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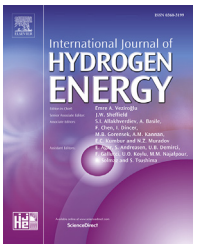

Application of graft-type poly(ether ether ketone)-based polymer electrolyte membranes to electrochemical devices – Fuel cells and electrolytic enrichment of tritium

Atsuko Fukaya [a,*], *Akira Tateno* [b], *Nobuaki Iimura* [c], *Yuko Ohta* [a], *Katsumi Takahashi* [b], *Tatsuya Sodekoda* [b], *Kazuyuki Suzuki* [d], *Hiroshi Takahashi* [d], *Shin Hasegawa* [e], *Akihiro Hiroki* [e], *Yasunari Maekawa* [e]

[a] *Corporate Business Development Div., IHI Corporation, 3-1-1, Toyosu, Koto-ku, Tokyo, 135-8710, Japan*
[b] *Research Laboratory, IHI Corporation, Shin-Nakahara-cho, Isogo-ku, Yokohama, Kanagawa, 235-8501, Japan*
[c] *IHI Inspection & Instrumentation Co., Ltd., 2-6-17, Fukuura, Kanazawa-ku, Yokohama, Kanagawa, 236-0004, Japan*
[d] *IHI Agri-Tech Corporation, 1-1-1 Ishishiba, Matsumoto, Nagano, 390-8714, Japan*
[e] *National Institutes for Quantum and Radiological Science and Technology, Takasaki, Gunma, 370-1292, Japan*

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ABSTRACT

The polymer electrolyte membrane consisting of poly(styrenesulfonic acid)-grafted poly(-ether ether ketone) (PEEK-PEM) was investigated for application to two electrochemical devices; a fuel cell and electrolytic enrichment of tritium. For fuel cells, high temperature operation has been required from the viewpoints of simplification of cooling systems, heat recovery systems and so forth, and durability is one critical issue affecting practical use. We performed a long term durability test for PEEK-PEM (ion exchange capacity = 2.4 mmol/g, conductivity = 0.15 S/cm) under the condition of 110 °C and 50% relative humidity, and achieved a lifetime of 1500 h at a constant current of 0.3 A/cm^2. The cell voltage maintained 97% of initial voltage after 1300 h of operation. There have been only a few reports that PEMs exhibit longer lifetime than 1000 h at temperatures above 100 °C. For quantitative evaluation of tritium concentration in low-level tritiated water such as environmental water, the tritium enrichment by a solid polymer electrolysis (SPE) method is required prior to the tritium concentration measurements. The SPE device composed of PEEK-PEMs with IECs of 0.9–1.2 mmol/g showed a tritium enrichment ratio of 1.35 at 30 °C, which is 20% higher than that of Nafion. Higher tritium enrichment ratios in PEEK-PEM are explained by the smaller amount of transported water. The water transport coefficient in PEEK-PEM is ~1, which is a half value of Nafion. In addition, the water transport coefficient of PEEK-PEM shows less temperature dependence, at least, up to 60 °C. These features have advantages in electrolytic enrichment of tritium for practical use.

* *Corresponding author.*
E-mail address: atsuko_fukaya@ihi.co.jp (A. Fukaya).

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Introduction

Polymer electrolyte membranes have been applied to various kinds of electrochemical equipment, for example, electrodialysis and redox flow batteries. Perfluorosulfonic acid (PFSA) membranes have been extensively used as a polymer electrolyte membrane (PEM) due to their chemical durability. PFSA membranes, however, have issues such as thermal durability, cost, safety during manufacture and use, and so forth [1,2]. In addition to the improvement and modification of PFSA, the investigation and development of alternative membranes, for example, hydrocarbon and composite membranes, have been promoted [3,4].

Poly(ether ether ketone) (PEEK) is one of the super-engineering plastics having the highest thermal stability (a glass temperature (T_g) of 146 °C and a melting temperature (T_m) of 338 °C) [5], mechanical stabilities (tensile strength 83 MPa) [6], and chemical resistance to various solvents (Dimethyl Formamide, N-Methyl-2-Pyrrolidone, aqueous alkaline solution and so forth) [7]. Two types of PEMs based on PEEK, sulfonated PEEK (sPEEK) [2] and poly(styrene sulfonic acid)-grafted PEEK (PEEK-PEM) [8,9], have been investigated. In sPEEK, sulfonic acid groups randomly and directly bond to the base PEEK backbone [2]; thus, the hydrophilic and hydrophobic regions are not clearly separated from each other and the backbone of the base material cannot maintain sufficient hydrophobicity. Thus, sPEEK with a degree of sulfonation (DS) larger than 75% is soluble in hot water, while the proton conductivity of sPEEK with low DS is not sufficiently high [10]. On the other hand, in PEEK-PEM, sulfonic acid groups bond to PEEK backbone through grafted aromatic chains; thus, the PEEK backbone maintains hydrophobicity. Therefore, PEEK-PEM with a wide range of grafting degree has both high mechanical properties and high proton conductivity. Taking advantage of these features, we studied PEEK-PEM performance for two kinds of electrochemical devices. We also studied PEEK-PEMs with additives, because PEM composites with additives are one of the common strategies to improve properties, for example, scavenging radical and suppression of water swelling [4].

