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Technical Communication

Preparation and characterisation of porous poly(2,5benzimidazole) (ABPBI) membranes using surfactants as templates for polymer electrolyte membrane fuel cells

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ABSTRACT

The first instance synthesis of porous poly(2,5benzimidazole) (ABPBI) membranes using sodium dodecyl sulfate (SDS) surfactants as templates is reported. The membranes were characterised by SEM, TGA, DSC and tensile tests. The tensile test results revealed that the porous ABPBI membranes exhibited unique mechanical properties compared with the original ABPBI membrane. Moreover, the porous ABPBI membranes showed high proton conductivity at 180 °C with high thermal stability when compared with the original ABPBI. A maximum conductivity of 2.23×10^{-2} S cm^{-1} of the porous ABPBI membranes was achieved at 180 °C in dry conditions, double the 1.1×10^{-2} S cm^{-1} obtained in the case of the ABPBI membrane. The porous ABPBI membrane demonstrated excellent properties on mechanical strengths, thermal stability and electrochemical performance when compared with those of the original ABPBI membrane, suggestive of a promising polymer electrolyte for fuel cells at high temperature.

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1. Introduction

Poly(2,5benzimidazole) (ABPBI) doped phosphoric acid (H_3PO_4) membranes exhibit high proton conductivity and durability at temperatures up to 180 °C [1–3], and high CO tolerance which allows the use of H_2 with up to 3% of CO impurities with only a small power loss in fuel cells [4]. ABPBI doped H_3PO_4 membranes have previously been used as a polymer electrolyte in super capacitors [5]. Furthermore, these ABPBI with very high molecular weights can be synthesized via simpler and cheaper methods than with PBI [6]. ABPBI exhibit the same or better conductivity compared to PBI owing to the increased acid-adsorbing capability of ABPBI, which contributes to the structural differences between ABPBI and PBI [7,8]. However, this is achieved at the expense of deterioration in the physical properties of ABPBI [9]. During normal fuel cell operation, the MEA is usually put under compressive force between the bipolar plates. Under this constant compressive stress, polymer electrolyte membranes (PEM) undergo creep. Polymer creep can cause permanent membrane thinning resulting in eventual failure [10]. Therefore, the mechanical property of PEM is also an important factor, leading to degradation in fuel cells. The concept of doping porous membranes with electrolytic solution was firstly applied to the lithium battery [11]. Although some reports have used this idea on the lithium salt conducting electrolytes [12,13], fewer papers have reported on proton conducting materials. A general observation is that an increase in porosity correlates

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with electrolyte solution uptake which involves a positive increase in ionic conductivity. Recently, Thomas et al. reported on the synthesis of a mesoporous PBI membrane using silica nanosol as a template to generate a continuous porosity within PBI [14]. Mecerreyes [15] prepared a porous PBI membrane by leaching out a low-molecular weight compound (porogen) to increase the ionic conductivity of the membrane. Following doping with phosphoric acid, a linear increase of the ionic conductivity with the initial porosity was observed. To date, no papers have reported on porous ABPBI membranes.

Here, we took advantages of the function of surfactants using as templates for synthesis of materials. In this work, porous ABPBI polymer materials were synthesized using sodium dodecyl sulfate as a template, which show retiform porous ABPBI polymer architectures. To our knowledge this is first study reported for the synthesis of porous ABPBI polymer.

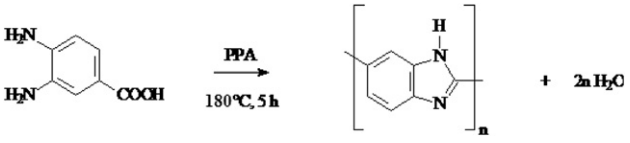
2. Experimental

2.1. Materials

3,4-Diaminobenzoic acid (DABA), 97%, used without further purification with 99% methanesulfonic acid (MSA), polyphosphoric acid (PPA) 85%, white mineral oil, sodium dodecyl sulfate (SDS) including phosphoric acid (85%) were purchased from Aldrich.

2.2. Synthesis of ABPBI

ABPBI was synthesized by condensation of DABA monomer in PPA as indicated in the scheme below.



