



Short communication

Performing of novel nanostructure MEA based on polyaniline modified anode in direct methanol fuel cell

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ARTICLE INFO

Article history:

Received 12 December 2011

Received in revised form 29 January 2012

Accepted 21 February 2012

Available online 7 March 2012

Keywords:

Direct methanol fuel cell (DMFC)

Novel nanostructure MEA

Polyaniline modified anode

Methanol crossover

ABSTRACT

In this work, a novel nanostructure membrane–electrode assembly (MEA) has been successfully prepared by employing of the polyaniline (PANI) modified anode for DMFC and characterized by SEM and polarization curves in DMFC under different conditions. PANI modified anode made by electro-polymerization of aniline and trifluoromethane sulfonic acid (TFMSA) under galvanostatic conditions on the surface of conventional DMFC's anode.

The DMFC test results under steady state conditions indicate that the novel nanostructure MEA exhibits higher performance compared to the conventional MEA in term of maximum power density and resistivity against methanol crossover from the anode side to the cathode side. Maximum power density of 105 mW cm^{-2} was obtained by new PANI modified anode compared to 75 mW cm^{-2} by conventional anode in the same conditions. The enhanced performance could be attributed to the higher activity of the PANI modified anode and lower methanol crossover caused by the PANI as barrier in the modified anode.

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1. Introduction

Direct methanol fuel cells (DMFCs) are promising and low temperature power source for portable applications due to their advantages, such as simple construction, compact design, high theoretical energy density, and relatively high energy-conversion efficiency [1,2]. However, DMFCs have several barriers to commercialization: (a) deactivation and poisoning of anode catalyst by CO or other methanol oxidation byproducts, (b) crossover of methanol through the membrane from the anode side to the cathode side and (c) high cost electrode because of high loading of noble metal in both anode and cathode sides.

Up to now many efforts have been directed at improving poison resistance of Pt by its alloying, catalyst surface modifying, overall Pt content reducing and finally decreasing of the methanol crossover from anode side to the cathode side by employing of the composite membranes in DMFC [3–7]. Researchers finding indicates Pt-Ru has remained the most commonly used catalyst in the anode of direct methanol fuel cells [8]. Regardless of which type of catalyst can be used, reduction of the noble metal content is essential for the decreasing of the electrode cost and generation of high power

density [9]. By considering of methanol crossover articles, they have led to not only a significant reduction in methanol transport within membrane but also result in an undesirable reduction of proton conductivity both key factors in determining overall DMFC performance.

A review on recently methanol oxidation on modified electrode articles indicates polyaniline (PANI) modified anode has a high potential for employing in DMFCs. PANI is one of the most important and widely studied conducting polymers which is a conductor in its partially oxidized state, which occurs in the potential range where most organic fuels oxidize [10–13].

Herein after several electrochemical and morphological studies on activity and stability of PANI modified electrodes in different reactions, mostly in three electroodic compartments, which have been done by us and others [14–22], we report on first time our successful attempts to employ new nanostructure PANI modified anode in DMFC under different operational conditions.

2. Experimental

2.1. Preparation of DMFC anodes

A mixture comprised of a homogeneous suspension of Pt-Ru/C (20–10%) (electrochem), nafion solution 5% (Aldrich), isopropanol (Merck) and water was homogenized using a sonicator for 20 min

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and then painted onto carbon cloth LT1200 (E-Tek) and lets it to dry after painting of each layer in oven at 60 °C. The resulting composite structure was dried in air at 120 °C for 1 h and divided into two identical parts. The amount of catalyst loading in both electrodes was 4 mg cm⁻². One electrode was modified by electrochemical polymerization of aniline and trifluoromethane sulfonic acid (TMFSA) and the other was used as conventional anode to make conventional MEA. In order to modify the surface of the first anode, it was placed as a working electrode together with a Pt counter electrode and Ag/AgCl electrode in an electrolytic cell containing an electrolytic polymerization solution 0.1 M aniline (Merck) and 0.5 M TFMSA (Merck). The temperature of the electrolytic polymerization solution was maintained at 0 °C. An electric current was passed between the electrodes at a fixed amperage of 2 mA cm⁻² for 1 s and then at a fixed amperage of 20 mA cm⁻² for 2 s to effect the electropolymerization, where a potentiostat–galvanostat (EG&G Princeton Applied Research Model 273A) was used to control the electropolymerization. This process led to the formation of a thin film having TFMSA retained within a PANI network on the surface of the catalyst particles as we studied it in our previous publications [14–18].

