species with distinct molecule sizes (He, H_2, CO_2, O_2, CH_4, N_2) were utilized for measuring the gas permeability of Nafion membranes. The gas permeation system was custom-built designed to determine gas transport properties based on the time-lag method [14–16]. A circular sample was masked with aluminum tape and sealed with epoxy to prevent leaks. The gas purity used in this study was 99.99%. All experiments used a feed pressure of 4 atm and varied temperature from 30 to 90 °C.

3. Results and discussion

3.1. Electron Spectroscopy for Chemical Analysis (ESCA)

The metal ion content was determined using Electron Spectroscopy for Chemical Analysis (ESCA). The mole ratio of metal ion to sulfur (Y:S) was used to evaluate the neutralization degree of Nafion-H^+, Na^+, K^+, and Ca^{2+} summarized in Table 1. Lithium, which has a low atomic number and electron density, was not measurable by this instrument.

3.2. Morphology

The morphology of Cs^+ stained Nafion was examined using TEM. Microtomed samples were created by cutting normal or parallel to the membrane surface. TEM images

Table 1
Elemental analysis in Nafion-Y with various cation forms.

	Nafion-H^+	Nafion-Li^+	Nafion-Na^+	Nafion-K^+	Nafion-Ca^{2+}
Y:S	–	–	1.00	1.29	1.42