Photo-Cross-Linking of Sulfonated Styrene−Ethylene−Butylene Copolymer Membranes for Fuel Cells

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Polystyrene−ethylene−butylene sulfonate copolymer membranes (PSEBS) were photochemically cross-linked using benzophenone as the photo-initiator. Benzophenone decomposed by first-order kinetics during the cross-linking process. The cross-linked PSEBS had lower water swelling, lower proton conductivity, and higher chemical stability than un-cross-linked PSEBS. The cross-linking process did not change the ion exchange capacity (IEC); the sulfonic acid groups were stable during the UV photo-cross-linking process. The photo-cross-linked PSEBS membranes degraded more slowly during fuel cell operation than non-cross-linked membranes. A layered membrane with PSEBS sandwiched between thin Nafion layers degraded at almost the same rate as PSEBS membranes. Nafion layer contacted with electrodes cannot prevent membrane from degradation during the fuel cell operation; degradation reaction carried out all through the membrane between cathode and anode.

Introduction

Polymer electrolyte membranes fuel cells (PEMFCs) are being developed for transportation and residential applications because of their high energy conversion efficiency, zero pollution emission, and low operation temperature.[1−3] Nafion (produced by DuPont), a perfluorosulfonic acid polymer, is the most widely used proton conductor in the PEMFCs due to its high ionic conductivity, good thermal stability, high chemical stability, and good mechanical strength.[3,4] However, its high price (presently, \$800/m^2 for ∼100 μm thick membranes)[5] and the difficulty of its disposal has led to the investigation of low-cost, environmentally friendly, nonperfluorinated ionomer membranes. Some of the polymer electrolytes investigated to date, include polysulfonated triflurostyrene,[6] polyether ether ketone (PEEK),[7,8] poly(arylene ether sulfone) (PSU),[9−11] PVDF-graft styrene,[12−14] acid-doped polybenzimidazole (PBI),[15,16] and polyphosphazene.[17,18] The ideal fuel cell membranes should have low cost (less than \$10/kW in a PEMFC), high chemical stability, high mechanical strength, and high conductivity. No material has yet to satisfy all the desired specifications.

Polystyrene−ethylene−butylene sulfonate (PSEBS) is a copolymer of styrene−ethylene−butylene with the aromatic rings being sulfonated. Membranes of PSEBS are inexpensive, and their conductivity can be easy changed through varying the degree of sulfonation. However, PSEBS has limited chemical stability and swells substantially with water absorption. PSEBS membranes lose mechanical strength when swollen with water. Cross-linking may be used to increase the mechanical strength and to decrease the swelling of fuel cell membranes. The sulfonation may be carried out pre-
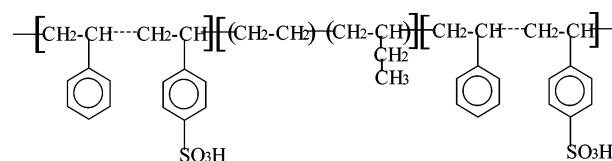

Figure 1. Structure of Dais polymer electrolyte. The polymer is a block copolymer of blocks of polystyrene and then blocks of ethylene/butylenes. A portion of the phenyl rings is sulfonated.

or post-cross-linking. Post-sulfonation is done by first cross-linking a polymer membrane and then exposing the cross-linked membrane to a sulfonation agent.[19−22] The sulfonation is slow and not uniform across the membranes because the sulfuric acid penetrates the hydrophobic membranes slowly. Pre-sulfonation exposes a membrane to a sulfonation agent, and then the cross-linking is done after sulfonation. In this case, the cross-linking usually take place between the sulfonic acid groups on different molecules,[10] resulting in a decrease of conductivity.

Recently, Graves and Pintauro cross-linked poly-[(alkylphenoxy) (phenoxy) phosphazene] films under UV(365 nm) radiation using benzophenone as the photoinitiator.[23] In the present paper, this method was successfully used to cross-link PSEBS membranes. The cross-linked PSEBS had lower water swelling, lower proton conductivity, and greater chemical stability than un-cross-linked PSEBS. The cross-linking process did not change the ion exchange capacity (IEC) of the membranes. Nafion layers placed between the electrodes and PSEBS membranes did not prevent membrane from degradation during the fuel cell operation.

