A tubular direct methanol fuel cell with Ti mesh anode

Zhi-Gang Shao [a],[b],*, Wen-Feng Lin [b], Fuyun Zhu [b],
Paul A. Christensen [b], Huamin Zhang [a], Baolian Yi [a]

[a] *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China*
[b] *School of Chemical Engineering and Advanced Materials, Bedson Building, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, UK*

Abstract

A novel tubular cell structure for a direct methanol fuel cell (DMFC) is proposed based on a tubular Ti mesh and a Ti mesh anode. A dip coating method has been developed to fabricate the cell. The characterization of the tubular MEA has been analyzed by scanning electron microscopy (SEM), energy dispersive X-ray (EDX), half cell and single cell testing. The tubular DMFC single cell comprises: a Ti mesh, a cathode diffusion layer and catalyst layer, a Nafion recast membrane and a PtRuO$_x$/Ti anode. Half cell tests show that the optimum catalyst loading, Ru/(Ru + Pt) atomic ratio and the Nafion loading of a PtRuO$_x$/Ti mesh anode are: 4 mg cm^{-2}, 38% and 0.6 mg cm^{-2}, respectively. Single cell tests show that the Nafion loading of the recast Nafion membrane and the concentration of the methanol in the electrolyte have a major influence on cell performance.
© 2006 Elsevier B.V. All rights reserved.

Keywords: DMFC; Tubular; Ti mesh

1. Introduction

With the development of information technology, the power consumption of portable electronic devices such as cellular phones, portable computers, digital cameras, and so on, is increasing. Because of its characteristics such as simple construction, easy operation, liquid fuel and high efficiency, the direct methanol fuel cell (DMFC) is considered a promising candidate for the power supply of portable equipment [1–3]. So far, many planar type DMFCs for portable applications have been developed [4–6]. However, compared with a tubular type DMFC, the planar type fuel cells have some disadvantages, for example: (1) a small electrode surface to volume ratio and (2) a lower flexibility in shape. Up to now, little research on tubular DMFC has been reported except that Okada et al. [7] reported a prototype of a DMFC utilizing tubular polymer electrolyte membranes. Nevertheless, it is difficult to coat the catalyst layer on the inside of a tubular polymer electrolyte membrane.

Ti mesh anodes prepared by deposition of the catalyst directly on the Ti mesh have been used in a DMFC [8,9]. Compared with the conventional structure of the anode, the mesh anode has many advantages, e.g.: (i) simplicity; (ii) easily produced on a mass scale; (iii) low cost; (iv) allowing flexibility in terms of shape; (v) collects current easily. Following on our previous work, a new design of a small-scale DMFC implementing a tubular type Ti mesh is further developed. In this design, a tubular Ti mesh is used as the backing layer of the cathode, and a Ti mesh is coated with a PtRuO$_x$ catalyst as the anode.

2. Experimental

2.1. Preparation of the anode

Following on from the work of Scott and co-workers on Ti mesh anodes [8], hydrophilic anodes were prepared by direct deposition of a PtRuO$_x$ catalyst onto titanium mesh using a thermal decomposition method. The procedure was as follows: firstly, Ti mesh was immersed in 10% oxalic acid at 80 °C for 1 h then, rinsed with De-ionized (Millipore) water (18 MΩ cm). The mesh was then dipped into the catalyst precursor solution and allowed to dry in air. This process was repeated several times until the desired catalyst loading was achieved. The precursor solution was a mixture of H$_2$PtCl$_6$ and RuCl$_3$ (0.2 M) in isopropanol. Afterwards, calcination was performed in air at 450 °C in a ceramic tube furnace for 1 h. Finally, the electrode was allowed to cool down to room temperature and weighted. The electrodes so prepared are denoted as PtRuO$_x$/Ti.

* Corresponding author. Tel.: +86 411 84379669; fax: +86 411 84665057.
E-mail address: zhgshao@dicp.ac.cn (Z.-G. Shao).

