

# Development of proton-conducting membrane based on incorporating a proton conductor 1,2,4-triazolium methanesulfonate into the Nafion membrane

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## Abstract

In this paper, 1,2,4-triazolium methanesulfonate ( $C_2H_4N_3^+CH_3SO_3^-$ , [Tri][MS]), an ionic conductor, was successfully synthesized. It exhibited high ionic conductivity of  $18.60\text{ mS}\cdot\text{cm}^{-1}$  at  $140\text{ }^\circ\text{C}$  and reached up to  $36.51\text{ mS}\cdot\text{cm}^{-1}$  at  $190\text{ }^\circ\text{C}$ . [Tri][MS] was first applied to modify Nafion membrane to fabricate [Tri][MS]/Nafion membrane by impregnation method at  $150\text{ }^\circ\text{C}$ . The prepared composite membrane showed high thermal stability with decomposed temperature above  $200\text{ }^\circ\text{C}$  in air atmosphere. In addition, the membrane indicated good ionic conductivity with  $3.67\text{ mS}\cdot\text{cm}^{-1}$  at  $140\text{ }^\circ\text{C}$  and reached up to  $13.23\text{ mS}\cdot\text{cm}^{-1}$  at  $180\text{ }^\circ\text{C}$ . The structure of the [Tri][MS] and the composite membrane were characterized by FTIR and the compatibility of [Tri][MS] and Pt/C catalyst was studied by a cyclic voltammetry (CV) method. Besides, the [Tri][MS]/Nafion membrane (thickness of  $65\text{ }\mu\text{m}$ ) was evaluated with single fuel cell at high temperature and without humidification. The highest power density of [Tri][MS]/Nafion membrane was  $3.20\text{ mW}\cdot\text{cm}^{-2}$  at  $140\text{ }^\circ\text{C}$  and  $4.90\text{ mW}\cdot\text{cm}^{-2}$  at  $150\text{ }^\circ\text{C}$ , which was much higher than that of Nafion membrane.

## Key words

high temperature PEMFC; membranes; triazole; Nafion; ionic conductor

## 1. Introduction

High temperature proton exchange membrane fuel cell (HT-PEMFC), enhanced electrode electrochemical kinetics, simplified water management and the cooling system, and increased CO tolerance, has been widely investigated recently [1–5]. Proton exchange membrane (PEM) is one of the key components in high temperature PEMFC, whose function is to conduct proton and separate reactants. With high proton conductivity, the perfluorinated sulfonic membranes like Nafion are widely applied in PEMFC. However, the proton conductivity of the traditional membrane is seriously dependent on water present in membrane [6]. The membrane will be dehydrated with temperature above the boiling temperature of water decreasing the proton conductivity and further degrading the fuel cell performance. As a result, development of

high temperature proton exchange membranes with high proton conductivity, high chemical and mechanical stability, and low permeability to fuel is the core obstacle in high temperature PEMFCs and has attracted much interest [7–9]. To improve the performance of Nafion<sup>®</sup> membranes for PEMFC in high temperature and no-humidification conditions, many researchers try modified membrane using various methods. An effective approach is incorporating Nafion membrane with protonic ionic liquids (PILs) [10–13]. PILs, as a kind of non-aqueous proton-conducting electrolyte with low volatility and relatively high ionic conductivity, are formed by proton transfer between Brønsted acids and bases. Noda [14] introduced imidazole into PEMFC firstly. Henceforth, great attentions have been paid to ILs and composite membranes contained ILs and polymer electrolyte such as imidazole, triazole, and tetrazole [15]. Doyle et al. [16] reported the influence

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between Nafion membranes and ILs and immersed 3-methylimidazolium triflate (MNI-Tf) into Nafion membranes. The ionic conductivity of the composite membrane exhibited  $6 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$  and  $1 \times 10^{-1} \text{ S}\cdot\text{cm}^{-1}$  between 150 and 180 °C. Yang et al. [17] fabricated a composite membrane Nafion/BMIm/PA based on Nafion115, ionic liquid and phosphoric acid and the membrane had potential to be used in the high temperature PEMFC with a tensile stress at break of 5.3 MPa and a proton conductivity of  $10.9 \text{ mS}\cdot\text{cm}^{-1}$  at 160 °C without humidification. Sevim et al. [18] fabricated a new copolymer doped with  $\text{H}_3\text{PO}_4$  based on 1-vinyl-1,2,4-triazole (VTri) and diisopropyl-p-vinylbenzyl phosphonate (VBP), which showed a proton conductivity of  $0.005 \text{ S}\cdot\text{cm}^{-1}$  at 150 °C. To improve the compatibility of Nafion-TEA membranes, Iojoiu et al. [19] doped Trifluoromethanesulfonate of triethylamm-monium (TFTEA) into Nafion-TEA. By casting they fabricated Nafion-TEA membrane containing 20 wt% TFTEA. Under 100 °C, 100% RH (relative humidity), and 1 atm relative pressure, current density of fuel cell reached  $0.85 \text{ A}/\text{cm}^2$  at 0.6 V. However, it was pity that no corresponding data about high temperature and no-humidifying conditions.

