

Grafting of styrene on to Nafion membranes using supercritical CO₂ impregnation for direct methanol fuel cells

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Received 3 November 2003; accepted 17 January 2004

Abstract

Grafting of styrene on to Nafion membranes is carried out by impregnation and radical polymerization in supercritical carbon dioxide (scCO₂) as a solvent and swelling agent. Styrene monomer and the initiator 2,2'-azoisobutyronitrile (AIBN) are first impregnated into Nafion membranes using scCO₂ at 38 °C and 25 MPa. After releasing CO₂, the polymerization is carried out at 80 °C and 10 MPa. The Nafion-grafted-polystyrene (N-g-ps) is sulfonated in concentrated sulfuric acid (98% H₂SO₄). The grafted membranes are characterized by measuring their ion-exchange capacities, ion conductivity and methanol permeation. The morphology and structure of these membranes are observed with Fourier transform infrared spectroscopy and scanning electron microscopy. The Nafion-grafted-polystyrene sulfonic acid (N-g-pssa) exhibits higher ion conductivity and lower methanol permeability than that of Nafion 115. The N-g-pssa membranes are tested as electrolytes in a direct methanol fuel cell.

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Keywords: Nafion-grafted-polystyrene sulfonic acid; Supercritical carbon dioxide; Impregnation; Direct methanol fuel cell; Ion-exchange capacity; Ion conductivity

1. Introduction

A fuel cell is an important energy-conversion system—it transforms chemical energy direct into electricity. Currently, direct methanol fuel cells (DMFCs) using methanol as a fuel are promising candidates for application in portable power sources and electric vehicles, due to the simplicity of the system and the adaptability of liquid fuel [1–3]. Despite the advantage of DMFCs, two major obstacles inhibit their commercial realization, namely, low activity catalysts and cross-over of methanol through the polymer electrolyte membrane to the cathode. Both the diffusion and the electro-osmotic drag of the methanol contribute to the latter. The methanol cross-over leads to a serious decrease in the cathode performance, and to a loss in overall fuel cell efficiency [4–9].

Recently, many efforts have been devoted to the development of polymer electrolyte membranes to reduce the material cost and to improve the power densities of fuel cells. The DMFC performance using other membranes is, however, inferior to that obtained with Nafion membranes [10].

Nafion membranes have several advantages such as good current profiles and good mechanical, chemical properties, but also have disadvantages such as temperature limitation and methanol cross-over through the membrane [11]. Modified Nafion membranes have been studied by various authors, for example, radiation-modified Nafion membranes have been obtained and characterized [12].

Supercritical carbon dioxide (scCO₂) has fast mass-transport properties during impregnation applications. Using scCO₂ as a swelling agent, it is possible to obtain polymer modifications by avoiding thermal stresses and plasticizing effects on polymers during impregnation [13]. Muth et al. [14] conducted a systematic investigation of the scCO₂-aided impregnation properties of three technically important polymers with three common vinylic monomers [14]. Liu et al. [15] reported that grafted copolymer could be prepared by free radical polymers in a swollen isotactic polypropylene (iPP) matrix with the aid of scCO₂ as a solvent for methyl methacrylate (MMA) and a swelling agent for an iPP matrix.

This study aims to improve the conductivity of Nafion membranes and to inhibit methanol permeation by the radical grafting of styrene monomer on to Nafion 115 membranes using scCO₂. In all cases, the initiator was

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azoisobutyronitrile (AIBN). The morphology and structure of grafted-Nafion membranes are determined by using Fourier transform infra-red spectroscopy (FT-IR) and scanning electron microscopy (SEM). Furthermore, the ion-exchange capacities (IEC), ion conductivity and methanol permeation are measured and compared with those of Nafion 115 membrane. The performance of the grafted membranes is examined in DMFCs using purpose-built equipment.

2. Experimental

2.1. Materials

Nafion 115 (Dupont) membranes were converted to the proton form by treating for 1 h at 80 °C in 0.5 M H₂SO₄ (98%, Aldrich). The membranes were then soaked in de-ionised water for 1 h at 80 °C in order to remove the excess acid [16]. The inhibitor in the monomer styrene (99.5%, JUNSEI) was removed before use by an alumina column and dissolved oxygen was removed through nitrogen purging. The initiator, 2,2'-azoisobutyronitrile (Aldrich), was used after recrystallization in methanol. Carbon dioxide with a purity of 99.99% was purchased from Korea Industrial Gas and used as-received.

