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Experimental study to distinguish the effects of methanol slip and water vapour on a high temperature PEM fuel cell at different operating conditions

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HIGHLIGHTS

- Operational constraints while using reformed methanol for HTPEM.
- Distinguishing methanol and water vapour effect on HTPEM fuel cell performance indirectly.
- Equivalent circuit model fitting carried out and different resistances deduced.
- The best operational temperature and current density for reformed methanol coupled HT-PEMFC (RMFC) is deduced.

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ABSTRACT

The objective of this paper is to separate out the effects of methanol and water vapour on a high temperature polymer electrolyte membrane fuel cell under different temperatures (160 °C and 180 °C) and current densities (0.2 A cm^{-2}, 0.4 A cm^{-2} and 0.6 A cm^{-2}). The degradation rates at the different current densities and temperatures are analysed and discussed. The results are supported by IV curves and impedance spectroscopy. The individual resistance variations are extracted by equivalent circuit model fitting of the impedance spectra. The presence of water in the anode feed enhances the performance while the presence of 5% methanol tends to degrade the cell performance. However, the presence of H_2O mitigates some of the adverse effects of methanol. The effect of varying fuel compositions was found to be more prominent at lower current densities. The voltage improves significantly when adding water vapour to the anode after pure hydrogen operation at 180 °C. A decrease in the total resistance corresponding to the voltage improvement is observed from the impedance spectra. There is minimal variation in performance with the introduction of 3% and 5% methanol along with water vapour in the anode feed at all current densities and operating temperatures. The overall degradation over a period of 1915 h is −44 μV h^{-1}. The test time includes 595 h of test with pure H_2 and 300 h test each with 15% H_2O, 3% CH_3OH + 15% H_2O and 5% CH_3OH + 15% H_2O at varying current densities and temperatures.

1. Introduction

In the last few decades, the polymer electrolyte membrane (PEM) fuel cell has matured and is now being considered as an alternative power source with high energy density and low environmental impact. Among the various kinds of PEM fuel cells, high temperature phosphoric acid (PA)-doped, PBI-based fuel cells have advantages in terms of higher CO tolerance, simpler water management and lower operational complexities [1–4]. To harness the aforementioned advantages more work is needed to overcome the various constraints (i.e., durability, cost, fuel storage and PA distribution, etc.).

The use of H_2 as a fuel is both difficult and costly due to lack of distribution infrastructure and efficient storage systems. The ability of an HT-PEMFC to withstand higher contents of impurities like carbon monoxide (CO) and carbon dioxide (CO_2), has led the research to different fuel options for HT-PEMFC's [5–7]. Jiao et al. [8] investigated the relationship between different flow channel designs and CO poisoning in an HT-PEMFC. They concluded at high CO percentage in the fuel, parallel flow channels have minimum poisoning effects from CO. At lower CO % the effect was insignificant. Najafi et al. [9] developed an operational strategy for HT-PEMFC based combined heat and power (CHP) system. The fuel

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was natural gas and the focus was to increase the efficiency of the overall system by controlling the fuel flow to adjust the thermal and electrical output from the unit. As an alternative, reformed methanol is also being explored as a fuel in HT-PEMFCs. Methanol as a fuel has advantages in terms of reduced handling complexities and the possibility of low cost on-site H_2 production. Methanol has the lowest reforming temperature (250–300 °C) compared to other fuels. As a liquid fuel, methanol also has higher volumetric energy density compared to hydrogen [10,11].

In an HT-PEMFC, proton conductivity is induced by PA present in the membrane electrode assembly (MEA). Thus, the parameters which affect the conductivity of PA are of great importance in this kind of fuel cell. The conductivity of PA is influenced by a number of parameters, such as temperature, viscosity of PA, PA doping level of the membrane, the distribution of PA within the cell and presence of water vapour in the cell [12].

The temperature has both positive and negative effects on the performance of an HT-PEMFC. All other things being equal, higher temperature increases the ionic conductivity and enhances the reaction kinetics. However, higher temperature at a constant water vapour pressure dehydrates the acid, which leads to lower proton conductivity [13,14]. On the other hand, an excess quantity of water vapour in the cell can also lead to adverse effect on cell performance. The mass transport issues become more prominent as a result of two phenomena. Firstly, an increase in the acid volume due to increased water absorption pushes acid to the catalyst layer and blocks the pores. Secondly, the presence of water vapour in the reacting gases reduces the mole fraction of the reactants [15–17].

The relationship between temperature, weight fraction of H_3PO_4, water vapour pressure, and ionic conductivity of PA is shown in Fig. 1. Part (a) of the figure shows how the conductivity varies with acid concentration at different temperatures. The conductivity decreases with increasing concentration. The decrease is faster when the H_3PO_4 weight fraction approaches 1 at temperatures above 100 °C [18,19]. Part (b) shows the relation between concentration and water vapour pressure above the acid. At a constant vapour pressure, the acid concentration increases with increase in temperature. The effect becomes more prominent at higher water vapour pressures. On the other hand, at a constant temperature, a small change in vapour pressure can produce a large change in concentration at acid concentrations above 100% H_3PO_4 [18]. Thus, increasing the temperature will produce two opposite effects on the conductivity. The increase with temperature will generally be dominant, but dehydration may become important at very dry conditions.

