



## Organic–inorganic hybrid titanophosphite proton conductive membranes with graded monomer conversion

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### ABSTRACT

Further advances in polymer electrolyte fuel cells require membranes that can operate at intermediate temperatures between 100 and 150 °C. In this study, we report a unique organic–inorganic hybrid titanophosphite membrane possessing high proton conductivity at such intermediate temperatures. The membrane was prepared to have a graded monomer conversion from its surface to its inner parts, by ultraviolet light (UV) absorption of titanate during UV-initiated photopolymerization. The surface of the membrane was completely polymerized to be water durable, whereas its inner parts were weakly polymerized, thus allowing VPA to function as a proton donor. This gives proton conductivities that are as high as  $6.3 \times 10^{-4} \text{ S cm}^{-1}$  at 130 °C under a dry atmosphere.

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### 1. Introduction

Future advances in fuel cell technology are contingent on the development of new materials. One such material is the Nafion® membrane (DuPont, Wilmington, DE, USA); it is a proton-conducting membrane and has been employed in polymer electrolyte fuel cells (PEFCs). However, the PEFC faces problems including poor carbon monoxide tolerance and heat rejection in temperatures between 60 and 80 °C. In order to overcome these drawbacks, a proton-conducting membrane is required to operate at intermediate temperatures around 100–150 °C [1] and should possess good durability and thermal stability. However, the proton conductivity of Nafion is reported to be low at such intermediate temperatures because proton conduction in Nafion requires the presence of water [2] and the density of acidic sites is as low as 0.9 mmol/g [3–9].

To solve the abovementioned problems, membranes of polyvinylphosphonic acid (PVPA) have been proposed [3]. The proton conductivity of PVPA membranes at intermediate temperatures is higher than that of Nafion because of the higher number of acidic sites present in PVPA. Accordingly, several types of PVPA-related membranes have been developed; however, these membranes are not water durable [10]. Copolymerization with hydrophobic monomers has been attempted to enhance the water durability of such membranes

[11]. Unfortunately, copolymerization with a hydrophobic monomer substantially decreases the concentration of acidic sites, i.e., –POH, leading to a decrease in the proton conductivity.

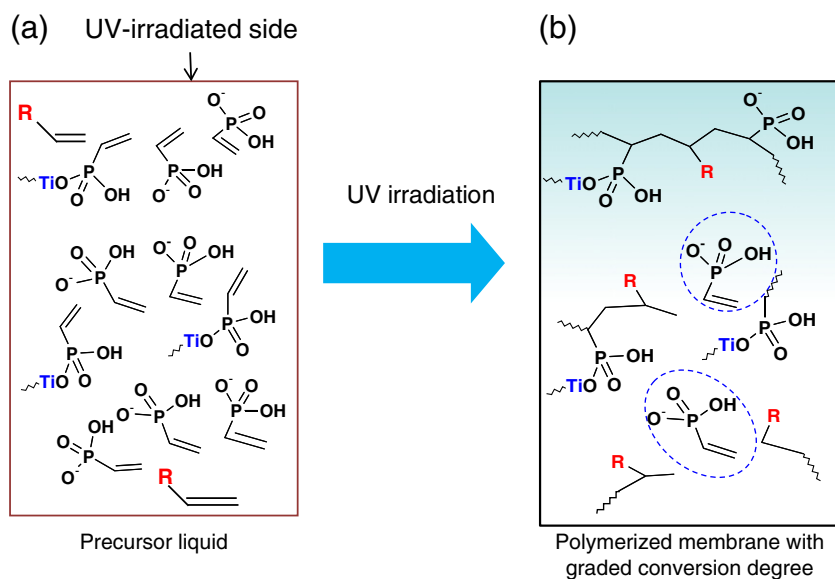
In this study, we describe a novel technique to prepare a membrane with a graded monomer conversion using ultraviolet light (UV) irradiation during radical photopolymerization. A schematic procedure is shown in Fig. 1. High conversion at the surface of the membrane enhanced durability while low conversion at the inner part of the membrane facilitated proton conductivity. This incremental change in the proton conductivity is possible because  $pK_{a1}$  of vinylphosphonic acid (VPA) is 2.74 and  $pK_{a2}$  is 7.34 [12], while  $pK_a$  of PVPA is around 5–6. Copolymerization of VPA with an additive monomer of hydrophobic nature having a low chain transfer constant leads to an increase in the conversion of the additive polymer. This procedure produces a PVPA-additive copolymer having high conversion at the surface, whereas the additive polymer in the inner part has low conversion of PVPA. Thus, the membrane consists of a shell made of a PVPA-additive copolymer for blocking moisture and a core of high proton density.

