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Improvement of chemical stability of polymer electrolyte fuel cell membranes by grafting of new substituted styrene monomers into ETFE films

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Polymer electrolyte membrane is the most important component of the polymer electrolyte membrane fuel cell (PEMFC). The membrane acts as a separator to prevent mixing of the reactant gases and as an electrolyte for transporting protons from the anode to the cathode [1]. Long-term fuel cell performance is mainly governed by the stability of the polymer electrolyte membranes. The most generally acceptable and widely used membrane is the Nafion® membrane, which has excellent properties in terms of thermal and chemical stability, proton conduction and mechanical strength. Today, the operational stability of Nafion® membrane in a PEMFC as reported by Osaka Gas Co. Ltd., Japan has exceeded 20,000 hr, which is close to the requirements of actual applications [2]. However, the high cost and environmental inadaptability have limited its commercial application. The new polymer electrolyte fuel cell membranes under development include the sulfonated hydrocarbon membrane [3], organic/inorganic hybrid membrane [4], and the radiation-grafted membrane [5, 6]. However, the chemical stability of these membranes has not yet reached the satisfactory level for the commercial use [6].

Due to the low fabrication cost, high proton conductivity and satisfactory dimensional stability, the radiation-grafted membrane may be the most promising material for the PEMFC applications [3–10]. Generally, the radiation-grafted membrane has a special chemical structure, composed of fluorinated main chain and sulfonated side chains. The former acts as a stable backbone that gives the necessary strength, dimensional stability, and gas barrier while the latter gives the ability of proton transportation. Binary monomers of styrene/divinylbenzene (DVB), where the DVB is used as a crosslinker, have been the most widely used grafts for the side chains. The best performance of these membranes was reported to be stable over several thousands of hours in a working fuel cell [7]. Even then, the lifetimes of these membranes are not long enough for a commercial application [8]. The main challenge in this field is how to improve the membrane durability.

It has been reported that the lower durability comes from the degradation of the styrene/DVB-grafted polymer electrolyte membrane, due to the lower chemical stability of the sulfonated side chains in the oxidant environment of the fuel cell [9]. Therefore, the strategy in our development of the radiation-grafted membrane is to find alternatives to replace the styrene monomer. On the other hand, grafting of a substituted styrene monomer is a well known approach to improve the stability of radiation-grafted membranes. For example, Momose *et al.* reported grafting of trifluorostyrene into polystyrene and poly (ethylene-co-tetrafluoroethylene) (ETFE) films, respectively [10, 11]. The grafted films were converted to polymer electrolyte membranes by sulfonation, and their chemical stability was evaluated.

In this study, we grafted two new substituted styrenic monomers, *p*-methylstyrene (MeSt), *p*-*tert*-butylstyrene (*t*BuSt) into ETFE film with and without the DVB crosslinker, and sulfonated the grafted ETFE films to prepare a new polymer electrolyte fuel cell membrane. For the actual application in fuel cell, we focused our attention on the improvement of chemical stability of the new membranes.

The MeSt and *t*BuSt monomers, and DVB crosslinker (Aldrich) were used without further treatment. The 0.2 M chlorosulfonic acid (Wako Chemical Co., Japan) solution in 1,2-dichloroethane was prepared for the sulfonation reaction. The base polymer ETFE (Asahi Glass Co., Japan) in the form of a 50 μm thick film was washed with acetone to remove any impurity on its surface before use.

The ETFE-based radiation-grafted membranes were synthesized by a process based on γ-ray pre-irradiation, subsequent grafting and sulfonation procedure. The pre-irradiation dose was 15 kGy, performed in the argon atmo-

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sphere at room temperature with a dose rate of 15 kGy/h. The pre-irradiated films were grafted in the monomer solution at 50 °C under argon atmosphere. The DVB content was 5% of the total monomers, and the weight of *t*BuSt was equal to that of the MeSt in the MeSt/*t*BuSt mixture monomers. The degree of grafting was calculated as $(W_g\text{-}W_0)/W_0 \times 100$, where W_g and W_0 are the film weights before and after the grafting reaction, respectively. The grafted film was sulfonated in the chlorosulfonic acid solution at 60 °C for 8 hr and followed by hydrolyzing in water at 80 °C for 12 hr. The proton conductivity of the water-saturated polymer electrolyte membrane at room temperature was measured by impedance spectroscopy using a Solartron 1269 analyzer with an AC perturbation of 10 mV.

In a working PEMFC, the polymer membrane in a higher acidic environment faces stringent conditions such as high temperature, oxidation and, reduction reactions, and the by-product of hydroxyl radicals [12]. Therefore, the high chemical stability of the polymer electrolyte membrane was required for a long-term PEMFC. However, testing polymer electrolyte membrane lifetimes in actual fuel cells is both time-consuming and expensive. Thus, it is desirable to develop rapid and simple methods for evaluating the new candidate membranes. In this study, an accelerated testing of the chemical stability of candidate membranes was carried out using a 3% H_2O_2 aqueous solution, by measuring the weight and conductivity changes of the membrane.

