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Graft-type polymer electrolyte membranes based on poly(ether ether ketone)/nanosilica hybrid films for fuel cell applications

Takashi Hamada, Hideyuki Fukasawa, Shin Hasegawa, Atsumi Miyashita, Yasunari Maekawa*

Department of Advanced Functional Materials Research, Takasaki Advanced Radiation Research Institute, Quantum Beam Science Research Directorate, National Institutes for Quantum and Radiological Science and Technology (QST), 1233 Watanuki, Takasaki, Gunma 370-1292, Japan

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ABSTRACT

The effect of nanosilica addition on the ionic conductivity, water uptake, and mechanical properties of poly(styrenesulfonic acid)-grafted poly(ether ether ketone) polymer electrolyte membranes (PEEK-PEMs) were investigated using silica-containing PEEK-PEMs (PEM-Si1, -Si3, and -Si5) prepared by radiation-induced graft polymerization to nanosilica (1, 3, and 5 wt%)-dispersed PEEK films (PEEK-Si1, -Si3, and -Si5). PEEK-Si3 and -Si5 exhibited 10%–50% higher grafting degrees (GDs) compared with those of a silica-free PEEK film. PEM-Si3 and -Si5 showed similar and slightly higher water uptakes in the lower- and higher-relative-humidity (RH) ranges compared with that of the silica-free PEMs. Under the fully humidified condition at 80 °C, PEM-Si3 exhibited the highest tensile strength (TS) (16.4 MPa), which is 1.27 and 1.64 times greater than those of the silica-free PEM and Nafion 212. The membrane electrode assembly (MEA) prepared from PEM-Si3 with an IEC of 3.30 mmol/g showed a maximum power density of 612 mW/cm² under 30% RH, which was 7% higher than that of the silica-free PEM-based MEA. On the basis of the aforementioned results, we concluded that (1) nanosilica was introduced into both hydrophilic (ion channel) and hydrophobic (matrix PEEK) phases in the PEMs; (2) nanosilica in the hydrophilic phase exhibits greater water absorption tendency but not greater water retention character, under high- and low-RH conditions, respectively; and (3) nanosilica in the hydrophobic phase increases the mechanical properties of silica-containing PEMs.

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Introduction

Polymer electrolyte fuel cells (PEFCs) can produce electricity via the reactions of hydrogen and oxygen, producing only water without CO₂ emission; they have therefore attracted

attention for use in next-generation energy applications such as fuel cell vehicles and stationary cogeneration systems to replace fossil-fuel resources [1]. A polymer electrolyte membrane (PEM) is one of the key components for PEFCs because its ionic resistance directly determines the power generation

* Corresponding author. Fax: +81 27 346 9385.

E-mail address: maekawa.yasunari@qst.go.jp (Y. Maekawa).

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efficiency [2,3]. Thus far, sulfonated perfluoropolymers such as Nafion™ have been predominantly used as PEMs. However, these materials raise several critical problems such as high fuel crossover and a maximum operating temperature of 80 °C [4–6].

PEMs are required to exhibit high proton conductivity and good mechanical properties under both low- and high-relative-humidity (RH) conditions because these properties control the power generation efficiency and durability under extreme operating conditions in fuel cell systems. Recently, we reported the RH dependence of the electrochemical and mechanical properties of poly(styrenesulfonic acid)-grafted poly(ethylene-co-tetrafluoroethylene) polymer electrolyte membranes (ETFE-PEMs) [7–10] and poly(styrenesulfonic acid)-grafted poly(ether ether ketone) (PEEK-PEM) [11–15] with a wide range of ion-exchange capacities (IECs). Unlike the proton conductivity of conventional PEMs, those of ETFE-PEMs and PEEK-PEMs exhibit less RH dependence. In particular, PEEK-PEM with high IECs exhibited similar conductivity even at 30% RH and a 1.4 times greater tensile strength (TS) under 100% RH at 80 °C compared with those of Nafion 212. Thus, PEEK-PEMs have the potential to solve the trade-off relationship between conductivity and mechanical properties and thus have potential applications as alternatives to Nafion.

Recently, the incorporation of inorganic fillers into a polymer matrix has attracted attention because the inorganic fillers can improve the proton conductivity, mechanical property and water-retention property, which is defined as water uptake at dry condition, of the polymer [16–31]. Among the investigated inorganic filler materials, silica nanoparticles have been extensively studied because of their low cost and ease of handling. Furthermore, silica nanoparticles have hydrophilic silanol groups on their surface; thus, hybrid membranes with silica nanoparticles might exhibit enhanced water retention even under low-RH conditions. Therefore, we anticipate that the introduction of silica nanoparticles into PEEK-PEMs would further improve the proton conductivities under low-RH conditions and the mechanical properties under high-RH conditions. To the best of our knowledge, the literature contains no reports of hybrid films of graft-type PEMs having high crystallinity and silica nanoparticles.

