



Immobilization of imidazole moieties in polymer electrolyte composite membrane for elevated temperature fuel cells



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HIGHLIGHTS

- Reinforced imidazole-g-SiO₂/Nafion/ePTFE composite membranes were developed.
- Mechanical properties of the formed membranes is greatly improved.
- Anhydrous proton conductivity reaches $1.8 \times 10^{-2} \text{ S cm}^{-1}$ at 180 °C.
- Assembled cell is continuously operated at 110 °C for 20 h without performance loss.

ARTICLE INFO

Article history:

Received 4 June 2015

Received in revised form

13 August 2015

Accepted 14 August 2015

Available online 22 August 2015

Keywords:

Polymer electrolyte membrane fuel cell

Imidazole

Silica nanoparticles

Surface-attachment

Proton conductivity

ABSTRACT

Development of membrane electrolyte with reasonable proton conductivity at elevated temperature without external humidification is essential for practical applications of elevated temperature proton exchange membrane fuel cells. Herein, a novel polymer electrolyte composite membrane using imidazole as anhydrous proton carriers for elevated temperature fuel cells is investigated. The imidazole moieties are immobilized inside the Nafion/poly(tetrafluoroethylene) (PTFE) composite membrane through *in situ* formation of imidazole functionalized silica nanoparticles in Nafion dispersion. The thus-formed membrane exhibits strong Coulombic interaction between negatively charged sulfonic acid groups of Nafion and protonated imidazole moieties, leading to an anhydrous proton conductivity of 0.018 S cm^{-1} at 180 °C. With the introduction of PTFE matrix, the mechanical strength of the membrane is greatly improved. The peak power density of a single cell assembled from the hybrid membrane is observed to be 130 mW cm^{-2} under 350 mA cm^{-2} at 110 °C without external humidification and it remains stable for 20 h continuous operation. The obtained results demonstrate that the developed composite membranes could be utilized as promising membrane electrolytes for elevated temperature fuel cells.

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1. Introduction

Proton exchange membrane fuel cell (PEMFC) has been considered as a promising clean energy technology for a wide variety of applications ranging from transportation to stationary power systems due to their high power density, rapid start-up, and high efficiency [1]. Since water is the proton transporting medium of a fuel cell, current PEMFC typically operates at <100 °C under humidified conditions. Recent progress in PEMFC has been focused

on increasing their operating temperature, because they could benefit from increased electrode kinetics, improved tolerance of the catalyst to impurities in fuel gases, improved water management and gas transport, and potentially recovered waste heat as a practical energy source at higher operating temperature [2,3]. An optimal operating temperature is generally believed to be 120–150 °C [4].

Although operating PEMFCs at elevated temperatures has many advantages, there are several technical barriers restricting their practical applications [5]. For instance, as the most commonly used electrolyte materials for commercialized fuel cell applications, perfluorosulfonic acid (PFSA) membranes such as Nafion became less conductive towards protons at low relative humidity. Aiming at

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this problem, many research efforts are devoted to develop different alternative electrolyte materials such as polybenzimidazole (PBI) [6,7], sulfonated poly(ether ether ketone) (SPEEK) [8,9], sulfonated copolyimides (SPIs) [10,11]. However, due to the robust structure and prominent physicochemical stability, PFSA membranes are still the most promising candidate for electrolyte materials [12]. Thus, modification of Nafion membranes is still an attractive approach for the development of elevated temperature PEMFCs [13].

The high proton conductivity of hydrated Nafion membranes relies on the presence of liquid water. Similar to water, heterocyclic compounds like imidazole are amphoteric molecules, being able to undergo autoprotolysis to a high degree via the hydrogen-bond networks, leading to high proton conductivity [14,15]. In addition, the volatility of imidazole is much lower than that of water, which makes it a potential substitute for water as the proton carrier at elevated temperature. Thus, incorporation of electrolyte membrane with imidazole is an attractive method to develop elevated temperature PEMFCs. However, as imidazole is soluble with water, it can leach out from the membrane to the electrode during the fuel cell operation. This leakage of incorporated imidazole results in not only the reduction of the proton conductivity of the electrolyte, but also the risk of poisoning the Pt-electrode, leading to a permanent damage to the assembled fuel cell [16]. Therefore, the immobilization of imidazole moieties is necessary in order to prevent the imidazole leaching. Schuster et al. have first reported an anhydrous electrolyte of imidazole-terminated ethyleneoxide oligomers, which behaves proton conductivity as high as $5 \times 10^{-3} \text{ S cm}^{-1}$ at 120°C [17]. Based on this model system, imidazole moieties have been immobilized on polymers [18–20] and polysiloxane using various methods [21,22]. The anhydrous proton conductivities of such composite membranes incorporated by proton donors range from 10^{-6} to $10^{-3} \text{ S cm}^{-1}$. More recently, heterocyclic compounds modified by silica nanoparticles and ionomers have been developed for anhydrous proton exchange membranes at elevated temperature [23–28]. However, the often associated decrease in mechanical strength with the improved anhydrous proton conduction hinders their practical application in fuel cells. Besides, the stability of anhydrous proton conductivity during a long-termed fuel cell operation requires further investigation.

