



Toward Anhydrous Proton Conductivity Based on Imidazole Functionalized Mesoporous Silica/Nafion Composite Membranes



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ABSTRACT

Although Nafion is regarded as the most preferred electrolyte membrane and often used as a benchmark for comparative evaluation of other electrolyte membranes, its wide spread for commercial PEM fuel cells is limited by the poor electrochemical properties at elevated temperatures and low relative humidity conditions. Herein, sol–gel synthesized mesoporous silica functionalized with a protogenic molecule (imidazole) is introduced into the Nafion matrix via a colloid mediated process. The formation of a stable colloid enables homogeneous dispersion of the silica-imidazole nanoparticles without aggregation. Under non-humidified conditions, the amphoteric and self-dissociative character of the tethered imidazole within the matrix functions as a transporting medium to facilitate proton conductivity. The structural and chemical phases are characterized, and qualitatively evaluated by XRD, TEM, FT-IR, TGA, and DMA. The results show that the average proton conductivity of the composite membrane with the optimal amount of functionalized nanoparticles increases progressively to $1.06 \times 10^{-2} \text{ S cm}^{-1}$ at 130°C , corresponding to an activation energy of 6.95 kJ mol^{-1} under non-humidified conditions. The mechanism governing the dynamics of proton conductivity and structural limitations as a function of temperature is discussed.

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1. Introduction

Nafion, a perfluorosulfonic acid (PFSA) polymer, is one of the most researched proton exchange membrane fuel cell (PEMFC) electrolytes and often used as point of reference for comparative study and evaluation of other solid proton exchange electrolytes. Although significant efforts have been made towards PEMFCs commercialization, there are still technical challenges such as the poor conductivity at elevated temperatures and low humidity conditions, in addition to the complexity associated with the water-thermal management and cost which still need to be addressed. Dehydration of Nafion at elevated temperatures typically above 80°C is often regarded as the major cause of the decline in proton conductivity at extreme conditions. On the one hand, Nafion membrane exhibits good proton conductivity under relatively high humidity state attributed to the proton hopping mechanism aided by the hydrated water molecules. On the other

hand, Nafion suffers a remarkable decline in proton conductivity as temperature rises above 80°C and relative humidity/hydration decreases. However, elevated temperature conditions are considered favorable for purging fuel gas contamination, as well as enhancing reaction kinetics and catalytic activities during cell operation [1–3].

Based on the view that the proton migration mechanisms in Nafion are enhanced in a considerably humidified/hydrated state, various modifications such as doping with metal oxides or metal oxide binary composites have been reported. Metal oxides have good water retention properties due to their hygroscopic nature and surface properties, as well as excellent thermochemical stability characteristics. Generally, PFSA polymers are modified by doping with; ~ 0.5 – $20 \text{ wt.}\%$ metal oxides (SiO_2 , ZrO_2 , TiO_2 , Al_2O_3) [4,5], heteropolyacids (HPA) [6,7], ionic liquid doping [8,9], or histidine modified carbon nanotubes with imidazole groups (Im-CNT) [10]. Incorporated bare metal oxide particles in Nafion improve water uptake and thermochemical degradation characteristics, but often lead to reduced ionic conductivity of the composite, particularly at very high concentration and temperatures below 80°C [11]. The decline in conductivity at high metal

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oxide concentrations is attributed to the blockage of proton transport channels by the impregnated nanoparticles [12]. Heteropolyacid in Nafion relatively improves conductivity but suffers from solubility and subsequently leaches out at elevated temperatures and/or in aqueous environment, thus rendering it unsuitable for long-term cell performance. Impregnating membranes with protic ionic liquids often leads to improved thermo-electrochemical properties, but may still require some level of humidification to achieve maximum performance. For example, a conductivity of 0.05 S cm^{-1} at 90°C and 30% of relative humidity (RH) was reported [13]. Enhanced ionic conductivity has also been reported in various studies for acid functionalized mesoporous silica, yet external humidification seems inevitable [14,15]. At low humidity and high temperature operation conditions, mesoporous silica is reported to augment water concentration at the anode catalyst layer and facilitates back diffusion to reduce anode over potential for stable and reversible current–voltage response [16]. Consequently, various research groups believe that infiltrating polymer matrices with metal oxides has beneficial properties for fuel cell membrane development, and have therefore devoted much effort to the study of metal oxide based hybrid and composite membranes. Kevork et al. [17] investigated Nafion doped with various metal oxides (SiO_2 , TiO_2 , and ZrO_2), and reported an improved performance of the hybrid membranes. The enhanced properties were assigned to the effect of the metal oxide particles on the temperature-dependent structure of the polymer matrix rather than the acidity and/or water retentivity property of the oxide fillers. The change in polymer structure relative to the glass transition temperature (T_g) of the hybrid membrane was regarded as the major factor accounting for the loss of water at elevated cell temperatures contrary to direct evaporation mechanism. Proton transfer in Nafion is due to the diffusion of hydrated protons in the so-called vehicle mechanism or through intermolecular proton migration between water molecules and hydronium ions, both of which are dependent on water of hydration.

