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Membrane modification by liquid phase deposition using small amount of TiO_2 for high-temperature operation of polymer electrolyte fuel cells

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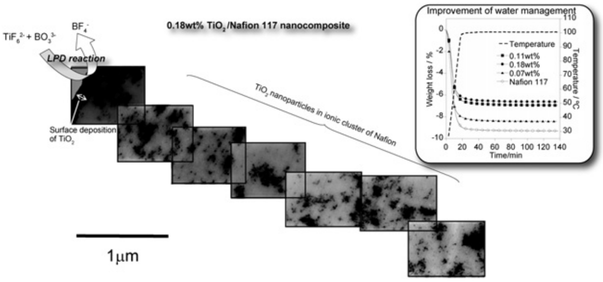
HIGHLIGHTS

- ► We prepared TiO_2-dispersed Nafion membrane by the liquid phase deposition method.
- ► Such membrane can improve the water management by existing hydrophilic filler.
- ► The amount of loading TiO_2 is much lower than previous reports.
- ► Water management was much improved after deposition despite the amount was so low.
- ► This material can contribute to PEFCs operating at high temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

A TiO_2-dispersed Nafion (Nafion–TiO_2) membrane is prepared by the liquid phase deposition (LPD) method by carrying out a hydrolysis reaction of titanium–fluoro complex in an aqueous solution. The conductivity of the TiO_2-modified membrane is studied. The obtained composite membrane has dispersed TiO_2 nanoparticles which enhance the membrane's hydrophilic and hygroscopic properties of polymer electrolyte fuel cells (PEFCs) under high temperature conditions. Change in the amount of TiO_2 deposited on the Nafion membrane from 0.07 to 0.18 wt% for LPD reaction periods ranging from 3 to 9 h does not result in any change in the membrane's ion-exchange capacities. High resolution transmission electron microscopy (HRTEM) images indicate the growth and agglomeration of TiO_2 particles at the surface during the LPD reaction. The diffusion of TiO_2 is observed in the membrane from its surface up to a depth of ca. 20 μm by means of XPS measurement. The water retention capacity of the membrane is improved from 63% to 83% at 200 °C by the deposition of 0.18 wt% of TiO_2. Consequently, we find the small amount of TiO_2 improved water management and increase the proton conductivity.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) are considered to be promising candidates for clean and efficient power generation. However, several factors; such as cost, reliability, and durability pose major challenges in the commercialization of PEFCs [1]. The core component of PEFCs is the polymeric membrane that functions as a charge carrier for protons, a separator for the reactant gases, and an electronic insulator that prevents electrons from passing through [2]. Perfluorinated sulfonic acid (PFSA) polymers such as Nafion (from DuPont) are the most commonly employed electrolyte membranes for PEFCs operating in ambient temperatures of less than 80 °C; Nafion exhibits good chemical stability, high mechanical strength, and high proton conductivity under well-humidified conditions [3,4]. However, it is known that PEFCs operating at temperatures higher than 100 °C offer significant advantages such

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as reduced CO poisoning at the anode, increased energy efficiency, improved heat rejection, improved quality of waste heat, and easy water management control [5,6]. In order to achieve good performance at high temperatures, the PFSA membranes need to be fully wet because proton conduction in the membrane relies on the dissociation of protons from the sulfonic acid groups (SO_3H) in the presence of water. Cell operation at temperatures around 100 °C causes dehydration of the PFSA membranes, thereby resulting in a rapid loss of conductivity and leading to degraded cell performance. Therefore, it is necessary to develop a proton exchange membrane for high-temperature fuel cell applications. Many studies have focused on the development of such membranes. A number of these researches have dealt with the modification of PFSA membranes in order to meet the operational requirements of high-temperature fuel cells. Hybrid Nafion-inorganic oxide electrolytes belong to this category [7]. The preparation of organic–inorganic membranes by incorporating hygroscopic metal oxide particles such as TiO_2 [7–11], ZrO_2 [7,8], SiO_2 [8–13], and other such materials [7,14–16] into membrane resin is considered one of the most effective approaches to ensure a certain relative humidity (RH) in cells operating at temperatures above 100 °C. In such electrolytes, the contribution of ceramic nanoparticles to increased PEFC performance at high temperature is frequently attributed to both the enhanced water retention and improved transport properties of the electrolyte. The most common technique in the modification of a PFSA membrane by incorporation of inorganic oxides is the use of the in-situ sol–gel method; this method results in higher water retention. This technique consists of complex procedures such as the use of an organic solvent, hydration, and heating [8,10–13]. While several researchers have focused on the water retention capabilities of the membrane, very few have considered focusing on the quantity and distribution of inorganic fillers throughout the inner region of the membrane. These inorganic fillers may affect the membrane's intrinsic properties to a certain extent and lead to a reduction in the proton conductivity and mechanical strength of the membrane. The quantity of inorganic fillers used in previous studies has been in the range of 2.5–25 wt% [7–15], and it has been found that, for a fixed level of water content, the proton conductivity in the membrane depends on the quantity of inorganic filler used. Therefore, the filler content should be reduced to a minimum level in order to maintain the ionic conductivity.