In prior work, we have reported an inorganic–organic hybrid proton exchange membrane of Nafion doped with *in situ* formed silica nanoparticles via an electrostatic self-assembly process [29,30]. Due to the even distribution of silica nanoparticles in the membrane and their insolubility in water, they can serve as the good “anchor” for the imidazole groups inside the polymeric membrane. To improve the mechanical strength of hybrid membranes degraded by the incompatibility between the inorganic particles and polymeric resins, the ImSiO₂ incorporated Nafion (ImSiO₂–Nafion) were impregnated into porous expanded poly(tetrafluoroethylene) (ePTFE) membranes. The anhydrous proton conductivity and the single cell performance at high temperatures of the formed ImSiO₂–Nafion/PTFE hybrid membranes were studied.

2. Experimental section

2.1. Materials

Nafion solution (DE-520, EW1100) was purchased from DuPont Ind., Co., which consists of 5 wt% of perfluorosulfonate resin (H⁺ form) and 95 wt% of solvents (IPA:water mixture = 10:9 by weight). Tetraethyl orthosilicate (TEOS) was purchased from Shanghai Reagent Co., Ltd. (China). 1-Benzylimidazole, sodium hydride, and palladium/carbon (Pd/C, 10 wt% Pd) were purchased from Alfa

Aesar. Triton X-100 (polyethylene glycol tert-octylphenylether) was purchased from Sigma Aldrich. ePTFE membranes (85% porosity, pore size 0.1–0.2 μm , thickness 8–10 μm) were purchased from Shanghai Dagong Co. (China). Water was deionized through a Milli-Q system (Barnsted Nanopore, resistivity = $18.0 \text{ M}\Omega \text{ cm}^{-1}$). Tetrahydrofuran (THF) was dried through reflux over sodium using benzophenone as indicator. N-methyl-2-pyrrolidone (NMP) was dried over CaH₂.

2.2. Synthesis of ImSiO₂ precursor

The synthetic procedure of ImSiO₂ precursor was schematically displayed in Fig. 1. N-benzyl-2-imidazolyl-methanol (I) was synthesized and purified according to literature [17].

2.2.1. Synthesis of N-benzyl-2-(3-triethoxysilanyl-propoxymethyl)-imidazole (II)

To a dispersion of NaH (110 mmol) in dry THF (50 ml) cooled using ice-bath under nitrogen atmosphere, a solution of compound I (100 mmol) in dry THF (100 ml) was added slowly. After stirring for 4 h, a solution of γ -chloropropyltriethoxysilane (105 mmol) was added dropwise. After overnight stirring, the mixture was heated to 45°C for 8 h. The solid was then filtered off and the solvent was evaporated completely. After purification of the raw material using column chromatography, the final product, yellowish oil, was obtained after evaporation of eluant (anhydrous ethyl acetate/ethanol) with a yield of 48% (48 mmol). ¹H NMR (CD₂Cl₂, 300 MHz, ppm): 7.16–7.27 (m, 2H, Ph), 7.03–7.10 (m, 3H, Ph), 6.91 (d, 1H, Im), 6.82 (d, 1H, Im), 5.13 (s, 2H, N–CH₂–Ph), 4.47 (s, 2H, Im–CH₂–O), 3.64 (m, 6H, SiO–CH₂–), 3.33 (t, 2H, O–CH₂–), 1.51–1.62 (m, 2H, C–CH₂–C), 1.12 (s, 9H, C–CH₃), 0.49–0.57 (m, 2H, Si–CH₂–).

2.2.2. Synthesis of 2-(3-triethoxysilanyl-propoxymethyl)-imidazole (III)

To a solution of compound II (40 mmol) in dry methanol (200 ml), Pd/C catalyst (2 g) was added. The mixture was continuously stirred with flushing hydrogen at 50°C for 72 h. After removal of catalyst through filtration, the solvent was evaporated. The quantity final product was obtained as yellowish oil. ¹H NMR (CD₂Cl₂, 300 MHz, ppm): 6.88 (s, 2H, Im), 4.52 (s, 2H, Im–CH₂–O–), 3.67 (m, 6H, SiO–CH₂–), 3.36 (t, 2H, O–CH₂–), 1.53–1.59 (m, 2H, C–CH₂–C), 1.16 (s, 9H, C–CH₃), 0.58 (m, 2H, Si–CH₂–).

2.3. Preparation of ImSiO₂–Nafion dispersion

ImSiO₂–Nafion dispersion was prepared as previously described

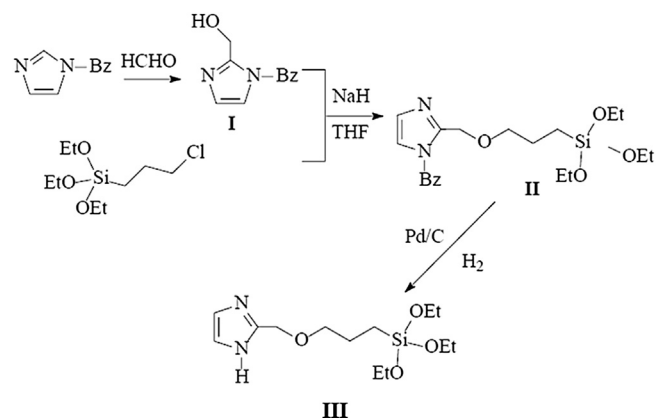


Fig. 1. Synthesis of ImSiO₂ precursor.

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