



Short communication

## High-performance anode for Polymer Electrolyte Membrane Fuel Cells by multiple-layer Pt sputter deposition

Sadesh Kumar Natarajan, Jean Hamelin\*

Institut de recherche sur l'hydrogène, Université du Québec à Trois-Rivières, 3351, Boul. des Forges, C.P. 500, Trois-Rivières (QC), Canada G9A 5H7

## ARTICLE INFO

## Article history:

Received 22 March 2010

Received in revised form 9 June 2010

Accepted 10 June 2010

Available online 18 June 2010

## Keywords:

PEMFC

Sputtering

Multi-layers

Platinum

Carbon nanotubes

Anode

## ABSTRACT

We investigate the sputtering deposition as a tool for preparing Polymer Electrolyte Membrane Fuel Cell (PEMFC) electrodes with improved performance and catalyst utilization. Anodes of PEMFC with ultra-low loading of Pt ( $0.05 \text{ mg cm}^{-2}$ ) are developed by alternate sputtering of Pt and painting layers of carbon nanotube ink with Nafion directly on the gas diffusion layer. Sputter depositing alternate layers of Pt on carbon-Nafion layer (CNL) has increased the anode activity over single-layer Pt deposited anode due to improved porosity and the presence of Pt nanoparticles in the inner CNL. Also, we investigated the influence of Nafion content in the CNL. The optimal Nafion content giving less resistance and better performance in an anode is 29 wt.%. This is significantly lower than for standard MEA anodes, indicating sufficient interfacial contact between each CNL. We studied the anodes prepared with 50 wt.% Nafion, which revealed larger ohmic resistance and also, blocks the CNL pores reducing gas permeability. Excellent mass transfer and performance is obtained with three-layer Pt sputter deposited anode with CNL containing 29 wt.% of Nafion.

© 2010 Elsevier B.V. All rights reserved.

### 1. Introduction

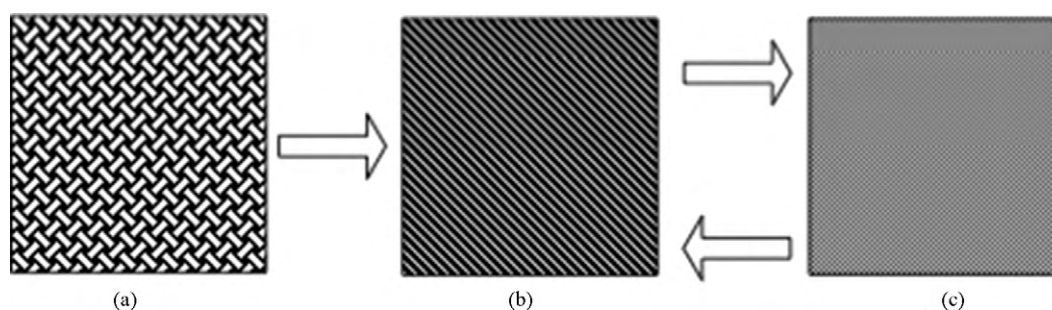
PEMFCs have great potential to replace batteries in portable devices and in the automotive industry. Platinum and its alloys have been used for PEMFC electrodes due to their high catalytic activity and stability under acidic environment in such fuel cell. However, for such applications mentioned above, PEMFC must be capable of operating at a high power density with an ultra-low content of electro-catalyst to reduce its weight, volume and cost [1,2]. Enormous research work has been carried out to explore the possibility of minimizing the Pt loading by reducing the particle size, employing stable and more durable carbon supports, applying sputtering techniques, and by increasing the catalyst utilization [3–5].

Electro-catalysts for PEMFCs must have high intrinsic activity for the electrochemical oxidation of hydrogen at the anode as well as for oxygen reduction at the cathode. Conventionally, these electro-catalysts, which are nanoparticles of Pt or its alloy, have been prepared by the chemical reduction of Pt salts. Subsequently, these Pt particles are adsorbed on high surface area carbon to prepare Pt/C powder, which are then mixed with solubilized cation exchange ionomer and applied on a porous carbon substrate by painting the gas diffusion layers (GDLs), spraying directly on the membrane method, or forming a decal. The electrochemical reac-

