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Notes

Preparation of Hybrid Proton Conductor by Sol-Gel Process from Nafion Solution

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Abstract: Proton-conducting hybrid materials composed of silica and Nafion polymer were prepared from the sol-gel synthesis of silica in aqueous Nafion solution. The compositions of hybrid proton conductors were adjusted with the changing ratios of tetraethyl orthosilicate to Nafion. The thermal analysis, FTIR, SEM, and X-ray diffraction studies have proved the formation of Nafion/silica hybrid materials and no remarkable phase separation was observed, which led to an assumption that the macromolecular chain of silica and Nafion was homogeneously interlaned.

Keywords: proton conductor, Nafion, hybrid.

Introduction

Perfluorosulfonate ionomers are specifically used in several industrial applications that require an ion-conducting polymer membrane with good thermal and chemical stability. The well-known fields of their applications are the electrochemical processes and devices such as fuel cells, chlor-alkali cells, and battery separtators. Nafion, developed by E.I. du Pont, is the most widely used perfluorosulfonate ionomer. However, Nafion and Nafion-like polymers have a few drawbacks such as high cost, water dragging during operation, and low thermal stability. These defects of Nafion and Nafion-like polymers have resulted in intensive efforts to develop a low-cost solid polymer electrolyte to replace them.

One way improving the defects of Nafion is to replace it with other polymers, which requires the development of new polymers that have good proton-conducting properties and other required physical properties.[1-6] The other way is the modification of a perfluorinated ionomer film itself through irradiation of γ-ray, grafting of other monomer, or blending with other polymers.[7] Making composite of Nafion with inorganic materials is an easily approachable method for the modification of Nafion.[8-12] Ceramic powders such as silica, alumina, and zeolite are frequently used in making the composites of Nafion.

The composite of Nafion with ceramic fillers results in phase separation of membrane films, which acts usually positive to the modification as proton conductor, with increased thermal and mechanical properties as well as increased proton conductivity. The insertion of ceramic fillers into Nafion films was performed through blending of both components or catalized condensation of metal alkoxide such as tetraethyl orthosilicate (TEOS) or its analogues.[13]

In this study, we discuss the preparation of proton-conductive hybrid materials through the condensation of TEOS in the Nafion solution, which differs from the other processes using Nafion films or melts.

Experimental

Materials. 5% solution of Nafion in mixed solvents of water and methanol, TEOS, and diethoxydimethylsilane (DEDMS) were purchased from Aldrich and used without further purification.

Synthesis of Nafion/Silica Hybrid. Table I shows the weight ratios of three main ingredients which were used in the synthesis of Nafion/silica hybrid materials. Four-neck flask was equipped with an oil bath, condenser, and dropping funnels. The given amounts of TEOS, DEDMS, and Nafion solution as shown in Table I were added with 0.1 g of sodium hydroxide. The reaction was carried out for 1 hr at 120 °C. The Product was filtered and dried at vacuum.

Instrumental Analysis; FT-IR spectra were recorded with 30 scanning with resolution of 4 cm^{-1} on MAGNA-506 of NICOLS. SEM images were obtained with XA 30S FEG of Philips. TGA measurements were performed on TA 2950 of TA instruments at the heating rate of 10 °C/min under nitrogen atmosphere, starting from room temperature up to 800 °C. DSC curves were obtained at the rate of 10 °C at nitrogen atmosphere with PERKIN ELMER DSC7. XRD

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Table I. The Weight Ratios of Ingredients in the Synthesis of Nafion/Silica Hybrid Materials

Sample Code[a]	TEOS	DEDMS	Nafion
TND-0	1.0	0.0	1.0
TND-10	1.0	0.1	1.0
TND-30	1.0	0.3	1.0
TND-50	1.0	0.5	1.0
TND-100	1.0	1.0	1.0
TDN-33	1.0	0.3	0.33
TDN-52	1.0	0.3	0.52
TDN-142	1.0	0.3	1.42
TDN-200	1.0	0.3	2.00

[a] Capital alphabet T, N, and D in the sample codes denote TEOS, Nafion, and DEDMS, respectively. Numericals combined with last capital by dash denote weight percent of DEDMS (D) or Nafion (N) to TEOS. Two kinds of samples were synthesized. One is TND series that are distinguished in the amount of DEDMS and the other is TDN series that are distinguished in the amount of Nafion.

patterns were recorded with a Rigaku D/Max-IIB X-ray diffractometer.