In this study, the effects of hydrophilic and amorphous nanosilica addition on the ionic conductivity, water uptake, and mechanical properties of PEEK-PEMs with high proton conductivities and high tensile strength (TS) under low- and high-humidity conditions were investigated using silica-containing PEMs prepared by radiation-induced graft polymerization to PEEK films containing 1, 3, and 5 wt% dispersed nanosilica (PEEK-Si1, -Si3, and -Si5, respectively). Moreover, the fuel cell performance of the nanosilica-containing PEMs was characterized and compared with that of silica-free PEMs.

Experimental

Materials

Silica-containing PEEK substrates (PEEK-Si1, -Si3, and -Si5) consisting of a PEEK (Victrex, Japan) and 1, 3, and 5 wt% dispersed nanosilicas with a diameter of 12 nm (NIPPON

AEROSIL Co. Ltd.) with a film thickness of 15 μm were provided by IHI Co. Ltd. These substrates were prepared by extrusion of the molten PEEK containing nanosilicas with a diameter of 12 nm, followed by uniaxial stretching. Ethyl 4-styrenesulfonate (ETSS) was purchased from Tosoh Co., Japan and was used as received. Divinylbenzene (DVB) (technical grade, 80%) was purchased from Sigma–Aldrich Co., Japan and was used without further purification. 1,4-dioxane was purchased from Wako Pure Chemical Industries Ltd. and was dried over molecular sieves before use. Other solvents were purchased from Wako Pure Chemical Industries Ltd. and were used as received. Analytical-grade sodium chloride (NaCl), sodium hydroxide (NaOH), and hydrochloric acid were purchased from Wako Pure Chemical Industries Ltd. Pure water was obtained from a Millipore Milli-Q UV system. Nafion 212 obtained from DuPont was pretreated by being boiled for 1 h in a 3% H₂O₂ solution, washed in hot pure water for 1 h, boiled for 1 h in 1 M H₂SO₄, and finally rinsed in hot water again for 1 h. Nafion perfluorinated ion-exchange resin and a 20 wt% solution of lower aliphatic alcohols/H₂O mixture were purchased from Sigma–Aldrich Co., Japan and were used without further purification. Pt/C catalyst was purchased from Tanaka Kikinzoku Kogyo Ltd., Japan.

Preparation of silica-containing PEMs

PEEK-Si1, -Si3, and -Si5 were added to a dried Schlenk tube, respectively. After the air was removed and the tube was purged with argon, a solution of DVB/1,4-dioxane (25 vol%) was added to this Schlenk tube under an argon atmosphere. The tube was then heated in a water bath at 50 °C for 24 h. The obtained films were washed with 1,4-dioxane and immersed in 1,4-dioxane at 50 °C for 12 h to remove residual monomers. The obtained films were dried in vacuum at 40 °C for 24 h.

The DVB-containing PEEK film in a Schlenk tube was irradiated with ⁶⁰Co γ-rays at a dose rate of 10 kGy/h for 16 h under an argon atmosphere at room temperature. A 50% (vol/vol) solution of ETSS and 1,4-dioxane, after being degassed and purged with argon, was added to the Schlenk tube. The resulting mixture was heated at 80 °C under an argon atmosphere for 6–46 h. The grafted silica-containing PEEK films were removed, washed several times with acetone, and soaked in acetone again for 12 h to remove residual ETSS and free polymers on the film surfaces. The obtained films were dried under vacuum at 40 °C for 24 h. The hydrolysis of ethyl ester was conducted in distilled water at 95 °C for 24 h to obtain poly(styrenesulfonic acid)-grafted PEEK-Si1, -Si3, and -Si5 (PEM-Si1, -Si3, and -Si5). Silica-free PEMs were prepared from the PEEK substrates, which were prepared by the same uniaxial stretching method used for PEEK-Si1, -Si3, and -Si5.

Electrolyte properties of the silica-containing PEMs

The amounts of DVB incorporated into the nanosilica-containing PEEK substrates were determined by TG analysis according to the following equation.

$$\text{The amount of DVB (\%)} = \frac{(1 - x/100)W_{\text{DVB}} - W_0}{W_0} \times 100 \quad (1)$$

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