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# Covalent organic/inorganic hybrid proton-conductive membrane with semi-interpenetrating polymer network: Preparation and characterizations

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**Abstract**

A series of new covalent organic/inorganic hybrid proton-conductive membranes, each with a semi-interpenetrating polymer network (semi-IPN), for direct methanol fuel cell (DMFC) applications is prepared through the following sequence: (i) copolymerization of impregnated styrene (St), *p*-vinylbenzyl chloride (VBC) and divinylbenzene (DVB) within a supporting polyvinyl chloride (PVC) film; (ii) reaction of the chloromethyl group with 3-(methylamine)propyl-trimethoxysilane (MAPTMS); (ii) a sol–gel process under acidic conditions; (iv) a sulfonation reaction. The developed membranes are characterized in terms of Fourier transform infrared/attenuated total reflectance (FTIR/ATR), scanning electron microscopy/energy-dispersive X-ray analysis (SEM/EDXA), elemental analysis (EA) and thermogravimetric analysis (TGA), which confirm the formation of the target membranes. The developed copolymer chains are interpenetrating with the PVC matrix to form the semi-IPN structure, and the inorganic silica is covalently bound to the copolymers. These features provide the membranes with high mechanical strength. The effect of silica content is investigated. As the silica content increases, proton conductivity and water content decrease, whereas oxidative stability is improved. In particular, methanol permeability and methanol uptake are reduced largely by the silica. The ratio of proton conductivity to methanol permeability for the hybrid membranes is higher than that of Nafion 117. All these properties make the hybrid membranes a potential candidate for DMFC applications.

*Keywords:* Proton-conductive membrane; Organic/inorganic hybrid membrane; Semi-interpenetrating polymer network; Direct methanol fuel cell

## 1. Introduction

Fuel cells have recently attracted considerable attention as an alternative energy-conversion technology [1]. Compared with conventional energy-conversion systems based on heat engines and fossil fuels, fuel cell systems directly transform chemical energy into electrical energy with the advantages of producing no waste products and causing no environmental problems. Among the various types of fuel cell, the direct methanol fuel cell (DMFC) is probably the most developed low-temperature system particularly for portable devices, such as laptops, handphones and personal digital assistants (PDAs). The DMFC has no the problems of the difficult storage of hydrogen gas or a complex reforming auxiliary compared with the hydrogen-fuelled proton-exchange membrane fuel cell (PEMFC). One of the vital components of the DMFC is the proton-conductive membrane, which serves as a physical separator between the anode and the cathode with the function of transporting protons and blocking electrons. Nowadays, the most utilized proton-conductive membrane is Nafion, which is a perfluorinated polymeric membrane developed by DuPont in the late 1960s [2]. Although Nafion has high proton conductivity, excellent chemical stability and good mechanical strength for fuel cells operating below 90 °C, high methanol crossover and high cost restrict its large-scale industrial application. For this reason, a number of studies have been carried out to develop alternative membrane materials [3–6].

One interesting alternative is a hybrid organic/inorganic membrane which has the potential to provide unique combi-

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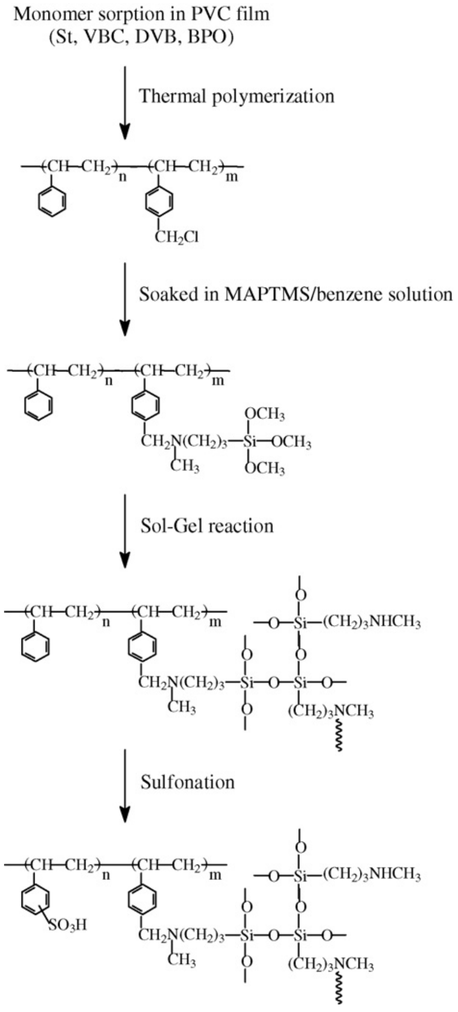

