

Short communication

Novel multilayer Nafion/SPI/Nafion composite membrane for PEMFCs

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Abstract

A novel multilayer membrane for the proton exchange membrane fuel cell (PEMFC) was developed. Nafion was dispersed uniformly onto both sides of the sulfonated polyimide (SPI) membrane. The Nafion/SPI/Nafion composite membrane was prepared by immersing the SPI into the Nafion-containing casting solution. Through immersing both membranes into the Fenton solution at 80 °C for 0.5 h for an accelerated ex situ test, chromatographic analysis of the water evacuated from the cathode and the anode of the cells and a durability test of a single proton exchange membrane fuel cells, it was proved that the stability of the composite membrane has been greatly improved by adding the Nafion layer compared with the SPI membrane. The fuel cell performance with the SPI and Nafion/SPI/Nafion membranes was similar to the performance with the commercial product Nafion[®] NRE-212 membrane at 80 °C.

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Keywords: Fuel cell; Composite membrane; Sulfonated polyimide; Nafion; Multilayer

1. Introduction

Fuel cells are efficient devices that generate electricity via chemical reaction of fuels and oxygen and therefore have been attracting more and more attention as a clean energy system [1]. One of the big challenges in the current fuel cell research is to develop an alternative membrane to the perfluorinated ionomers, for example, Nafion (DuPont). The perfluorinated ionomer membranes are highly proton conductive and chemically and physically stable at moderate temperatures, however, these preferable properties are deteriorated above their glass transition temperature (T_g) ca. 110 °C. High gas permeability, high cost, and environmental inadaptability of the fluorinated materials are serious shortage for the practical fuel cell applications. In the past decade, a variety of proton conductive materials have

been proposed as an alternative membrane. Non-fluorinated hydrocarbon ionomers, acid-doped polymers, inorganic/organic nanohybrids, solid acids with superprotonic phase transition, and acid/base ionic liquids fall into this category [2–6]. Although each material has its own advantages, most of them have failed to meet the requirements of high conductivity and durability under fuel cell operating conditions. The degradation is probably the major drawback of these hydrocarbon materials. The perfluorinated ionomers still stand as the state-of-the-art membrane.

Yu et al. [7] used Nafion membrane bonded with the PSSA membrane by hot press and located it at the cathode side. The composite membrane was designed to prevent oxidation degradation of the PSSA membrane. Ren et al. [8] used sulfonated poly (ether ether ketone) (SPEEK) membranes as the support material to prepared Nafion–SPEEK–Nafion (NSN) composite membranes. The NSN composite membrane was prepared by immersing SPEEK in Nafion-containing casting solution.

In this work, we developed a multilayer composite membrane by sulfonated polyimide (SPI) and Nafion. The two Nafion coated layers were added onto the sulfonated polyimide

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membrane by immersing to protect the SPI membrane from degradation.

2. Experimental

2.1. Materials

The 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA, 96%) was bought from Beijing Multi.Technology Co. Ltd. and used as received. The 4,4'-diamino-biphenyl 2,2'-disulphonic acid (BDSA, 95%) was bought from Shanghai World-prospect Industrial Co. Ltd. and purified before polycondensation reaction. The 4,4'-oxydianiline (ODA, 90%) was bought from Changshu Huishun Chemistry Co. Ltd. and recrystallized from ethanol prior to use. *m*-Cresol, methanol and benzoic acid were used as received. Triethylamine (TEA) was dried with molecular sieve 4A prior to use.

2.2. Random copolyimide preparation

The random copolyimides were prepared by the method reported by Genies et al. [9]. In a three-necked flask equipped with mechanical stirrer, nitrogen inlet, 1.027 g (0.003 mol) of BDSA and 0.6 ml of triethylamine were introduced with 30 ml of *m*-cresol. This mixture was stirred at room temperature until the BDSA was dissolved. Then 1.6761 g (0.006 mol) of NTDA, 0.6007 g (0.003 mol) of ODA and 1.31 g of benzoic acid were added. This reaction mixture was stirred for few minutes and then heated at 80 °C for 4 h and at 180 °C for 20 h. Before cooling, 20 ml of *m*-cresol were added and the viscous polymer solution was poured into methanol. The precipitated polyimide was collected by filtration, washed with methanol and dried under vacuum at 100 °C.

