

Short communication

MWCNTs reinforced Nafion[®] membrane prepared by a novel solution-cast method for PEMFC

L. Wang^{a,b}, D.M. Xing^a, H.M. Zhang^a, H.M. Yu^a, Y.H. Liu^c, B.L. Yi^{a,*}

^a Proton Exchange Membrane Fuel Cell Key Materials and Technology Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Science, 457 Zhongshan Road, Dalian, Liaoning 116023, PR China

^b Graduate School of the Chinese Academy of Sciences, Beijing 100039, PR China

^c Division of Chemical and Biomolecular Engineering, Nanyang Technological University, Singapore 637722, Singapore

Received 31 July 2007; received in revised form 30 September 2007; accepted 1 October 2007

Available online 11 October 2007

Abstract

An improved solution-cast method is presented to prepare multi-wall carbon nanotubes (MWCNTs)/Nafion[®] reinforced membrane with different MWCNTs content (from 1 to 4 wt. %). MWCNTs were oxidized by H₂O₂ and sodium hydroxide (NaOH) was added into the MWCNTs/Nafion[®]/*N,N*-dimethylacetamide (DMAC) solution. The long-term stability of the resulting dispersions was much better than the unmodified dispersions. The as-cast membrane was observed by scanning electron microscope (SEM). The MWCNTs were uniformly dispersed in the Nafion[®] resin. The tensile strength and the elongation at break were greatly improved for the reinforced membranes compared to the recast Nafion[®] membranes (54 and 27%, respectively). The fuel cell performance of the reinforced membranes with different MWCNTs contents was also tested at 80 °C under fully humidified conditions. By comparing the mechanical properties, proton conductivity and fuel cell performance of the reinforced membranes, we concluded that the content of MWCNTs in the reinforced membranes should not exceed 3 wt. %. The MWCNTs/Nafion[®] reinforced membrane with 3 wt. % MWCNTs content showed the best mechanical characteristics and excellent fuel cell performance.

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Keywords: PEMFC; MWCNTs; Nafion[®]; Reinforced membrane; NaOH

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been considered for electrical power sources as a suitable alternative to internal combustion and diesel engines because of their high power density, high energy conversion efficiency and low pollution emissions [1]. The proton exchange membranes (PEMs) currently used in fuel cells, such as Nafion[®] membranes, are highly proton conductive, chemically and are physically stable at moderate temperatures [2,3]. However, the membranes dehydrate due to high temperature and the lowering in relative humidity. The high temperature leads to reduction of the tensile strength and the conductivity for the membranes.

In the past decade, a variety of proton conductive materials have been proposed as alternative membranes. 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 [4–8]. Although each material has its own advantages, most of them have failed to meet the requirements of high proton conductivity and durability under fuel cell operating conditions. The perfluorinated ionomers still stand as the state-of-the-art membrane.

Carbon nanotubes (CNTs) have attracted particular attention for their unique structural, mechanical, and electrical properties, with extensive applications in many fields [9,10]. Studies using MWCNTs in polymer-composites report an increased storage modulus [11]. However, the dispersion of CNTs in polymer matrix is still an issue. Wang et al recently reported that the addition of NaOH to the aqueous solutions of Nafion[®] could suppress the aggregation of Nafion[®] and make the Pt in the solution distribute more uniformly [12]. In our previous works, Liu used MWCNTs to reinforce Nafion[®] through the ball-milling and solution-cast method. When the content of MWCNTs is 1 wt. %, the proton conductivity of the

* Corresponding author. Tel.: +86 411 84379097; fax: +86 411 84665057.
E-mail address: blyi@dicp.ac.cn (B.L. Yi).

membrane had not decreased and the maximum tensile strength of the membrane was greatly improved [13]. However, the ball-milling method used to disperse the MWCNTs is expensive and too complicated to mass produce.

The present study is concerned with a more convenient and effective method to prepare MWCNTs reinforced Nafion[®] membranes with better MWCNTs dispersion. MWCNTs were oxidized by H₂O₂ and an improved solution-cast method by NaOH addition was used to prepare the membranes. The as-prepared reinforced membranes show potential for application in PEMFCs.