2.2. Preparation of the cathode

The cathodes were prepared by a dip coating method. A tubular Ti mesh pre-coated with carbon was used as the diffusion layer. The procedure for carbon coating on Ti mesh was as follows: a tubular Ti mesh (Ø 3 mm, provided by Heggemann) was dipped into the mixture of the uncatalysed carbon (Vulcan XC-72), PTFE and isopropanol, and then dried in the air. This process was repeated several times until 3.5 mg cm^{-2} carbon loading was reached. The weight ratio of the uncatalysed carbon and PTFE was 1:1. After that, a mixture including Pt/C catalysts (50% Pt, Johnson Matthey), 30 wt.% Nafion® was dipped on the outside surface of the diffusion layer as the catalyst layer. The Pt catalyst loading of the cathode was about 3.5 mg cm^{-2}.

2.3. Fabrication of the membrane electrode assembly (MEA)

The tubular cathode supported inside with a stainless steel rod was dipped into a 20% Nafion solution (Aldrich) and dried in the air. This process was repeated several times until the desired Nafion loading (dry weight) was achieved. The electrode was dried at 120 °C for 30 min and so a cathode with a Nafion recast membrane was completed. Finally, a 5 wt.% Nafion solution (EW 1100) was sprayed onto the PtRuO$_x$/Ti anode, equivalent to a dry Nafion loading of about 0.6 mg cm^{-2}. The membrane electrode assembly was prepared by wrapping a PtRuO$_x$/Ti anode on the outside surface of the recast membrane, and the anode was connected by spot-welding.

2.4. Half cell testing

Half cell testing was performed in a conventional three-electrode cell at room temperature. The reference electrode was a silver/silver chloride (Ag/AgCl) electrode in saturated KCl, which was connected to the cell via a glass capillary. In this paper, unless otherwise specified, all electrode potentials are quoted versus the Ag/AgCl reference electrode. Its potential versus RHE is 0.199 V at room temperature. The counter electrode was a 2.5 cm × 2.5 cm Pt foil. The working electrode was a 1 cm × 0.5 cm PtRuO$_x$/Ti. The instrument used to control potential/current was a Voltlab PGZ301 Dynamic-EIS.

Firstly, cyclic voltammetry was carried out on all of the anodes in N$_2$-de-aerated electrolyte containing 0.5 M H$_2$SO$_4$ at room temperature (20 °C). The electrodes were cycled between −0.2 and 0.7 V at a scan rate of 50 mV s^{-1} until a stable state of the electrode was reached. Linear sweep voltammetry (LSV) was performed on the anodes in N$_2$-de-aerated electrolyte containing 0.5 M H$_2$SO$_4$ + 0.5 M CH$_3$OH at room temperature between −0.2 and 0.5 V at a scan rate of 1 mV s^{-1}.

2.5. Single cell testing

Fig. 1 shows a schematic diagram of the apparatus for single cell testing. A mixture of 0.5 M H$_2$SO$_4$ and the methanol water solution was used as the electrolyte. Room temperature and atmospheric air was fed to the cathode inlet at a flow rate of
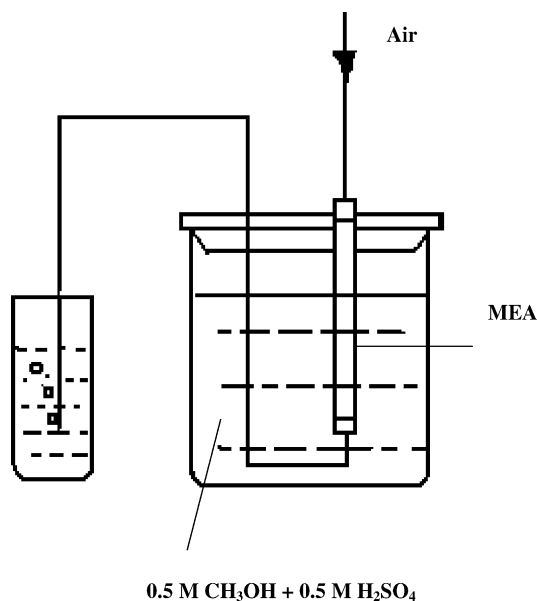

Fig. 1. Schematic diagram of the apparatus for single cell testing.

