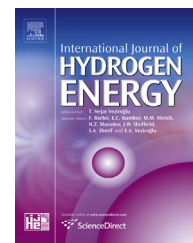




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Study on the alkaline stability of imidazolium and benzimidazolium based polyelectrolytes for anion exchange membrane fuel cells

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ABSTRACT

Imidazolium and benzimidazolium groups containing anion exchange membranes (AEMs) were synthesized by the functionalization of poly(styrene-co-vinylbenzyl chloride) with methylimidazole and methylbenzylimidazole, respectively. The essential properties for AEMs used in anion exchange membrane fuel cells (AEMFCs) including ion exchange capacity, water uptake, hydration number, and ionic conductivity were investigated. A comparative study of these two AEMs focusing on the alkaline stability was conducted in the present work. We have used TGA, FTIR, ¹H NMR, and ¹³C NMR techniques to evaluate the susceptibility to alkaline degradation. Meanwhile, we have performed density functional theory (DFT) calculations to confirm the experimental results of the alkaline degradation study. It has been found that the benzimidazolium cations would be more easily attacked by OH⁻ anions leading to ring-opening compared to the imidazolium cations.

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Introduction

Anion exchange membrane fuel cell (AEMFC) is a new type of fuel cell, which has been received increased attention recently. AEMFCs have a number of attractive features such as allowance to use a lower quantity of noble metal catalyst and metal based bipolar plates, as well as no electrode deterioration resulting from the deposition of carbonate salts and the

electrolyte leakage problems. Since AEMFCs have advantages in cost and operation reliability over proton exchange membrane fuel cells (PEMFCs) and alkaline fuel cells (AFCs), respectively. AEMFC is considered as an ideal fuel cell device having potential to realize the commercialization in the portable applications [1–3].

However, alkaline stability issues exist for most of anion exchange membranes (AEM) when they are placed in a

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hydrous mediate at a temperature above 60 °C in presence of hydroxide ions. This kind of fuel cell requires long-term stable ionic conductivity and mechanical strength. To improve the property decay resulting from alkaline degradation will be necessary [4].

In 2010, J. Feng et al. prepared AEMs based on the copolymer derived from allyl methylimidazolium chloride and methyl acrylate. They found the prepared membrane exhibited an ionic conductivity reaching 3.33×10^{-2} S/cm in deionized water at 30 °C [5]. They first suggested that imidazolium containing polymer membranes have good perspectives and great potential for AEMFCs. Almost at the same time, F. Yan et al. produced cross-linked AEMs having imidazolium groups via in-situ cross-linking of vinyl methylimidazolium iodide with styrene and acrylonitrile. The resulting copolymer membranes exhibited high ionic conductivities (above 10^{-2} S/cm) [6]. The membranes displayed an excellent chemical stability up to 400 h in high pH solution without an obvious loss of ion conductivity and mechanical properties. Since the works of J. Feng's group and F. Yan's groups successfully demonstrated the improved chemical and thermal stabilities of imidazolium groups compared to ammonium groups used as anion exchange sites [5,6]. Studies focusing on the AEM based on imidazolium containing polymer have been attracted growing attentions recently [7–14].

Benzimidazolium is one of imidazolium derivatives, are expected to exhibit the similar characteristic of anion conduction. Recently, X. Lin et al. synthesized new AEMs based on poly(phenylene oxide) containing pendant benzimidazolium groups. Their AEM with an IEC of 2.21 mmol/g was reported to exhibit a pretty high ionic conductivity at 25 °C as high as 3.7×10^{-2} S/cm [15]. On the other hand, poly(benzimidazolium) is a quaternized polybenzimidazole (PBI) having benzimidazolium moiety in the polymer backbone, synthesized from PBI via a facile methylation process [16–18]. In the work of H. Hou et al., poly(benzimidazolium) based AEM exhibited a good ionic conductivity as high as 2.2×10^{-2} S/cm at room temperature. And, the ethanol permeability of which was pretty low (5.4×10^{-8} mol cm²/s) [17]. However, Henkensmeier et al. studied the alkaline degradation mechanism of poly(benzimidazolium) and suggested the alkaline stability of which was required to be improved [19].

