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Synthesis of inorganic-organic hybrid membranes consisting of organotrisiloxane linkages and their fuel cell properties at intermediate temperatures

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ABSTRACT

Inorganic-organic hybrid membranes consisting of an aliphatic main-chain polymer and trisiloxane bond were synthesized using a simple, one-pot process from a trisiloxane derivative, phosphonic acid acrylate, and vinylbenzotriazole. 1,5-Divinyl-3-phenylpentamethyltrisiloxane (DPPMTS) was copolymerized with 2-hydroxyethyl methacrylate acid phosphate (HEMAP), and *N*-vinylbenzotriazole (VBT), yielding inorganic-organic hybrid composites. The formation of the inorganic-organic hybrid structure was confirmed by IR, ^{13}C, and ^{29}Si NMR spectroscopy. The membranes exhibited good thermal stabilities up to 200 °C. The aliphatic chains of the methacrylate derivative copolymerized with trisiloxane in the hybrid membranes improved the mechanical properties of the membranes. The tensile modulus of the VBT/HEMAP/DPPMTS membrane with a composition of 1:9:5 was 1.19 GPa. The conductivities of the 1:9:5 membranes were 5.3×10^{-2} S cm^{-1} and 4.1×10^{-4} S cm^{-1} at 100 and 19.3% relative humidity (RH), respectively, and 130 °C. The membrane electrode assembly (MEA) using the hybrid membrane exhibited a peak power of 7.8 mW cm^{-2} at 140 °C and 30% RH.

1. Introduction

Perfluorosulfonic polymers, such as Nafion, are widely used as membranes in polymer electrolyte fuel cells (PEFCs) because of their high proton conductivity, good mechanical strength, and chemical stability below 100 °C [1,2]. However, the operating conditions should be optimized to maintain 100% relative humidity (RH) at around 80 °C and a low CO concentration (<20 ppm) in the H_2 gas [3] (a high concentration of CO degrades the catalytic activity of Pt). The operation of PEFCs at higher temperatures increases the tolerance concentration of CO poisoning for the Pt catalysts from >20 to 2000 ppm [3]. In addition, the raised operation temperature improves the cell efficiency and simplifies the management system [4]. Therefore, membrane electrolytes exhibiting high proton conductivities at intermediate temperatures from 100 to 150 °C are required.

Inorganic-organic hybrid membranes have the merits of both the organic and inorganic phases. As the flexibility and functionality of organics are combined with the chemical, thermal, and mechanical stability of inorganics, the inorganic-organic hybrid membrane is suitable for use at intermediate temperatures [5–28]. Silica forms a network structure and has high chemical and thermal stabilities: thus, various silica-based hybrid membranes including proton conductive species, such as Nafion [8], sulfuric acid [9], tungstic acid [10], and polyheterocycle [11], have been reported. Although the doping or mixing of acid groups (sulfuric acid, tungstic acid, etc.) into these silica-based matrices is a simple method for the fabrication of the membranes, the water generated during the cell reaction rapidly dissolves the acid species because no chemical bond is formed between the proton carriers and the matrices. The loss of the proton carriers decreases the proton conductivity and cell performance, especially at a high RH. Thus, the proton carrier should be bound to the matrix via covalent bonds to suppress the leaching of proton carriers during fuel cell operation. Membranes with proton carriers that are strongly fixed by

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