2.2. Preparation of Nafion-grafted-polystyrene membranes

The grafting experiments were carried out in a SUS316 reactor (30 ml capacity) that was fitted with a window to allow observation of the phase change. Carbon dioxide was supplied with a gas booster pump (Maxpro Technologies Inc., Model DLE 75-1). To minimize the fluctuation from the pump and to maintain a steady feedrate, a 300-ml reservoir was used between the pump and the reactor. A schematic diagram of the impregnation and polymerization apparatus is given in Fig. 1. The Nafion 115 membranes were cut into strips (4.5 cm × 5 cm), cleaned and weighed. The membranes were then placed inside the vessel. Styrene monomer

(0.1–3 g) and AIBN (1 wt.% based on monomer) solutions were loaded in the reactor and a thermocouple was fixed. Certain amounts of CO₂ were charged into the apparatus until the desired pressure was reached. Nafion membranes were impregnated at 38 °C for 4 h. After a desired impregnation time, the fluid in the system was released. The polymerization step then was started by raising the temperature to 80 °C and was conducted at a pressure of 10 MPa for 4 h. Finally, after cooling to room temperature and total release, the samples were dried in a vacuum oven at 70 °C and reweighed. The degree of grafting was determined from the increase in weight after the grafting process, i.e.

$$\% \text{ grafting } (G) = \frac{W_t - W_0}{W_0} \times 100 \quad (1)$$

where W_0 is the initial weight of Nafion 115 and W_t is the weight of Nafion-grafted-polystyrene (N-g-ps).

After grafting reaction, the grafted membranes were sulfonated to various degrees at room temperature. Sulfonation was effected by immersing the grafted membranes for the desired time in concentrated sulfuric acid (98% H₂SO₄), which served as a mild sulfonating agent [17]. After sulfonation, the membranes were washed with de-ionised water until pH neutral, and then dried in a vacuum oven.

2.3. Membrane characterization

Infrared (IR) attenuated total reflection (ATR) spectra of the Nafion-grafted-polystyrene sulfonic acid (N-g-pssa) membranes were measured with a FT-IR spectroscope (Jasco-200). The phase and morphological characteristics of grafted membranes after impregnation and polymerization were observed by means of a field emission scanning electron microscope (FE-SEM, JSM-6700F). The surface was coated with platinum to avoid charging effects.

The IEC was obtained by titration. Pieces of N-g-pssa membrane (2.5 cm × 2.5 cm) in the proton form were held in 0.5 M KCl at 80 °C for 2 h to exchange with potassium ions. The solution was titrated with 0.05 M KOH to pH 7. The IEC was calculated from the dry mass of the membrane

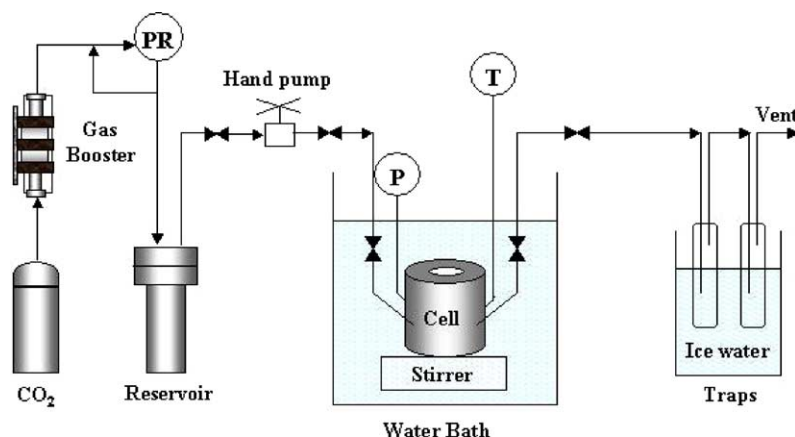


Fig. 1. Schematic diagram of impregnation and polymerization apparatus (P: pressure gauge; T: temperature gauge; PR: pressure regulator).

and the proton density in the membrane. To convert back to the proton form, the membrane was immersed overnight in 0.5 M H₂SO₄ [18].

The ion conductivity of each sample was measured at room temperature by means of ac electrochemical impedance spectroscopy (EG&G Model 273A potentiostat/galvanostat). The amplitude of the ac voltage was 10 mV. The four-probe method was used to determine the area resistance of each membrane [19]. The methanol permeability of each membrane was measured using an in-house diffusion cell at room temperature. The concentration of methanol in the permeate stream increased with time and was measured by a refractive index detector (NAR-3T, ATAGO) to calculate the methanol permeability.