2.2. MEAs fabrication and DMFC testing

Conventional MEA fabricated by as-prepared conventional anode and commercial cathode (Fuel Cell store) on Nafion 117 membrane electrolyte without hot pressing. Nafion 117 (Fuel Cell store) was used after usual pretreatment with 3% of H₂O₂, 0.5 M of H₂SO₄ and water for 30 min at 80 °C.

Novel MEA fabricated by PANI modified anode and the same commercial cathode on Nafion 117 without hot pressing. Both MEA subsequently installed in a homemade gold plated fuel cell test fixture made by one channel serpentine flow pattern on SS 316 end plates with 5 cm² of active areas. Both cells were later connected to a test station Scribner compact 850C and performed under different conditions. Most experiments have been done in the optimized methanol concentration of 1 M which gave better performance and led to lesser methanol crossover compared to other methanol concentrations. The methanol was recycled during the experiments. Oxygen with purity of 99.8% was used as oxidant in the cathode side. The experiments were carried out by keeping the anode and cathode at atmospheric pressure. The anode and cathode flow rates were kept constant at the rate of 1 ml min⁻¹ of the methanol solution and 200 ml min⁻¹ of the oxygen respectively.

To investigate the possible effects of PANI on durability of DMFC, the durability of the conventional anode and PANI modified anode was tested in a single cell at 80 °C. The DMFCs were discharged at a constant voltage of 0.45 V for a period of time. During the discharging process, methanol solution was recycled.

3. Results and discussion

3.1. Anodes structure investigation

Fig. 1 indicates the conventional anode catalyst layer made by PtRu/C and 30% Nafion ionomer within. Fig. 2a and b demonstrates the formation of PANI nanofibers within the anode catalyst layer and confirms the PANI nanofibers formation within the electrode. Such nanofibers layer improve mechanical properties of catalyst layer and alleviate their migration and agglomeration during experiments and even after a long time of methanol electrooxidation, so catalytic properties, performance and life time of the modified catalyst would be increased as it has been demonstrated recently [17].

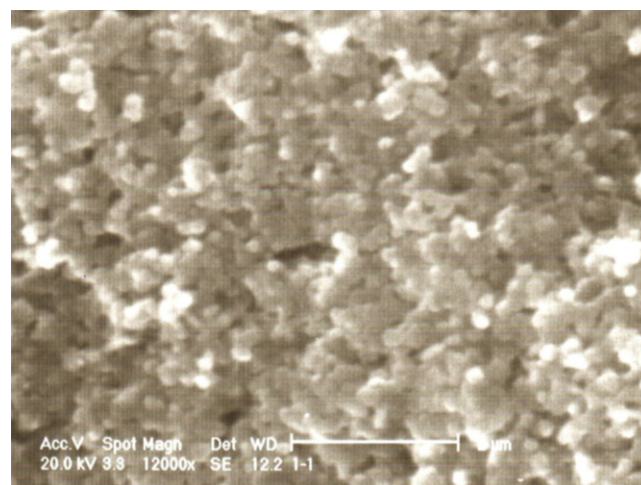


Fig. 1. Top view of scanning electron microscopy micrograph of the conventional anode.