200 ml min^{-1} without pre-heating and humidification. The temperature was controlled by the water bath at 50 °C. The active area of all the electrodes was ca. 5 cm^2.

2.6. Physico-chemical characterization

A Jeol JSM-5300LV scanning electron microscope (SEM) was employed to investigate the structures and morphology of the MEA. Energy dispersive X-ray (EDX) spectroscopy was also employed for the characterisation of the anode electrodes using a RONTEC spectrometer (made in Germany).

3. Results and discussion

3.1. Microscopic structure of the tubular MEA

An image of a tubular DMFC single cell is shown in Fig. 2. Scanning electron microscopy (SEM) photographs of the cross-
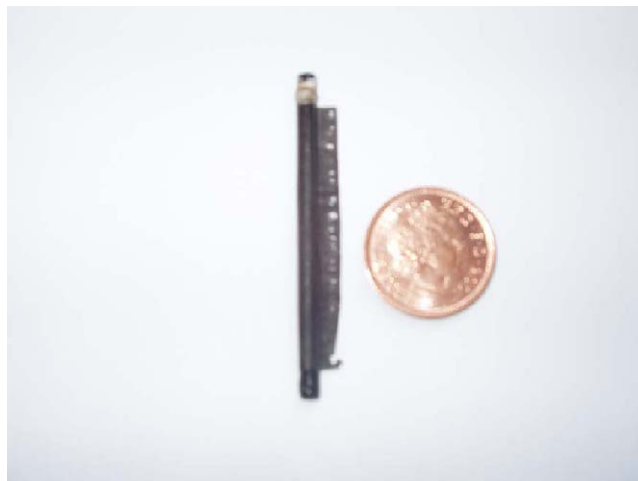

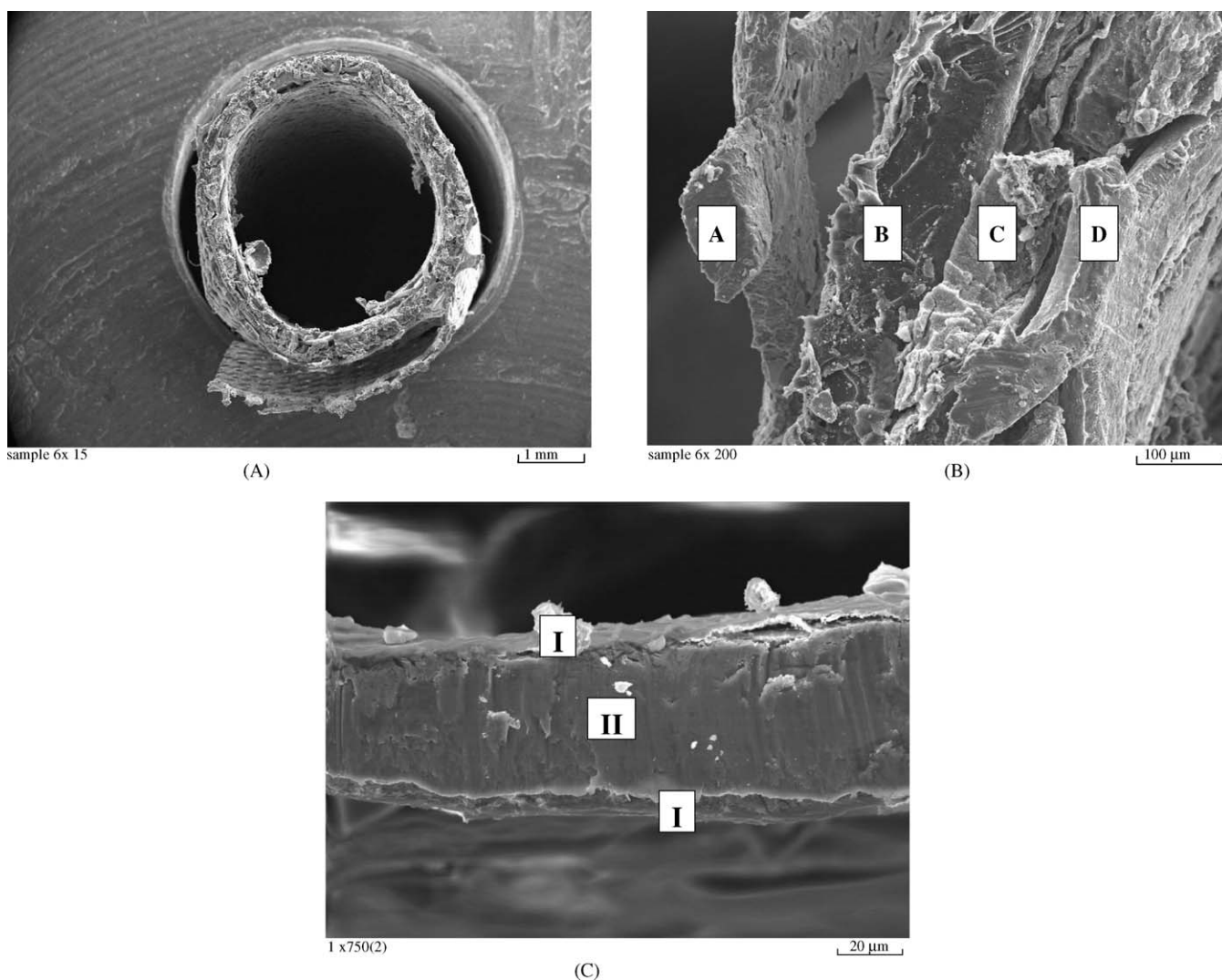Fig. 2. A photograph of a tubular DMFC single cell.