2. Experimental

2.1. Pretreatment of the MWCNTs

About 50 mg as-received MWCNTs (Shenzhen Nanotech Port Co. Ltd., purity higher than 95 wt.%) with 20–40 nm mean range of diameter and 1–2 μm length were refluxed in 50 ml concentrated HNO₃ and concentrated H₂SO₄ (3:1, v/v) solution at 80 °C for 2 h, and were washed several times with distilled water [14,15]. Then, they were dried in an oven at 80 °C for 24 h. The oxidation of MWCNTs by H₂O₂ was carried out [16]. The acidified products were refluxed in 30% H₂O₂ at 80 °C for 6 h. Finally they were dried at 80 °C for 24 h.

2.2. Membrane preparation

Reinforced membranes were prepared by the following procedure. The Nafion[®] resin was obtained from Nafion[®] dispersion (Nafion[®] R-1100 resin, DuPont Fluoroproducts, USA). The Nafion[®]/DMAC solution (2%, w/v), MWCNTs and NaOH were mixed ultrasonically for at least 2 h in an ultrasonic cleaning instrument (KUDOS SK5200H, operated at 40 kHz and 200 W). The amount of NaOH was 10 times the amount required to exchange all the protons of the sulfonic acid groups in Nafion[®] to the sodium salt form. Then, the MWCNTs/Na-Nafion[®]/DMAC solution was filtrated to remove the residual NaOH and was poured onto a glass plate. The glass plate was heated in an air oven at 120 °C for 4 h and in a vacuum oven at 150 °C for 2 h. Finally, the membranes underwent the following standard treatment: 1 h in boiling 3% H₂O₂, 1 h in boiling 0.5 M H₂SO₄, 3 washings with H₂O followed by drying in a vacuum oven. The thickness of the reinforced membranes was in the range of 40–55 μm. The membrane prepared with NaOH was denoted as the NaOH-MWCNTs/Nafion[®] membrane. The membrane prepared without NaOH was denominated as the MWCNTs/Nafion[®] membrane. The same conditions were also used to prepare pure recast Nafion[®] membrane without treatment with NaOH.

2.3. Fourier transform infrared spectroscopy (FTIR) analysis of the oxidized MWCNTs

The infrared spectra of the MWCNTs oxidized by H₂O₂ were recorded at a resolution of 2 cm⁻¹ with a FTIR spectrometer (JASCO FT/IR-4100).

2.4. Solution stability test

The solutions of the MWCNTs/Nafion[®]/DMAC and the MWCNTs/Na-Nafion[®]/DMAC mixed ultrasonically for 1 h were stored at ambient conditions for 2 weeks. The photographs of the solution after the long-term stability test were recorded.

2.5. SEM analysis of the membrane with MWCNTs

A JEM-1200EX microscope was used to observe the surface and the morphology of the cross-sectioned, reinforced membranes. The membranes were cut with a scalpel to expose their cross-sections.

2.6. Tensile strength and elongation at break of the membranes

The tensile strength and the elongation at break of the membranes were measured with a tensile tester AG-2000A (Shimadzu, AUTO graph) at room temperature. Tensile conditions were based on Chinese Standard QB-13022-91 and samples were measured using a programmed elongation rate of 50 mm min⁻¹.

2.7. Proton conductivity measurements

Proton conductivity was measured using a four-point probe and an electrochemical impedance spectroscopy (EIS) technique over the frequency range from 10 Hz to 100 kHz (Princeton Applied Research PARSTAT 2273). The cell was placed in deionized water. The resistance value associated with the membrane conductance was determined from the high-frequency intercept of the impedance with the real axis. Proton conductivity was calculated using the following equation:

$$\sigma = \frac{L}{RDW} \quad (1)$$

where L is the distance between the two reference electrodes, R the measured membrane resistance, and D and W are the thickness and the width of the sample membrane at the ambient conditions, respectively.

2.8. Electron conductivity measurements

The samples were sandwiched between two copper plates which had been plated with gold on both sides. An electrical current of 1 A, sourced by means of a PSP-2010 programmable power supply (Manufactured by INSTEK), was provided via the two plated copper plates. During the experiments, the compacting force was increased with a step of 5 N s⁻¹ controlled by a WDW Electromechanical Universal Testing Machine. The voltage of between the two copper plates was recorded. All the samples had the same area 2.65 cm⁻². The diameter of the copper plates was 60 mm. When the sample was placed between the plates, a 35 μm polytetrafluorethylen (PTFE) gasket with a 2.65 cm⁻² holes was used to prevent the contact of the copper

plates. It was presumed that there was no plastic deformation for all the samples during the test.