Experimental Section

Poly(styrene−ethylene−butylene) sulfonate (Figure 1) was obtained as a solution in a mixture of propanol, dichloroethane, and THF from Dais-Analytic Co. The molecular weight of the polymer and the monomer stoichiometry were proprietary. The ion exchange capacity (IEC) was 1.50 mmol/g. Nafion solution with equivalent weight 1100 g/mol of SO$_3$ was obtained from Ion Power (LIQUION 1100, 5% solution). 2-Propanol was purchased from Fisher Chemicals.

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The membranes were recast from alcohol solutions of polystyrene−ethylene−butylene sulfonate. The membrane recasting setup consists of three parts: a cylindrical glass tube (6.35 cm diameter), a glass plate, and a level adjustment. The ends of wall on the glass tube were carefully polished flat. When the cylindrical tube was place on the glass plate and liquid is introduced into the cylinder, it does not leak out. The level of the glass plate was adjusted to make the membrane thickness uniform.

To prepare membranes suitable for cross-linking, benzophenone to a desired concentration was added into the PSEBS solution from Dais. The solution was diluted with 2-propanol to ∼6 wt % PSEBS, stirred for several minutes, and transferred into the membrane casting setup. The level of the glass plate was adjusted carefully; membrane thicknesses were uniform to ±2 μm. The solvents were evaporated at 50−60 °C in a drying oven. After the solvent completely evaporated, the membranes were annealed at 135 °C in Ar for 15 min. The membranes irradiated with a UV lamp (365 nm, 556 mW/cm^2) in Ar atmosphere at room temperature (25 °C). After 12 h of irradiation, the membranes were turned over and irradiated on from the other side for 12 h. After irradiation was complete, the membranes were soaked in 1 M H_2SO_4 for 24 h and then washed thoroughly with DI H_2O to remove any metallic ion impurities. The same procedures were used to cast un-cross-linked PSEBS membranes except no benzophenone was added and the membranes were not exposed to UV irradiation.

For Nafion-PSEBS layered membranes, 10 μm Nafion membranes were cast from Nafion solution from Ion Power as described elsewhere.[24] The dry PSEBS membrane was placed between two dry 10 μm Nafion membranes. The sandwich structure was pressed between Teflon plates at 100 °C and 50 MPa for 2 min.

The kinetics of the structure change of PSEBS during cross-linking was followed by FTIR. A benzophenone-containing PSEBS film of ∼10 μm thickness was cast on a sodium chloride plate from the PSEBS solution containing a known amount of benzophenone. After air-drying for several hours, the film was irradiated with a UV lamp (365 nm, 556 mW/cm^2) in an Ar atmosphere at room temperature (25 °C). During the irradiation, the sample was removed from UV light source periodically, and FTIR spectra were recorded using a Nicolet 730 FT-IR spectrometer.

The conductivity measurements were performed in a controlled environment bomb using a two-probe method with a Princeton Applied Research potentiostat/galvanostat model 273A and Princeton Applied Research lock-in amplifier model 5210. The desired humidity was reached by injecting a certain amount of water into a container holding the sample at controlled temperature and measuring the water vapor pressure.[25] The IEC of membranes was obtained by titration.[10]

Membranes ∼3 cm × 3 cm × 100 μm thick were vacuum-dried at ∼80 °C for 3 h and then weighed, and the length was measured. The membranes were then placed in liquid H_2O for 10 h at 25 °C, the external water was wiped off, the samples were weighed, and the length was measured. The water uptake and linear swelling were recorded for the membranes contacted with liquid water.