Fig. 3. SEM analysis of the cross-section view of the tubular membrane electrode assembly (MEA) and PtRuO$_x$/Ti anode: (a) top view of MEA, magnification ×15; (b) part of MEA, magnification ×200: (A) PtRuO$_x$/Ti anode, (B) Nafion recast membrane, (C) the cathode diffusion layer and catalyst layer and (D) Ti mesh; (c) PtRuO$_x$/Ti anode: (I) PtRuO$_x$ catalyst layer and (II) Ti mesh.

section of the new tubular DMFC are shown in Fig. 3a and b. It is seen from Fig. 3a that the diameter of the Ti mesh, which is used as the backing layer of the cathode, is about 3 mm. Fig. 3b shows that the tubular DMFC single cell comprises a Ti mesh, the cathode diffusion layer and catalyst layer, Nafion recast membrane, and PtRuO$_x$/Ti anode from inside to outside in the radial direction. A cross-sectional view of the PtRuO$_x$/Ti anode is shown in Fig. 3c; it is observed that the PtRuO$_x$ layer is a ca. 5 µm coating on top of the ∼50 µm Ti mesh. The PtRuO$_x$ catalyst layer was found to adhere well to the Ti mesh.

3.2. Half cell tests

Fig. 4 shows the effect of the catalyst loading on the activity of the anodes for the methanol oxidation. It is seen, the optimum catalyst loading was 4 mg cm^{-2}. This can be explained by that the specific surface area of the electrodes decreases with the catalyst loading increases. Thus, the catalyst loading of the tubular anode is chosen as 4 mg cm^{-2}.
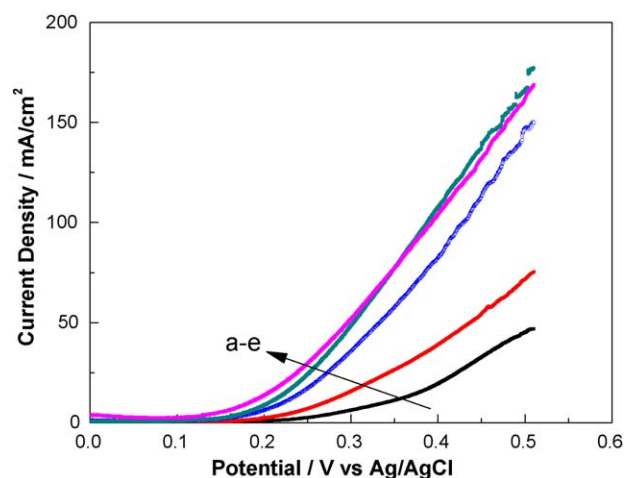