2.9. Fuel 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 preparation. The Pt/C catalyst loading at the anode and the cathode were both 0.5 mg Pt cm⁻². Two electrodes with effective area 5 cm² were hot-pressed onto a membrane to form a membrane electrode assembly (MEA). The MEA was mounted in a single cell with stainless steel end plates and stainless steel mesh flow fields as the current collectors. The fuel cell performance was evaluated from *I-V* curves at 80 °C. The fuel and the oxidant were fed in with co-flow. The flow rates of inlet gases were maintained at H₂ 40 ml min⁻¹ and O₂ 80 ml min⁻¹. The fuel cell was started by heating the fuel cell to the 80 °C and heating the humidifiers to their respective values. Similarly, the H₂ and O₂ pipeline temperatures were also maintained 5 °C higher than that of the humidifiers to prevent the vapor condensation. All tests were performed under the following conditions: humidifier temperature $T_{H_2}/T_{O_2} = 80/80$ °C; cell temperature $T_{cell} = 80$ °C; gas pressure $P_{H_2}/P_{O_2} = 0.30/0.30$ MPa. The data were recorded after 12 h fuel cell operation.

3. Results and discussion

3.1. FTIR spectrums of the oxidized MWCNTs

The FTIR is a good method for the carbon materials characterization [17–19]. Fig. 1 shows the FTIR spectrum of the oxidized MWCNTs. The peaks of the corresponding groups in Fig. 1 are listed in Table 1 [20]. The –COOH and –OH groups on the oxidized MWCNTs perhaps allowed a more uniform dispersion through the interaction between the polar groups resulting

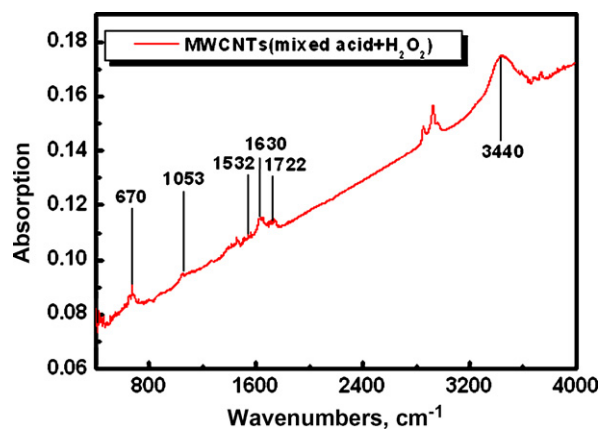


Fig. 1. FTIR image of the MWCNTs after the mixed acid and H₂O₂ treatment.

Table 1

Assignment of absorbance peaks in FTIR spectrum of the oxidized MWCNTs

Vibrational bands (cm ⁻¹)	Assignment
3440	OH str.
1722	C=O str.
1630	H-b and (C=O str.)
1532	–C=C– str.
1053	CH ₂ –O–H
670	–C=C– str.

in an increase in the proton conductivity of the composite membranes.

3.2. Solution stability test

After 1 h of sonication, the two kinds of dispersions became homogeneously ink-like, and close inspection revealed that aggregates of nanotubes were not found at the bottom of beaker. When the stability of the MWCNTs/Nafion[®]/DMAC and the MWCNTs/Na-Nafion[®]/DMAC solutions were compared after prolonged standing of 2 weeks under ambient conditions, it was found that the MWCNTs/Nafion[®]/DMAC/NaOH