The detailed procedure followed was: 13.0 g of 3.4-diaminobenzoic acid and 100 ml of white mineral oil were added in 3-neck glass flask equipped with mechanical stirrer under nitrogen atmosphere. The mixture was stirred well and 60 g of polyphosphoric acid was added while stirring. The mixture was heated to 180 °C, and held at this temperature for 5 h while continuously been stirred, forming dark brown materials. After the mixture has been cooled, the product was removed from the mixture by filtration. The product was neutralized with sodium carbonate, filtered and washed with deionised-water and then acetone. Then it was dried in a vacuum oven at 110 °C over night.

Porous ABPBI polymers using SDS as templates were synthesized in PPA from the DABA monomer at 180 °C for 2 h. The detailed procedure followed was: 13.0 g of 3.4-diaminobenzoic acid (Sigma–Aldrich), 1.0 g sodium dodecyl sulfate (SDS) (Sigma–Aldrich) and 100 ml of white mineral oil (Sigma–Aldrich) were then added in a 3-neck glass flask equipped with a mechanical stirrer under nitrogen atmosphere. The mixture was then stirred well and 60 g of polyphosphoric acid (Sigma–Aldrich) was added with stirring over night. Then the mixture was subsequently heated to 180 °C, and held at this temperature for 5 h while continuously been stirred, forming dark blue materials. When the mixture cooled down, the composite was removed from the mixture by filtration. To remove SDS templates and PPA remains, the product was neutralised with sodium carbonate, filtered and washed with deionised-water followed by acetone, dried in a vacuum oven at 110 °C over night.

2.3. Preparation of ABPBI membranes, porous ABPBI membranes, and H_3PO_4 doping

The ABPBI or porous ABPBI was dissolved in MSA at 130 °C to make a 4% solution. The 4% solution was then poured on flat bottom glass plates and the solution was removed by heating the hot plates in a ventilated oven at 200 °C until volatility ceased. Then, the plates were cooled down to 100 °C and hot water poured over it to peel off the membranes. Subsequently the membranes were dried in a vacuum oven at 110 °C over night. The thicknesses of membranes were 0.06–0.07 mm.

The dried ABPBI and porous ABPBI membranes were immersed in 85%H_3PO_4/H_2O (70:30 by volume) for 3 days at 70 °C.

The acid uptake measurement of membranes was done by drying them in a vacuum-dried oven at 110 °C for 3 h followed by weighing for results. The acid uptake was measured for the membranes placed into in 85%H_3PO_4/H_2O (70:30 by volume) for 3 days at 70 °C. After the acid sorption, samples were vacuum-dried at 110 °C over night. The absorbed amount of H_3PO_4 (W %) was obtained with $W\% = (W_1 - W_0)/W_1 \times 100\%$. Where W_1 and W_0 are the masses of the membranes before impregnation and after drying, respectively.

2.4. Characterisations

The membrane surface morphology was studied using a Scanning Electron Microscope (SEM, Hitachi X650). Cross section specimens for the SEM were prepared by freezing the dry membrane samples in liquid nitrogen (77 K) and subsequently breaking the membranes into small pieces. The samples were Au-sputtered under vacuum before the SEM examination.

Thermal gravimetric analyses (TGA) were analyzed by using Thermal Analyzer STA 1500 (CCI-3, Rheometric Scientific) at air with 10 °C/min.

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Differential scanning calorimetry (DSC) measurements were done by using DSC Q2000 under nitrogen atmosphere heating from room temperature up to 400 °C at a rate of 20 °C/min.

AC conductivity measurements as a function of temperature were made in air at a fixed frequency of 500 Hz–2 kHz by Hioki 3560 AC milliohm meter (HiTester). The area of electrode is 4 cm^2. The membrane was sandwiched between carbons electrode and was packed in a sealed cell. In order to eliminate the effect of absorbed humidity of the sample, the cell was heated at 180 °C and the measurements were recorded while cooling. The membrane proton conductivity σ was calculated, using the relationship:

$$\sigma = d/RS,$$

where d, R and S are the thickness, resistance and surface area of the membranes, respectively.

