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Characterisation of PAMPS–PSS pore-filling membrane for direct methanol fuel cell

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ABSTRACT

A novel, low cost polymer electrolyte membrane for direct methanol fuel cell (DMFC) has been fabricated using the pore-filling technique with copolymer composed of poly-2-acrylamide-2-methylpropanesulphonic acid (PAMPS) and poly-styrene sulphonic acid (PSS) impregnated in a porous polyimide (PI) substrate. The pore-filling membranes, as well as a Nafion membrane as a reference, were subjected to proton conductivity, methanol permeability and DMFC performance tests at various methanol concentrations to understand the effect of ion-conductive copolymer component towards the DMFC applications. PAMPS–PSS pore-filling membranes showed a decrease in methanol permeability whilst they retained their proton conductivity, consequently improving the DMFC performance compared to commercial Nafion membrane. The steric and hydrophobic properties of PSS allow to improve methanol crossover, achieving high DMFC performance in methanol concentration up to 5 mol L^{-1}, demonstrating that PAMPS–PSS pore-filling membranes are attractive for the DMFC applications.

1. Introduction

A direct methanol fuel cell (DMFC) is one of the polymer electrolyte fuel cells that have a potential advantage of simple system concept with an excellent fuel storage capability and high efficiency of energy conversion at low temperature operation, in addition with the innocuous waste emission [1–7]. Although DMFC attracts great attention as a candidate for new portable power devices, DMFC shows far less energy density compared to hydrogen polymer electrolyte membrane fuel cells (PEMFCs) or Li ion batteries. The power density of DMFC strongly depends on the quality of the membrane electrode assembly (MEA), and thus the latter has been a key component in the development of the DMFC. In general, MEA consists of a polymer electrolyte membrane (PEM) sandwiched between anode and cathode painted with respective electrode catalysts. Methanol fuel directly reacts at the anode, without additional reformation process. Protons produced by this process permeate through the proton-exchange electrolyte membrane to react with oxygen molecules at the cathode, generating water molecules and electric current.

The conversion efficiency of DMFC depends on the performance of MEA elements, such as proton-exchange PEMs, metal catalysts and binders. Among those, great effort has been devoted to the R&D on the PEM for several decades [7–10]. Commercially available membranes mainly of the perfluorosulphonate type such as a Nifion® (DuPont) and Aciplex® (Asahi Chemical) are widely used in the fuel cell applications due to their high proton conductivity and mechanical strength, as well as its thermal and chemical stability [11–14] However, Nafion shows a high methanol crossover at its high concentrations and moreover is an expensive material. Achieving a high resistance towards methanol and a sufficient ionic conductance as well as a high chemical and mechanical stability at low manufacturing and material cost is the main challenge in the commercialisation of DMFC with power densities higher than PEMFC and Li ion batteries.

Many of the hydrocarbon polymer electrolyte membranes have been proposed as alternatives to Nafion. Most of the proposed membranes possess a sulphonic acid group within the chemical structure as a functionality to secure a high ionic conductivity [15–26]. When the sulphonated polymer membrane contacts an aqueous medium, sulphonic acid moieties attract protons associated to water molecules, creating an effective pathway for the proton transport. However, methanol molecules can also permeate through the hydrophilic channels, significantly deteriorating the cell performance. Moreover, it is important to control the water uptake within the PEMs. An excess swelling of the membrane causes a loss of its dimensional stability, while a low swelling decreases the proton conductivity of the polymer due to a loss of proton mediators in the membrane. In this way, controlling the water uptake as well as proton and methanol mobility of PEMs are the key issues for the design of a high-performance proton conductive PEMs [15,16].

Poly(2-acrylamido-2-methyl-1-propanesulphonic acid) (PAMPS) contains sulphonic acid groups in its chemical structure and was reported to show a good chemical stability and high proton

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conductivity [26–35]. Poly-4-styrenesulphonic acid (PSS) impregnated membranes were also found to manifest a high proton conductivity, methanol resistance as well as mechanical stability, allowing a high DMFC performance compared to that of Nafion [36,37]. Therefore, PAMPS and PSS might become a potential alternative as a proton conductive phase for PEM, improving the performance of DMFC. To further optimise the PEM properties, these two types of electrolyte polymer can be mixed and co-polymerised at various ratios. However, these polymers are highly soluble in water and have a low structural stability in the DMFC performance [26,31]. In order to increase the structural stability of the PAMPS/PSS copolymer in MEA, while maintaining its high proton conductivity, two strategies are proposed to fabricate a structurally stable PEM: (1) cross-linking with co-polymers and (2) employing a pore-filling method that utilises mechanically stable substrates [2,4,38–43]. The former strategy is an effective way to control the swelling as well as to retain dimensional and thermal stability of the membranes [26–30]. Moreover, methanol crossover can be controlled effectively by choosing appropriate cross-linking components in the PEM.