In order to improve these abovementioned properties of the PFSA membrane, we fabricated a TiO_2-dispersed Nafion membrane with high hydrophilic and hygroscopic properties using the liquid phase deposition (LPD) method. It is well-known that the LPD method is the one of the available soft solution processes for the preparation of metal oxides and/or thin films with large surface area and complex morphology [17,18]. TiO_2 thin films can be prepared by a simple and ambient process that involves the following two reactions, therefore hydrolysis of metal-fluorocomplex (1) and reaction of fluorine scavenging (2) [18];

$$TiF_6{}^{2-} + 2H_2O \leftrightarrow TiO_2 + 6F^- + 4H^+ \quad (1)$$

$$H_3BO_3 + 3H^+ + 4F^- \rightarrow BF_4{}^- + 3H_2O \quad (2)$$

In this reaction process, the metal oxide species (TiO_2) infiltrate into the nano-sized spaces in the electrolyte. The reaction solution can penetrate the micro or nanopores in various kinds of substrate materials and on the surface of each pore. Deki et al. have developed such a deposition process by means of the liquid phase infiltration method using nano-ordered templates such as 2D arrays or trench structures prepared by deep reactive ion etching (RIE) [19,20], inverse opal structures using 3D colloidal crystals [21], nano-ordered oxide species using inverse micelles [22], the addition of aqueous polymer solution [23], and on-site synthesis using solid fluorine scavenger [24]. In such cases, the LPD method realized the deposition on the soft matter surface including polymer substrate. Additionally, the LPD method has been applied for fabrication of organic–inorganic composite materials [25].

In this study, the TiO_2 nanoparticles are embedded in the vicinity of the membrane surface. Such a unique incorporation state is thought to be important because the membrane is required to maintain its intrinsic properties such as conductivity and ion exchange capacity, especially at the inner region. Therefore, the oxide amount in the membrane is reduced by the deposition of the metal oxide (by the LPD process) in limited spaces such as the ion-channel structure. Further, we have attempted to improve water management in the process without changing the membrane's intrinsic properties (such as ion exchange capacity and proton conductivity) with LPD process.

2. Experimental

2.1. Samples

As a substrate matrix polymer, Nafion® 117 (DuPont) was pretreated by immersion and stirring in mixed aqueous solution of 1.0 mol dm^{-3} HNO_3 and 1.6 mol dm^{-3} H_2O_2 at 70 °C for 1 h. Afterward the membrane was washed using distilled water at 70 °C for 1 h. Subsequently, this pretreatment procedure was done twice. The pretreated Nafion membrane was cut into 20 mm × 20 mm for LPD reaction.

For preparation of the parent solutions for the LPD reactions, $(NH_4)_2TiF_6$ (Morita Chemical Industries Co. Ltd.) and H_3BO_3 (Nacalai Tesuque Inc.) were dissolved and diluted in deionized distilled water purified by Advantec GSH-200 to give concentrations of 0.5 mol dm^{-3}. Aqueous H_3BO_3 solution was added to aqueous $(NH_4)_2TiF_6$ solution for the LPD reaction. The final concentrations of $(NH_4)_2TiF_6$ and H_3BO_3 in reaction solution were 0.1 mol dm^{-3} and 0.2 mol dm^{-3}, respectively.

For the preparation of TiO_2-dispersed Nafion, a piece of Nafion® 117 membrane was immersed in 20 ml of the reaction solution at 30 °C. Reaction periods ranged from 3 to 9 h. Each prepared membrane was thoroughly washed by ion-exchange water and dried in a vacuum oven at 100 °C for 6 h.

2.2. Quantitative analysis of ionic species

We employed inductive coupled plasma atomic emission spectrometry (ICP-AES; Horiba Ultima 2000) for quantitative analysis of ionic species in reaction solution. The membrane was immersed into 1.0 mol dm^{-3} HCl solution. After all cationic species eluted in the HCl solution, the amount of dispersed TiO_2 in the membrane was measured by ICP.

A neutralization titration was carried out in order to determine the ion-exchange capacity of the membrane. Since ammonium ions were remained in Nafion membrane after LPD reaction using $(NH_4)_2TiF_6$, the membranes were immersed in 0.1 mol dm^{-3} citric acid aqueous solution for 12 h to ion-exchange into proton for normalization three times. The H^+ form membrane was immersed in 2.0 mol dm^{-3} NaCl (Nacalai Tesuque Inc.) and 0.01 mol dm^{-3} NaOH aqueous solution titrated with phenolphthalein.

2.3. Observation of deposited TiO_2

Distribution and elemental analysis of dispersed TiO_2 in Nafion were observed by cross-sectional SEM imaging and elemental