Results and Discussion

The mixture of Nafion solution, TEOS, and DEDMS was clear and transparent, which was assumed to form homogeneous mixture. As shown in Table I, bifunctional DEDMS and tetrafunctional TEOS were used for the hydrolysis and condensation sol-gel reaction to silica. The input of bifunctional DEDMS was objected to prepare the silica containing linear and flexible poly(dimethylsiloxane) short chains. Our main interest was whether phase separation occured between the Nafion polymer and silica network, and what was the domain size if the phase separation was done. But any phenomena of phase separation were not observed with naked eye during synthesis of hybrid material from Nafion and silica.

Figure 1 and Figure 2 show FT-IR spectra of two series of samples synthesized according to Table I. The characteristic absorption peaks for the identification of Nafion and silica are as follows; The stretching and bending vibrations of dimethylsilyl group based on DEDMS appear at 2960~2970, 1260, and 850 cm^{-1} respectively. The stretching vibration of Si-O-Si bond is known to appear at 1100~ 1000 cm^{-1}. The relative intensities of these characteristic peaks increase and decrease in proportion to the amount of DEDMS and Nafion. It is deduced from these results that the impregnation of Nafion polymer chain into the network of silica occurs from homogeneous mixture of all the monomers, polymer, and solvents.

Figure 3 and Figure 4 show the curves of thermogravimetric analysis of all samples divided into two series. The increase of bifunctional DEDMS by the synthesis resulted

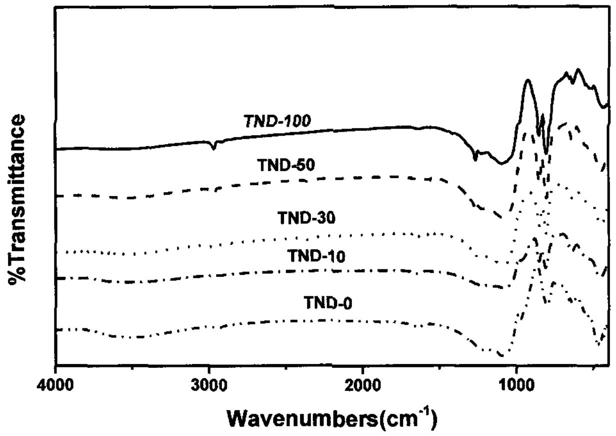

Figure 1. FT-IR spectra of samples that are synthesized with different ratio of DEDMS.

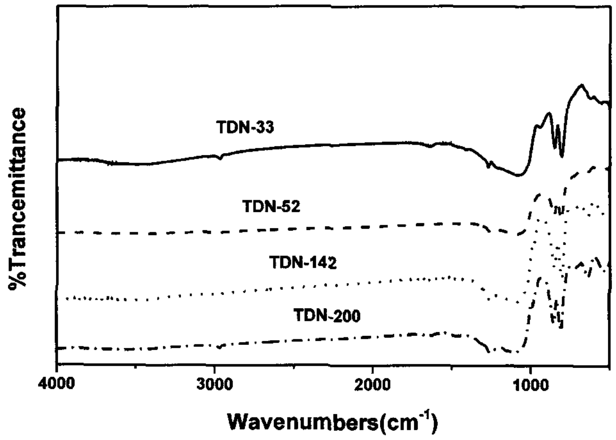

Figure 2. FT-IR spectra of samples that are synthesized with different ratio of Nafion polymer.