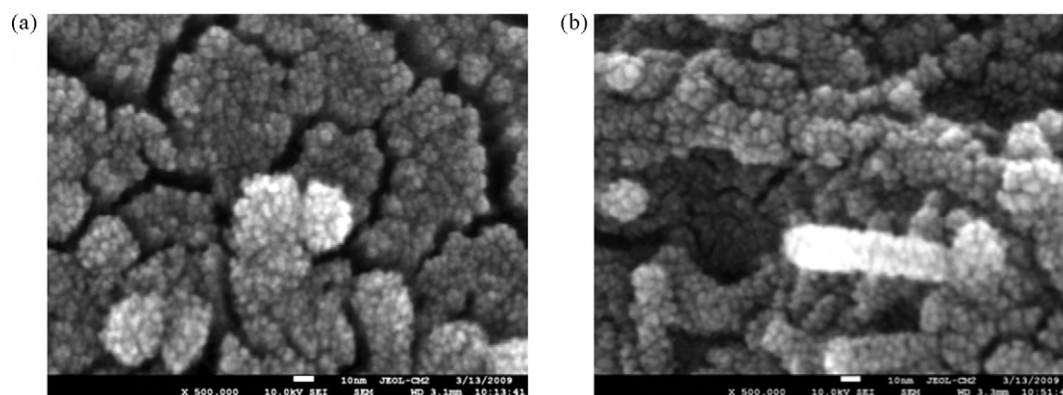
tion is limited to the interface between the electrolyte membrane and the Pt catalyst that is exposed to the reactant, known as the three-phase reaction zone. Thus, a high-surface-to-mass ratio provided by small Pt nanoparticles is certainly desirable on grounds of improved catalyst utilization. However, not all-geometric specific-surface area contributes to the heterogeneous catalysis, only a small proportion of electro-catalysts is electrochemically active while an overriding majority of the noble metal nanoparticles are not accessible to reactions.

Several research groups have suggested that thin film deposition of Pt on carbon backing prior to ionomer impregnation made the proton access to the catalytic sites much easier [1,6,7]. Also, other attempts have been made to etch the surface of polymer electrolyte and deposit the catalyst using the sputtering method [8,9]. In general, their main intention is to deposit nanoparticles of Pt at the polymer electrolyte–electrode interface. This method facilitates not only the fabrication of nano-scale Pt layer with uniform distribution, but it allows the preparation of precise Pt content and thickness as well as a well defined micro-structure morphology. Applying a Pt film having a surface density of  $0.5 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$  to the front surface of a blank or catalyzed gas diffusion layer or to the polymer electrolyte can reduce the loading ten-fold without reduction in performance [6–9]. However, the success of this technique depends on whether the thickness of the catalyst film hinders the transport of gas molecules, thereby reducing the number of triple access points available for protons, electrons and gas molecules. The objective of this work is to improve the utilization

\* Corresponding author. Tel.: +1 819 376 5011; fax: +1 819 376 5164.  
E-mail address: [Jean.Hamelin@uqtr.ca](mailto:Jean.Hamelin@uqtr.ca) (J. Hamelin).



**Fig. 1.** Schematic of electrode preparation; (a) GDL, (b) GDL painted with CNT–Nafion ink, (c) Pt sputtered on dry ink. Sequence (b) and (c) is repeated twice for sample EA2 and PA2, and thrice for sample EA3 and PA3.



**Fig. 2.** FEG-SEM images of the surface of (a) one (EA1) and (b) three-layer (EA3) Pt sputtered CNL substrates.

efficiency of the catalyst through the proposed multiple alternate layers of CNL and Pt deposition for the anode of PEMFCs. Following this strategy, we prepared multi-layers sputtered electrodes with larger concentration of catalyst particles for the layer closest to the membrane to study the changes in electrochemical performance. Also, we compared the influence of ionomers concentration for two different mass ratios of ionomers/carbon.

## 2. Experimental

Previous studies have shown that catalyst particles supported on structured carbon materials such as carbon nanotubes, exhibit better electrochemical performance than those supported on carbon black (generally Vulcan XC-72<sup>TM</sup>) [10,11]. In this study, multi-wall carbon nanotubes (Cheap Tubes Inc., outer diameter <8 nm; length 10–30 µm; purity >95 wt.%; surface area >500 m<sup>2</sup> g<sup>-1</sup>) are used as received. A 10 wt.% Nafion<sup>TM</sup> solution (Dupont Inc.) is used as the proton conductive agent and binder for the catalyst layer. A carbon cloth (LT1200-W, E-TEK) is used as GDL and 20 wt.% Pt on Vulcan XC-72 serves as the electro-catalyst for the cathode electrode.