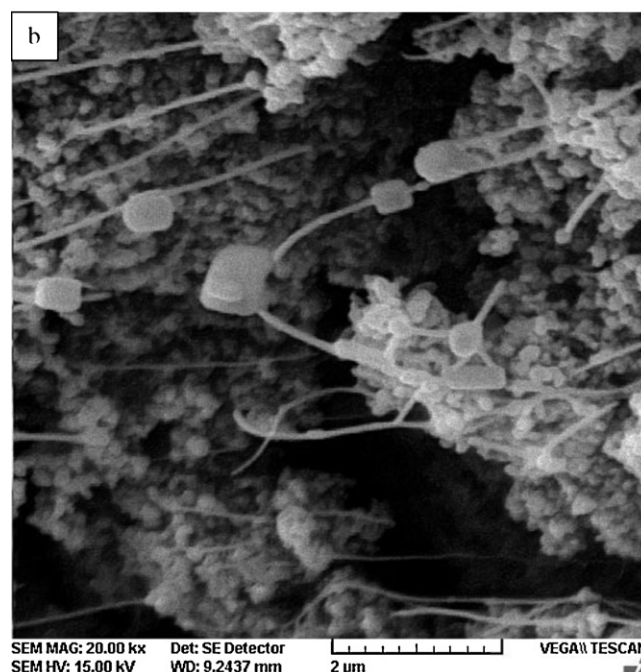
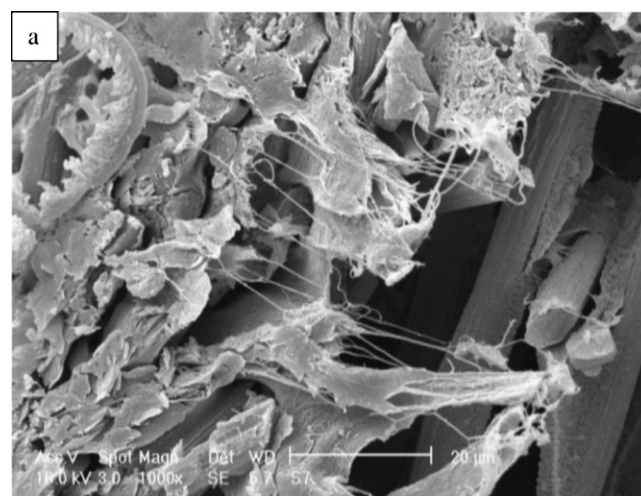


Fig. 2. Top view of scanning electron microscopy (SEM) image of the PANI modified anode (a). SEM image of the PANI modified catalyst layer (b).

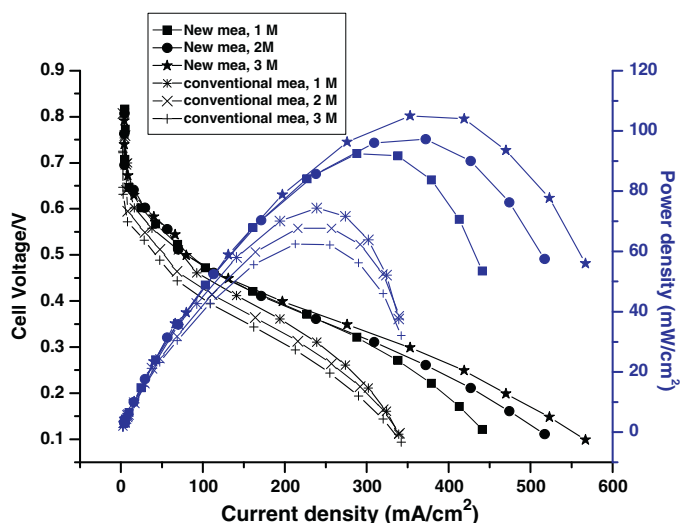


Fig. 3. Performance of the novel MEA and conventional MEA at 80 °C and different methanol concentrations: 1, 2 and 3 M, P_{O_2} : ambient, O_2 flow rate: 0.2 ml min⁻¹, anode and cathode catalyst loading: 4 and 2 mg cm⁻², respectively.

The effect of the polyaniline nanofibers on the electrochemical activity of the electrode in methanol oxidation, electrode structure morphology and its anti-poisoning effect have been studied in full details previously [14–19] so herein does not present any electrochemical three electroodic compartment results.

3.2. Performance comparison in DMFC

Fig. 3 shows the performance of the new MEA made by PANI/PtRu/C anode in DMFC with different feeding methanol concentration compared to conventional MEA performance in the same conditions. Results indicate the conventional MEA has lower performance than the modified MEA over the entire current density region. As it has been pointed out in Fig. 3 by increasing methanol concentration in the anode side of the conventional MEA the cell performance reduces gradually because methanol crossover increases through the membrane and cell performance reduces. But in case of the novel MEA by increasing methanol concentration in the anode side cell performance increases in spite of expecting performance decreasing. It can be pointed to the effect of the polyaniline nanofibers in decreasing of the methanol crossover through the membrane and increasing of the electrochemical activity of the PANI modified anode in methanol oxidation reaction [17]. It seems PANI acts as barrier against methanol crossover from the anode side to cathode side.