The first application is a fuel cell, for which investigation and development have been promoted with growing interest in the field of hydrogen economics. PFSA membranes such as Nafion have been extensively used for fuel cells due to their chemical durability; however, the operating temperature is limited to below 80 °C. One requirement of fuel cells is a high temperature operating range above the boiling temperature of water (100 °C), from the viewpoints of simplification of cooling systems, heat recovery systems, CO tolerance and so forth [4]. Operation under low humidity conditions has also been also required for the simplification of humidification systems. Various kinds of PEM materials have been studied as candidates for operation under high temperature and low humidity conditions; for example, modified PFSA, hydrocarbon, polysiloxanes and composites [4]. Chen et al. have achieved the 1000 h operation under a condition of 95 °C and 80% relative humidity (RH) by using PEEK-PEM, indicating that PEEK-PEM has a potential for high temperature operation. Durability is one critical issue affecting practical use. In this study, we performed durability tests under the condition of a temperature above 100 °C and low humidity.

The second application is electrolytic enrichment of tritium. Tritium (T) is the radioactive isotope of hydrogen, and is used as a tracer for the leakage of radioactive isotopes. Most tritium exists as a form of tritium water, HTO. The tritium concentration of environmental water has been evaluated for the purpose of hydrological and oceanographic research [11]. The tritium concentration in precipitation was also monitored after the accident in 2011 at Fukushima Daiichi Nuclear Power Plant in Japan [12]. The tritium concentration of environmental water is generally around 1 Bq/L. Such a tritium level is not sufficiently high for measurements of tritium concentrations using a liquid scintillation counter. Before tritium concentration is measured, tritium enrichment using water electrolysis [11] is required, and this is known as the solid polymer electrolyte (SPE) method. PFSA membranes have been used as an electrolyte in SPE devices, and few investigations have been made into other types of materials. Therefore, we applied the PEEK-PEM to electrolytic enrichment of tritium.

Experimental

Preparation and properties of PEEK-PEM

PEEK-PEMs with/without additives were prepared by grafting functional groups into base films, similar to Ref. [8, 13]. The additive-free PEEK films were purchased (Aptive2000-016G for thickness of 16 μm, Aptive2000-100 for thickness of 100 μm, Victrex). Two kinds of base films for PEMs with additives were prepared: (1) nanosilica with a diameter of 12 nm (AEROSIL 200, Nippon AEROSIL Co. Ltd.), and (2) composite with two kinds of additives, talc ($Mg_3Si_4O_{10}(OH)_2$) with a diameter of 0.6 μm (D-600, Nippon TALC Co. Ltd.) and a small amount of perfluoroalkoxy alkane (PFA, P-62XPT, Asahi glass Co. Ltd.). PEEK powder (380P, Victrex) and the additives were mixed at temperatures above the melting point of PEEK by a twin screw extruder (HK-25D, PARKER Co.), and pellets of the composites were obtained. Then, the base films were formed by T-dei method using a single screw extruder (2D25S, Toyo Seiki Seisaku-sho, Ltd.). The chill roll was kept at temperatures below the crystalline temperature of PEEK, 170–180 °C. The thermal properties of the obtained base films were evaluated by differential scanning calorimetry (DSC). The crystallinity degree is 5–8%, which is the equivalent to PEEK films without additive [8,13].

Synthesis was carried out in three steps (Fig. 1); thermal grafting of divinylbenzene (DVB) into PEEK films, radiation-induced grafting of ethyl styrenesulfonate (ETSS) using γ-ray or electron beam, and hydrolysis of sulfonic acid protecting group (ethyl ester). The chemical structure of PEEK-PEM is shown in the right figure of Fig. 1; poly(styrene sulfonic acid) grafted on the PEEK base film.

For fuel cell tests, PEEK-PEMs were prepared by the following synthetic conditions. PEEK films (16 μm thickness, size 10 × 10 cm^2) were immersed in a 25 wt% DVB solution in 1,4-dioxane at 80 °C for 1 h to induce thermal DVB-grafting, and then dried in vacuum at 40 °C for 16 h. The films were packed in plastic bags filled with inert gas and were irradiated

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