The carbon-Nafion ink is prepared by the addition of an appropriate amount of Nafion solution to CNTs to achieve a total carbon loading of 0.5 mg cm<sup>-2</sup>. Two batches of ink slurry are prepared by maintaining the weight ratio of carbon to Nafion at 2.5 and 1, respectively. Each batch of ink slurry is used to prepare electrodes A1, A2 and A3 with one-, two- and three-layered Pt sputtering, respectively. A prefix of “E” is added to the electrode identities that are painted using equal proportion (1:1) of Nafion and CNTs. The rest of the samples are identified with a prefix “P” as proportional (0.29:1).

The first layer of ink is painted on the MPL of the GDL and dried at 80 °C for 2 h. The carbon loading depends on the number of sputtering layers assigned for each electrode. We carried out coating experiments on the painted GDL using a turbo sputter coater (Emitech K575X, Emitech Ltd.). The Pt sputtering target used in the present experiment is a piece of 99.99% pure Pt foil. The distance between the target and electrodes is about 55 mm. The sputtering is carried out under an Ar atmosphere at room temperature and a bleeding gas pressure of 0.2 mbar. In a standard process for a single-layer sputtering, the film is deposited for a period of 100 s with a sputter-current of approximately 40 mA, whereas sputtering coating time is splitted for electrodes that require multiple sputtering.

**Table 1**  
Summary of sample composition and sputtering time.

Sample ID	EA1	EA2	EA3	PA1	PA2	PA3
C/Nafion	1	1	1	2.5	2.5	2.5
Pt layers	1	2	3	1	2	3
Layer 1 Pt loading (mg cm <sup>-2</sup> )	0.05	0.025	0.015	0.05	0.025	0.015
Layer 1 sputter time (s)	100	50	30	100	50	30
Layer 2 Pt loading (mg cm <sup>-2</sup> )	–	0.025	0.015	–	0.025	0.015
Layer 2 sputter time (s)	–	50	30	–	50	30
Layer 3 Pt loading (mg cm <sup>-2</sup> )	–	–	0.02	–	–	0.02
Layer 3 sputter time (s)	–	–	40	–	–	40

Multiple Pt catalyst layer electrodes are prepared by repeating the above sequence until the desired number of layers is achieved. The proposed multi-catalyst layer sputtering on the gas diffusion layer is shown in Fig. 1. The electrodes are fabricated under the conditions listed in Table 1.

A Field Emission Gun Scanning Electron Microscope (FEG-SEM) provides high spatial resolution (1.5 nm at 15 kV) with a very good contrast, allowing us to easily observe the Pt particles. FEG-SEM is performed on electrodes with single- and three-layered Pt, namely EA1 and EA3. The membrane electrode assemblies (MEAs) are prepared using Nafion membrane NRE212, sputtered electrodes as anode and a standard  $0.2 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$  as cathode. Fabrication of standard cathode involves preparing the ink for the catalytic layer from Pt/C powder (20 wt.%) and Nafion solution in the ratio 2.5:1. After the ink becomes homogeneous with mixing, it is painted on the gas diffusion layer to achieve a Pt loading of  $0.2 \text{ mg cm}^{-2}$ . The complete fabrication of a MEA involves hot pressing the membrane and electrodes of a  $5 \text{ cm}^2$  cross-sectional area. The temperature and pressure of the hot-pressing machine used are  $130^\circ\text{C}$  and 1000 psi, respectively. Prior to pressing the MEA, the temperature of the cell components is stabilized for 1 min, followed by applying the pressure for 2 min.

The MEA is placed between two Furon gaskets 0.25 mm thick and inserted between two graphite plates with serpentine grooves, and then placed in a single cell test fixture ( $5 \text{ cm}^2$ ) from Fuel Cell Technologies. A uniform torque of 10.5 Nm is applied onto the eight bolts that were used to assemble the PEMFC. Humidified hydrogen and air are fed into the cell at a flow rate of 200 and 450 sccm, respectively. In order to maintain the membrane's low resistance, a 100% relative humidity is preferred. The experiment is carried out at a cell temperature of  $80^\circ\text{C}$  and at pressure of 1 atm.

