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Imidazolium-based organic–inorganic hybrid anion exchange membranes for fuel cell applications

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A B S T R A C T

Imidazolium-based ionic liquids and imidazolium-based organic–inorganic hybrid alkaline anion exchange membranes (AEMs) are synthesized and investigated in the present work. The imidazolium-based hybrid AEMs are prepared via in situ cross-linking of styrene, acrylonitrile, 1-vinyl-propyl-triethoxysilaneimidazolium chloride ([VPSIm][Cl]) and 1-vinyl-3-butylimidazolium bromide ([VBIm][Br]), followed by anion exchange with hydroxide ions. The water uptake and swelling degree of the hybrid AEMs decrease with increasing [VPSIm][Cl] content due to the formation of an Si–O–Si inorganic network in the membranes. The resulting organic–inorganic hybrid AEMs show good thermal stability, excellent mechanical properties and high conductivity (above 10^{-2} S cm^{-1} at room temperature in liquid water). Compared with samples without the addition of [VPSIm][Cl], the hybrid membranes show much higher alkaline stability, and the hybrid AEMs displayed excellent chemical stability up to 480 h in 2 M KOH solution at 60 °C.

1. Introduction

With the increasing demand for clean and efficient energy worldwide, fuel cell as an environmentally friendly power source and substitute for conventional fossil fuel processes, are attracting more and more attention [1]. Among several types of fuel cells, polymer electrolyte fuel cells using proton exchange membranes (PEMs) and alkaline anion exchange membranes (AEMs) as solid electrolytes, are being considered as renewable and portable energy devices due to their high energy conversion efficiency, environmental friendliness, and their flexibility for use in various kinds of electric vehicles [2,3]. In the past decades, much effort has been devoted to developing PEMs for proton exchange membrane fuel cell (PEMFC) applications. Perfluorosulfonic acid membranes, represented by Nafion as the archetype, are most commonly used in PEMFCs due to their high proton conductivity and excellent chemical stability in acidic conditions. However, the exhaustible precious metal electrocatalysts required in PEMs (such as platinum) and the high cost of Nafion membranes are hindering the widespread commercialization of PEMFCs.

Replacing PEMs with AEMs is a solution to the problem of cost, in principle, because the use of abundant transition metal electrocatalysts (such as Ni, Co and Fe) is feasible in anion exchange membrane fuel cells (AEMFCs) with high pH AEMs as electrolytes [4–6]. Furthermore, AEMFCs offer fuel flexibility, reduced fuel crossover, and enhanced reaction kinetics that may make these devices desirable in certain applications [7,8]. Therefore, AEMs and AEMFC have attracted much attention in recent years. However, meeting the comprehensive requirements of high hydroxide anion conductivity, robust mechanical properties and good chemical stability in alkaline environment, not to mention robust device performance, is a key challenge for the application of AEMs in AEMFCs [9].

Recently, much research effort has been spent on developing high-performance AEM materials with quaternary ammonium cationic groups based on polysulfone [10], poly(arylene ether sulfone) [11–17], poly(arylene ether ketone) [18,19], poly(phenylene oxide) [20,21] poly(fluorenyl ether ketone sulfone) [22,23] and polypropylene [24]. It should be pointed out that the practical

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application of AEMs is strongly limited by their alkaline stability and mechanical properties. A growing effort is underway to develop AEM materials that simultaneously possess high hydroxide conductivity, good mechanical properties, and robust alkaline stability under the operating conditions of AEMFCs [25–37]. However, most of these membranes were unstable in alkaline media especially at temperatures above 60 °C and at high KOH concentrations (above 1 M). Therefore, developing AEMs with high alkaline stability is still an urgent issue [38,39].

Most AEMs that have been reported were prepared by solution casting, and the treatment of hazardous organic solvents is a problem for large-scale production of membranes. Chemical crosslinking is a common but effective method for the preparation of AEMs, which could both suppress the water swelling and improve the mechanical strength of AEMs [40]. Beside quaternary ammonium cationic groups, guanidinium [41], phosphonium [42], benzimidazolium [43], metal-cation [44] and imidazolium [45–50] based AEMs have been investigated. Imidazolium-based ionic liquids (ILs) are mostly room-temperature organic salts, have attracted much attention as electrolytes for various processes due to their excellent thermal stability, low volatility and high conductivity. The AEMs with imidazolium cations showed better stability in alkaline solution at elevated temperature compared with AEMs containing quaternary ammonium cationic groups [50]. However, the mechanical strength of AEMs must be enhanced.

In this paper, we propose a new type of cross-linked alkaline hybrid AEM based on imidazolium-based ILs, [VBIm][Br] (1-vinyl-3-butylimidazolium bromide) and [VPSIm][Cl] (1-vinyl-propyltriethoxysilaneimidazolium chloride). In this investigation, [VPSIm][Cl] acts both as a monomer and cross-linker which resulted in the formation of an Si–O–Si inorganic network in the membranes. An Si–O–Si inorganic network phase was chosen because it can effectively resist water swelling of the AEMs, thus assuring good mechanical strength and lowering fuel crossover. Zhang [51] and Xu [52] have fabricated polysilsesquioxane-based AEMs and PPO/SiO_2 hybrid AEMs with Si–O–Si inorganic network phase, respectively, and the membranes showed good alkaline stability and suitable for potential AEMFC applications. In the present work, it is expected that the cross-linked alkaline hybrid membrane will offer good mechanical strength, high hydroxide ion conductivity and excellent alkaline stability. The properties of the membranes, such as water uptake, swelling degree, ion exchange capability (IEC), hydroxide ion conductivity, thermal stability, mechanical properties and chemical stability in high pH solution were investigated.

