



Imidazolium-Functionalized Anion Exchange Polymer Electrolytes with High Tensile Strength and Stability for Alkaline Membrane Fuel Cells



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ABSTRACT

This study reports novel kinds of high tensile strength alkaline anion-exchange membranes composed of imidazolium-functionalized anion exchange polymer electrolytes. The membranes were prepared by a combined thermal and chemical cross-linking of poly (vinyl alcohol) and poly (3-methyl-1-vinylimidazolium chloride)-co-(1-vinylpyrrolidone) (PMVIC-co-VP). Characterizations by AC impedance technique, mechanical property, FTIR spectroscopy, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), along with the water uptake, alkaline resistance and oxidation stability were carried out on the membranes consisting of different PVA/PVA-PMVIC-co-VP mass ratios to evaluate their applicability in alkaline fuel cells. The membrane in a mass ratio of 1:0.4 exhibited high tensile stress at break in the range of 59.3~76.6 MPa, and the elongation at break around 9.2~14.9%, depending on the annealing temperature from 130~190 °C. The OH⁻ conductivity of the membranes was found to be increased with increasing annealing temperature and mass ratio, and reached high up to $1.7 \times 10^{-2} \text{ S cm}^{-1}$. Besides, the membranes showed perfect oxidation stability in 30% H₂O₂ for 250 hours with no obvious weight loss was observed. XPS analysis indicated that some degradation occurred when the membrane was exposed to 8 M KOH at 85 °C for 312 h, but no lessened OH⁻ conductivity was detected. SEM pictures revealed an ordered microvoid structure with pore size ca. 100~150 nm uniformly dispersed on the membrane surface, which imparted the PVA/PVA-PMVIC-co-VP membrane with good OH⁻ conductivity.

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1. Introduction

Polymer electrolyte membrane (PEM) fuel cell devices are currently being investigated for a variety of applications, as they efficiently convert the chemical energy stored in a fuel (e.g., H₂ or CH₃OH) directly into electrical energy [1–3]. According to the PEMs used, the fuel cell can be divided into proton-exchange membrane fuel cells (PEMFCs) and alkaline anion membrane fuel cells (AMFCs), where the PEMs conduct proton (H⁺) and hydroxide ion (OH⁻), respectively. In recent years, the researches on AMFCs have made a noticeable comeback from PEMFCs dominant era [1–3]. This is because that compared to fuel cell operated in a strong acidic media, the AMFCs can get faster electrokinetics, lower

fuel crossover, reduced CO poisoning, and the possible of using non-precious metal catalysts such as silver (Ag) and nickel (Ni) [1–3]. In addition, due to the less corrosive nature of an alkaline medium, higher durability is expected for AMFCs. The water management can also be improved due to the electro-osmotic drag transporting water away from the cathode, therefore, the so-called alcohol 'crossover' problem is highly reduced because of the opposite movement of OH⁻ anions to the movement of H⁺ ions in acidic membrane [4,5].

To date, some new alkaline anion-exchange membranes (AEMs) have been evaluated for use in AMFCs, where the membranes are composed of polymer matrix and quaternized ammonia groups which feature an anion as the charge carrier, such as fluorinated polymers including poly(ethylene-co-tetrafluoroethylene) (PETFE) and poly(vinylidene fluoride)(PVDF) [4,6], polysulfone (PSO) [7], poly(arylene ether sulfone) (PAES) [8], poly(2,6-dimethyl-1,4-phenyleneoxide) (PPO) [9] and quaternized poly(phentlene) [10]. However, these polymers are generally of high price and their

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quaternization is complex process, which is even very toxic and carcinogenic. In particular, the stability of the quaternary ammonia groups has to be improved which are likely to decompose in concentrated alkali solutions, especially at elevated temperatures (above 60 °C) via by either an E₂ Hofmann elimination or by an SN₂ substitution reaction [11–13].

In principle, an ideal AEM candidate should be expected to meet the following requirements: low cost, high ionic conductivity, high chemical and thermal stability, low gas or fuel permeability in order to reduce crossover, thin enough (50–80 μm) to reduce ionic resistance, and high mechanical strength and low degree of swelling when immersed in water [14]. However, no AEMs can fulfil all the above requirements because of the trade-off relations between these parameters. Based on the above conceptions, we here proposed a new kind of AEMs composed of Luviqat 370 modified with cross-linked poly(vinyl alcohol) (PVA), which show high tensile strength and membrane stability with reasonable ionic conductivity. PVA is a polyhydroxy polymer which is very commonly used in practical applications because of its easy preparation and biodegradability [15]. Also, PVA has film-forming capacity, hydrophilic properties, and a high density of reactive chemical [16]. Luviqat[®] is a brand of BASF with a serious of polymers. Their aqueous solutions of cationic polymers are widely used in cosmetics, personal care, cleansing and conditioning [17,18], hence it is nontoxic and environmentally friendly. Luviqat 370 has a chemical composition of poly(3-methyl-1-vinylimidazolium chloride)-co-(1-vinylpyrrolidone)(PMVIC-co-VP). Due to the property of water soluble quaternized copolymer, it can offer anions as charge carrier conduction hydroxide (OH⁻) after ion exchanged. In particular, because the cationic species appended to polymer backbone are imidazolium cations and the cyclic quaternary imidazolium structure in PMVIC-co-VP, it is expected to contribute the membrane excellent chemical stability and mechanical property along with the high dense of cross-linkages of PVA [19–21]. Therefore, in this work, we try to fabricate PVA/PMVIC-co-VP composite membranes, ie., PVA/PMVIC-co-VP blend by a combined thermal and chemical cross-linking technique. The simplicity of the blending technique allows the membrane to be cost-effective, provides the potential for combing the attractive features of each blend component while at the same time reducing their deficient characteristic. The membrane characteristics such as hydroxide (OH⁻) conductivity, water uptake, mechanical property, membrane structure and stability were thoroughly characterized using AC impedance technique, FT-IR spectra, SEM images and XPS analysis. The results suggest that the membranes proposed in this work provide an attractive alternative for AMFC applications.