Fig. 4 shows the polarization and power density curves of the DMFC containing new MEA at 60, 70 and 80 °C. The fuel solution containing 1.0 M methanol was pumped to the anode at a rate of 1.0 ml min⁻¹ and dry oxygen was fed to the cathode at a flow rate of 200 standard cubic centimeters per minute (sccm).

As shown in Fig. 4, both power density and open-circuit voltage (OCV) increase significantly with increasing of the cell temperature. The power density and OCV of the DMFC increase from 74 to 96 mW cm⁻² and from 755 to 822 mV, respectively, when the temperature is increased from 60 to 80 °C. The increased performance can be attributed to the improved kinetics of the reactions on both anode and cathode electrode at higher temperatures.

The cell performance results in Figs. 3 and 4 are also comparable to typical DMFCs performance and PANI employed DMFCs listed in Table 1. A review of this table shows that identical performance can be obtained by novel MEA at lower temperature or lower precious metal in the anode side, translating into a low cost power

Table 1
Comparison of performance obtained by different authors Forced- O_2 Fed DMFCs literature data.

Cathode catalyst	Cathode catalyst loading (mg/cm ²)	Anode catalyst	Anode catalyst loading (mg/cm ²)	Methanol conc. (M)	Methanol flow rate (ml min ⁻¹)	O_2 flow rate (ml min ⁻¹)	P_{O_2} (kPa) _{abs}	Membrane	Cell performance (mW/cm ²)	Cell Temp. (°C)	Ref.
Pt/C	3	Pt/Pani	3	2	3	100	100	N 115	21	60	[11]
Pt/C	5	PRu/C	4	2	20	200	—	N/Pani	40	60	[23]
Pt/C	1	PRu/C	1	1	5	200	—	N 117	42	80	[24]
Pt/C	5	PRu/C	4	2	20	200	—	N 117	60	60	[23]
Pt/C	2	PRu/C	2	2	2	200	—	N/Pani	35	25	[24]
Pt/C	0.50	PRu/CSA ^a	0.50	1	12	200	—	117	105	80	[25]
Pt/C	2	PRu/C	1.8	1	—	—	—	117	7	25	[26]
Pt/C	2	PRu/C	1.5	2	5	100	200	117	35	30	[27]
Pt/C	1.37	PRu/C	2.5	2	—	—	200	117	125	85	[28]
Pt/C	2	Pani/PtRu/C	4	1	5	200	100	117	105	80	Current study

^a Sulfuric acid and chlorosulfuric acid functionalized carbon black as PtRu electrocatalyst support.

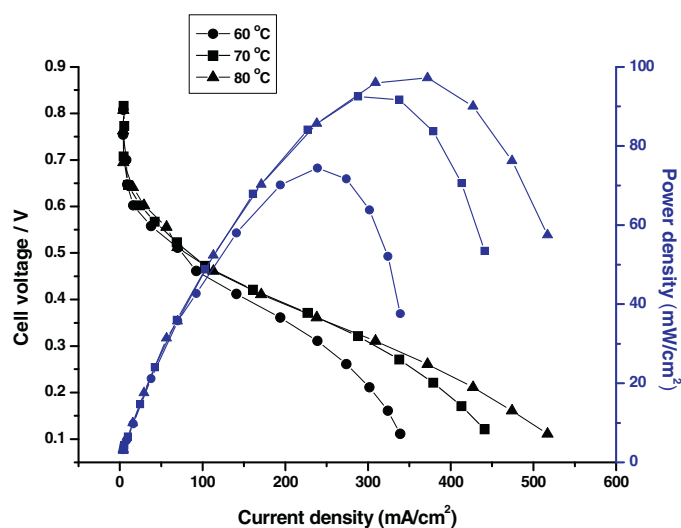


Fig. 4. Performance of the novel MEA made by PANI modified anode at different cell temperatures: 60, 70 and 80 °C, anode feed: 1 M CH₃OH by flow rate of 1 ml min⁻¹, cathode feed: dry O₂ by flow rate of 200 ml min⁻¹ and ambient pressure.

source based on PANI modified anode for DMFC can be achieved. By considering the obtained results in this study and other reported articles on DMFC which employed PANI as catalyst support or as membrane composite agent [11,23,25], it seems the employment PANI as surface catalyst modifier is more effective procedure than the employment of the PANI as a catalyst support or as a membrane composite agent.