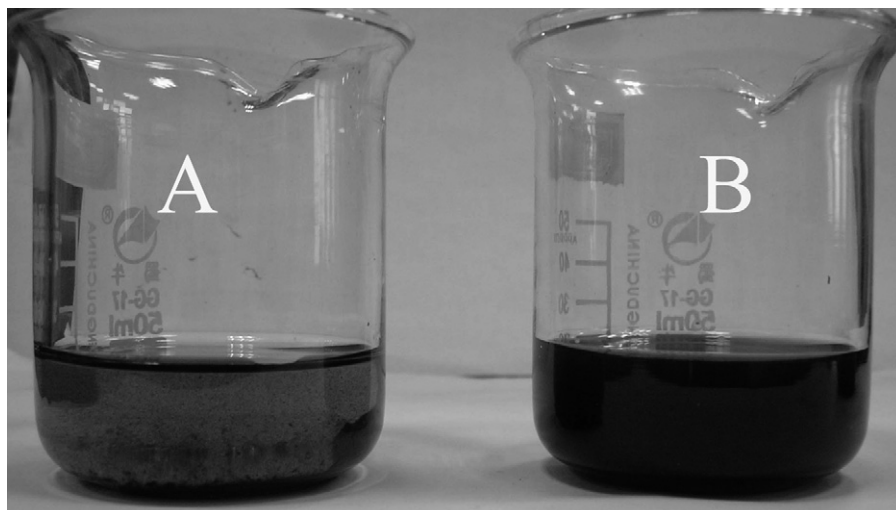


Fig. 2. Images of the MWNT-Nafion[®] in DMAC after 2 weeks, (A) without NaOH; (B) with NaOH.

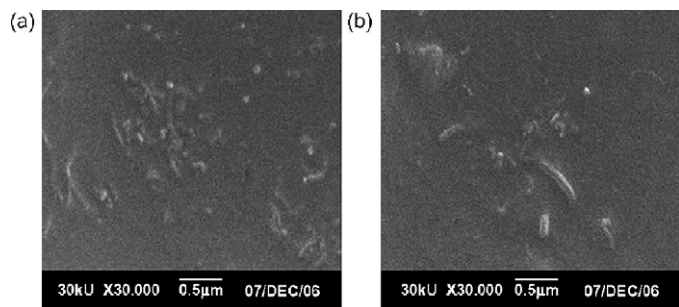


Fig. 3. SEM surface images of 2% MWCNTs/Nafion[®] reinforced membranes, (a) MWCNTs/Nafion[®] membrane; (b) NaOH-MWCNTs/Nafion[®] membrane.

solution remained homogeneous (Fig. 2(B)), whereas, the MWCNTs/Nafion[®]/DMAC had a precipitate at the bottom of the beaker (Fig. 2(A)). The long-term stability test shows that the added NaOH could exchange the proton form Nafion[®] into sodium ion form Nafion[®] at ambient conditions. It prevents the secondary aggregation of Nafion[®] and thereby prevents the aggregation of the MWCNTs [21]. Also, the oxidized MWCNTs could be dispersed into Nafion[®] more easily because of interactions between the –OH and –COOH groups of the oxidized MWCNTs and the sodium sulfonate groups of the Nafion[®]. This hypothesis needs to be further validated with more effective characterization methods.

3.3. SEM analysis of the membrane with MWCNTs

Fig. 3(a) and (b) shows that the surface of the MWCNTs/Nafion[®] and the NaOH-MWCNTs/Nafion[®] reinforced membranes. From the SEM microphotograph Fig. 3(a), the surfaces of the MWCNTs/Nafion[®] membrane show MWCNTs as agglomerates. However, the surface of the NaOH-