2.3. Membrane preparation

The NMP solution of SPI in TEA salt form was cast onto glass plates and dried in air at 60 °C for 12 h, then dried under vacuum at 120 °C for 2 h, 160 °C for 1 h. The as-cast membrane was soaked in 0.5 M H₂SO₄ at room temperature for 12 h. The membrane was thoroughly washed with de-ionized water. The membrane thickness was about 15 μm.

The composite membrane was prepared as the following procedure. Another SPI membrane which was made 11 μm thick was immersed in the 5% Nafion[®] dispersion (Nafion[®] R-1100 resin, DuPont Fluoroproducts, USA). The coated membrane was dried in an oven at 60 °C for 12 h to remove the residual solvents and at 120 °C for 12 h to make the Nafion crystallization. The thickness of the Nafion side layer was 2 μm. The composite membrane thickness was about 15 μm. The IEC was measured by means of a traditional titration method. A membrane sample which is about 0.500 g was soaked in 100 ml of 1.0 M NaCl solution for 2 days. Released proton concentration was titrated using 0.01 M NaOH solution. The inherent viscosities of the sulfonated polyimide were measured by using an Ostwald viscometer at 30 °C.

2.4. IR and SEM study

The infrared spectra of the membranes were recorded with a FT-IR spectrometer (JASCO FT/IR-4100). For scanning electron microscope (SEM) measurement, selected samples of the membranes were cut into pieces with scalpel. The cross-section of the membrane was examined with the JEOL (JSM 6360LV SEM) scanning electron microscope.

2.5. Electrochemical impedance spectroscopy (EIS) measurements

To investigate the ohmic resistances of the membranes under wet operation, EIS measurements were performed. For this purpose, a frequency response detector (EG&G model 1025) and a potentiostat/galvanostat (EG&G model 273A) were used.

2.6. Stability study

Thermal analysis of the SPI and Nafion[®] NRE-212 membranes were performed via thermogravimetry (TG) with a Pyn's-diamond TG-DTA-THERMOSTSR instrument at a heating rate of 10 °C min⁻¹ under nitrogen.

The SPI and Nafion/SPI/Nafion membranes were hot-pressed with two frames made of polyester then immersed in 80 °C Fenton solutions (3% H₂O₂ aqueous solution containing 10 ppm FeSO₄) for 0.5 h. After immersing, the membranes was separated from the frames and washed with de-ionized water.

Analysis of the residual water of both the anode and cathode with SPI and Nafion/SPI/Nafion operated for 20 h were performed in a JASCO (JASCO, Japan) HPLC system, consisting of a PU-2089 quaternary gradient pump, a UV-1575 intelligent UV-vis detector and an AS-2055 intelligent sampler. The chromatographic data were recorded and processed by JASCO Chrompass software. A Hypersil C18 column (5 μm, 120 Å, 250 mm × 4.6 mm) was employed for the separation of the water samples. The binary mobile phase consisted of solvents A (100 mM ammonium acetate) and B (acetonitrile). A mobile-phase gradient was used as follows: 0–30 min; 5–100% B; 30–45 min; 100% B. Injection volume was 50 μl. Flow rate was 1.0 ml min⁻¹. The effluent was detected at 254 nm by a UV detector.

For the durability test of the cells with 15 μm SPI and 15 μm Nafion/SPI/Nafion membranes, the cells were operated at a constant current density of 500 mA cm⁻² at 80 °C under fully humidified condition. The flow rates of inlet gases were kept at H₂ 50 ml min⁻¹ and O₂ 100 ml min⁻¹. The voltage at 500 mA cm⁻² and the open-circuit voltage (OCV) were recorded [10].

