



Novel approach for the preparation of ionic liquid/imidazoledicarboxylic acid modified poly(vinyl alcohol) polyelectrolyte membranes



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ABSTRACT

This paper first time describes the preparation of the novel ionic proton exchange membrane (ILPEM). Ionic liquid, 1-butyl-3-methylimidazol-3-ium hexafluorophosphate, has immobilized into 4,5-imidazoledicarboxylic acid (IDC) modified PVA matrix. ILPEMs optimized by measuring the swelling properties at varying cross-link time. Membranes were characterized to evaluate functional groups, % swelling, gel content, molecular weight between cross-link, cross-link density, thermal stability and proton conductivity. The single cell performances of the membrane evaluated using a microbial fuel cell set-up (Biogenerator). Ionic membranes exhibited higher thermal stability, and proton conductivity of the membrane obtained was in order of 2.8–3.6 mS cm⁻¹. The Biogenerator equipped with ILPEM showed maximum current density of 1260 mA cm⁻² and power density of 245 mW cm⁻², which was higher than any of the existing conventional cathodic microbial fuel cell.

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1. Introduction

The Biogenerator (Fe²⁺/H₂ microbial fuel cell) is the first biotechnological electrochemical conversion device that harvests electrical energy from hydrogen (H₂). Oxidation of hydrogen at anode continuously produces protons and electrons. Electrons flow through outer circuit and generate electricity while protons transport through polyelectrolyte membrane (PEM) from anode to cathode where reduction of Fe³⁺ to Fe²⁺ takes place. The cathode is usually coupled with bioreactor where metal ions (Fe²⁺) oxidized in the presence microorganisms to ferric ions (Fe³⁺). Thus, analogous to conventional H₂/O₂ polyelectrolyte membrane fuel cells (PEMFC), it employs a PEM to transfer protons from anode to cathode and generates power [1]. After summarizing all the main electrochemical and biological reactions [2], the overall reaction takes place in the Biogenerator can be written as Eq. (1); i.e., the same as that of the conventional H₂/O₂ fuel cell.



Modified poly(vinyl alcohol) (PVA) as well as their blend and

composite has found enormous application as a PEM due to its very good film forming characteristics, cross-link ability, biodegradability and low cost [3–5]. Presence of enormous number of hydroxyl groups that form the proton-transfer bridges in presence of solvent-water makes the PVA an ultimate candidate for the PEM [6]. In attempt to constrain the water solubility and to increase mechanical stability in electrochemical environment cross-linking of PVA has been received much attention to induce physico-chemical modification [7]. Cross-linking reactions of the PVA can be achieved either in the presence or in the absence of catalyst by thermal treatment [8,9] or by irradiation method [10,11] in solid or in solution form. These reactions are also accomplished using organic or inorganic low molecular weight compounds [12,13] or polymers [14,15] containing at least two reactive functional groups that can react with the hydroxyl groups of PVA via aldol condensation [16] or esterification [17] to form a 3D network structure. Besides cross-linking, it is essential to combine PVA matrix with the monomer, oligomer or polymer that comprises of negatively charged ions such as carboxylic and/or sulfonic acid groups. Hereafter, to produce PEM via cross-linking route, PVA has been reacted using different cross-linking agents that have reactive sites as well negatively charged ions such as sulfosuccinic acid [18], poly(styrene sulfonic acid-co-maleic acid) [14], poly(acrylic acid-co-maleic acid) [19], p-sulfonate phenolic [20] and sulfonated polyhedral oligosilsesquioxane/ethylene diaminetetraacetic dianhydride [21]. This method has minimized the sacrificial effect of a certain amount of the hydroxyl groups of PVA by introducing the

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new proton conducting ionic sites. Nevertheless, in the practice, preparation of PEM having high ionic (proton) conductivity along with mechanical, chemical and thermal stability is a very big challenge to come across. Usually, membranes that exhibited high proton conductivity showed poor mechanical stability and vice versa. Contemporary, ionic liquid (IL) salts that are liquid at below 100 °C, have received more and more consideration as potential electrolytes for applications in electrochemical devices because of their high ionic (proton) conductivity, thermal stability and non-volatile nature [22,23]. Consequently, IL doped poly(benzimidazole) (PBI) [24] and IL/poly(vinylidene fluoride-hexafluoropropylene) blend [25] membranes were studied for fuel cell application. Tang and et al. [26] developed high temperature PEM by doping ionic liquid, 1-methylimidazolium trifluoromethanesulfonate dopant into a 3D framework of poly(acrylic acid)-poly(ethylene glycol). Membrane exhibited proton conductivity value of 19.4 mS cm⁻¹ at 200 °C under anhydrous conditions. While the IL 1-H-3-methylimidazolium bis(trifluoromethanesulfonyl)imide doped PBI PEM reached a proton conductivity value of 1.86 mS cm⁻¹ at 190 °C [27].

