



# Guanidimidazole-quanternized and cross-linked alkaline polymer electrolyte membrane for fuel cell application

Jie Cheng<sup>a</sup>, Guoqing Yang<sup>a</sup>, Kuibo Zhang<sup>a</sup>, Gaohong He<sup>a</sup>, Jia Jia<sup>b</sup>, Hongmei Yu<sup>b</sup>, Fangyuan Gai<sup>a,c</sup>, Lingdong Li<sup>a</sup>, Ce Hao<sup>a</sup>, Fengxiang Zhang<sup>a,\*</sup>

<sup>a</sup> School of Chemical and Petroleum Engineering, Dalian University of Technology, State Key Laboratory of Fine Chemicals, 2 Dagong Road, Liaodongwan New District, Panjin 124221, China

<sup>b</sup> Division of Fuel Cells, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

<sup>c</sup> Division of Materials Science, Luleå University of Technology, SE-97187 Luleå, Sweden

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## ABSTRACT

A modified imidazole, namely guanidimidazole (GIm) was designed and synthesized as a novel quaternizing- and cross-linking agent for alkaline polymer electrolyte membrane fabrication. The resulting membrane was more alkali tolerant and swelling resistant than that quaternized purely by 1-methylimidazole owing to the enhanced resonance and cross-linking ability of GIm, the former confirmed by a LUMO (lowest unoccupied molecular orbital) energy calculation. The membrane also showed good ionic conductivity, mechanical strength and thermal stability. A H<sub>2</sub>/O<sub>2</sub> fuel cell using the synthesized membrane showed a peak power density of 39 mW cm<sup>-2</sup> at 50 °C. This work preliminarily demonstrates the beneficial effect of imidazole modification by both experimental and computational investigation; it provides a new cation design strategy that may potentially achieve simultaneous improvement of alkali stability and swelling resistance of alkaline electrolyte membranes.

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## 1. Introduction

As a next-generation energy conversion technology, fuel cell has advantages of high efficiency and low or even zero emission compared to fossil based energies. Among different fuel cells, proton exchange membrane fuel cell (PEMFC) has been thought of a promising one and its application has been widely demonstrated; however, its high cost (due to expensive Nafion membrane and noble metal electrocatalyst such as platinum) is an obstacle hindering more widespread application and commercialization. By contrast, alkaline polymer electrolyte membrane fuel cell (APEMFC) may be potentially more cost effective; this is because its fast oxygen reduction reaction in basic operating condition allows the use of non-precious catalyst such as silver, nickel, cobalt and transition metal oxides in place of platinum [1–4]. In addition, fuel crossover and hydroxide ion transport in APEMFC are along opposed direction so that fuel crossover can be better suppressed than in PEMFC. Other advantages of APEMFC include device compactness, avoidance of liquid leakage, and minimized carbonate formation. All these benefits make APEMFC a more promising energy technology and have received extensive

interests in recent years.

As the key material of APEMFC, the alkaline polymer electrolyte membrane (APEM) plays a vital role in determining the cell performance. It transports hydroxide ions produced at the cathode to the anode, and serves as the separator between the two electrodes, preventing fuel crossover and short circuit. To guarantee a high power density, long-term operation of the cell, APEM should possess high hydroxide conductivity and superior stability (in chemical, dimensional, thermal and mechanical ways). It should also be inexpensive, and easy to make so that APEMFC can be applied practically. Conventional APEM materials are made of a polymer functionalized with quaternary ammonium (QA) cations, and often synthesized by quaternizing chloro- or bromomethylated polymers with amines [5–10]. Various polymers such as polysulfones, [11–14] poly(etherketone), [15] poly(ether ether ketone), [16] polystyrene, [17,18] poly(phenylene) [19] and so on have been used to prepare QA functionalized APEM.

The biggest problem with QA functionalized APEM is the insufficient stability of QA groups against hydroxide attack at elevated temperature [20–22]. This will result in decreased ion exchange capacity and conductivity of the membrane. In order to overcome the low stability issue, many efforts have been made in recent years to explore the possibility of employing non-QA cations such as phosphonium, [23–25] guanidinium, [26–29] imidazolium [30–32] and piperazinium [33]. Among these,

\* Corresponding author.

E-mail address: [zhangfx@dlut.edu.cn](mailto:zhangfx@dlut.edu.cn) (F. Zhang).

imidazolium cations have attracted tremendous interest because they are potentially advantageous in terms of alkaline stability owing to their resonance effect. Resonance means charge delocalization or reduced charge density, giving rise to weakened interaction between the cation and the hydroxide ions so that the hydroxide attack can be alleviated to some extent [34]. However, the resonance effect may be disturbed by the substituents on the imidazolium ring. If the substituent is a strong electron donor or acceptor, the resonance might not be strong enough to offset the substituent's influence. Therefore, several studies have been carried out to enhance alkaline stability by introducing suitable substituents at C2- and N3- positions [35–37]; some of these substituents (e.g. butyl group) not only participate in the resonance effect but also mitigate hydroxide attack due to steric hindrance [38,39].

In this work, we explored modification of imidazolium by introducing a substituent of guanidine nature, and synthesized a novel quaternizing agent, namely 2-(1,1,3,3-tetramethylguanidine)-imidazole, or simply guanidimidazole (GIm). The guanidine moiety's resonant characteristic [40] may contribute to the resonance effect of imidazolium; in other words, the GIm-derived cation, or  $[GIm]^+$  will have an enhanced resonance effect relative to imidazolium alone. Therefore, the GIm-quaternized APEM could exhibit improved alkaline stability relative to that quaternized purely by N-methylimidazole. We also performed a density functional theory (DFT) calculation of the Lowest Unoccupied Molecular Orbital (LUMO) energy of various imidazolium structures; the calculation outcome is in good agreement with the experimental result. In addition, the bi-functional nature of GIm leads to a cross-linked structure of the APEMs, which can inhibit water swelling of the membrane effectively and also contributes to its mechanical strength and thermal stability.