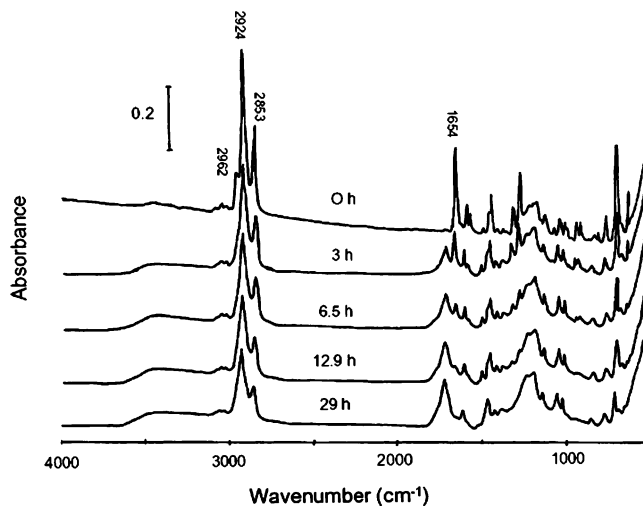Membrane electrode assemblies (MEA) were prepared with commercial E-TEK electrode (0.4 mg/cm^2 Pt load-

Figure 2. FT-IR spectra of benzophenone-containing PSEBS during photo-cross-linking process. The 1654 cm^{-1} peak is the benzophenone's C=O stretch vibration. The 2924 cm^{-1} and 2853 cm^{-1} peaks are the C−H stretching vibration of CH_2. The 2962 cm^{-1} peak is the C−H stretching vibration of CH_3. The broad peak at 3700∼3200 cm^{-1} is the OH stretching peak.

ing carbon cloth). The 5 cm^2 electrodes were made by impregnating 0.6 mg of Nafion /cm^2 into the E-TEK electrodes and then pressing electrodes onto both sides of the membrane at 135 °C and 20 MPa for 1 min. The MEAs were tested in a Globltech fuel cell test station. Pure H_2 was fed to the anode at 100 mL/min. Either 100 mL/min O_2 or 250 mL/min air was fed to the cathode. The flow rates are much greater than the stoichiometric, so the gas phase compositions at the anode and cathode are nearly uniform. The humidity of the feed gases was fixed by bubbling the gas streams through bottles of water at controlled temperature. Our standard test conditions were with the fuel cell at 80 °C, the anode humidification bottle was at 88 °C, and the cathode humidification bottle was at 86 °C. The feed humidification was estimated to be ∼80−90% relative humidity (RH) at 80 °C. After the fuel cell had reached stable conditions, cyclic voltammograms were done at a sweep rate of 100 mV/S and in the range of 0.1−1 V versus hydrogen electrode for 1 h. Once the CVs were reproducible, the cell potential versus current−potential data was obtained with an electronic load.

Membrane lifetime was tested by operating the fuel cell at a controlled potential of 0.6 V for various periods of times. Polarization curves were subsequently obtained to estimate the change in membrane resistance.

Results and Analysis

Cross-Linking/FT-IR Experimental Results. FT-IR spectra recorded as a function of irradiation time are shown in Figure 2. The 1654 cm^{-1} peak is the C=O stretch vibration for benzophenone. The decomposition rate of benzophenone was determined by plotting the log absorbance (ln[A_{1654}]) as a function of irradiation time, as shown in Figure 3; the first-order rate constant of photodecomposition was ∼0.25 h^{-1}.

The 2924 and 2853 cm^{-1} peaks are the CH_2 asymmetric stretch and the symmetric stretch, respectively. The 2962 cm^{-1} peak is the CH_3 asymmetric stretch. It is obvious that the 2924 cm^{-1} (CH_2) peaks got smaller with irradiation time. The CH_2 peaks were de-convoluted by fitting the spectra with Gaussian peaks. The
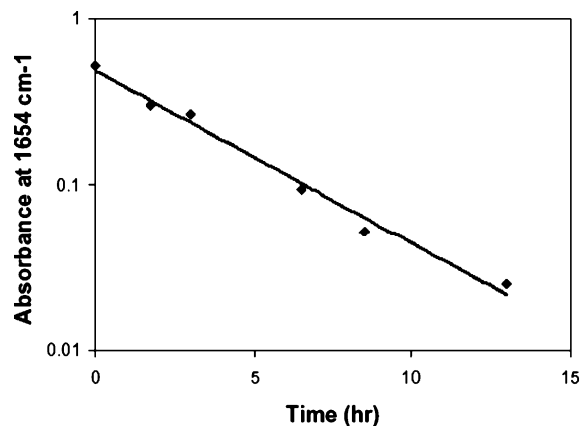
Figure 3. Depletion of benzophenone with time. The absorbance of the carbonyl stretch of benzophenone at 1654 cm^{-1} as a function of irradiation time. The data fit is $A(t) = A(0)e^{-0.25t}$.