The effect of a constant stress on the different membrane materials was evaluated by tensile testing on a H10KT tensile test machine (Tinius olsen). The membranes were cut into samples with a length and width of 4 cm and 1.0 cm. Stress–strain curves were generated using a strain rate of 0.5 mm/min and an initial static force of 50 N at room temperature.

3. Results and discussion

3.1. SEM morphology

The morphology of the ABPBI and porous ABPBI membranes was studied from the Scanning Electron Microscope (SEM) as presented in Fig. 1. Fig. 1a and c shows uniform surfaces without pinhole defects, but differing surface morphology between ABPBI membranes and porous ABPBI membranes. Braid structures were observed on the surface of porous ABPBI membranes. Fig. 1b and d shows the cross-sectional fractures of ABPBI and porous ABPBI membranes. It can be observed that no pores penetrate into the ABPBI matrix. Fig. 1d shows the retiform porous structure that was introduced into backbone of porous ABPBI membranes.

3.2. Mechanical properties

Stress–elongation behavior at room temperature is illustrated in Fig. 2 and Table 1 summarizes the results obtained during the mechanical characterisation of ABPBI and porous ABPBI membrane.

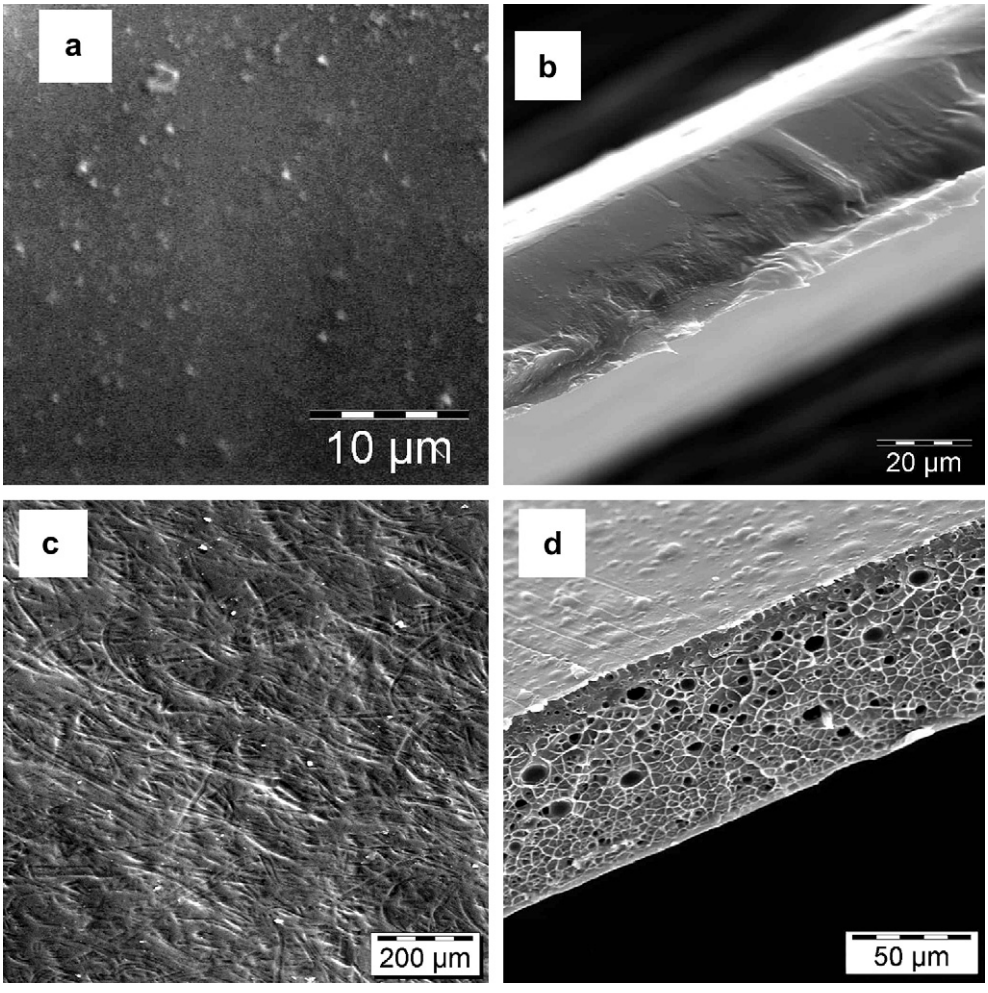

Fig. 1 – SEM images of ABPBI and porous ABPBI membranes (a, ABPBI; b, cross section of ABPBI; c, porous ABPBI; d, cross section of porous ABPBI).