Fig. 1 shows the weight change of the *t*BuSt-grafted (grafting, 56%) membrane in the H_2O_2 solution. For comparison, the weight changes of MeSt-grafted (grafting, 53%) and MeSt/DVB-grafted (grafting, 52%) membranes are also plotted. As shown in Fig. 1, it was found that the membranes were continuously swelling and then quickly decomposed. The durability time, which is defined as the lasting time till the weight loss gets started in 3% H_2O_2 solution, were 36, 78, and 116 hr for the MeSt, MeSt/DVB, and *t*BuSt-grafted membranes, respectively. The MeSt/DVB-grafted membrane showed much longer durability time than that of the MeSt-grafted one. It was due to the crosslinking structure in the former membrane introduced by the DVB crosslinker. However, it should be noted that the *t*BuSt-grafted membrane even without the crosslinking structure showed the longest durability time of 116 hr, until then, the durability times in our studies were always less than 100 hr. It may be due to the large hydrophobic groups of *tert*-butyl substituted into the benzene rings.

The *t*BuSt-grafted membrane possessing significantly high chemical stability gives us a new direction to further explore its feasibility as a high performance membrane. Different degrees of grafting of the *t*BuSt-grafted membranes were synthesized and the proton conductivities were determined. However, as shown in Fig. 2, the initial result showed that the proton conductivity of the *t*BuSt-grafted membrane was considerably lower than that of the MeSt/DVB-grafted one. For instance, the proton conductivity of the *t*BuSt-grafted membrane at a high degree of grafting of 77% was only 0.03 S/cm. In addition, the highly grafted membrane was considerably brittle. On the other hand, in the acceptable flexibility region with the degree of grafting of about 38%, the conductivity was less than 0.015 S/cm, which was too low for the fuel cell applications.

Based on the findings of the high conductivity of the MeSt-grafted membrane and the high chemical stability of the *t*BuSt-grafted membrane, we designed a composite grafting structure of MeSt/*t*BuSt to graft into the ETFE films. In addition, DVB crosslinker was added to further improve the chemical stability. Both the MeSt/*t*BuSt and MeSt/*t*BuSt/DVB were successfully grafted into the ETFE films up to a high degree of grafting of 70%. The proton conductivities of the corresponding membranes are also shown in Fig. 2. We found that the conductivity of the

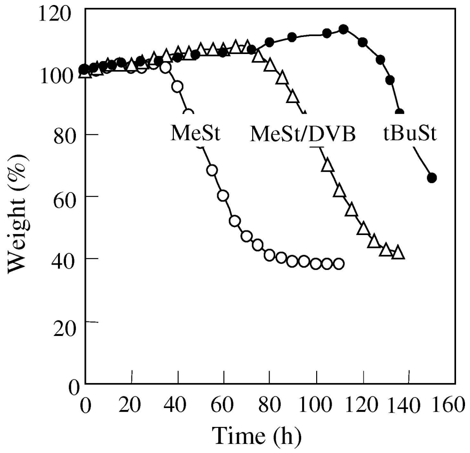

Figure 1 Chemical stability of the MeSt, MeSt/DVB and *t*BuSt-grafted membranes in the 3% H_2O_2 aqueous solution at 60 °C. The degrees of grafting of these membranes were 53%, 52%, and 56%, respectively.

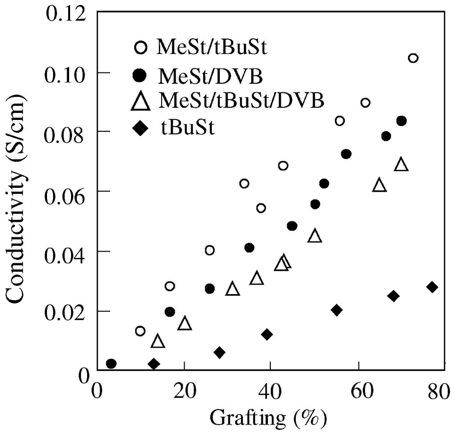

Figure 2 Proton conductivity of the MeSt/*t*BuSt, MeSt/DVB, MeSt/*t*BuSt/DVB, and *t*BuSt-grafted membranes plotted as a function of the degrees of grafting.