Scheme 1. Chemical reactions in membrane preparation.

nations of organic and inorganic properties [7,8]. The organic component may provide mechanical strength and proton conductivity, whereas the inorganic phase can reduce methanol permeation and improve both thermal and chemical stability. Furthermore, in order to control the dosage and dispersion of the inorganic component and make it more compatible with the organic phase, a covalent linking could be designed and formed between the two phases. For example, a covalent organic/inorganic hybrid material was synthesized with 2-hydroethyl methacrylate (HEMA) as a covalent-bonding agent: the hydroxyl group in HEMA polycondensed with prehydrolyzed tetraethyl orthosilicate (TEOS), while the C=C double bond copolymerized with styrene [8,9]. The monolithic membrane from the sulfonated hybrid material was, however, too brittle and too mechanically weak when the inorganic content was relatively high.

The mechanical strength of the membrane could be enhanced by utilizing a semi-interpenetrating polymer network (semi-IPN) technology based on a supporting film and a monomer solution [10]. In this method, the impregnated monomer within the supporting film is polymerized, and the propagated polymer chains are interpenetrated with those of the supporting film, thereby forming a physical network. The two polymer chains become miscible due to the semi-IPN structure, and a high mechanical stability can be achieved from the supporting film whereas the propagated polymer chains bring the proton conductivity after a post-sulfonation reaction.

In this research, the above two concepts, covalent organic/inorganic hybrid and semi-IPN technology, are combined together to develop a series of new proton-conductive membranes. Fig. 1 schematically illustrates the preparation procedures and Scheme 1 shows the corresponding chemical reactions. The non-porous supporting polyvinyl chloride (PVC) film is swollen in the monomer solution containing styrene (St), *p*-vinylbenzyl chloride (VBC) and divinylbenzene (DVB). The impregnated monomers are thermally polymerized within the PVC film, thereby forming a semi-IPN structure. The chloromethyl groups in VBC then react with 3-(methylamine)propyl-trimethoxysilane (MAPTMS). After a sol–gel process, the developed inorganic ≡Si–O– network is covalently bound to the organic poly(St-co-VBC) network. A covalent organic/inorganic hybrid proton-conductive membrane with a semi-IPN structure is obtained after a subsequent sulfonation reaction. Styrene has been chosen due to its high thermal stability and suitability for the sulfonation process of the aromatic ring to incorporate the sulfonic group responsible for high proton conductivity [8,11]. The developed membranes are then characterized in terms of Fourier transform infrared/attenuated total reflectance (FTIR/ATR), scanning electron microscopy/energy-dispersive X-ray analysis (SEM/EDXA), elemental analysis (EA), thermogravimetric analysis (TGA), ion-exchange capacity, water content, methanol uptake, proton conductivity, methanol diffusivity, mechanical stability and oxidative stability.

## 2. Experimental

### 2.1. Materials

A PVC film was supplied by Hwashin Engineering Co. (Seoul, Korea) with a thickness of 80 μm. Styrene, VBC and DVB were supplied by Aldrich (Milwaukee, WI, USA) and then purified with Aldrich inhibitor removers. The thermal initiator benzoyl peroxide (BPO) from Fluka (Buchs, Switzerland) was purified by recrystallization in a methanol/water mixture at −5 °C. MAPTMS and chlorosulfonic acid from Aldrich, 1,2-dichloroethane from Junsei Chemical Co. (Tokyo, Japan) and other reagents were used as received.

### 2.2. Membrane preparation

As shown in Scheme 1, the membrane preparation procedures can be divided into four steps. The first step is thermal polymerization. The PVC film was cleaned in *n*-hexane for 4 h before it was soaked in a monomer solution of St, VBC, DVB and BPO for 3 h at room temperature. The monomer-swollen PVC film was placed between two glass plates and sealed with aluminum foil to prevent the evaporation of the monomers. Thermal polymerization was carried out in an oven at 80 °C for 8 h. During