Table 1. Relative Peak Area of CH$_2$ FT-IT Absorption

	normalized peaks area				
irradiation time	0 h	3.0 h	6.5 h	13.0 h	29.0 h
2924 cm^{-1} (CH$_2$)	1.0	0.62	0.6	0.53	0.46

area of each Gaussian was determined as a function of irradiation time; the peak areas for CH$_2$ relative to their initial area are shown in Table 1. The area of CH$_2$ peaks decreased with time, indicating the CH$_2$ groups participated in the cross-linking process. Because the intensity of the CH stretch associated with the styrene was too weak relative to the CH$_2$ stretches, it was not possible to show if the CH group was involved with the cross-linking reaction during the cross-linking process. But it is suspected that the CH groups also reacted as they are expected to be chemically more reactive than the CH$_2$ groups. A board peak in the range of 3700−3200 cm^{-1} emerged during the cross-linking reaction indicating formation of OH groups from the benzophenone. On the basis of the FT-IR results, a possible sequence of chemical reactions of the cross-linking process is shown in Figure 4.

Physical−Chemical Characteristics of the Membranes. The physical−chemical characteristics of the membranes are shown in Table 2, and for comparison, the properties of Nafion 115 are also included. The water uptake and swelling of the cross-linked PSEBS was lower than that of PSEBS. The water swelling of both PSEBS membranes were greater than Nafion 115. The IEC of PSEBS was reduced by cross-linking. However, the IEC of PSEBS membranes based on the density of sulfonic acid groups was the same before and after cross-linking, indicating that the sulfonic acid group was stable during the UV photo-cross-linking process. Cross-linking reduced the ion conductivity and
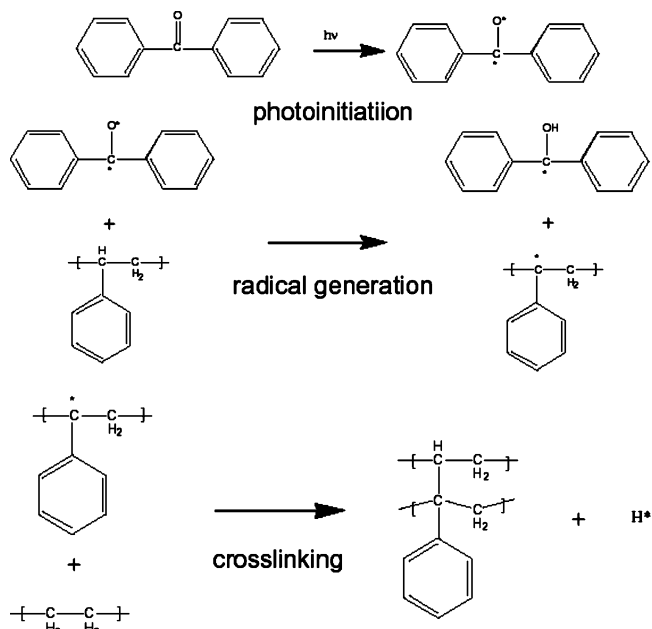

Figure 4. Chemical reactions of PSEBS photo-cross-linking using benzonphenone as initiator. The process starts with photoexcitation of the benzophenone to generate radicals. The radicals take a tertiary or secondary hydrogen atom from the polymer chain, making a radical center on the polymer. The radicals attack another polymer chain forming a cross-link.

swelling. The cross-linking may have resulted in less and smaller hydrophilic channels for water absorption and proton mobility. The conductivity of PSEBS was twice that of Nafion 115, approximately scaling with the IEC.