The alkaline stability of an electrolyte membrane used in AEMFC is of crucial importance [20]. However, there are few studies concerning the difference in the alkaline stability between imidazolium and benzimidazolium based AEMs up to now. In this work, we prepared two kinds of AEM based on poly(styrene-co-vinylbenzyl chloride) containing imidazolium and benzimidazolium groups, respectively. We attempt to compare the alkaline stability of these AEMs using TGA and FTIR techniques. Their ion exchange capacity, water uptake, hydration number, and ionic conductivity were also investigated. Furthermore, we tried to identify the alkaline stability of two model compounds, one with imidazolium group and the other with benzimidazolium group, using ¹H NMR, and ¹³C NMR techniques, as well as theoretical DFT calculations.

Experimental

Materials

Styrene, vinylbenzyl chloride, azobisisobutyronitrile (AIBN), 1-methylimidazole, 1-methylbenzimidazole, bromobutane, potassium chromate (K₂CrO₄), and all the d-solvents used in this work including dimethyl sulfoxide-d₆ (DMSO-d₆) and potassium deuteroxide solution were purchased from Aldrich. Sodium sulfate (Na₂SO₄), sodium chloride, potassium hydroxide (KOH), and silver nitrate (AgNO₃) were obtained from SHOWA. All the solvents used in this work including dimethylformamide (DMF), diethyl ether, hexane, and methanol were ACS grade and provided from ECHO Chemical Co., Ltd. DMF was dried and purified by distillation over calcium hydride before use. All the reagents and solvents except for DMF were used as received without further purifications.

Synthesis of poly(styrene-co-vinylbenzyl chloride) [poly(St-co-VBC)]

A mixture of styrene (10.963 g, 0.105 mol), vinylbenzyl chloride (7.631 g, 0.045 mol), AIBN (0.082 g, 0.0005 mol), and toluene (about 15 mL) were placed in a 100 mL of two-necked flask reactor equipped with a magnetic stirrer and a condenser. The molar ratio of styrene and vinylbenzyl chloride was set at 7:3. The reaction was carried out by vigorously stirring the mixture at 80 °C under a nitrogen atmosphere for 16 h. After cooling to room temperature, the resulting polymer was precipitated by pouring the mixture into excessive methanol. The residual solvent within the resulting polymer was removed under reduced pressure at 100 °C for 6 h. Then, the poly(St-co-VBC) powder was obtained.

Synthesis of poly(styrene-co-vinylbenzyl methylimidazolium) [poly(St-co-VBMI)]

A mixture of poly(St-co-VBC) (0.1424 g, 0.012 mol), 1-methylimidazole (0.373 g, 0.0045 mol), and anhydrous DMF (30 mL) were placed in a 250 mL of two-necked flask reactor equipped with a magnetic stirrer and a condenser. The mixture was vigorously stirred at 80 °C under a nitrogen atmosphere for 16 h. After cooling to room temperature, the resulting polymer was precipitated by pouring the mixture into excessive diethyl ether. The residual solvent within the resulting polymer was removed under reduced pressure at 100 °C for 6 h. Then, the poly(St-co-VBMI) powder was obtained.

Synthesis of poly(styrene-co-vinylbenzyl methylimidazolium) [poly(St-co-VBMBI)]

A mixture of poly(St-co-VBC) (0.1424 g, 0.012 mol), 1-methylbenzimidazole (0.6 g, 0.0045 mol), and anhydrous DMF (30 mL) were placed in a 250 mL of two-necked flask reactor equipped with a magnetic stirrer and a condenser. The mixture was vigorously stirred at 80 °C under a nitrogen

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