



# Effect of the addition of hydrated titanium oxide on proton conductivity for aromatic polymer electrolyte membrane



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## ABSTRACT

To improve the proton conductivities of a polymer electrolyte membrane which is composed of multi-block copolymers, in low humidity conditions, the effect of adding hydrated titanium oxide into a membrane was investigated. Membranes containing hydrated titanium oxide were prepared by using tetraethoxy titanium. Membranes containing hydrated titanium oxide showed higher proton conductivity than the membrane not containing the additives regardless of humidity. This result showed that adding hydrated titanium oxide improved proton conductivity. By contrast, all the polymer electrolyte membranes showed almost the same water content rate. The content rates of hydrated titanium oxide in membranes were lower than 3 wt%. Thus, adding hydrated titanium oxide was not considered to affect the water content rate of membranes. This result showed that proton conductivity was improved by adding hydrated titanium oxide without increasing water content rate. From the scanning transmission electron microscope observation, micro-phase-separated structures were observed clearly in membranes containing hydrated titanium oxide. It seemed that hydrated titanium oxide enhanced the hydrophilic segments aggregation during the film-forming process. Probably, the well-defined hydrophilic domains functioned as proton paths and enhanced the proton conductivity of the membrane.

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## 1. Introduction

Polymer electrolyte fuel cells (PEFCs) are clean and highly efficient energy conversion systems that are anticipated for use in alternative portable, automotive, and stationary power sources [1–3]. Membrane electrode assembly (MEA) is a main component of PEFC, and it is composed of a polymer electrolyte membrane (PEM) sandwiched between an anode and a cathode. Perfluorosulfonic acid (PFSA) membranes are commonly used because of their high proton conductivity and chemical stability. Aromatic polymer electrolyte membranes have also been widely studied for PEM [4–16]. For example, sulfonated polyether sulfone (S-PES), sulfonated polyether ether ketone (S-PEEK), sulfonated polyphenylene (S-PP), and sulfonated polyimide (S-PI) have been investigated because these materials show good thermal stability and

mechanical strength. Recently, the number of peripheral equipment such as humidifiers needs to be decreased to reduce the production cost of the PEFC system. PEMs should be used in low humidity conditions for the PEFC system. Therefore, PEMs should be developed that show high proton conductivity in low humidity. Although proton conductivity is increased by increasing the ion exchange capacity of the PEM, the water content rate is also increased and the mechanical characteristics worsen. To improve proton conductivity of the PEM, many researchers have studied PEMs that have micro-phase-separated structures [12,13,15,16]. They reported that micro-phase-separated structures were formed in a PEM composed of a multi-block copolymer. Additionally, these PEMs had higher proton conductivities than PEMs composed of random copolymers. Hydrophilic domains are considered to function as a proton path, which improves the proton conductivity, and thus, the micro-structure of PEMs needs to be controlled to improve the proton conductivity of the PEM. Micro-structures of PEMs are affected by not only block length of the multi-block copolymer but also the film-forming method [13,17]. It is considered that the factors that affect proton conductivity of the PEM, such as the film-forming method, must be controlled to obtain the PEM that

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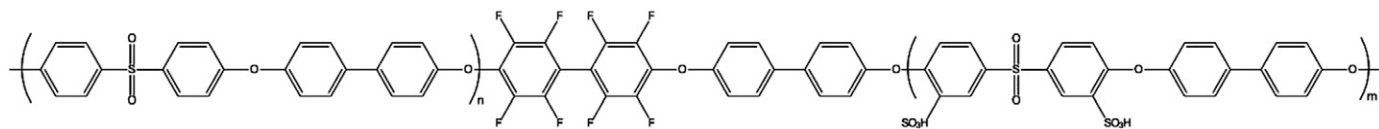


Fig. 1. Chemical structures of the copolymer.

shows high proton conductivity. One method that controls the micro-structure of PEM is to add additives during the film-forming process.

Moreover, putting additives into a PEM is considered to effectively improve the proton conductivities of PEMs. Many researchers have studied PEMs containing metal oxides that have hygroscopic properties. Hagihara et al. and Uchida et al. prepared PEMs containing TiO<sub>2</sub> and SiO<sub>2</sub>, respectively [18,19]. Some other reports have investigated aromatic polymer electrolyte membranes containing additives [20–22]. These PEMs are composed of random copolymers and zirconium oxide, phosphated zirconia, and heteropoly acid used as additives. However, there have been few reports about additive-containing PEMs that are composed of a multi-block copolymer.

In this study, the effect of adding hydrated titanium oxide into PEMs composed of multi-block copolymers was investigated in order to improve proton conductivities in low humidity conditions. Tetraethoxy titanium (TET) was used as a precursor of hydrated titanium oxide. The effect of the addition of tetraethoxy titanium on the micro-structures of PEM was also investigated.