2. Experimental

2.1. Materials and membrane preparation

The membranes were prepared by a simple solution-casting method. A stock PVA (99% hydrolyzed, average molecular weight M_w = 86,000–89,000, Aldrich) aqueous solution was prepared by dissolving PVA in distilled water and then heated at 90 °C with continuous stirring until a transparent solution was obtained. Luviqat[®] FC370 (40% as active ingredients in H₂O, average molecular weight M_w = 400,000, Aldrich) was separately prepared, then mixed with the above PVA solution under stirring for at least 2 h to make sure that the new solution was completely homogeneous. Appropriate amounts of the two solutions were then mixed in the selected blending ratios: 1:0.2, 1:0.4, 1:0.6, 1:0.8, 1:1 and 1:1.2 of PVAPVA/PMVIC-co-VP by mass, respectively. The resulting solutions were poured into plastic Petri dishes, and water was evaporated under ambient conditions. When visually dry, the

membrane was peeled from the plastic substrate with a thickness of about 60–100 μm.

2.2. Thermal and chemical cross-linking of PVA/PMVIC-co-VP membranes

The annealing temperature was varied from 130 to 190 °C for 1 one hour, in order to investigate the thermal cross-linking effect on membrane performance. The chemical cross-linking time was kept at 1 one hour, which was previously demonstrated to be optimal [2]. Then the samples of square pieces of membranes (ca. 1.5 × 2 cm) were soaked in a reaction solution containing 10 mass% glutaraldehyde (GA) (25 wt% solution in water, SCRC) in acetone at 30 °C with a small amount of hydrochloric acid added, where the cross-linking between the –OH of PVA and the –CHO of GA in the membrane was catalyzed.

2.3. Alkaline PVA/PMVIC-co-VP membrane preparation

Fig. 1 schematically illustrates the preparation of PVA/PMVIC-co-VP alkaline membranes using both thermally and chemically cross-linked procedures. Immersion in 2 M KOH and equilibration for 24 hours rendered the membranes conductive by converting from Cl⁻ form into OH⁻ form. After that, the membranes were taken out and rinsed repeatedly with deionized (D.I.) water to remove the KOH on membranes surface for final conductivity measurements. The postulated model of the inner structure of PVA/PMVIC-co-VP membrane and, the representative photographs of the membranes before and after ion-exchange are illustrated in Fig. 2.

2.4. OH⁻ conductivity measurement and swelling behavior of the membranes

The OH⁻ conductivity of the formed membranes was measured by an AC impedance technique using an electrochemical impedance analyzer (CHI760), where the AC frequency was scanned from 100 kHz to 0.1 Hz at a voltage amplitude of 100 mV. Fully hydrated membranes were sandwiched in Teflon conductivity cell equipped with Pt foil contacts on which Pt black was plated [22]. The membranes were in contact with water throughout the measurements. The impedance was measured by placing the cell in a room temperature. Then OH⁻ conductivity (S cm⁻¹) was

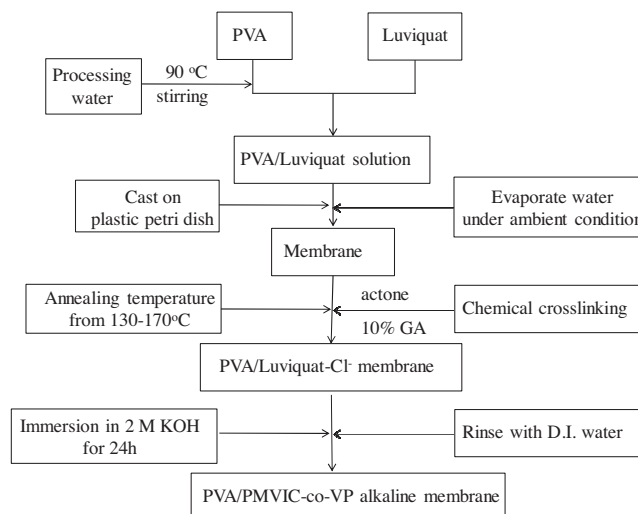


Fig. 1. Preparation procedure of thermally and chemically cross-linked PVA/PMVIC-co-VP alkaline membranes.

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