Fig. 4. Linear sweep voltammetry (LSV) for PtRuO$_x$/Ti with different catalyst loadings in 0.5 M H$_2$SO$_4$ + 0.5 M CH$_3$OH at room temperature (30 at.% Ru); scan rate: 1 mV s^{-1}: (a) 0.6 mg cm^{-2}; (b) 1.2 mg cm^{-2}; (c) 2 mg cm^{-2}; (d) 4 mg cm^{-2}; (e) 6 mg cm^{-2}.
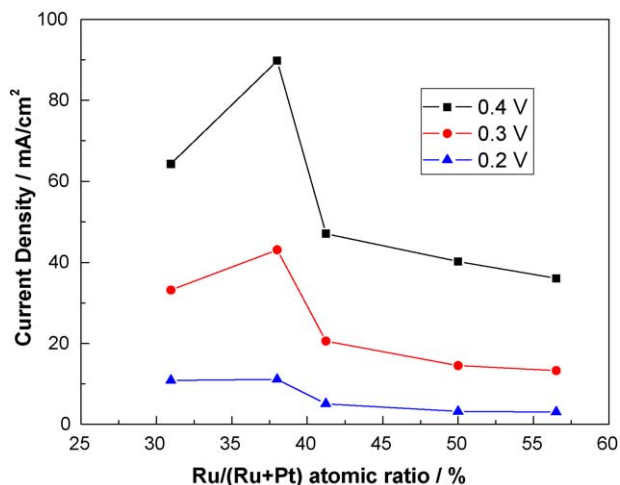
Fig. 5. Activity of PtRuO$_x$/Ti anodes as a function of the Ru/(Pt + Ru) atomic ratio, taken from LSVs (scan rate: 1 mV s^{-1}; 2 mg PtRuO$_x$ cm^{-2}; 0.5 M H$_2$SO$_4$ + 0.5 M CH$_3$OH; room temperature).

It is well known that the ratio of Pt to Ru has a dramatic effect on the performance of the catalyst for methanol oxidation. Fig. 5 shows current densities of methanol oxidation at various potentials during linear sweep voltammetry measurements on the PtRuO$_x$/Ti mesh anodes with 2 mg cm^{-2} catalyst as a function of Ru/(Ru + Pt) atomic ratio. The atomic ratio of Ru and Ru + Pt on the PtRuO$_x$/Ti mesh anode is from the EDX measurements. The potentials 0.2, 0.3 and 0.4 V were chosen because these covered the practical DMFC operating range. As may be seen in Fig. 5, the optimum Ru/(Pt + Ru) atomic ratio at room temperature was 38% with the highest output current densities of 11.1, 43.1 and 89.8 mA cm^{-2} at 0.2, 0.3 and 0.4 V, respectively. This is consistent with the report by Arico et al. [10], who found the optimum surface composition to be ca. 40 at.% Ru for an unsupported PtRu alloy as the anode catalyst in a DMFC. However, Iwasita et al. [11] showed that the activity of smooth Pt–Ru electrodes with Ru contents between 10 and 40 at.% was similar. Gasteiger et al. [12] reported an optimum surface composition was near 10 at.% Ru on the basis of the need for having three sites on Pt for methanol adsorption. Chu and Gilman [13] reported a maximum in activity for 50 at.% Ru in the bulk between 25 and 65 °C in the presence of sulfuric acid. This can be explained by the fact that the conditions of catalyst preparation and the electrolyte are different, as pointed out by Arico et al. [10]. In our work, the composition of the PtRuO$_x$/Ti anodes for the tubular cell is 38 at.% Ru.