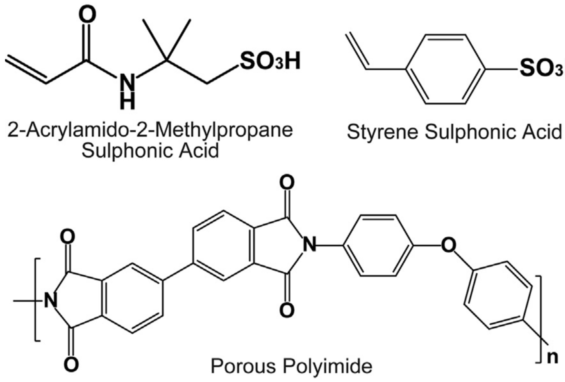
The pore-filling method using hard porous films has been described in several works [2,4,17,30,38–40]. A porous substrate has to be chemically inert and mechanically stable during the cell performance, where the expansion of soft polymer electrolyte polymers in pores is dimensionally restricted by the hard substrate matrix. At the same time, small amount of water can be added in the resulting pore-filling PEM in order to increase the proton transfer. Yamaguchi et al. have widely investigated pore-filling membranes for DMFC applications and demonstrated several advantages of this method [2,17,38,41].

In this study, pore-filling electrolyte membranes were prepared by filling a porous polyimide (PI) substrate. The latter is a rigid and mechanically stable platform preventing swelling in the course of the cell performance [17,40]. We have employed the copolymer composed of PAMPS and PSS with different mixing ratios. All materials used in this study are commercially available and are more than 10 times cheaper than Nafion membranes. Co-polymerisation was triggered by visible light, which is an extremely easy process with a high reproducibility and low manufacturing cost. It is known to fabricate homogeneous membranes. The pore-filling PEM was scrutinised by various experimental techniques focusing on the morphology, methanol permeability, proton conductivity and DMFC performance at various methanol concentrations. Nafion was also investigated for comparison. We aim to understand the electrochemical features of PAMPS/PSS copolymers in the impregnated membranes systems and to evaluate the DMFC performance of the pore-filling membranes.

2. Experimental

2.1. Preparation of the pore filing membrane

A porous polyimide (PI) was purchased from Ube industries, LTD (thickness of 17 μm, pore diameter of 50 nm and porosity of 49%). A monomer impregnation polymerisation method was used to prepare the pore-filling polymer PEM in this work, following procedure reported in Ref. [41]. In detail, a 50 wt% aqueous solution of mixed monomer was prepared mixing 2-acrylamido-2-methylpropanesulphonic acid (99%, Aldrich) and 4-styrenesulphonicacid sodium salt hydrate (Aldrich) at different mixing ratios (Scheme 1). Furthermore, 1 mol% of N,N′-methylene-bis(acrylamide) (Aldrich) and 2.2′-azobis (2-amidino propane) dihydrochloride (Aldrich) was added. Firstly, the PI substrate was soaked in acetone, followed by the sonication in the above mixed monomer solution for 10 min. Subsequently, the photo-polymerisation was initiated by irradiating the membrane by visible light for 2 h at 25 °C. After the reaction, the resulting sample was kept at 55 °C for 30 h to complete the polymerisation reaction. Such prepared membranes were then soaked in a large volume of 1 mol L^{-1} aqueous HCl for 1 h to achieve the protonation. The membrane sample was then repeatedly rinsed with ultrapure water supplied by the Milli-Q system (Milli-pore, Inc.) to remove excess HCl before characterisation and evaluation processes. Several membrane samples with different PAMPS/PSS ratios were prepared in this study as listed in Table 1. Nafion 112 (thickness 59 μm, DuPont) was used as a standard membrane for comparison. Nafion was first soaked into 30% of H_2O_2 solution at 60 °C for 1 h, rinsed with ultrapure water and then immersed into 1 mol L^{-1} aqueous H_2SO_4 at 60 °C for 1 h. This process was repeated three times in order to completely protonate Nafion membranes.



Scheme 1. Chemical structures of cross-linked sulphonated polymer electrolytes, AMPS and SS, and the porous-polyimide substrate.

Table 1
Characterisation of the PAMPS/PSS pore-filling PI membranes examined in this work.

Sample	PAMPS–PSS mixing ratio	Proton conductivity κ (S cm^{-1})	Methanol permeability coefficient *P* (10^6 cm^2 s^{-1} mol^{-1})	Thickness (μm)
PSS-0	100:0	0.058	2.22	18
PSS-20	80:20	0.068	NA	18
PSS-50	50:50	0.080	0.91	18
PSS-80	20:80	0.062	0.30	18
Nafion 112	–	0.100	8.22	59

2.2. Characterisation of membranes

Methanol permeation was evaluated by the electrochemical method using a two-compartment electrochemical cell (compartments A and B) [33], separated by the membrane to be examined. Compartment A includes a Pt wire as a counter electrode, Pt polycrystalline working electrode (diameter of 1.0 cm) and a Hg/Hg_2SO_4/0.5 mol L^{-1} H_2SO_4 reference electrode (all potential are quoted against a standard hydrogen electrode SHE). Firstly, both compartments contain 125 mL of deaerated 0.5 mol L^{-1} H_2SO_4 electrolyte. Subsequently methanol is added in compartment B (final concentration 2 mol L^{-1}). Cyclic voltammograms were recorded at 50 mV s^{-1} between 0.05 and 1.20 V to monitor the concentration of methanol in compartment A permeated through the membrane. Electrolyte solution in both compartments was continuously stirred by magnetic stirrers during measurement to minimise a methanol concentration gradient. Charges obtained by