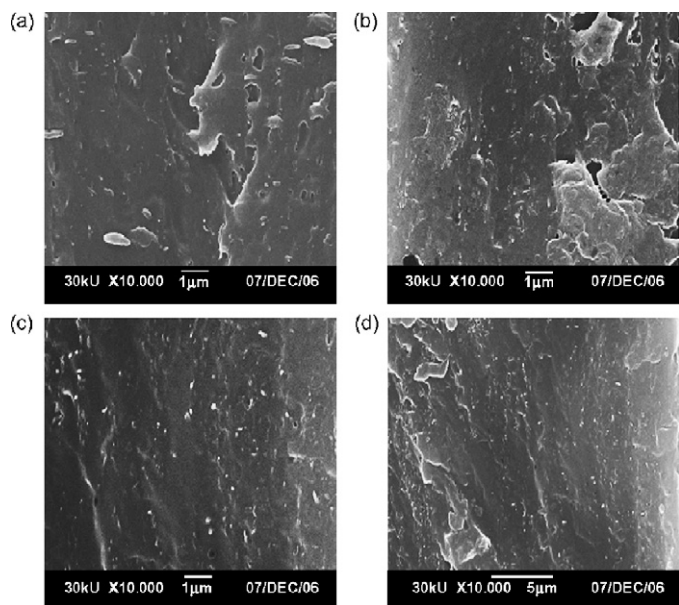


Fig. 4. SEM cross-section images of 2% MWCNTs/Nafion[®] reinforced membranes: (a) and (b) MWCNTs/Nafion[®] membrane (10,000 \times); (c) NaOH-MWCNTs/Nafion[®] membrane (10,000 \times); (d) NaOH-MWCNTs/Nafion[®] membrane (5000 \times).

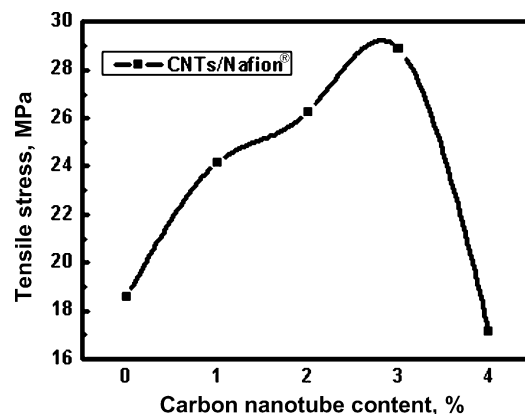


Fig. 5. Tensile strength of NaOH-MWCNTs/Nafion[®] reinforced membranes with different MWCNTs contents.

MWCNTs/Nafion[®] membrane shows the isolated form of MWCNTs (Fig. 3(b)). Fig. 4(a)–(d) are the cross-sections of the MWCNTs/Nafion[®] reinforced membranes with the MWCNTs content of 2 wt.%. The white dots represent the MWCNTs. The MWCNTs dispersed more uniformly in the NaOH-MWCNTs/Nafion[®] (Fig. 4(c and d)) than in MWCNTs/Nafion[®] (Fig. 4(a and b)). There are more white dots in images representing the same area of the NaOH-MWCNTs/Nafion[®] membranes, and this proves that the carbon nanotubes can be effectively dispersed when NaOH is added via the described solution-cast method with the oxidized MWCNTs. The improved dispersion is probably because of covalent or ionic bond formation between the carbon nanotubes and the Nafion[®].

3.4. Tensile strength and elongation at break of the membranes

Fig. 5 indicates the tensile characteristic of NaOH-MWCNTs/Nafion[®] reinforced membranes with different contents of MWCNTs. Adding MWCNTs to Nafion[®] increased the tensile characteristics of the membrane. When the MWCNTs content reached 3 wt.%, the tensile strength of the NaOH-MWCNTs/Nafion[®] reinforced membrane increased from 18.5 MPa (recast Nafion[®]) to 28.5 MPa (an increase

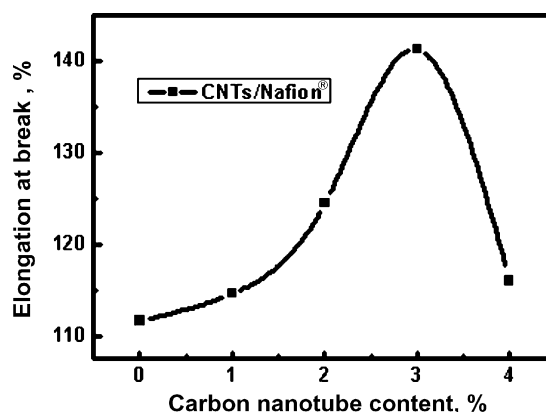


Fig. 6. Elongation at break of NaOH-MWCNTs/Nafion[®] reinforced membranes with different MWCNTs contents.