## 2. Experimental

### 2.1. Materials

Oxalyl chloride, 1,1,3,3-tetramethylurea, dichloromethane, 2-Aminoimidazole sulfate, acetonitrile are all of analytical grade, provided by Aladin Reagents and stored over 4 Å molecular sieves. Oxalyl chloride was purified by distillation immediately before use. Polysulfone was purchased from Solvay. All other chemicals such as chloroform, ethyl acetate, tin chloride, chloromethyl methyl ether, methanol, ethanol, 1-methylimidazole and N,N-dimethylacetamide (DMAc) were obtained commercially and used as received.

### 2.2. Synthesis of 2-(1,1,3,3-tetramethylguanidine)-imidazole

Under a nitrogen atmosphere, 1,1,3,3-tetramethylurea (9.6 mL, 80 mmol) was added to 20 mL dichloromethane ( $CH_2Cl_2$ ) in a round bottom flask, and oxalyl chloride (10.15 mL, 120 mmol) was then added at 20 °C. After reacting for 2 h at 60 °C,  $CH_2Cl_2$  was evaporated under reduced pressure, and a solid product Vilsmeier salt was obtained. In the next step, 2-Aminoimidazole sulfate (6.6045 g, 50 mmol) was added to 20 mL acetonitrile solution of Vilsmeier salt (8.55 g, 50 mmol) in a round bottom flask under nitrogen atmosphere. After the mixture was refluxed for 24 h, a 4 M NaOH aqueous solution was added to adjust the PH to 9–10; the new mixture was stirred vigorously until it became clear. The organic phase was extracted with ethyl acetate ( $5 \times 100$  ml) and dried over anhydrous  $MgSO_4$ , filtered and evaporated to remove the solvent, extraction solvent and other byproducts. A reddish brown oily liquid was obtained which is named GIm.

### 2.3. Membrane fabrication

Chloromethylated polysulfone (CMPSf) was synthesized by chloromethylation of PSf using chloromethyl methyl ether (CMME) as the chloromethylating agent and chloroform as solvent as described in previous work [14]. Then a 5% (w/v) solution of CMPSf was prepared using N,N-dimethylacetamide (DMAc) as solvent; equimolar guanidinoimidazole (GIm) and 1-methylimidazole (MIm) were added and stirred at 50 °C for about 1 h. The resulting mixture was then cast on a pre-cleaned glass plate and heated in the open air at 60 °C for 24 h and 80 °C for another 24 h to get rid of the solvent and the un-reacted reagents. The resulting membrane PSf-GIm-MImCl (chloride form of polysulfone AEM quaternized with a GIm/MIm mixture, mole ratio of GIm/MIm being 1:1) was rendered into hydroxide form by soak in 1.0 M aqueous solution of NaOH for 24 h. For comparison purpose, we prepared PSf-2GIm-MImCl (chloride form of polysulfone AEM quaternized with GIm/MIm=2:1, mole ratio) and PSf-MImCl (chloride form of polysulfone AEM quaternized with only MIm) membranes following the same procedure as above.

### 2.4. Membrane characterization

Hydrogen Nuclear Magnetic Resonance ( $^1H$  NMR) spectroscopy was performed using INOVA-400M spectrometer with deuterated dimethylsulfoxide (DMSO) as the solvent and tetramethylsilane as the internal standard.

Fourier transform infrared spectroscopy (FTIR) was performed on a Lambda950 spectrometer using thin membrane as a sample. FTIR spectra were recorded in the wave number range of 400–4000  $cm^{-1}$  with a resolution of 4  $cm^{-1}$ .

Ion exchange capacity (IEC) was measured using the conventional back titration method. A certain mass of membrane sample (in hydroxide form) was equilibrated with de-ionized (DI) water for at least 24 h and then soaked in an aqueous hydrochloric acid (HCl) solution of known concentration (about 0.01 M) and volume for 24 h to render the membrane to  $Cl^-$  form. The HCl solution was then titrated against 0.01 M NaOH standard solution with phenolphthalein as the indicator. The measured IEC ( $IEC_m$ ) of membranes was calculated by the following equation:

$$IEC = \frac{C_1V_1 - C_2V_2}{m}$$

where  $C_1$  and  $V_1$  denote, respectively, the concentration and volume of HCl standard solution before titration;  $C_2$  and  $V_2$  stand for the concentration and volume of NaOH standard solution used in titration, respectively;  $m$  is the mass of dried membrane sample.

Water uptake (WU) and swelling ratio (SR) of the fabricated membranes were studied by comparing the dimension (length and width) and mass of wet and dry membranes. The weight and dimension of wet membranes were measured after soaking in DI water for 24 h at room temperature. Then, the membranes were vacuum-dried at 50 °C for 24 h, and the weight and dimension of dry membranes were measured again. WU and SR were calculated by the following equations:

$$WU = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%, \quad SR = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100\%$$

where  $W_{wet}$  and  $W_{dry}$  are the mass of wet and dry membrane samples, respectively,  $L_{wet}$  and  $L_{dry}$  are the average length of wet and dry membrane samples, respectively. And  $L_{wet} = (L_{wet1} \cdot L_{wet2})^{1/2}$ ,  $L_{dry} = (L_{dry1} \cdot L_{dry2})^{1/2}$ , in which,  $L_{wet1}$ ,  $L_{wet2}$  and  $L_{dry1}$ ,  $L_{dry2}$  are the lengths and widths of wet and dry membrane samples, respectively.

Ionic conductivity of the membranes was measured by four-

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