Triazole has three nitrogens in the ring and has similar proton-transfer mechanism with imidazole [20]. Moreover, the proton can be transferred easier than imidazole due to the structure of single-double alternated bond and three nitrogens in the ring of triazole. And the chemical stability and the ability of ionic transform of triazole are better than imidazole. 1H-1,2,4-triazole is a potentially useful heterocycle which has a relatively high proton conductivity up to  $1.2 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$  at its melting point [21]. Luo et al. [22] prepared 1,2,4-triazolium methanesulfonate ( $\text{C}_2\text{H}_4\text{N}_3^+\text{CH}_3\text{SO}_3^-$ ) using 1H-1,2,4-triazole ( $\text{C}_2\text{H}_3\text{N}_3$ ) and methanesulfonic acid ( $\text{CH}_3\text{SO}_3\text{H}$ ). The resulting of its thermal property, proton conduction behaviour and electrochemical stability suggested 1-methanesulfon-1,2,4-triazol would be a suitable candidate for high temperature PEMFC electrolytes.

In this paper, a ionic conductor of 1,2,4-triazolium methanesulfonate ([Tri][MS]) was synthesized and was first to be applied to incorporate into Nafion membrane to fabricate Nafion/[Tri][MS] composite membrane by impregnation method. The structural, thermal and electrochemical properties of the composite membranes were investigated. Moreover, fuel cell performance at high temperature and the compatibility between [Tri][MS] and Pt/C catalyst were systematically explored.

## 2. Experimental

### 2.1. Materials

1 H-1,2,4-triazol (Tri, 99.5%) was supplied from ACROS Co., USA, methanesulfonic acid (MSA, 98%) from Tianjin Guangfu Fine Chemical Research Institute, the Nafion (NRE212) membrane from DuPont, USA. N-methyl-2-pyrrolidone (NMP, >99%) and methanol (99.9%, AR) were

purchased from Tianjing kemiu Chemical Ltd, China. Acetone (DMK, >99.5%) was supplied from Dalian inorganic chemical Co. Besides, polybenzimidazole (PBI), used in the gas diffusion electrode (GDE), was synthesized as reported previously [9]. Pt/C (70% Pt on Vulcan XC-72 carbon) was purchased from Johnson Matthey.

### 2.2. Fabrication of 1,2,4-triazolium methanesulfonate ([Tri][MS])

The [Tri][MS] was synthesized from methanesulfonic acid (MSA) and 1H-1,2,4-triazol (Tri) by acid-base neutralization reaction. Firstly, Tri was dissolved with acetone and stirred to get transparent solution of Tri. Then, the MSA was added into the solution dropwise, which was stirred for 4 h. Herein, the mole ratio of MSA and Tri was 1 : 1.5. The produced white particles was washed several times with acetone to remove residual MSA and dried at 60 °C to obtain purified [Tri][MS] ( $\text{C}_2\text{H}_4\text{N}_3^+\text{CH}_3\text{SO}_3^-$ ).

### 2.3. Preparation of the [Tri][MS]/Nafion membrane

The [Tri][MS]/Nafion composite membrane was prepared as follows. Firstly, the Nafion (NRE212) membrane was dried in the vacuum drying oven at 80 °C for 2 h. Then, the Nafion® membranes were immersed into [Tri][MS]-saturated methanol solution at 60 °C for 12 h and dried for 12 h. Put the above membranes into molten [Tri][MS] at 150 °C for 7 h and 36 h, respectively, to make the membrane saturated with [Tri][MS] (marked by the [Tri][MS]/Nafion membrane-7 h, the [Tri][MS]/Nafion membrane-36 h). Finally, the residual melt [Tri][MS] on the surface of the membrane was scraped off with filter paper at 150 °C and dried to obtain the [Tri][MS]/Nafion composite membrane. The content of [Tri][MS] in the [Tri][MS]/Nafion membrane-36 h was 25 wt%. By comparison, the content of [Tri][MS] of the [Tri][MS]/Nafion membrane-7 h was 8 wt%.

### 2.4. Physical characterization

Fourier-transform infrared (FTIR) of [Tri][MS] and the [Tri][MS]/Nafion membrane was recorded with a Bruker Equinox 55 FTIR spectrometer. The thermal stability was measured by thermogravimetric analysis (TGA, STA449F3, NETZSCH, Germany) at the rate of  $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$  under air and  $\text{N}_2$  atmosphere. Differential scanning calorimetry (DSC) was carried out on a Seiko Instrument DSC 811 under air atmosphere. The sample was heated to 200 °C and then cooled to ambient temperature and heated again to 200 °C at the rate of  $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ . The morphology of the [Tri][MS]/Nafion membrane was observed with a field emission scanning electron microscopy (FESEM; Hitachi, S-4800).

### 2.5. Ionic conductivities

The ionic conductivity of [Tri][MS] was measured by the conductivity meter (DSA-11, Shanghai LEI-CI Co. Ltd,

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