Fuel Cell Performances of Membranes. Polarization curves were taken as a function of time on line to characterize the stability of the membranes in use. Figures 5 and 6 show the polarization curves for PSEBS membranes without and with cross-linking. The power density loss at 1 A/cm^2 due to the MEA resistance of the non-cross-linked PSEBS membrane increased from 0.27 to 0.47 W/cm^2 over 55 h of operation, while the power density loss at 1 A/cm^2 due to the MEA resistance of the cross-linked PSEBS membrane was 0.32 W/cm^2, a little bit higher than that of non-cross-linked PSEBS membrane, but only increased to 0.40 W/cm^2 after 85 h on-line.

To reduce the rate of membrane degradation at the electrode−membrane interface, a thin perfluorosulfonic layer of Nafion was introduced between the electrode and the PSEBS membrane. Nafion-layered membranes were made by pressing 10 μm Nafion membrane on both sides of PSEBS membranes. The fuel cell performance of a layered membrane is shown in Figure 7. The

Table 2. Characterization of the Membranes

membranes	PSEBS	PSEBS-CL 5.6%[a]	PSEBS-CL 10.2%[b]	Nafion 115
ion exchange capacity, IEC (mequiv/g)	1.50	1.40	1.35	0.91
	Water Swelling (in Liquid Water)			
linear expansion, %	41.2	32.9	32	13.3
H$_2$O take up, wt %	213	140	140	22
	Conductivity, at 100% RH (S cm^{-1})			
60 °C	0.280	0.221	0.235	
80 °C	0.304	0.252	0.262	0.142
100 °C	0.320	0.255	0.267	0.154
120 °C	0.303	0.243	0.264	0.166

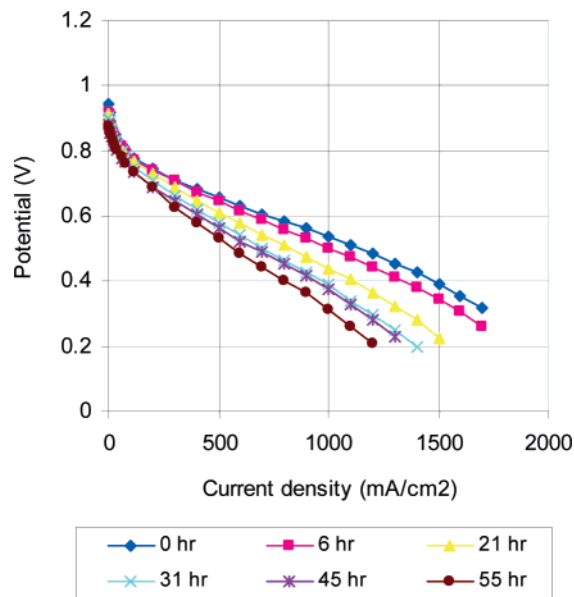[a] The benzophenone in the PSEBS is 5.6 wt %. [b] The benzophenone in the PSEBS is 10.2 wt %.

Figure 5. Performance of a fuel cell over time with a PSEBS membrane. Membrane thickness: 90 μm, anode: 88 °C, cell: 80 °C, cathode: 86 °C, total P = 1 atm, H$_2$/O$_2$.

Figure 7. Performance of fuel cell over time with a PSEBS membrane sandwiched between Nafion. Membrane: Nafion/PSEBS/Nafion (10/90/10 μm, anode: 88 °C, cell: 80 °C, cathode: 86 °C, total P = 1 atm, H$_2$/O$_2$.

Figure 6. Performance of fuel cell over time with a cross-linked PSEBS (PSEBS-CL 5.6%) membrane. Thickness: 90 μm, anode: 88 °C, cell: 80 °C, cathode: 86 °C, total P = 1 atm, H$_2$/O$_2$.