2.7. Membrane electrode assembly preparation and single cell test

The membrane electrode assembly (MEA) was prepared by a hot pressing process. The 20 wt.% Pt/Vulcan XC-72 (Pt/C) catalyst from E-TEK, carbon paper from Toray, PTFE suspension and Nafion solution (DuPont) were used in the MEA

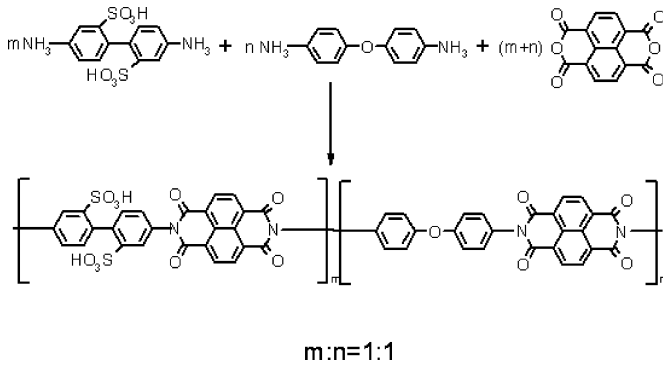


Fig. 1. Structure of sulfonated polyimide.

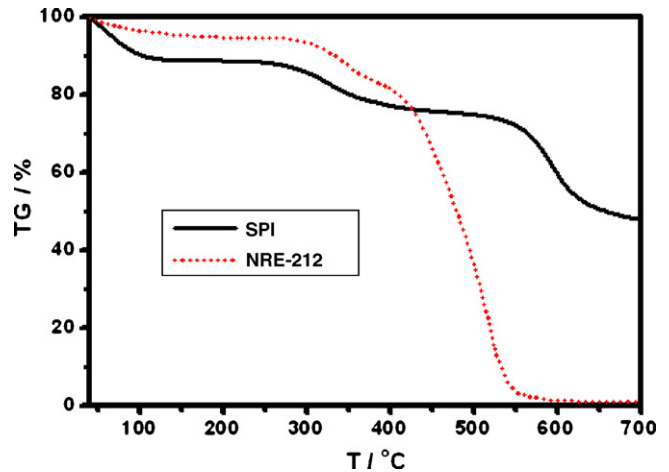


Fig. 3. TG image of SPI membrane.

preparation. The Pt/C catalyst loading of the anode and the cathode were both $0.5 \text{ mg Pt cm}^{-2}$. Two electrodes with effective area 5 cm^2 were hot-pressed onto a membrane to form a MEA. The MEA was mounted in a single cell with stainless steel end plates and stainless steel mesh flow field as current collectors. The fuel cell performance was evaluated by I - V curves at 80°C . The fuel and oxidant were fed in with co-flow. The flow rates of inlet gases were kept at H_2 40 ml min^{-1} and O_2 80 ml min^{-1} .

The cell was started by increasing the cell temperature set point to 80°C and raising the humidifier temperatures to their respective values. Similarly, the H_2 and O_2 pipeline temperatures were also maintained 5°C higher than the humidifiers to prevent water condensation in the pipelines. All data were obtained at the following conditions: humidifier temperature $T_{\text{H}_2}/T_{\text{O}_2} = 80^\circ\text{C}$; cell temperature $T_{\text{cell}} = 80^\circ\text{C}$; gas pressure $P_{\text{H}_2}/P_{\text{O}_2} = 0.30/0.30 \text{ MPa}$. And the data were recorded after 12 h fuel cell operation.

3. Results and discussion

3.1. Membrane characterization

The copolymerization of BDSA, ODA and NTDA proceeded quantitatively in *m*-cresol to give the ionomer (Fig. 1). The copolymer composition was set at 1/1 by moles to obtain the ionomer with the ion exchange capacity (IEC) as about $1.98 \text{ mequiv. g}^{-1}$. This IEC value was close to the theoretic

cal value ($2.00 \text{ mequiv. g}^{-1}$) of this sulfonated polyimide. This indicates that the copolymerization was successfully and the sulfonate groups had been introduced into polymers. The inherent viscosity of the sulfonated polyimide is 0.54 dL g^{-1} . Others reported similar viscosity data of naphthalenic dianhydride based polyimides [11].