In order to increase the triple phase reaction area in the MEA of the DMFC, it is usual to coat a Nafion solution onto the catalyst layer surface of the anode. Fig. 6 shows that the effect of the Nafion loading on the mesh anode on the current density of methanol oxidation got from the LSV measurement at 0.2 V potential. As shown, a current density decay with a Nafion loading is observed. In the PtRuO$_x$/Ti anodes, the catalyst is coated on both two sides of the mesh (see Fig. 3c). The Nafion coating layer on the catalyst surface can block the mass transport of the methanol from the electrolyte to the catalytic site, which results in poor performance of the anode. In our experiments,
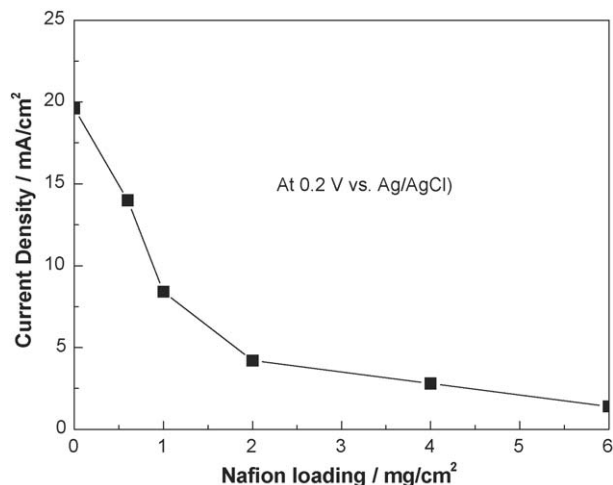

Fig. 6. Activity of PtRuO$_x$/Ti anodes as a function of the Nafion loading on the mesh anode, taken from LSVs (scan rate: 1 mV s^{-1}; 4 mg PtRuO$_x$ cm^{-2}; 38 at.% Ru; 0.5 M H$_2$SO$_4$ + 0.5 M CH$_3$OH; room temperature) at 0.2 V vs. Ag/AgCl.

the Nafion loading on the PtRuO$_x$/Ti anode for tubular DMFC is 0.6 mg cm^{-2}.

3.3. Single cell performance

The performance comparison of a tubular MEA with different Nafion loadings is shown in Fig. 7. The open circuit potential of the cell with 40 mg cm^{-2} of Nafion is higher than that with 10 mg cm^{-2} Nafion, but the performance of the latter is higher than that of the former. It may be caused by the difference of the membrane resistance. Fig. 8 shows the SEM analysis results of cross-section view of a part of the tubular cathode coating with recast Nafion membrane with different Nafion loadings. As shown, the thickness of the recast Nafion membranes with 40 and 10 mg cm^{-2} Nafion loading are 150 and 30 μm, respectively. The resistance of the recast membrane will increase with its thickness. Thus, a thin membrane is of benefit to improve the performance of a tubular DMFC. However, a thin membrane will cause serious methanol crossover problems from the anode
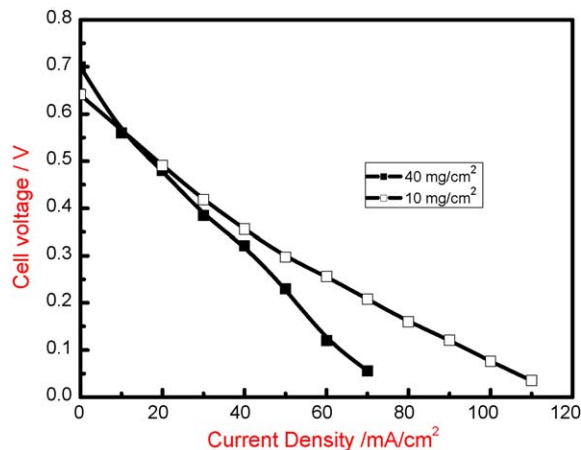