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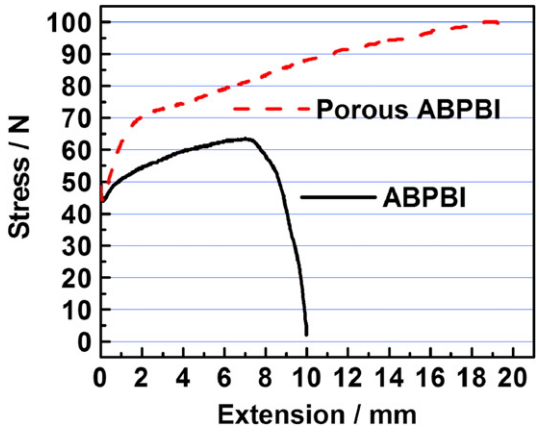

Fig. 2 – Stress–Extension curves of ABPBI and porous ABPBI membrane at room temperature.

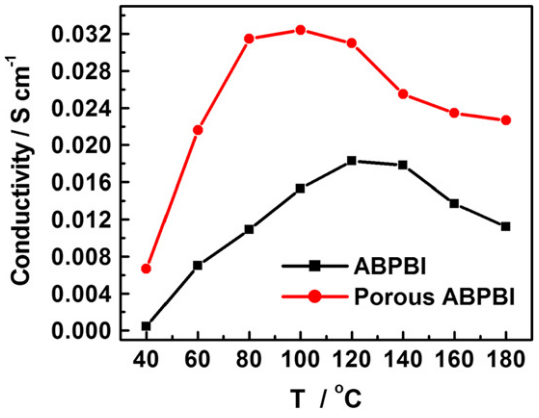

Fig. 3 – Conductivities of ABPBI and porous ABPBI membranes as a function of temperature.

As can be seen from Fig. 2 and Table 1, the original ABPBI specimens display rather brittle behavior, whereas the porous ABPBI membranes exhibit ductile behavior characterised by double elongation of the porous ABPBI (38.8%) membranes compared to the original ABPBI membrane (19.2%). For the porous ABPBI membranes, the stress at breakpoint is 66.7 MPa. Whereas only 0.6 MPa is obtained with the original ABPBI membranes. The yield stress of porous ABPBI membranes was 69.9 MPa, much higher than 19.1 MPa that was measured on the original ABPBI membranes. For porous ABPBI membranes, Young's modulus was 1.76 GPa, whereas it was 2.38 GPa in the case of ABPBI membranes. Yield stress is used as an indication of the onset of plastic deformation and Young's modulus as an indication of stiffness [16]. Young's modulus obtained by ABPBI casted at high temperature and low temperature is about 1.19 and 0.290 GPa [17], respectively and are smaller than those obtained in this work. A possible reason for there differences is through variability in manufacturing process or casting process. Mechanical properties in polymer membranes are attributed to differences in the morphology of the polymer backbone, ionic domains, or contributions from both [18]. The difference of mechanical properties between the ABPBI membrane and porous ABPBI membranes could be explained by the difference in the backbone structure between the porous ABPBI membranes and the original ABPBI membrane.