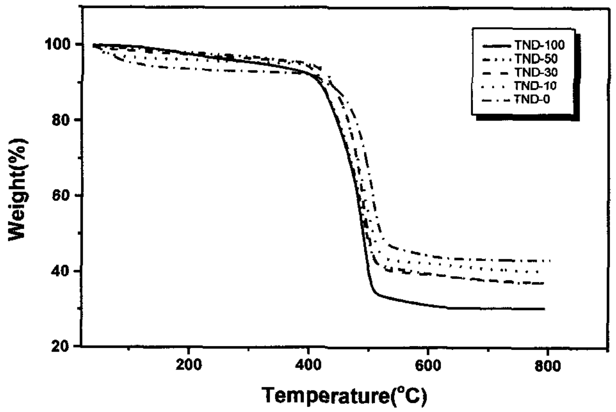

Figure 3. TGA curves of samples coded as TND-series.

in the samples that showed increased weight loss as shown in Figure 3. Similarly, the increased input of Nafion by the synthesis resulted in the samples with larger weight loss as shown in Figure 4. The curves in Figures 3 and 4 lead to the explanation that the organic chain and groups such as ethyl group of DEDMS or Nafion polymer itself cause the dominant weight loss of samples. Figure 5 and Figure 6 show DSC thermogram of samples. The measured values from DSC are summarized in Table II. The DSC thermogram of the dried Nafion from its solution was recorded in our laboratory, which was characterized to have a broad endothermal peak spreaded from 135 to 215 °C. Thus it is assumed that the endothermal peaks of Figure 5 and Figure 6 are due to the melting of Nafion domain in hybrid materials. From the analysis of TND series data on Table II, the increase of bifunctional DEDMS causes the decrease of melting point (m.p.) and ΔH of Nafion polymer. These phenomena are assumed to be resulted from two factors. One is the relatve decrease of Nafion contents in samples. The other is that the increase of DEDMS causes the expansion of interpenetrated portion of Nafion into the network of silica with weakening of polar interaction of Nafion. These phenomena were again observed in the samples of TDN series that were varied in the amount of Nafion. But the decrease of m.p. was relatively small and no trend was found in endothermal heat. These data are summarized as that the ratio of DEDMS, which determines chain density of silica, is the most critical factor for the interpenetration of Nafion polymer chains in this hybrid materials.

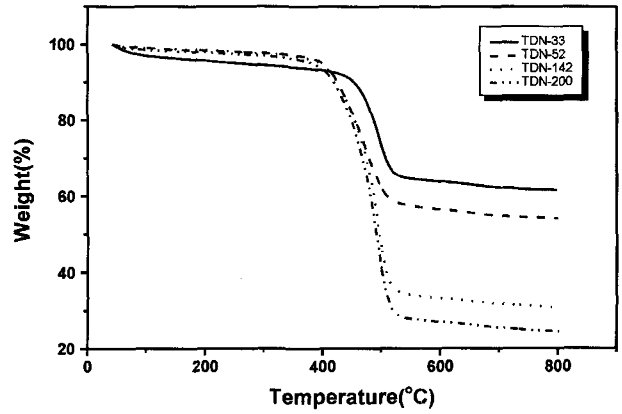

Figure 4. TGA curves of samples coded as TDN-series.

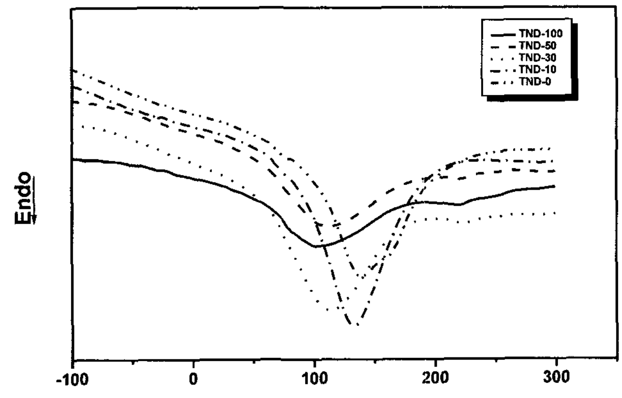

Figure 5. DSC curves of samples coded as TND-series.