2.4. Fuel cell experiments

A membrane electrode assembly (MEA) was fabricated by hot pressing the N-g-pssa with Pt black as the cathode and an Pt–Ru electrode as the anode. Compaction was achieved with a pressure of 13.8 MPa at 125 °C for 2 min. The electrode was supplied by E-TEK. The grafted membranes (N-g-pssa) were tested as electrolytes under fuel cell conditions (methanol concentration = 2 M; cell temperature = 65 °C; 2 kgf cm⁻² pressure between cathode and anode). The flow rate of O₂ was controlled by a mass-flow controller (300 ml min⁻¹).

3. Results and discussion

3.1. Grafting experiments

The impregnation and polymerization tests were conducted at 38 and 80 °C, respectively. To optimize the operation conditions, the effect of various amounts of styrene monomer on the mass gain were studied. During the grafting process, the fluid solution was homogeneous (single phase), which could be observed from the optical window at the top of the reactor. The impregnation process was conducted at 25 MPa with various amounts of monomer. The mass gain increased initially as the amount of monomer was increased, and then a steady value was reached after 0.5 g (see Fig. 2).

3.2. Infra-red spectroscopy and SEM measurement

The N-g-ps membranes were subjected to ATR-FT-IR analysis. The ATR spectra of Nafion 115 and N-g-ps membranes (0.3 g monomer concentration) are given in Fig. 3. It is clear that polystyrene has been grafted on to the Nafion membranes. The characteristic peaks in the Nafion membrane are 1202 and 1144 cm⁻¹, which represent the C–F stretching vibrations of the PTFE backbone, and 1052 and 980 cm⁻¹, which arise from the stretching vibration of SO₃⁻ and C–O–C, respectively. The existence of polystyrene in grafted membranes is verified by the decrease in the

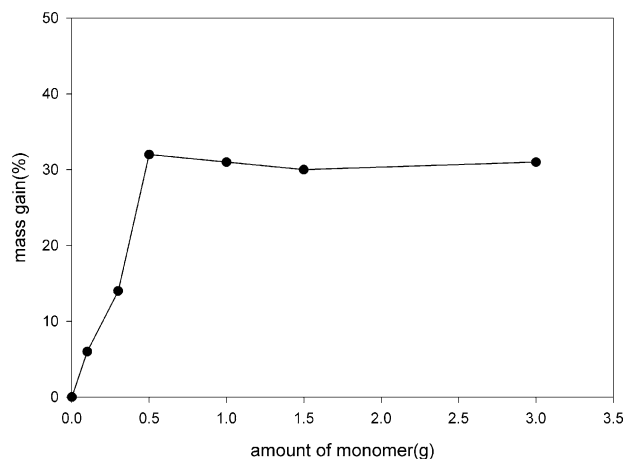


Fig. 2. Effect of various amounts of styrene monomer on mass gain.

absorbance peak for non-grafted Nafion. The absorption bands for polystyrene that appear in the regions 760 and 700 cm⁻¹ are due to aromatic C–H bonds and the out of plane benzene ring C–C bond, respectively. Also, it is notable that the peaks at 1601 and 1500 cm⁻¹ are due to aromatic C=C stretching vibrations.

The morphological changes in the surfaces of the non-grafted Nafion 115, scCO₂ processed Nafion and the N-g-ps membranes were examined by FE-SEM; the micrographs are shown in Fig. 4. When Nafion is processed by supercritical CO₂ at 38 °C and 25 MPa for 8 h, the morphology of scCO₂ processed Nafion, Fig. 4(b), is significantly different from that of non-grafted Nafion (Fig. 4(a)). The morphology of the surface of Nafion is caused by swelling and releasing of CO₂ in the reactor. The N-g-ps surface shows a markedly discrete structure (Fig. 4(c)). It is obvious that some polystyrene exists on the Nafion membranes.

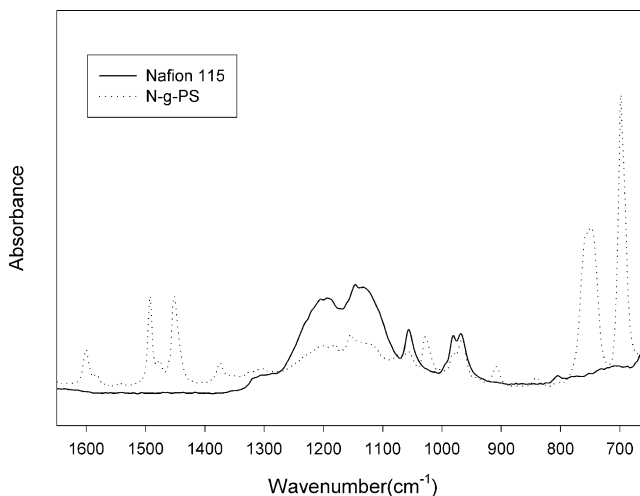


Fig. 3. IR reflectance (ATR) spectra of both Nafion 115 and N-g-ps membranes.