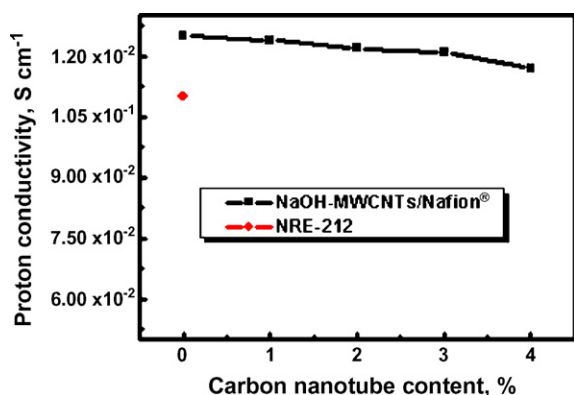


Fig. 7. Proton conductivities of NaOH-MWCNTs/Nafion[®] reinforced membranes with different contents immersed in liquid water at 80 °C.

of 54%). Fig. 6 shows the elongation at break of NaOH-MWCNTs/Nafion[®] reinforced membranes with different MWCNTs contents. The tendency of the increased elongation at break follows the same trend as that of the tensile strength. When the MWCNTs content reached 3 wt.%, the elongation at break of the NaOH-MWCNTs/Nafion[®] reinforced membrane increased from 112% (recast Nafion[®]) to 142% (an increase of 27%). Filler dispersion, aspect ratio, and orientation of the MWCNTs in polymer matrix are the critical factors, which affect the mechanical characteristic of the MWCNTs reinforced polymers. The good dispersion of MWCNTs prepared from improved solution-cast method increases the tensile strength of the membranes. The interface between the Nafion[®] and the treated MWCNTs also plays an important role in reinforcing the composites by effectively transferring the stress between the MWCNTs and the Nafion[®] resin. The oxidation of MWCNTs probably increases the interaction between Nafion[®] and MWCNTs. The increased tensile strength and elongation at break could help to delay membrane failure which occurs when pure Nafion[®] is hydrated at temperatures higher than 80 °C and might improve fuel cell durability.

3.5. Proton conductivities of the NaOH-MWCNTs/Nafion[®] reinforced membranes

Fig. 7 shows the proton conductivities of the NaOH-MWCNTs/Nafion[®] reinforced membranes immersed in liquid water. The results show that with the increase of MWCNTs content, the proton conductivities of the NaOH-MWCNTs/Nafion[®] membrane decreased slightly. When the content of MWCNTs exceeded 3 wt.%, the proton conductivity of the composite membrane decreased more obviously. This might be due to electron passage formed in the membrane when the content of MWCNTs exceeded 3 wt.%.

3.6. Electron conductivities of the NaOH-MWCNTs/Nafion[®] reinforced membranes

Fig. 8 shows the electron conductivities of the NaOH-MWCNTs/Nafion[®] reinforced membranes. The results show that when the content of MWCNTs was increased between

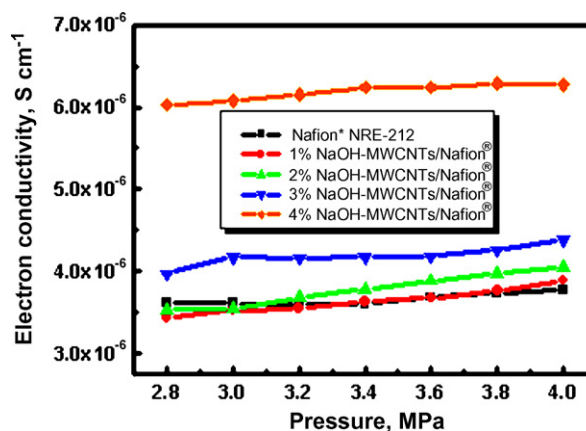


Fig. 8. Electron conductivities of the NaOH-MWCNTs/Nafion[®] reinforced membranes and NRE-212 with different contents of MWCNTs under different pressures at room temperature.

1 and 3 wt.%, the electron conductivities of NaOH-MWCNTs/Nafion[®] membrane increased slightly. The electron conductivities of reinforced membranes with 1 and 2 wt.% MWCNTs were almost the same as that of the electron conductivities of Nafion[®] NRE-212 membrane. When the content of MWCNTs exceeded 3 wt.% the electron conductivity markedly increased (from 3.0×10^{-5} to 4.5×10^{-5} S cm⁻¹). This is because when the content of MWCNTs exceeded 3 wt.%, the electron conduction passageway was formed in the membrane.