The sulfonated copolymer was identified by IR spectra. In Fig. 2, the IR spectra of the copolymer shows the peaks at 1714 and 1670 cm^{-1} are due to the naphthalimide absorption of the polyimides and peak at 1350 cm^{-1} represent the C–N vibration. The peak at 1499 cm^{-1} is due to the ether bridge absorption. The peaks at 1030 and 1098 cm^{-1} are due to the stretching vibration of the SO_2 [12]. These all prove the formation of sulfonated polyimide.

The thermal stability of the six-membered sulfonated polyimide and the Nafion[®] NRE-212 were analysed by thermogravimetric analysis. The results are given in Fig. 3. The figure shows that sulfonated polyimide thin films exhibited a three-step weight loss. The first step was observed at around 100°C due to the loss of water molecules absorbed by the highly hygroscopic SO_3 groups [12,13]. The second step of weight loss was

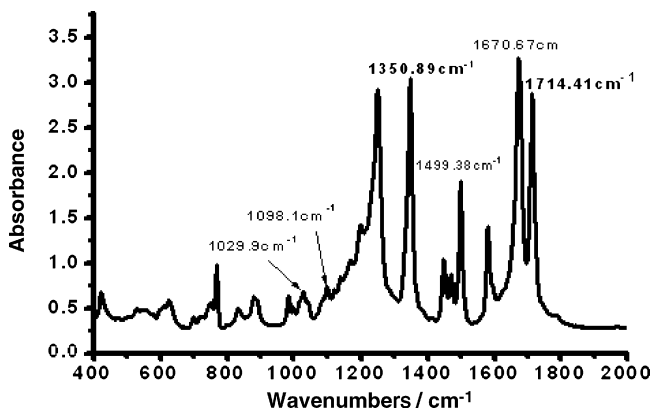


Fig. 2. IR spectrum of sulfonated polyimide.

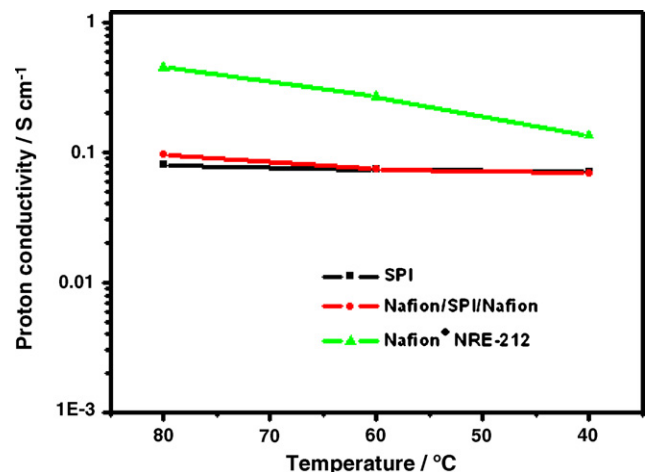


Fig. 4. Proton conductivity of membranes as a function of temperature at 100% RH.

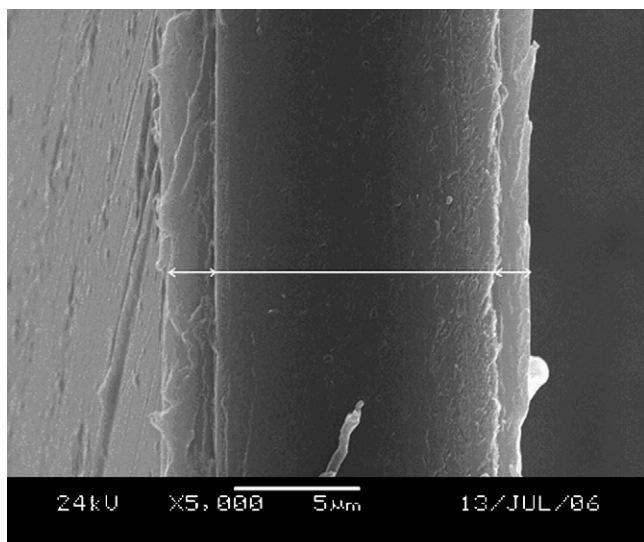


Fig. 5. SEM photomicrograph: cross-section of the Nafion/SPI/Nafion membrane.

observed at around 270 °C due to the decomposition of sulfonyl groups [12–14]. The onset of the second step is almost similar for the Nafion® NRE-212. The third step indicates the decomposition of the polymer backbones. For the Nafion® NRE-212, the onset for third step of weight loss started around 380 °C and there was a rapid weight loss observed beyond 380 °C. But the

sulfonated polyimide showed an onset at around 550 °C indicating their better thermal stability than Nafion® NRE-212. These results suggest that the synthesized sulfonated polyimide films can be used as polymer electrolyte membranes for medium and high temperature operation.