It is generally accepted that designing humidity independent electrolyte membranes is a promising approach to PEMFCs operated at elevated temperatures. At relatively high temperatures and low humidity conditions, protogenic molecules such as imidazole could play the role of water in the proton migration mechanism. For example, an improved conductivity at low RH was reported for SiO_2 –Imi doped sulfonated poly(ether ether ketone) (sPEEK) membrane [18]. The enhanced properties of the composite membrane was attributed to dissociation of proton from sulfonic acid groups on sPEEK relative to the basicity of the SiO_2 –Imi which enhanced proton conductivity by intermolecular proton transfer through hydrogen bonding. Li et al. [19] impregnated imidazole into Nafion through a hydrocarbon linker and reported a proton conductivity of $\sim 10^{-3} \text{ S cm}^{-1}$ under anhydrous state. The T_g was observed to increase in the composite due to the electrostatic interaction between imidazole moieties and sulfonic groups. Electrostatic interactions lead to the formation of interfacial ionic clusters which facilitate proton transport under anhydrous conditions. In a study of a polybenzimidazole membranes modified with sulfonated imidazole groups, the proton conductivity was reported to increase with a corresponding increase in both temperature (up to 160°C) and the ImiSA content [20].

Indeed, imidazole is a heterocyclic aromatic compound and clearly known to behave as both a proton acceptor or donor at the nitrogen sites due to its amphoteric and self-dissociation character; with acidic proton at $-\text{NH}-$ and the basic site at the $=\text{N}-$. Accordingly, protonation of imidazole gives symmetrical imidazolium cation. Treatment of imidazole with sulfuric acid creates protonic charge carriers at the sulfonic acid groups. The ensuing hydrogen bonding interaction between the imidazole moieties and sulfonic groups generates ionic paths to induce protonic charge

migration. The earlier electrochemical study by Kreuer et al. [21] reveals that even at 120°C , imidazole exhibits proton conductivity at a rate comparable to that of liquid water at room temperature. Unlike perfluorosulfonic polymer membranes in which the proton conductivity is inherently dependent on high relative humidity, imidazole based membranes may permit fuel cell operation above 100°C independent of humidification thereby eliminates the water management complexity and the effect of humidity induced membrane swelling or volumetric change. Therefore, it would be beneficial to incorporate the thermochemical resistive mesoporous silica and the anhydrous proton migration capability of imidazole in a Nafion matrix for elevated temperature/anhydrous application. Surface modification of mesoporous silica with molecules such as, (3-chloropropyl) trimethoxysilane (CIPTMS), triethoxysilyl butyraldehyde, or aminopropyltriethoxysilane, enables facile attachment of imidazole moieties which can be subsequently impregnated into Nafion matrix. Considerably, tethering imidazole molecules to mesoporous silica, relative to dense silica, could prevent surface dislodgement or leaching of the attached imidazole moieties as well as enables the introduction of excess protons as extrinsic charge carriers in the Imidazole/Silica/Nafion composite system. Thus, higher grafting density of the functionalizing agents is anticipated whereby imidazole moieties residing in the mesopores can interact with excess sulfonic groups within the pore domain to enhance the conductivity while remained thermally shielded.

In this communication, an investigation into the electrochemical properties of composite membranes based on imidazole functionalized silica nanoparticles doped Nafion with well ordered proton transfer channels is carried out. The composite materials are prepared via a simple thermally assisted colloidal formation and solution casting process. Herein, the imidazole moieties are expected to serve as medium for stable intermolecular proton transport under anhydrous conditions by interacting with sulfonic groups to form a uniform network of ionic clusters across the membrane. Structural reinforcement with the high thermo-resistive mesoporous silica provides thermochemical properties. The membranes are evaluated for ionic conductivity based on the influence of doped silica-imidazole over a wide temperature range. As a consequence, the hydrogen bonding dynamic as well as the interfacial chemistry for improved transport of protonic charges as a function of temperature are evaluated. In addition, the membranes are characterized to determine the physico-chemical structure, crystallinity, and morphological properties.

2. Experimental Section

2.1. Materials and Method

Nafion suspension (DE-520, EW1100) was purchased from DuPont Fluoroproducts. The suspension consists of perfluorosulfonate resin (5 wt.%), 1-propanol/water mixture (94 wt.%) and other VOCs (< 2 wt.%). Toluene (99.5%, Sinopharm chemical reagent Co. Ltd, China) was dried and stored over molecular sieve (3 Å) until used. All supplementary chemical reagents and solvents including tetraethoxysilane (TEOS-98%, Sinopharm Chem. Reagent Co., China), (3-Chloropropyl) trimethoxysilane (CIPTMS-98%, Aladin Chemical Co., Shanghai), imidazole (99.0%, Sinopharm Chem. reagent Co. Ltd, China), triethylamine, (Et_3N , 99%, Shanghai Reagent Co., China), methanol anhydrous (99.5%, Sinopharm Chem. reagent Co. Ltd, China), hydrogen peroxide ($\sim 30\%$, Sinopharm Chem. reagent Co. Ltd, China), ethylene glycol (99.0%, Sinopharm Chem. reagent Co. Ltd, China), ethanol (99.7%, Sinopharm Chem. reagent Co. Ltd, China), and sulfuric acid (98%, Shanghai Reagent Co., China) were used as supplied. De-ionized (DI) water was obtained from an up water purification system (Ulupure, China).

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