Recently, we have proposed solvent-free reactions for preparing organic–inorganic hybrid materials using orthophosphoric acid and organically modified silanes [13,14]. In a solvent-free reaction, the following metathesis occurs on heating:  $M-X + P-OH \rightarrow M-O-P + HX\uparrow$  ( $X=Cl$ , ethoxy). Groups that do not participate in this reaction are omitted from the reaction formula. Because of the absence of solvent evaporation, a crack-free monolith can be produced by simply mixing the starting reagents followed by post baking. Additionally, a product prepared by metathesis uniformly contains an almost complete

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**Fig. 1.** Schematic representation of membrane possessing graded degrees of polymerization: (a) titanophosphite precursor, (b) copolymerized membrane having graded degrees of polymerization.

alternating copolymer of oxide in the form of M–O–P. The above technique can be employed if UV-absorbable oxides such as titanophosphite are incorporated into the copolymer; the intensity of UV light during photopolymerization decreases as the penetration depth increases [15], according to the Beer–Lambert law. Gradation of monomer conversion occurs along the depth of the membrane.

In this study, titanium tetraisopropoxide (TTIP) and ethylmethacrylate (EMA) were selected as the alkoxide and additive monomer starting materials, respectively. Because of the low chain transfer constant of EMA, the EMA radical is expected to be sufficiently stable to promote a large conversion. In addition, EMA was also used as a diluent to decrease the reactivity between TTIP and VPA. Furthermore, water durability is improved because of the hydrophobic nature of polyethylmethacrylate (PEMA).

NMR spectroscopy was employed to confirm the structure and the graded monomer conversion of the membrane. Thermal and chemical stabilities of the membrane were assessed and the proton conductivity was determined.

## 2. Experimental

### 2.1. Sample preparation

Four types of membrane were prepared in this study. Vinylphosphonic acid (VPA), TTIP, and a polymerization initiator, Irgacure 1700, were used as received. EMA was purified by stirring in 1 M NaOH solution to remove a polymerization inhibitor. TTIP was first diluted with EMA to avoid any rapid reaction with VPA. The mixture was then added to VPA at 50 °C under N<sub>2</sub> atmosphere and stirred for 90 min to afford a precursor liquid. Irgacure 1700 (1.0 wt.%) was added to the precursor. The resulting mixture was poured into a polydimethylsiloxane mold (diameter 10 mm, thickness 1 mm). The mixture was irradiated from both sides using a high-pressure mercury lamp (UI-501 C, Ushio, Tokyo, Japan) for 2 h at 50 mW/cm<sup>2</sup> to afford the membranes (VET). Additionally, VET was further heat-treated (VET-ht) as shown in Fig. 2. Membranes of VPA–EMA copolymer (VE) and polyvinylphosphonic acid (PVPA) were also prepared for comparison, following the procedure described for VET. Thus, VPA and/or EMA was stirred at 50 °C for 90 min and irradiated with UV light following the addition of Irgacure 1700. The four types of membrane prepared are listed in Table 1.

Monoliths with thickness of 5 mm were also prepared by irradiating one of the two sides for 1 h to confirm polymerization gradation.

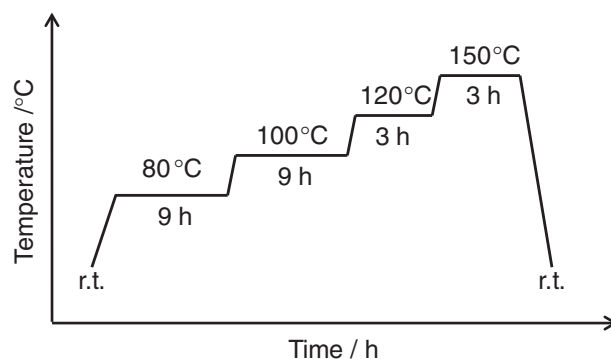
### 2.2. Analyses of the local structure and the monomer conversion in the membrane

Structural analyses were performed using an NMR spectrometer (JEOL, CMX 400, Tokyo, Japan). The 90° pulse and the delay time were 3 μs and 10 s, respectively. <sup>31</sup>P MAS NMR spectra were obtained at a spinning rate of 10 kHz for solid-state analysis of the membranes. Chemical shifts are expressed in parts per million (ppm) with respect to phosphoric acid (0 ppm). In order to confirm the conversion gradation, <sup>31</sup>P MAS NMR spectra for irradiated and non-irradiated sides of a 5-mm-thick monolith were also acquired.

Fourier transformed infrared spectroscopy (FT-IR, Thermo Nicolet Avatar 360, Thermo Nicolet, Madison, WI, USA) using the KBr pellet method was employed; a mixture of the membrane (2 mg) and KBr (250 mg) was ground using a pestle and mortar and pressed under a pressure of 60 MPa for 15 min to afford a KBr pellet.

### 2.3. Characterization of the thermal stability, water durability, and conductive property of membranes

Thermal stability was characterized by thermogravimetry (TG, Rigaku TG 8120, Rigaku, Tokyo, Japan) with a heating rate of 5 °C/min.



**Fig. 2.** Temperature program of heat treatment.

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