The proton conductivity of the SPI, Nafion/SPI/Nafion and Nafion® NRE-212 membranes at 100% RH was plotted as a function of temperature (as shown in Fig. 4). The results show that with the temperature increasing, the proton conductivities of Nafion increased more. The proton conductivity of SPI and composite membranes were $6\text{--}7 \times 10^{-2} \text{ S cm}^{-1}$ at 40 °C and increased to the order of $10^{-1} \text{ S cm}^{-1}$ at 80 °C. These results were close to the data reported in the literature [14].

From the cross-sectional morphology, the composite membrane was apparently composed of three layers (Fig. 5), the anode side Nafion layer, the cathode side Nafion layer and the SPI central layer. The side layers were with good adhesion to the native SPI membrane. The thickness of the side layers was uniform.

3.2. Stability

Fig. 6 shows the FT-IR spectrum of the sulfonated polyimide membranes. It displays the ether bridge of ODA absorption band at 1499 cm^{-1} (Fig. 6, top two). Meyer reported that the residues of the membrane after 600 h operation had a large quantity of

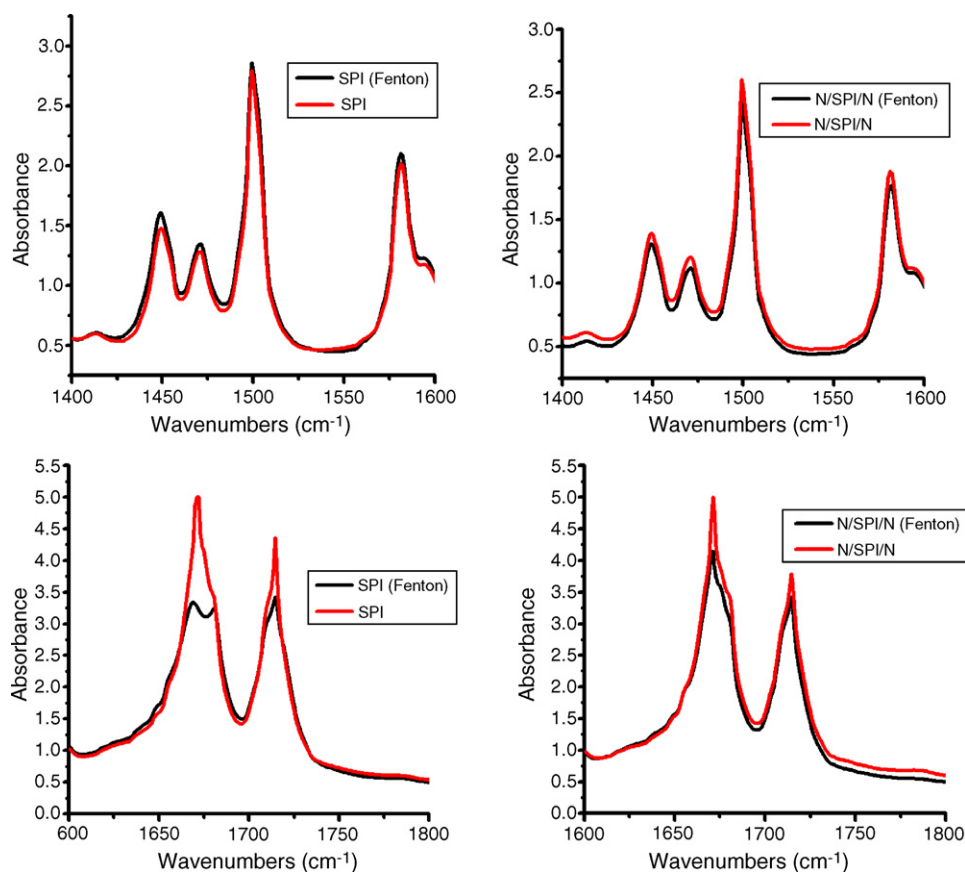


Fig. 6. FT-IR spectra of the native SPI and Nafion/SPI/Nafion membranes (top two) and SPI and Nafion/SPI/Nafion membranes treated with 80 °C Fenton solution for 0.5 h (bottom two).