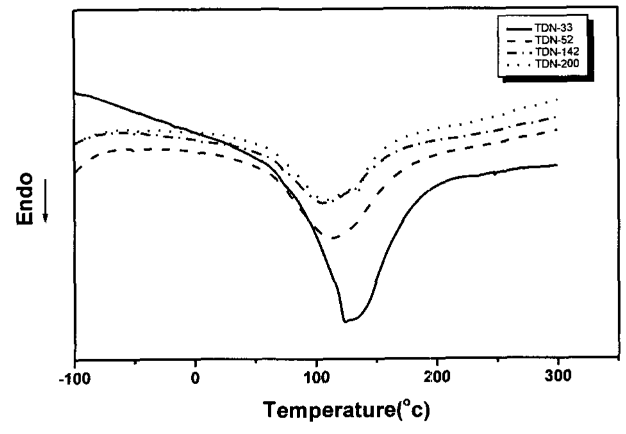

Figure 6. DSC curves of samples coded as TDN-series.

Figure 7 shows SEM image of sample TND-50 as an example. We obtained SEM images for the all samples. But we could not observe any remarkable differences from the images of nine samples. All the samples were prepared as a form of white powder and showed no remarkable differences in their appearances. Figure 8 shows a XRD pattern of sample TND-100, which indicates that there is no crystalline microdomain in powder samples.

Although diverse methods were tested, the samples could not be transformed to flexible films. The find-out of a proper binding material for hybrid powder is expected to make it possible to cast films for the measurement of proton conducting.

Table II. The Melting Temperature and Enthothermal Amount of Heat of the Synthesized Nafion/Silica Hybrid Materials

Sample Code[a]	m. p. (°C)	ΔH (J/g)
TND-0	137.8	159.5
TND-10	133.0	147.2
TND-30	111.7	114.2
TND-50	108.0	107.0
TND-100	101.6	51.3
TDN-33	120.5	110.6
TDN-52	114.8	95.4
TDN-142	108.5	102.3
TDN-200	106.6	94.4

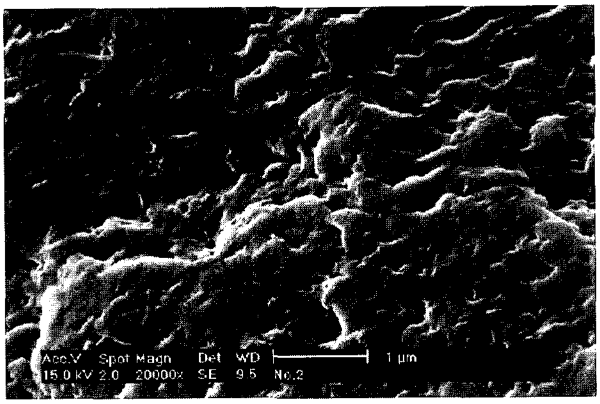

Figure 7. SEM micrograph of the powder of sample TND-50.

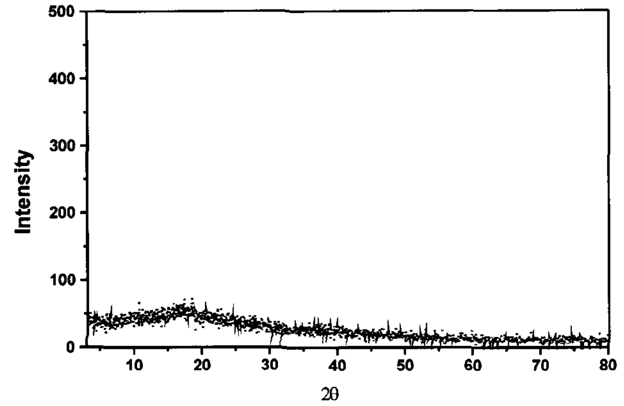

Figure 8. XRD pattern of the powder of sample TND-100.

Conclusions

The hybrid materials were prepared for the modification of physical properties of Nafion proton conductors. Sol-gel process in Nafion solution with TEOS including bifunctional DEDMS was chosen for the synthesis of hybrid materials. Through analysis of FT-IR, TGA, DSC, SEM and XRD, it is assumed that the prepared hybrid materials have well mixed or interlaned chain morphology between the silica network and Nafion. It is suggested that our method is more useful than the conventional one for the precise control of composition and morphology of hybrid or composite materials from Nafion.

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