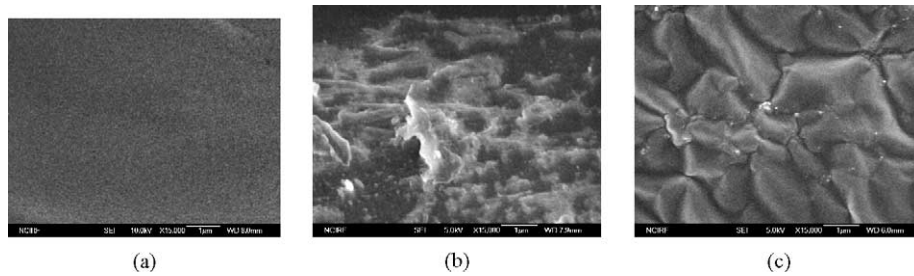


Fig. 4. Scanning electron micrographs of: (a) Nafion 115; (b) scCO_2 processed Nafion 115; (c) N-g-ps membranes.

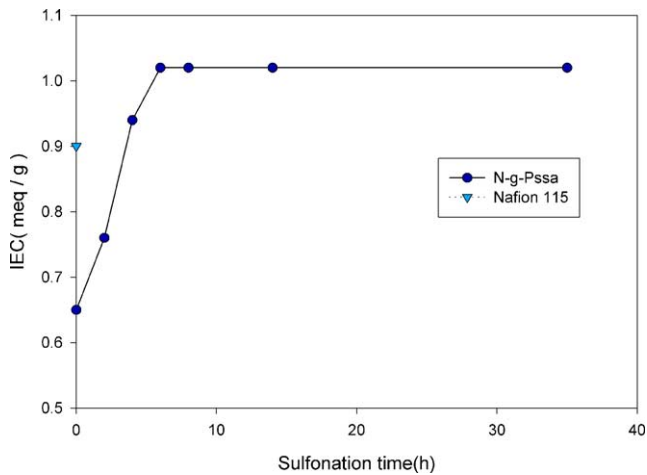


Fig. 5. Ion-exchange capacity (IEC) vs. sulfonation time with N-g-psa membranes in concentrated sulfuric acid.

3.3. IEC measurement

The effect of sulfonation time in the N-g-psa membrane on the IEC is shown in Fig. 5. Linear behavior is observed with increasing sulfonation time. An equilibrium state is reached after a sulfonation time of 6 h. The degree of sulfonation can be calculated from the ion-exchange capacity.

Table 1

Comparison of ion conductivity and methanol permeability of N-g-psa membranes at room temperature

Amount of monomer (g)	Mass gain (%)	Ion conductivity (S cm^{-1})	Methanol permeability ($\times 10^6 \text{ cm}^2 \text{ s}^{-1}$)
0.1	6	0.0407	1.41
0.3	14	0.0461	2.15
0.5	32	0.0398	3.06
Nafion 115	–	0.0385	3.29

N-g-psa has value of 1.02 meq g^{-1} . The IEC of the membranes are higher than that of Nafion 115.

3.4. Ion conductivity and methanol permeability

The change of ion conductivity as a function of monomer amount is listed in Table 1. The value of non-grafted Nafion 115 is used as a reference value and is 0.0385 S cm^{-1} . The ion conductivity increases initially with increasing mass gain when the sulfonation time is held constant. For 0.3 g of monomer, the highest ion conductivity is 0.0461 S cm^{-1} .