### 3. Results and discussion

Fig. 2(a) and (b) shows a FEG-SEM image of Pt sputtered on a surface of a CNTs–Nafion for sample EA1 (two-layer) and EA3 (three-layer), respectively. The CNTs–Nafion layer has a highly porous morphology due to the sparse packing of the CNTs. The CNT buried into the depressions of the carbon layer can be seen from the top through the pores, which suggests that Pt can be deposited even on the inside of the CNT layer as shown for EA3. Also, it can be seen in Fig. 2(a) and (b) that Pt particles do not form continuous films on the CNTs–Nafion substrate, but are rather evenly dispersed. After Pt sputtering on the CNTs–Nafion layer of EA1 with a loading of  $0.05 \text{ mg cm}^{-2}$ , the layers turned from black (typical, CNTs) to dark grey. However, the sample EA3 with a top layer Pt loading of  $0.02 \text{ mg cm}^{-2}$  has a lighter shade of grey. This indicates that longer sputtering time might give a dense and thick deposited Pt layer [12]. By comparing the performance of EA1 and EA3 electrodes in MEAs, it is apparently inferred that the short sputtering time in EA3 permits the formation of a deposited Pt layer with a larger porosity. A comparison of the  $I$ - $V$  polarization curves for the sputtered electrodes (EA1, EA2, and EA3) is given in Fig. 3. It is observed that the multiple layer sputtered electrodes (EA2 and EA3) have a higher power density than the single layer one (EA1). Therefore, the thick deposited Pt layer of EA1 with reduced porosity have caused the voltage drop due to mass-transport limitations of hydrogen fuel, thereby reducing the number of triple access points [13]. A thinner catalyst layer such as EA3 is believed to be associated with less mass transport loss. From this result, it is expected that for a given Pt loading, multiple sputtered electrodes have better mass transport and more triple access points than a single-layer Pt sputtered electrodes.

Fig. 3 compares the cell performance of a standard MEA to those onto which Pt has been sputtered on a substrate containing a ratio

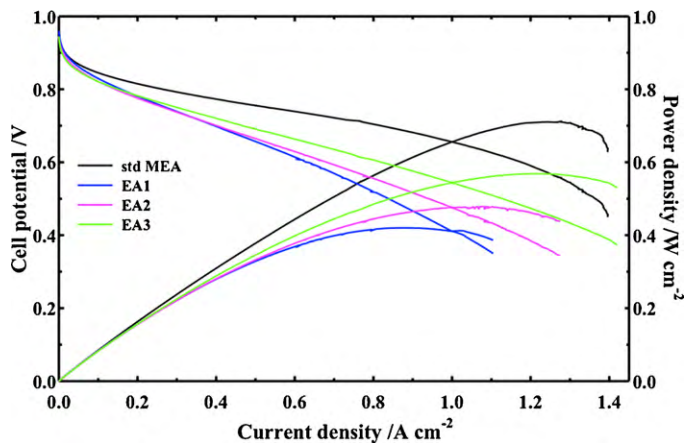


Fig. 3. Comparison of polarization and power curves of standard MEA with EA series MEAs elaborated in this work.

of 1:1 of CNTs/Nafion. The results reveal that the standard MEA with a Pt loading of  $0.2 \text{ mg cm}^{-2}$  exhibits the best cell performance, while sample EA3 with a Pt loading four times less than the standard MEA possesses similar anode catalyst activity. It is important and interesting that even when the Pt loading was decreased from  $0.2 \text{ mg cm}^{-2}$  to  $0.05 \text{ mg cm}^{-2}$ , the performance did not noticeably decline. However, the difference of performance between the MEAs is observed only when the pattern of loading is altered. It is well known from the FEG-SEM study that in order to gain the highest cell performance and catalyst activity, the electrode must have larger porosity, which can be achieved effectively by multiple-layer sputter deposition. Excluding for the standard MEA, there is no major difference in the cell performance at smaller current densities ( $<0.3 \text{ A cm}^{-2}$ ) for sample EA1, EA2, and EA3. But, at medium and larger current densities, the added sputter-deposited layers in EA2 and EA3 have improved the limit at which hydrogen can diffuse through the electrodes. Moreover, it can be observed from Fig. 3 that the larger content of Nafion in the sputtered MEAs has increased the ohmic resistance between the deposited Pt layers. As Fig. 3 shows, all of the sputtered MEAs present decreasing slopes in the linear region of the polarization curve, which implies that the cell resistance is caused by the CNTs/Nafion layers. Larger ohmic resistance in the electrode layers is observed in the order,  $R(\text{EA1}) > R(\text{EA2}) > R(\text{EA3})$ . Therefore, the thinner the electrode layer, the smaller the ohmic resistance in the electrode. At larger current densities, EA3 with three-layered Pt electrode exhibit better performance as compared to EA1 and EA2 electrodes. Generally, a