3.7. Performance of PEMFCs operated under fully humidified conditions

Fig. 9 shows the polarization curves of cells with NaOH-MWCNTs/Nafion[®] reinforced membranes operated under fully humidified conditions and at 80 °C cell temperatures. The cell performance with the reinforced membranes was a little better than that with the commercial NRE-212 membrane. This is possibly due to the good proton conductivity of the Nafion[®] prepared by the recasting method. When the MWCNTs content in the reinforced membrane increased, the fuel cell

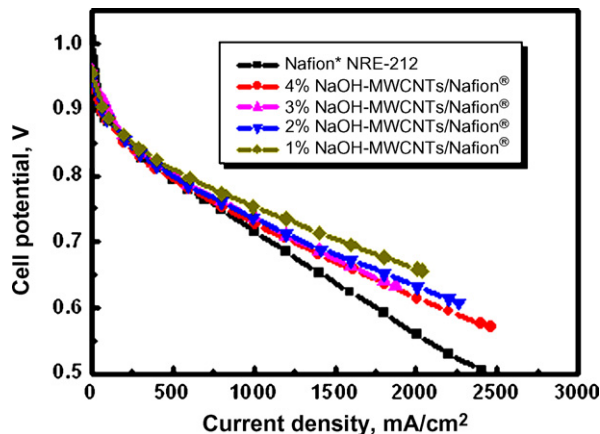


Fig. 9. Fuel cell performance of the NaOH-MWCNTs/Nafion[®] reinforced membranes with different contents of MWCNTs and NRE-212 at 80 °C under humidified conditions.

Table 2
The open circuit voltage (OCV) of the fuel cell made with different membranes

Membrane	OCV (V)
Recast Nafion [®] (50 μm)	0.965
Reinforced membrane (1%) (40 μm)	0.956
Reinforced membrane (2%) (55 μm)	0.961
Reinforced membrane (3%) (50 μm)	0.960
Reinforced membrane (4%) (50 μm)	0.930

performance decreased. The performance loss of the NaOH-MWCNTs/Nafion[®] reinforced membranes was due to the slight decrease of the membrane proton conductivity, which is caused by the replacement of polymer with MWCNTs. However, the fuel cell performances of the MWCNTs composite membrane compare favorably with state-of-the-art membranes in fuel cell applications.

Table 2 shows the open circuit voltages (OCV) of the fuel cell made with different membranes. The OCVs of the fuel cell with 1, 2 and 3 wt.% reinforced membranes were between 0.955 and 0.960 V. These values are similar to that of the recast Nafion[®] (0.965 V) prepared in our laboratory but are lower than that of pure Nafion[®] 212 (at about 0.98 V). When the content of the MWCNTs reached 4 wt.% in the membrane, the OCV decreased to 0.930 V due to the electronic conduction and the short circuit caused by the MWCNTs. Therefore, the MWCNTs content in the reinforced membrane prepared by present method should not exceed 3 wt.%.

4. Conclusions

A NaOH-MWCNTs/Nafion[®] reinforced membrane was prepared using MWCNTs to reinforce Nafion[®]. The oxidized MWCNTs and an improved solution-cast method by NaOH addition were used to prepare the membrane. The FTIR proved the formation of –COOH groups on the wall of MWCNTs after the oxidation of the MWCNTs. The long-term stability test shows the advantages to NaOH treatment and MWCNTs oxidation in improving dispersion quality in the Nafion[®]/DMAC solution. Because of the addition of MWCNTs, the tensile strength and elongation at break of the reinforced membranes were greatly improved. The surface and morphology the cross-sectioned, reinforced membrane with 2 wt.% MWCNTs were examined with SEM. The SEM results showed a homogeneous MWCNTs dispersion in the 2 wt.%

NaOH-MWCNTs/Nafion[®] membrane at the surface and in cross-section. The proton conductivity and fuel cell performances with NaOH-MWCNTs/Nafion[®] reinforced membranes were not much lower than that of the recast Nafion[®]. The fuel cell performances of the reinforced, MWCNTs composite membrane compare favorably with state-of-the-art membranes in fuel cell applications.

Acknowledgment

We gratefully acknowledge the financial support for this work provided by National Natural Science Foundation of China (20476104 and 20636060).

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