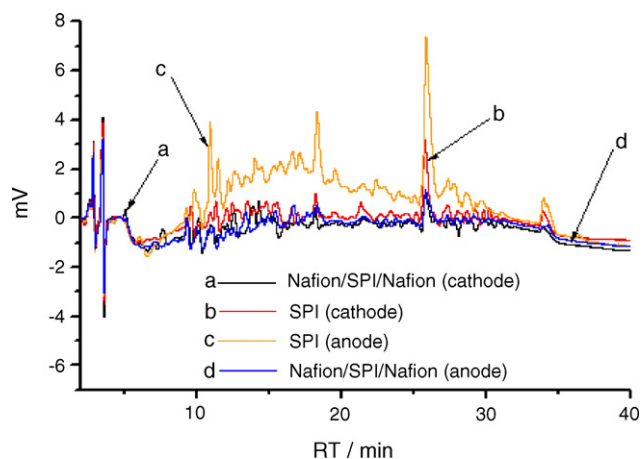


Fig. 7. High-performance liquid chromatograms of the water evacuated from the cathode (a and b) and the anode (c and d) of the cell with SPI and Nafion/SPI/Nafion membranes after operation for 20 h, respectively.

imide function groups and the characteristic components of the hydrophobic part of the polymer are not detected. In order to normalize the spectrum intensity, the absorption band located at 1499 cm^{-1} characteristic of the hydrophobic part of the polymer (ether bridge of ODA) was used as reference since it would be not affected by Fenton test [15].

We detected that the intensity of the peaks at $1714, 1670\text{ cm}^{-1}$ (Fig. 6, bottom two) of the SPI which refer to the naphthalimide absorption bands of SPI decreased greatly after immersing in 80°C Fenton solution for 0.5 h [12]. However, the intensity of the peaks at $1714, 1670\text{ cm}^{-1}$ of the Nafion/SPI/Nafion did not change very much. The IR results suggest that the SPI degradation in Fenton solution is due to the imide functions are degraded mainly in the ionic part of the polymer and some ionic oligomers are then slowly extracted by the water. Also, the IR results suggested that the coated Nafion layer could slower the SPI degradation [7].

Fig. 7 shows the high-performance liquid chromatograms (HPLC) of the water from fuel cell with SPI and Nafion/SPI/Nafion membranes. The peak area of c was larger than that of d. It suggested the degradation rate of the SPI membrane is larger than the Nafion/SPI/Nafion membrane. So, we concluded that the addition of the Nafion layer reduced the degradation of the SPI membrane.

The voltage at the current density 500 mA cm^{-2} and the OCV of PEM fuel cells with the Nafion/SPI/Nafion composite membrane and SPI membrane with time is shown in Fig. 8. It is found that the decrease of the cell voltage at 500 mA cm^{-2} and OCV of Nafion/SPI/Nafion is obviously less than the decrease of the cell voltage and OCV of SPI at the time scale of experiment. At 90 h, the OCV of SPI reduces to 0.739 V and therefore we stopped the fuel cell. These experimental results indicate that the Nafion layers located at both sides of the SPI membrane slower the degradation of the SPI membrane.