He [20] carried out studies to understand the proton conduction mechanism and the factors affecting conductivity of phosphoric acid-doped PBI membranes. Their studies showed strong influence of relative humidity on the proton conductivity at higher temperatures, while below 100 °C the effect of water on the conductivity was concluded to be negligible. The addition of water vapour increases the dissociation of acid and decreases the viscosity of the solution. Both these factors have a positive influence on the proton conductivity. The study also demonstrated that conductivity increases with temperature under higher acid doping levels [20]. Ma et al. [21] also studied the mechanism of proton conductivity in a PBI-H_3PO_4 fuel cell. The results show a positive effect of relative humidity on the proton conduction mechanism at temperatures above 130 °C. Higher relative humidity (RH) is suggested to reduce the formation of pyrophosphoric acid ($H_4P_2O_7$) and the presence of a higher concentration of $H_4P_2O_7$ reduces proton conductivity [21]. A study to understand the interaction of water and PA based membranes revealed the importance of water vapour to enhance HT-PEMFC performance. A higher performance with water vapour was attributed to two reasons; the increased charge carrier concentration and formation of PA as a result of reaction

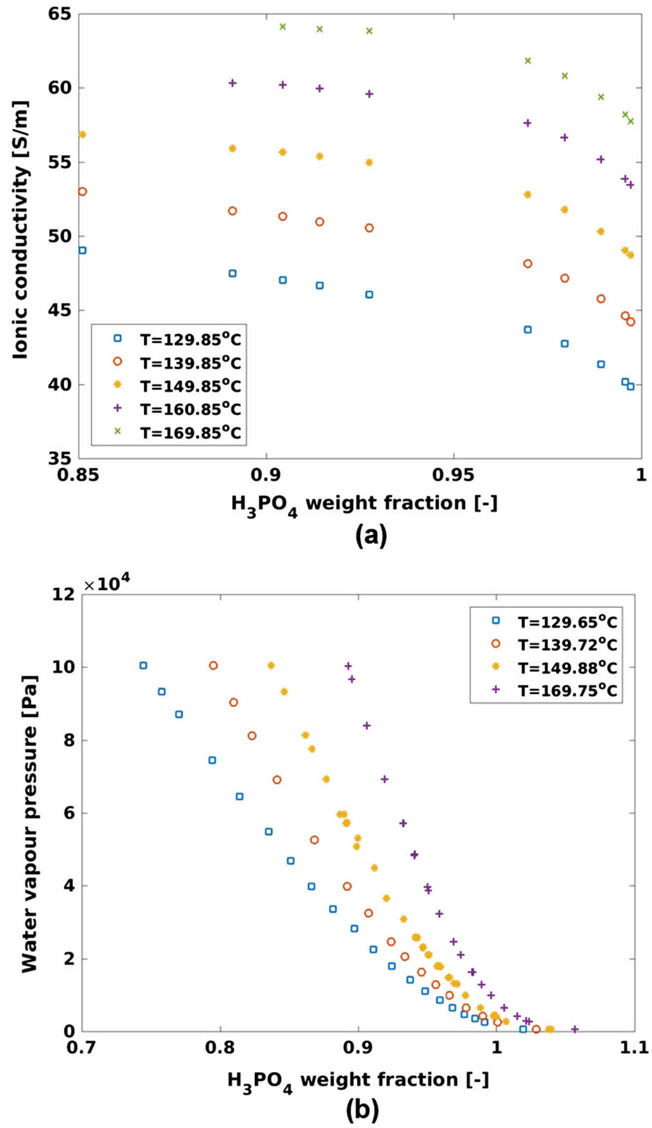

Fig. 1. The effect of temperature and weight fraction of H_3PO_4 on the ionic conductivity (a) and the H_2O vapour pressure (b) [18].

between pyrophosphoric acid and water [22]. The chemical reaction governing the phenomenon is shown by Eq. (1),

$$H_4P_2O_7 + H_2O \rightleftharpoons 2H_3PO_4 \quad (1)$$

Chen and Lai [16] analysed the effect of temperature and humidity on the fuel cell performance using impedance spectroscopy. Their study concluded minimal effect of humidity on the performance, while the membrane resistance changed with humidity. Performance and resistance comparison under different current densities and humidity levels was carried out. The charge transfer resistance decreased with increase in humidity at low current density, while it showed the opposite trend under higher current density [16]. The water transport phenomenon and its effect on HT-PEMFC performance was investigated by Zhang et al. [23]. Two operational modes, namely open-through mode and dead-end mode, were investigated to understand the movement of generated water from the cathode to anode. When operated under dead-end mode, the excess water on the anode reduced the performance, which was regained on changing to open mode. They concluded that the high affinity of phosphoric acid towards water enhances the phosphoric acid conductivity, which decreases