3.3. Durability test of DMFC with conventional and PANI modified anodes

Since the addition of PANI into anode catalyst layer of the MEA significantly improves DMFC performance, thus it is necessary to investigate its durability under constant current or voltage discharge for a long-term operation.

Fig. 5 shows the variation of the cell current density as a function of time at a constant voltage of 0.45 V under a normal operating condition without any recovery process. In this set of experiments, a time period of 6 h has been chosen since substantial performance loss occurred during the first few hours in discharge operating modes.

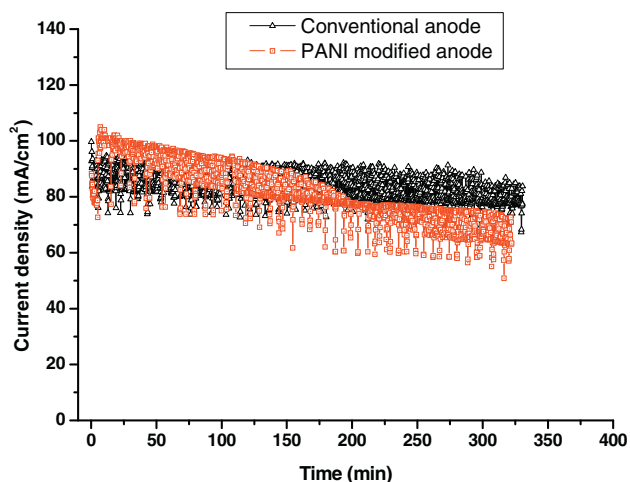


Fig. 5. Current density–time behavior of conventional and PANI modified anode in DMFC at a constant voltage of 0.45 V fed by recycled methanol.

The discharge curves for PANI modified anode can be divided into two regions. At the early stage the current density of MEA made by PANI modified anode is higher than the conventional MEA within 125 min. Then, the current density slightly decreases roughly in the same range of conventional anode performance. Higher current density in the first part of curves might be attributed to an increase in methanol crossover resistance and anode activity caused by employing of PANI modified anode which is consistent with polarization curves results.

However it clearly decays with time probably due to decreasing of the methanol concentration in the reservoir, not optimized modified anode and MEA structures and/or irreversible catalyst or membrane degradation itself [29].

As it can be seen in Fig. 5 there was no significant performance degradation of the conventional anode cathode. However, there is still a gradual and slow performance loss, which might be related to decreasing of the methanol concentration in the reservoir or catalyst poisoning and/or MEA components degradation.

4. Conclusion

This work demonstrates the performance of the novel nano-structure MEA based on polyaniline modified anode in DMFC under real condition. PANI was deposited on the surface of the PtRu/C anode catalyst as a methanol-blocking by over oxidation of methanol. It effectively reduces methanol crossover at elevated methanol concentration compared to conventional MEA.

Obtained results also indicate the employment of the PANI nanofibers as surface catalyst modifier (this study) is more effective than the employment of the PANI as a catalyst support (Pt/PANI, Pt/PANI-C) or as a membrane composite agent.

It can therefore be concluded that MEA based on PANI/PtRu/C anode could be a good alternative anode catalyst for methanol electrooxidation which is highly desirable for the small-scale DMFC importable devices and micro electromechanical systems.

However to realize the employment of PANI modified DMFC anode for practical applications a deeper understanding of various degradation routes and identification of performance restoration techniques are needed.

Acknowledgments

This work was carried out in Fuel Cell Laboratory of Isfahan University of Technology (IUT). The author would like to thank the Research Council of IUT. The support of the Iranian Nano Technology Initiative Council and Fuel Cell Steering Committee are also acknowledged.