Considering the above unique properties of PVA and IL, this paper first time reports the cross-linking as well chemical modification of PVA through hydroxyl groups using imidazoledicarboxylic acid (IDC) in the presence of ionic liquid (IL) for the preparation of the ionic PEM. Novel methodology aimed to produce high performance ionic PEM from the miscible blend of PVA/IL/IDC for Biogenerator application. Membranes were characterized to measure the swelling properties, proton conductivity and thermal stability.

2. Experimental

2.1. Materials

Polyvinyl alcohol (PVA) (Mw 146,000–186,000, 99+% hydrolyzed), 4,5-imidazoledicarboxylic acid (IDC), trihydroxydooxidophorus acid (PA) (85% phosphoric acid) and ionic liquid (IL) 1-butyl-3-methylimidazol-3-ium hexafluorophosphate, ≥ 96% (BMIM-PF₆) were procured from Sigma Aldrich. The standard gas diffusion electrodes with platinum catalyst loading of 0.5 mg cm⁻² were purchased from FuelCellsEtc (College station, Texas, USA). Solvent dimethyl sulfoxide (DMSO), acetone and methanol were

brought from Caledon Laboratories Ltd., (Georgetown, Canada). All the chemicals were used without any further purification.

2.2. Imidazole salt preparation

A solution of 4,5-Imidazoledicarboxylic acid (IDC) was prepared using aqueous ammonia as a solvent. To this, a concentrated trihydroxydooxidophorus acid (85% phosphoric acid, PA) was added drop wise over a 15 min under continuous stirring to avoid solution exothermic. Characteristically, IDC:PA mole ratio was 0.9:1. The white fibrous precipitates of imidazole phosphate (IDCPA) salt was isolated by filtration through a 0.45 μm pore size polycarbonate membrane and successively washed with mixture of methanol/acetone solvent to remove unreacted PA residues. Finally, the IDCPA salt was dried in oven at 70 °C for 12 h. Schematic of this process is shown in Supporting information S1.

2.3. Membrane preparation

A schematic of membrane preparation process is shown in Fig. 1. A 10 wt% PVA solution was prepared in dimethyl sulfoxide (DMSO). After that predetermined weight of PVA solution, IDAPA salt and IL-BMIM-PF₆ were charged into a clean glass vial and mixed. To get dispersion and to remove entrapped air, probe sonication (MISONIX, XL-2000) was used for 15 min. After that clear viscous solution was slowly heated at 70–80 °C with stirring to moderately evaporate the DMSO solvent. The solvent evaporation was monitored by weighing the content of the glass vial. After approximately, 25% DMSO removal, PVA-IDAPA-IL gel formation starts, at that point the viscous solution in hot condition (> 60 °C) was poured onto a clean glass plate and a thin film was casted by casting knife. As the solution cooled to a room temperature (23 °C) a semisolid film was formed. After drying at room temperature for 12 h, the membrane was kept in oven at 85–90 °C for 12 h, and cross-linked by thermal treatment at 140 °C for 90–150 min. Further, cross-linked membranes were washed with cold and hot water to remove unreacted IDCPA salt and stored for various characterizations.

2.4. Membrane characterization

Swelling study that includes % swelling, water uptake, gel content, molecular weight between cross-links and cross-link

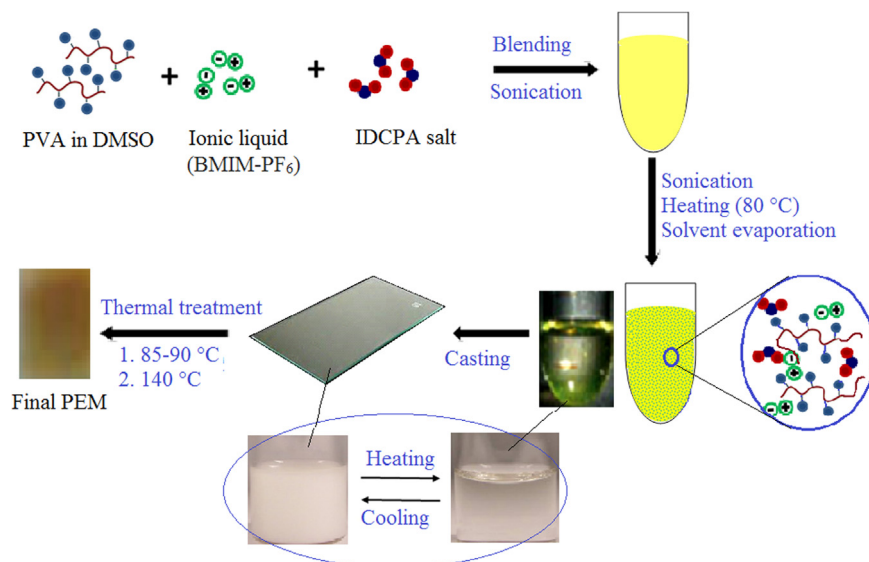


Fig. 1. Schematic of ILPEM preparation.

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