3.3. Performance of PEMFC under humidified condition

Fig. 9 shows the PEMFC performances of the SPI, Nafion/SPI/Nafion and Nafion[®] NRE-212 membranes at 80°C

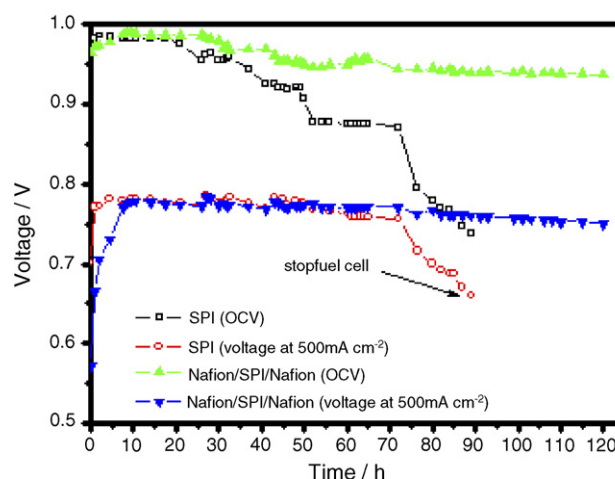


Fig. 8. Fuel cell stability test of a single cell with SPI and Nafion/SPI/Nafion membranes with fully humidified H_2/O_2 at 80°C . $P_{\text{H}_2}/P_{\text{O}_2} = 0.30/0.30\text{ MPa}$.

with humidified hydrogen/oxygen. It had been reported that higher fuel cell performance can be obtained with IEC increase and membrane thickness decrease [16]. The IEC of the SPI membranes was about $1.98\text{ mequiv. g}^{-1}$. The membrane thicknesses of the SPI and Nafion/SPI/Nafion were all $15\text{ }\mu\text{m}$. As shown in Fig. 9, the fuel cell performances of the SPI and Nafion/SPI/Nafion membranes were as high as that of Nafion[®] NRE-212. With an open circuit voltage (OCV) of $0.974\text{--}0.983\text{ V}$, SPI and Nafion/SPI/Nafion membranes showed cell voltages of $0.708\text{--}0.714\text{ V}$ at current density of 1 A cm^{-2} , which were comparable to Nafion[®] NRE-112 (0.716 V).

The performance of the Nafion/SPI/Nafion membrane was better than that of the SPI. This could be due to the ohmic loss of the Nafion/SPI/Nafion was smaller than that of the native SPI. And the proton conductor in the electrode was Nafion, the interfacial resistance could be decreased due to the good adhesion between the catalyst layer and membrane, thereby the cell resistance of the Nafion/SPI/Nafion.

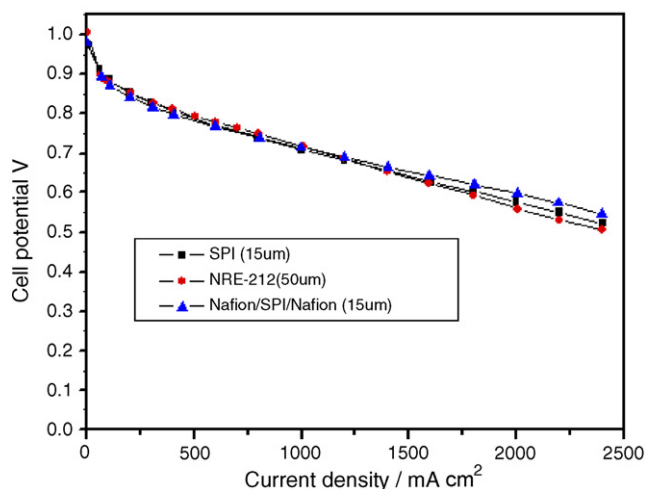


Fig. 9. Performance of H_2/O_2 fuel cells with SPI, Nafion/SPI/Nafion and Nafion[®] NRE-212 membrane under humidified conditions at 80°C .

4. Conclusions

A new Nafion/SPI/Nafion composite membrane, where Nafion membrane is bonded with the SPI membrane and located at both sides of the fuel cell, is designed to prevent the SPI membrane oxidation degradation in fuel cells. The cell performances with Nafion/SPI/Nafion composite membrane and SPI membrane were comparable to that of Nafion® NRE-212. The stability of the proton exchange membrane was obviously improved in the accelerated ex-situ Fenton solution test, analysis of the water evacuated from the cathode and the anode of the cell with SPI and Nafion/SPI/Nafion membranes and a durability test of single proton exchange membrane fuel cells.

Acknowledgments

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