3.3. *Proton conductivity*

By exposing the ABPBI membranes and the porous ABPBI membranes to a H_3PO_4 (85%)/H_2O solution (70:30 by volume) at 70 °C for 3 days, it was observed that the acid uptake increased from the value of 63% for ABPBI membranes to 116% for porous ABPBI membranes. Fig. 3 shows the proton conductivities of H_3PO_4 solution doped ABPBI membranes and porous ABPBI membranes as a function of temperature, conductivity on both membrane was increased with the increasing of temperature and reached to a maximum and then decreased with increased temperature. A maximum conductivity of 3.2×10^{-2} S cm^{-1} of porous ABPBI membranes was achieved at 100 °C, much higher than the maximum 1.8×10^{-2} S cm^{-1} for the ABPBI membrane at 120 °C. The conductivity of porous ABPBI at 100 °C is higher than that obtained by the ABPBI·3 H_3PO_4 with 30% RH (2.5×10^{-2} S cm^{-1}) [7], is lower than that by reported [19]. To further eliminate the effect of absorbed humidity of the membrane, the cell was heated at 180 °C until stabled and the measurements of conductivity were recorded while cooling and showed on Fig. 4. A maximum conductivity was 2.23×10^{-2} S cm^{-1} for porous ABPBI membranes at 180 °C in dry condition, more than double 1.1×10^{-2} S cm^{-1} obtained in the case of the ABPBI membrane. The increase of conductivity in the porous ABPBI membranes compared to the ABPBI ones is probably due to the fact that the large pores are reservoirs for the concentrated aqueous solution of H_3PO_4.

Table 1 – The Mechanical properties of ABPBI and porous ABPBI membranes

Mechanical properties	ABPBI	Porous ABPBI
Stress at break (MPa)	0.6	66.7
Yield Stress (MPa)	19.1	69.9
Elongation at break (%)	19.2	38.8
Young's modulus (G)	1.78	2.38

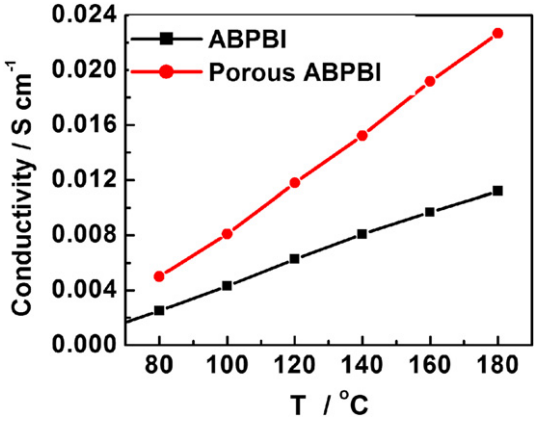

Fig. 4 – Conductivities of ABPBI and porous ABPBI membranes as a function of temperature while cooling.

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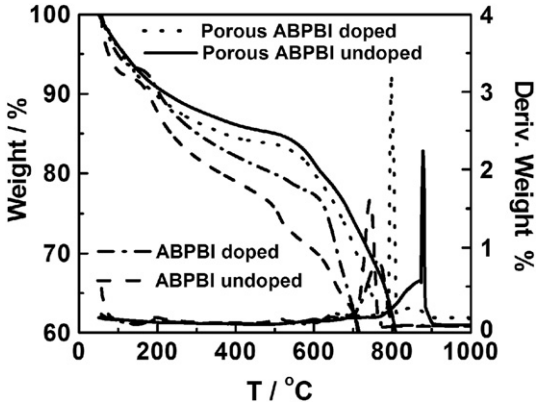

Fig. 5 – DTA and TGA curves of ABPBI and porous ABPBI membranes undoped/doped doped with H_3PO_4 at air atmosphere.

3.4. *Thermal analysis*

It is very important that polymer electrolyte membranes maintain a stable proton conductivity at elevated temperatures for PEMFC application. Thermal properties of the origin ABPBI membrane and the porous ABPBI membrane were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA and DTA (Fig. 5) of ABPBI membranes and porous ABPBI membranes before and after doped with H_3PO_4 were performed from 50 °C to 1000 °C to gain insight into their thermal stability. As depicted in Fig. 5, the first weight loss at below 100 °C is due to the water content in both membranes. The corresponding exothermic peak can be also found on the DTA curve (Fig. 5). There is an abrupt decrease of weight at about 520 °C in both membranes before doped with H_3PO_4, which may be due to the decomposition of the ABPBI matrix. Likewise, the highest corresponding exothermic peak was observed at 800 °C in the case of ABPBI, whereas the highest exothermic peak was observed on porous ABPBI membranes at 880 °C. The thermal stability was thus much higher than that of ABPBI composite membranes [3,20] and that of cross-linked porous PBI membranes [14]. From Fig. 5, it is clear that the porous ABPBI membrane and the ABPBI membranes after doped with H_3PO_4 have a significant weigh loss at about 200 °C, which can be caused by condensation reaction of phosphonic group with the dehydration. However, the porous ABPBI membrane still maintained a quite high thermal stability up to 740 °C, though after it was doped with H_3PO_4 the thermal stability of the ABPBI membranes and porous ABPBI membranes decreased.