Figure 8. Cell potential changes with time at 600 mA/cm^2 for different membranes (88/80/86 °C, total P = 1 atm, H$_2$/O$_2$).

performance of Nafion-layered membranes shows that the stability of Nafion-layered membranes was about the same as membranes without the Nafion protective layer. The stability of different membrane preparation is shown more clearly in Figure 8 where the cell voltage is shown as a function of time with the current maintained at 600 mA/cm^2. The voltage decline precipitously over 100 h for the non-cross-linked PSEBS membrane and the Nafion/PSEBS-layered membrane. In contrast, the cell voltage decayed by only ∼10% over 300 h with the cross-linked membranes.

A frequent assumption is that degradation of membranes in fuel cells occurs at the interface surface between the electrodes and membranes.[26,27] The results reported here show little effect of having a protective layer at the membrane−electrode interface, which suggests that degradation of PEMFC membranes occurs
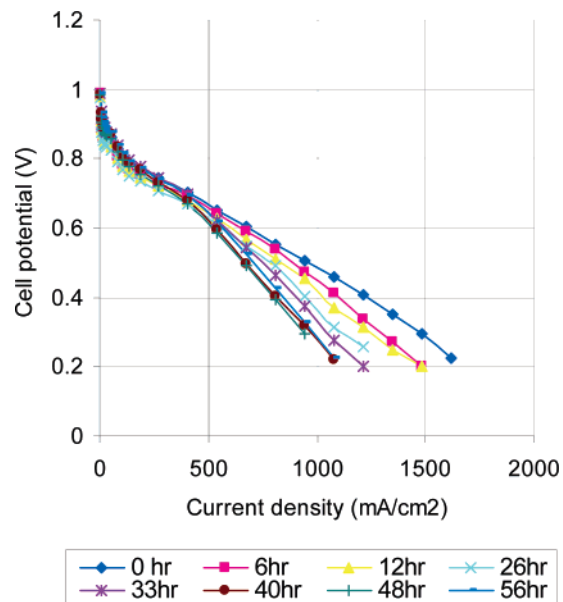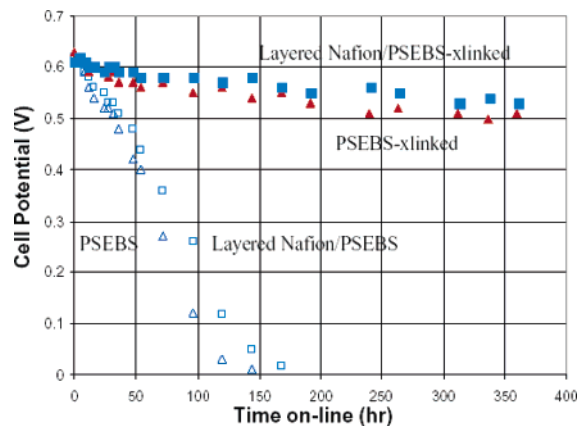
throughout the membranes and is not limited to the membrane−electrode interface.

The reduction of oxygen at the cathode may occur with the formation of free radicals, which could attack the polymer chains and degrade the performance of fuel cell. The accepted view is that the polystyrene structure can be attacked at the α-C forming stable tertiary radicals.[28] Cross-linking removes the most reactive centers in the PSEBS and reduces mobility in the polymer matrix. Both of these may contribute to the improved performance stability of the cross-linked PSEBS membrane in the fuel cell.

Conclusions

PSEBS membranes were successfully cross-linked through photoreaction using benzophenone as a photoinitiator. The benzophenone reacted by first-order kinetics during the cross-linking process. The cross-link takes place between CH$_2$ and CH groups in PSEBS membranes. The photo-cross-linked PSEBS are much more stable than PSEBS membranes during fuel cell operation. After cross-linking, the PSEBS conductivity was reduced, while the IEC kept constant, indicating

that the sulfonic acid group is stable during UV cross-linking process. Nafion layers between the membrane and the electrodes cannot prevent membrane from degradation during the fuel cell operation; the degradation reaction carries out all through the membrane between cathode and anode.

Acknowledgment

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