References

- [1] T. Wang, C. Lin, F. Ye, Y. Fang, J. Li, X. Wang, *Electrochem. Commun.* 10 (2008) 1261–1263.
- [2] V. Neburchilov, J. Martin, H. Wang, J. Zhang, *J. Power Sources* 169 (2007) 221–238.
- [3] E. Antolini, *Mater. Chem. Phys.* 78 (2003) 563–573.
- [4] V. Mehta, J.S. Cooper, *J. Power Sources* 114 (2003) 32–53.
- [5] H. Zhao, L. Li, J. Yang, Y. Zhang, H. Li, *Electrochem. Commun.* 10 (2008) 876–879.
- [6] R. Wang, Z. Zhang, H. Wang, Z. Lei, *Electrochem. Commun.* 11 (2009) 1089–1091.
- [7] Q.M. Huang, Q.L. Zhang, H.L. Huang, W.S. Li, Y.J. Huang, J.L. Luo, *J. Power Sources* 184 (2008) 338–343.
- [8] H. Liu, C. Song, L. Zhang, J. Zhang, H. Wang, D.P. Wilkinson, *J. Power Sources* 155 (2006) 95–110.
- [9] R. Dillon, S. Srinivasan, A.S. Arico, V. Antonucci, *J. Power Sources* 127 (2004) 112–126.
- [10] B. Habibi, M.H. Pournaghi-Azar, *Int. J. Hydrogen Energy* 35 (2010) 9318–9328.
- [11] Y.F. Huang, C.W. Lin, C.S. Chang, M.J. Ho, *Electrochim. Acta* 56 (2011) 5679–5685.
- [12] R.B. Moghaddam, P.G. Pickup, *Electrochem. Commun.* 13 (2011) 704–706.

- [13] Y.M. Wu, W.S. Li, J. Lu, J.H. Du, D.S. Lu, J.M. Fu, *J. Power Sources* 145 (2005) 286–291.
- [14] H. Gharibi, M. Zhiani, R.A. Mirzaie, M. Kheirmand, A.A. Entezami, K. Kakaei, *J. Power Sources* 155 (2006) 138–144.
- [15] H. Gharibi, M. Zhiani, R.A. Mirzaie, M. Kheirmand, A.A. Entezami, K. Kakaei, M. Javaheri, *J. Power Sources* 157 (2006) 703–708.
- [16] M. Zhiani, H. Gharibi, K. Kakaei, *Int. J. Hydrogen Energy* 35 (2010) 9261–9268.
- [17] M. Zhiani, B. Rezaei, J. Jalili, *Int. J. Hydrogen Energy* 35 (2010) 9298–9305.
- [18] H. Gharibi, K. Kakaei, M. Zhiani, *J. Phys. Chem. C* 114 (2010) 5233–5240.
- [19] H. Gharibi, K. Kakaei, M. Zhiani, M.M. Taghiabadi, *Int. J. Hydrogen Energy* 36 (2011) 13301–13309.
- [20] Z.A. Hu, L.J. Ren, X.J. Feng, Y.P. Wang, Y.Y. Yang, J. Shi, L.P. Mo, Z.Q. Lei, *Electrochem. Commun.* 9 (2007) 97–102.
- [21] F.J. Liu, L.M. Huang, T.C. Wen, C.F. Li, S.L. Huang, A. Gopalan, *Synthetic Met.* 158 (2008) 767–774.
- [22] S. Palmero, A. Colina, E. Muñoz, A. Heras, V. Ruiz, J. López-Palacios, *Electrochem. Commun.* 11 (2009) 122–125.
- [23] C.H. Wang, C.C. Chen, H.C. Hsu, H.Y. Du, C.P. Chen, J.Y. Hwang, L.C. Chen, H.C. Shih, J. Stejskal, K.H. Chen, *J. Power Sources* 190 (2009) 279–284.
- [24] B.G. Choi, H. Park, H.S. Im, Y.J. Kim, W.H. Hong, *J. Membrane Sci.* 324 (2008) 102–110.
- [25] M. Carmo, M. Brandalise, A.O. Neto, E.V. Spinace, A.D. Taylor, M. Linardi, J.G.R. Poco, *Int. J. Hydrogen Energy* 36 (2011) 14659–14667.
- [26] J. Kim, T. Momma, T. Osaka, *J. Power Sources* 189 (2009) 999–1002.
- [27] X. Xue, J. Ge, C. Liu, W. Xing, T. Lu, *Electrochem. Commun.* 8 (2006) 1280–1286.
- [28] A.K. Shukla, R.K. Raman, N.A. Choudhury, K.R. Priolkar, P.R. Sarode, S. Emura, R. Kumashiro, *J. Electroanal. Chem.* 563 (2004) 181–190.
- [29] S.J.C. Cleghorn, D.K. Mayfield, D.A. Moore, J.C. Moore, G. Rusch, T.W. Sherman, N.T. Sisofo, U. Beuscher, *J. Power Sources* 158 (2006) 446–454.