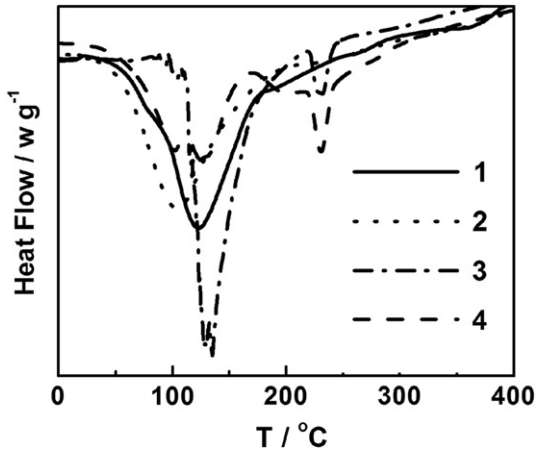

Fig. 6 – DSC curves of ABPBI and porous ABPBI membranes at air atmosphere curves: 1, porous ABPBI; 2, ABPBI; 3, porous ABPBI doped with H_3PO_4; 4, ABPBI doped with H_3PO_4.

Table 2 – Endothermic peak value (T) of ABPBI and porous ABPBI membranes

Membrane	T (°C)
ABPBI	104
Porous ABPBI	122
ABPBI-doped with H_3PO_4	100,125, 230
Porous ABPBI-doped with H_3PO_4	128,135, 230

The DSC of the ABPBI membranes and porous ABPBI membranes is presented in Fig. 6. Endothermic peak value shown in Table 2 indicate the existence of single endothermic peak for both membranes without doping H_3PO_4, attributable to the loss of absorbed water of ABPBI [21]. In the case of ABPBI doped with H_3PO_4 membranes, there are three endothermic peaks at 100, 125 °C and 230 °C, which can be ascribe to the loss of surface absorbed water of membrane, of the bound water of ABPBI matrix and condensation of PO_4 groups. In addition, the porous ABPBI doped with H_3PO_4 membranes show three endothermic peaks at 128 °C, 135 °C and 230 °C, which can be attributed to the loss of absored water, of absorbed water inside of pores and of water molecules from the condensation of PO_4 groups to give pyrophosphoric and then polyphosphoric acid, respectively [22–24]. These above results show there are more stable absorbed and bound water in the porous ABPBI membranes, which can be related with its higher conductivity than the ABPBI membrane.

4. Conclusion

Porous poly(2,5benzimidazole) (ABPBI) membrane using sodium dodecyl sulfate (SDS) surfactants as templates was synthesized resulting in a porous structured ABPBI membrane. The results of the investigation on tensile tests revealed that porous ABPBI membranes exhibit unique mechanical properties compared with the original ABPBI membrane. It has shown an increase in ductile behavior, anti-plastic deformation and an decrease in stiffness. Furthermore, this porous ABPBI membrane has shown high proton conductivity at 180 °C with high thermal stability compared to original ABPBI membrane. A maximum conductivity of 2.23×10^{-2} S cm^{-1} of porous ABPBI membrane was achieved at 180 °C in dry conditions, double the 1.1×10^{-2} S cm^{-1} obtained in the case of the ABPBI membrane. It seems likely that the adsorption and reserve capability of H_3PO_4 increased owe to the porous fabric in the case of porous ABPBI membranes, leading to a higher conductivity. The porous ABPBI membrane demonstrated excellent properties on mechanical strengths, thermal

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stability and electrochemical performance compared with those of the original ABPBI membrane, which suggests that it may be a suitable polymer electrolyte for fuel cells at high temperature. Further work is in progress to determine possible optimum conditions for enhancing the porous structure of ABPBI by operational temperature during the synthesis process to further increase the mechanical properties. On the other hand, whether the permeability of the porous membranes to hydrogen or methanol is low enough to allow high efficiency fuel cell operation remains to be tested.

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