Fig. 7. The performance comparison of tubular cell with different Nafion loading in the recast membrane, at 50 °C with atmospheric air feed at the cathode and 0.5 M methanol at the anode.
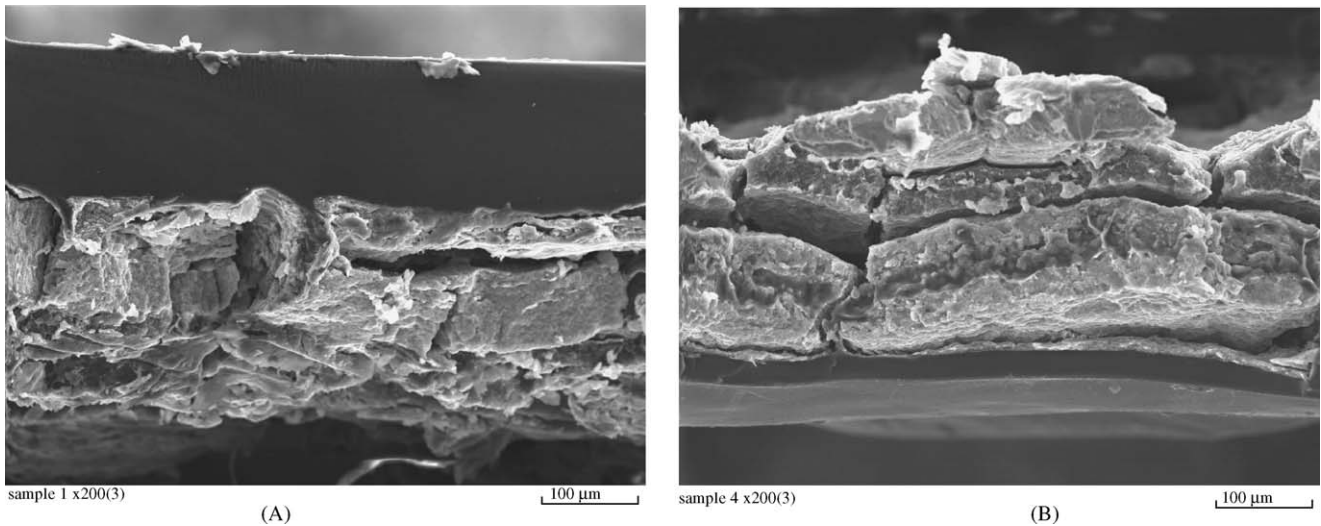
Fig. 8. SEM analysis of cross-section view of a part of the tubular cathode coating with recast Nafion membrane including: (a) 40 mg Nafion cm^{-2} and (b) 10 mg Nafion cm^{-2}.

to the cathode. In our experiment, 10 mg cm^{-2} Nafion was used in the recast membrane of a tubular MEA.

Fig. 9 shows the effect of the methanol concentration in the electrolyte on the performance of a tubular DMFC at 50 °C with atmospheric air as the cathode feed. As shown in Fig. 9, the optimum concentration of the methanol is 0.5 M. This can be explained by the fact that a higher concentration of methanol will cause serious methanol crossover, and a lower concentration will cause mass transport problems for the methanol from the electrolyte to the active sites of the catalyst, which will result in poor cell performance.

Fig. 10 shows a short-term stability test of a tubular DMFC single cell at 50 °C with an atmospheric air feed to the cathode in 0.5 M methanol. From Fig. 10, it is seen that the performance of the tubular cell decreased a little at the higher current densities after running for 72 h, while it kept stable at the lower current densities. It is considered that this decline in performance at higher current densities may be mainly due to the change of the cell structure which was caused by its immersion in the

Fig. 10. A short-term stability test of a tubular DMFC single cell at 50 °C with atmospheric air feed at the cathode and 0.5 M methanol at the anode.

0.5 M H$_2$SO$_4$ + 0.5 M CH$_3$OH solution. It may also be due to the insufficient removal of water produced in the cathode. However, the tubular cell provides a new structure to develop DMFC for the portable applications.