2. Experimental

2.1. Materials

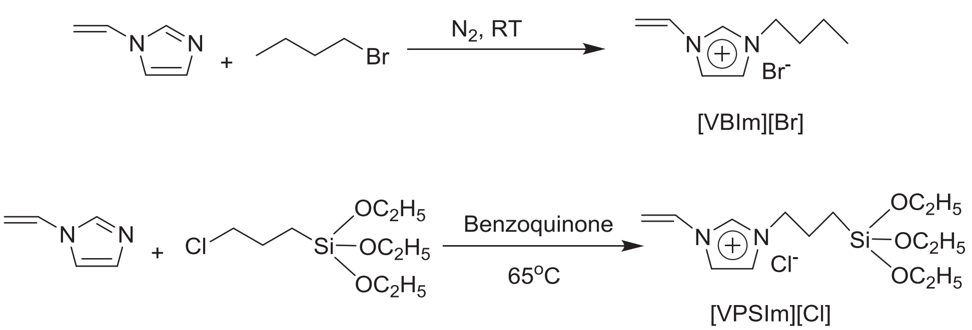
Styrene, acrylonitrile, N-vinylimidazole, N-butylbromide, ethylether, 3-chloropropyltriethoxysilane, pure para divinylbenzene (DVB), benzoin ethylether, ethyl acetate, tetraethyl orthosilicate (TEOS), potassium hydroxide, and sodium hydroxide were used as purchased. All of the vinyl monomers were made inhibitor-free by passing the liquid through a column filled with basic Al_2O_3 to remove the polymerization inhibitor. Distilled deionized water was used for all experiments.

2.2. Synthesis of 1-vinyl-3-butylimidazolium bromide ([VBIm][br])

[VBIm][Br] was synthesized as shown in Scheme 1. N-vinylimidazole (9.41 g, 0.1 mol) and an equivalent molar amount of n-butylbromide (13.7 g, 0.1 mol) were added into a 100 mL round bottomed flask equipped with a mechanical stirrer and a nitrogen inlet/outlet. The mixture was stirred at room temperature under nitrogen atmosphere for 48 h. The resultant viscous oil was washed with ethyl acetate three times, and dried in dynamic vacuum at 80 °C for 24 h before use. [VBIm][Br] was obtained as a yellow transparent viscous oil (17.10 g, 74% yield). ^{1}H NMR (400 MHz, DMSO) δ 9.47 (s, 1H, N–CH–N), 8.19 (s, 1H, N–CH=C), 7.93 (s, 1H, C=CH–N), 7.28 (dd, *J*=15.6, 8.7 Hz, 1H, N–CH=C), 5.95 (dd, *J*=15.6, 2.3 Hz, 1H, C=*H*CH), 5.43 (dd, *J*=8.7, 2.3 Hz, 1H, C=HC*H*), 4.20 (t, *J*=7.2 Hz, 2H, N–CH$_2$–C), 2.10 –1.65 (m, 2H, C–CH$_2$–C), 1.55–1.12 (m, 2H, C–CH$_2$–C), 0.92 (t, *J*=7.4 Hz, 3H, C–CH$_3$).

2.3. Synthesis of 1-vinyl-propyltriethoxysilane-imidazolium chloride ([VPSIm][cl])

As shown in Scheme 1, [VPSIm][Cl] was synthesized similar to [VBIm][Br]. N-vinylimidazole (9.41 g, 0.1 mol), an equivalent molar amount of 3-chloropropyltriethoxysilane (24.80 g, 0.1 mol), and benzoquinone (0.171 g, 0.5 wt% of the monomer) were added to a 100 mL round bottomed flask equipped with a mechanical stirrer and a nitrogen inlet/outlet. The mixture was stirred at 65 °C under nitrogen atmosphere for 48 h. The resultant viscous oil was washed with ethylether three times and then dried under dynamic vacuum at 80 °C for 24 h before use. [VPSIm][Cl] was obtained as a yellow transparent viscous liquid (25.31 g, 76% yield).^{1}H NMR (400 MHz, DMSO): δ 9.64 (s, 1H, N–CH–N), 7.93 (s, 1H, N–CH=C), 7.59 (s, 1H, C=CH–N), 7.17 (dd, *J*=15.8, 8.9 Hz, 1H, N–CH–C), 5.48 (dd, *J*=15.9, 1.1 Hz, 1H, C=*H*CH), 4.85 (dd, *J*=8.9, 1.0 Hz, 1H, C=HC*H*), 4.16 (t, *J*=7.2 Hz, 2H, N–CH$_2$–C), 3.77–3.68 (m, 6H, O–CH$_2$–C), 1.96–1.77 (m, 2H, C–CH$_2$–C), 1.17–1.08 (m, 9H, C–CH$_3$), 0.59–0.49 (m, 2 H, C–CH$_2$–Si).



Scheme 1. Reaction scheme for the preparation of [VBIm][Br] and [VPSIm][Cl].