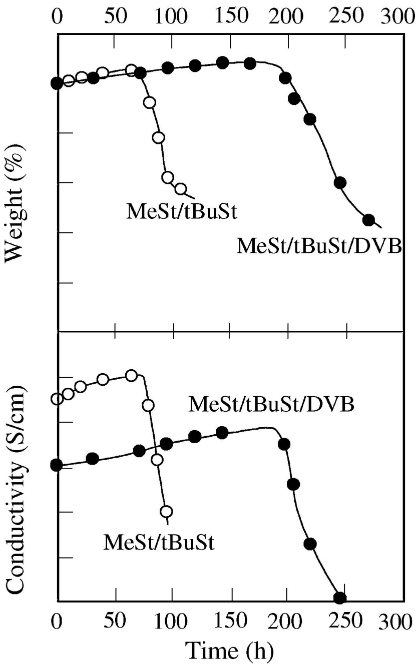

Figure 3 Chemical stability of the MeSt/*t*BuSt and *t*BuSt/DVB-grafted membranes in the 3% H_2O_2 aqueous solution at 60 °C. The degrees of grafting of the two membranes were 52% and 55%, respectively.

MeSt/*t*BuSt-grafted membrane distinctly increased from the single *t*BuSt-grafted one, and it was even higher than that of the MeSt/DVB-grafted one. At a degree of grafting of 38%, the conductivity of the MeSt/*t*BuSt-grafted membrane was 0.06 S/cm, which reached the same level as of the Nafion® membrane. With induced DVB crosslinking structure, the conductivity of the MeSt/*t*BuSt/DVB was not as high as that of uncrosslinked MeSt/*t*BuSt-grafted membrane, it may be caused due to the lower water absorbance of the crosslinked structure [3, 4]. Even though, at a degree of grafting of 36%, the conductivity of the MeSt/*t*BuSt/DVB-grafted membrane can still reach 0.037 S/cm, which is at the level of the Gore-Select® membrane determined under the same conditions. In addition, the MeSt/*t*BuSt/DVB-grafted membrane was relatively flexible even with a high degree of grafting of 65%, it gives a high possibility of being used as a fuel cell membrane.

The chemical stabilities of the *t*BuSt/MeSt and *t*BuSt/MeSt/DVB-grafted polymer electrolyte fuel cell membranes are shown in Fig. 3. The degrees of grafting of the two membranes are 52% and 55%, respectively. The weighing of the membranes and the measuring of the proton conductivity were simultaneously conducted. The weight and conductivity versus time are plotted in Fig. 3a and 3b, respectively. It was found that the durability time of the *t*BuSt/MeSt-grafted membrane was about 65 hr, which was shorter than that of the *t*BuSt-grafted membrane (116 hr) but longer than that of the MeSt-grafted membrane (36 hr). On the other hand, introducing the crosslinking structure into the membrane by DVB crosslinker, the durability time significantly increased. As shown in Fig. 3, the MeSt/*t*BuSt/DVB-grafted membrane showed a significantly long durability time of about 200 hr, about three times higher than that of the traditional styrene/DVB-grafted membrane. For reference, the traditional styrene/DVB-grafted membrane was reported to have a durability time of about 70 hr in a 3% H_2O_2 solution at 60 °C [13], and it can work in a H_2/O_2 fuel cell at 60–80 °C for several thousands of hours [7].

Both the weight and conductivity of the polymer electrolyte membranes showed an increase in the H_2O_2 solution before the weight loss. The weight increase was about 7% while the conductivity increase was about 15%. This may be due to the initial scission of the graft chains, especially the crosslink bonds, resulting in the membrane more swollen. The final weight and the dimensions of the tested membrane returned to the values of the original non-grafted ETFE film. It indicates that the weight loss is due to the graft chain and the sulfonic acid group leaving the ETFE substrate. From the analysis of the residual H_2O_2 solution, no free sulfuric acid could be found, indicating that the membrane decomposition in H_2O_2 solution was due to the C-C scission of the graft chain [9]. The *tert*-butyl on the *t*BuSt modifies the benzene ring electronic structure and increases the membrane hydrophobicity. The former increased the stability of the α-hydrogen, while the latter defended the hydrophilic ·OH radical to attack the α-hydrogen. Therefore, the *t*BuSt-grafted membrane showed much better durability than the styrene and MeSt-grafted one.

In conclusion, MeSt/*t*BuSt/DVB-grafted polymer electrolyte membrane showed a high performance for the fuel cell applications. The *t*BuSt contributed to a high chemical stability while the MeSt contributed to a high conductivity to the resulting membrane. The DVB crosslinker in the membrane further improved the chemical stability. The new polymer electrolyte membrane with a degree of grafting of 36% showed proton conductivity as high as that of the Gore-Select® membrane, and the durability time was about three times longer than that of the traditional styrene/DVB-grafted one. Therefore, the MeSt/*t*BuSt/DVB-grafted polymer electrolyte membrane was more possible to be used for the fuel cells.

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