4. Conclusions

A new tubular cell structure has been successfully developed for a low temperature DMFC. In this structure, the tubular cell is composed of: a Ti mesh, a cathode diffusion layer and catalyst layer, a Nafion recast membrane and a PtRuO$_x$/Ti anode. For the PtRuO$_x$/Ti mesh anode, the optimum catalyst loading, Ru/(Ru + Pt) atomic ratio and the Nafion loading are 4 mg cm^{-2}, 38% and 0.6 mg cm^{-2}, respectively. In addition, the Nafion loading of the recast Nafion membrane and the concentration of the methanol in the electrolyte have a major influence on the tubular cell performance. After running for 72 h, the performance of the tubular cell only decreased a little at the higher current densities.
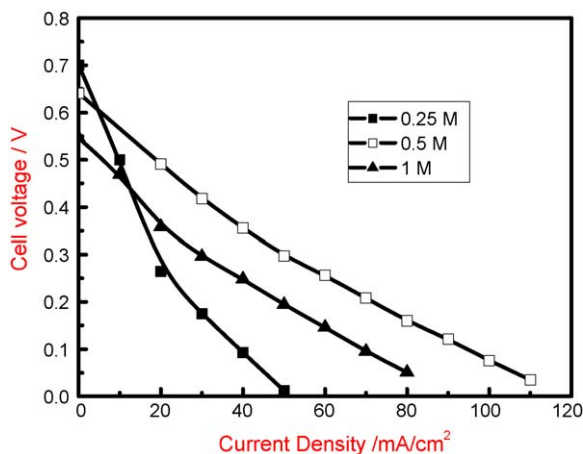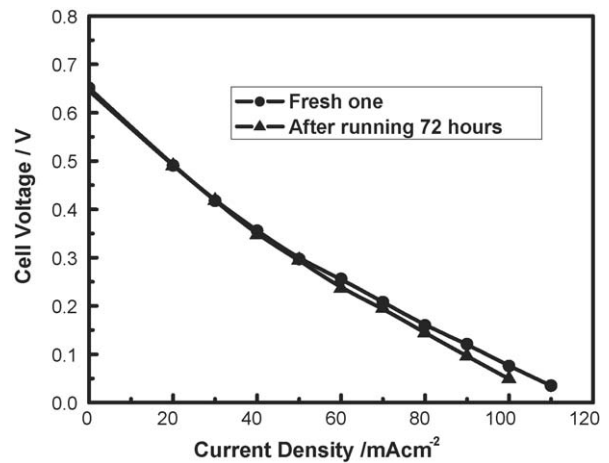

Fig. 9. The effect of the methanol concentration on the performance of the tubular DMFC single cell at 50 °C with atmospheric air feed at the cathode.

Acknowledgments

References

[1] X. Ren, P. Zelenay, S. Thomas, J. Davey, S. Gottesfeld, J. Power Sources 86 (2000) 111.
[2] R. Dillon, S. Srinivasan, A.S. Arico, V. Antonucci, J. Power Sources 127 (2004) 112.
[3] A. Missiroli, F. Soavi, M. Mastragostino, Electrochem. Solid-State Lett. 8 (2005) A110.
[4] A. Blum, T. Duvdevani, M. Philosoph, N. Rudoy, E. Peled, J. Power Sources 117 (2003) 22.
[5] C.Y. Chen, P. Yang, J. Power Sources 123 (2003) 37.
[6] M. Broussely, G. Archdale, J. Power Sources 136 (2004) 386.
[7] H. Qiao, M. Kunimatsa, T. Okada, J. Power Sources 139 (2005) 30.
[8] C. Lim, K. Scott, R.G. Allen, S. Roy, J. Appl. Electrochem. 34 (2004) 929.
[9] Z.-G. Shao, W.-F. Lin, F. Zhu, P.A. Christensen, M. Li, H. Zhang, Electrochem. Commun. 8 (2006) 5.
[10] A.S. Arico, P.L. Antonucci, E. Modica, V. Baglio, H. Kim, V. Antonucci, Electrochim. Acta 47 (2002) 3723.
[11] T. Iwasita, H. Hoster, A. John-Anacker, W.F. Lin, W. Vielstich, Langmuir 16 (2000) 522.
[12] H.A. Gasteiger, N. Markovic, P.N. Ross Jr., E.J. Cairns, J. Electrochem. Soc. 141 (1994) 1795.
[13] D. Chu, S. Gilman, J. Electrochem. Soc. 143 (1996) 1685.