An increase in mass gain leads to an increase in membrane thickness, which is not favorable for increasing the ion conductivity because of increasing membrane resistance. Otherwise, increasing mass gain should enhance the IEC. The two

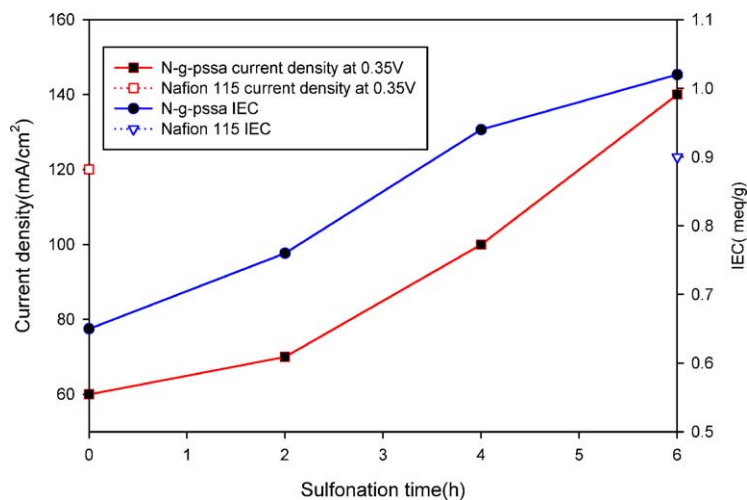


Fig. 6. Effect of IEC on cell performance with various sulfonation times.

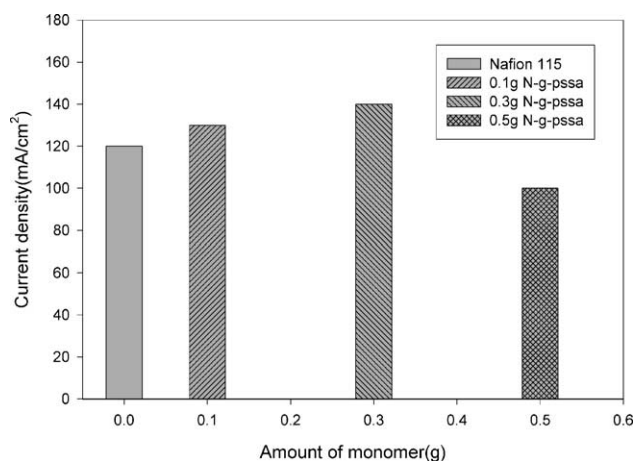


Fig. 7. Effect of various amounts of monomer in N-g-pssa membranes on performance of single-cell DMFC.

competing factors result in an optimum in the curves. The methanol permeability is shown as a function of monomer amount in Table 1. The samples used for methanol permeability measurement were N-g-ps membranes sulfonated for 6 h. The methanol permeability was determined from the equation developed by Tricoli [20]. The permeability of methanol in the Nafion 115 membrane is higher, with a value of $3.29 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, than that of a N-g-pssa membrane. The permeabilities of the N-g-pssa membranes increase with increasing mass gain, i.e. from 3.06×10^{-6} to $1.41 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. For 0.1 g of monomer, the permeability decreases by as much as 57%, from 3.29×10^{-6} to $1.41 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

3.5. Cell performance test

With increase in sulfonation time, the data in Fig. 6 show that the IEC increases. As the IEC is increased, the cell current density at 0.35 V is simultaneously increased. The effect of various amounts of monomer in N-g-pssa membranes on the performance of a single-cell DMFC is presented in Fig. 7. The three grafted membranes differ only in the amount of monomer. The 0.3 g N-g-pssa membrane gives the best cell performance at 0.35 V because this membrane probably has the highest ion conductivity and a lower methanol permeability than that of Nafion 115. Based on these results, enhanced performance of DMFCs can be obtained by increasing the ion conductivity and reducing the methanol permeability of N-g-pssa membranes using scCO_2 impregnation and polymerization. This implies that modification of Nafion membrane is an alternative way to increase cell performance. The grafted membrane system prepared in scCO_2 should provide active transport of H^+ to achieve high performance in DMFC system.

4. Conclusion

N-g-pssa proton exchange membranes have been prepared by grafting of styrene on to Nafion membranes in scCO_2 and subsequent sulfonation. The mass gain can be controlled by amount of styrene monomer in the fluid phase. Characterization and cell performance of these membranes have been undertaken. The N-g-ps has been sulfonated in concentrated sulfuric acid (98% H_2SO_4) under relatively mild sulfonation conditions. The IEC of the membranes are higher than that of Nafion 115. The morphology and structure of the membranes has been observed with FT-IR and SEM. ATR-FT-IR spectra of non-grafted Nafion and N-g-pssa confirm that styrene is indeed grafted on to Nafion. Scanning electron micrographs have allowed assessment of the effect of grafting on morphology. The N-g-pssa membranes show lower methanol permeability than that of Nafion 115. As the IEC and ion conductivity are increased, the cell performance is simultaneously increased. Enhanced cell performance of DMFCs can be obtained with N-g-pssa membranes using scCO_2 impregnation and polymerization.

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