## 2. Experimental

### 2.1. Preparation of polymer electrolyte membranes

The molecular structure of the copolymer is shown in Fig. 1. Multi-block copolymer based on poly(arylene ether sulfone) was synthesized in a process similar to the one described in the literature [11]. At first, hydrophilic and hydrophobic segments were synthesized. Multi-block copolymer was copolymerized by hydrophilic and hydrophobic segments. Table 1 lists descriptions of the copolymer used in this study. The molecular weights of the hydrophobic segments and copolymer were evaluated using gel permeation chromatography with a polystyrene standard. The molecular weight of hydrophilic segment was measured before hydrophilic and hydrophobic segments were combined.

Hydrated titanium oxide was obtained using a hydrolysis reaction of tetraethoxy titanium which is described in the literature [23]. PEMs' preparation processes are shown in Fig. 2. The PEM without additives was obtained by process 1 (Fig. 2(a)), in which the polymer was dissolved in N-Methyl-2-pyrrolidone (NMP) and its varnish was obtained. PEMs with additives were obtained by processes 2 and 3 (Fig. 2(b) and (c)). In process 2 (Fig. 2(b)), 10 wt% tetraethoxy titanium solution, which was diluted with ethanol, was mixed with NMP, and their mixed solution was obtained. The polymer was dissolved in the mixed solution, and its varnish was obtained. In process 3 (Fig. 2(c)), multi-block copolymer was first dipped in 10 wt% TET solution for 1 h. After multi-block copolymer was separated from TET solution and was washed with ethanol, multi-block copolymer with additive was obtained. Then, the polymer was dried and mixed with NMP, and varnish was obtained.

After varnish was obtained, all PEMs were prepared using the same process. The varnish was first cast on glass substrates with an applicator

and dried at 90 °C for 20 min. Second, the PEMs were dried at 200 °C for 2 h. Third, the obtained membranes were removed from glass substrates and washed with deionized water. Fourth, membranes were dipped in 1 mol/L NaOH for 30 min and washed with deionized water. Fifth, membranes were dried at 120 °C for 5 h again. Finally, membranes were acidified with 1 mol/L H<sub>2</sub>SO<sub>4</sub> for 1 h and then washed with deionized water, and PEMs were obtained (Table 2).

To evaluate the crystal structure, hydrated titanium oxide powder was synthesized using the same process for preparing PEMs. In this process, 10 wt% TET solution was first mixed with deionized water. Second, the solution was dried at 90 °C for 20 min. Third, the obtained powder was dried at 200 °C for 2 h and washed with deionized water. Fourth, the powder was dipped in 1 mol/L NaOH for 30 min and washed with deionized water. Fifth, the powder was dried at 120 °C for 5 h again. Finally, the powder was acidified with 1 mol/L H<sub>2</sub>SO<sub>4</sub> for 1 h and washed with deionized water.

### 2.2. Characterization of PEMs and hydrated titanium oxide powder

Content rates of hydrated titanium oxide in PEMs were analyzed using a thermo gravimetric analyzer (TG, EXSTER TG/DTA6200, Seiko Instruments Inc.). In this process, PEMs were heated to 500 °C, polymer in the PEM was burned, and the weight of residual solid was measured. The content rate of titanium oxide (C) was calculated as:

$$C = W_{\text{res}}/W_{\text{dry1}} \times 100 [\%] \dots (1)$$

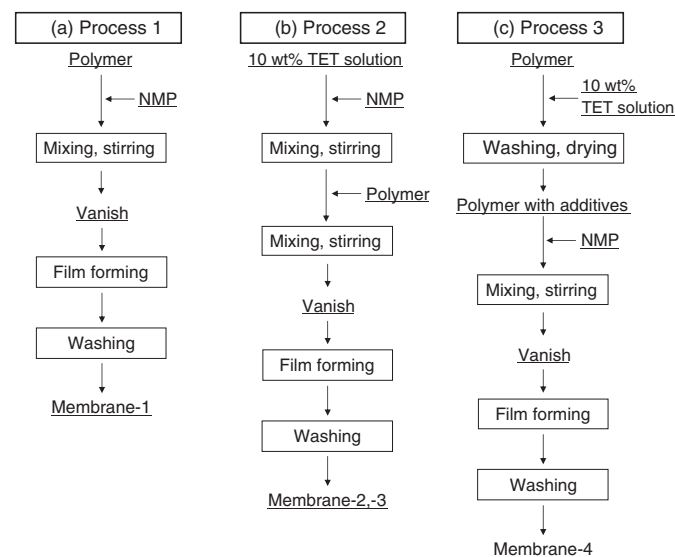


Fig. 2. Forming processes of membranes.

Table 1  
Characteristics of the copolymer.

Type of polymer	Hydrophobic segment		Copolymer		IEC (meq/g)
	$Mn \times 10^4$	$Mw / Mn$	$Mn \times 10^4$	$Mw / Mn$	
Multi-block	0.5	1.8	6.3	3.2	2.2

Table 2  
Film forming conditions of membranes.

Membrane	Type of polymer	Process	Content rate of added TET calculated as TiO <sub>2</sub> (wt%)
Membrane-1	Multi-block	1	0
Membrane-2	Multi-block	2	1.3
Membrane-3	Multi-block	2	2.6
Membrane-4	Multi-block	3	-

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