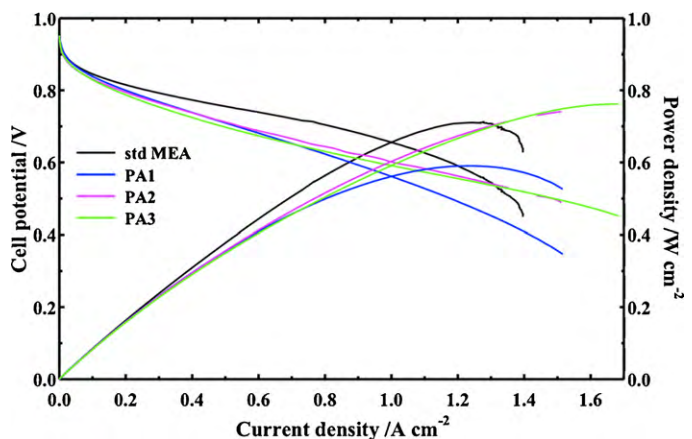


Fig. 4. Comparison of polarization and power curves of standard MEA with PA series MEAs elaborated in this work.



voltage drop at larger current density is due to mass-transport limitations occurring in the electrodes. In this case, the mass transport losses are assumed to be similar at the cathode. Any performance drop observed at larger current densities can be attributed to the starving of hydrogen at the triple access points at the anode. So, the better performance of EA3 in the large current density region can be explained by postulating fewer mass-transport limitations, due to much thinner catalyst layer. It is reasonable that the higher the current density, the more obvious the advantages of EA3 > EA2 > EA1, because thinner catalyst layers would promote the diffusion and transportation of hydrogen.

Fig. 4 compares the cell performance of a standard MEA to those onto which Pt has been sputtered on a substrate containing a ratio of 2.5:1 of CNTs/Nafion. It is observed from Fig. 4 that the reduction of Nafion content in the catalyst layer has strongly improved the performance of MEA with ultra-low platinum loadings. It is also evident from Fig. 4 when compared with Fig. 3 for a similar Pt loading pattern that lowering the Nafion content in the catalyst layer has significantly reduced the ohmic resistance in the catalyst layer. Hence, a better MEA performance is observed for electrodes that contain 29 wt.% dry Nafion in the CNTs/Nafion layers. For example, the current density at 0.7 V has increased from  $0.4 \text{ A cm}^{-2}$  in Fig. 3 to  $0.54 \text{ A cm}^{-2}$  in Fig. 4 for a single-layer sputtered electrode. Similarly, near the end of the linear decreasing region (0.4 V), the current density has increased from  $1.03 \text{ A cm}^{-2}$  in Fig. 3 to  $1.42 \text{ A cm}^{-2}$  in Fig. 4 for the same sample. This can be explained by the rising electronic conductivity of the catalyst layers as Nafion content decreases. Moreover, the large amount of Nafion in the EA series (EA1, EA2 and EA3) electrodes blocks the electrode pores, thus reducing gas permeability [12,13].

A similar trend of performance improvement using multi-layered Pt sputtering is observed for PA3 and PA2 as with EA3 and EA2. At larger current densities, three-layered Pt electrodes in the PA and EA series show better performance than single and double Pt-layered electrodes. This is due to the presence of a thinner porous catalyst layer in three-layered electrodes that reduces the mass-transport limitation that resulted from an increase in the distance through which the gas has to diffuse [14]. Furthermore, in EA3 electrode, thick layer of Nafion in the ink applied between the sputtered layers block access for hydrogen to a few Pt sites making them inactive. Therefore, the electrodes prepared with only 29 wt.% dry Nafion (PA series) have more triple access points than the EA series electrodes. In addition, the lower Nafion content and more Pt active sites in PA3 have also resulted in a better performance of the corresponding MEA when compared with standard MEA.

Similarly, Wan et al. [6] sputtered Pt on three layers of Vulcan XC72 and Nafion on a GDL (MEA 3L-C,  $0.15 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ ) and tested the MEA with oxygen instead of air. At 0.4 V, they achieved a current density of  $0.73 \text{ A cm}^{-2}$  when compared to  $1.69 \text{ A cm}^{-2}$  (PA3 in Fig. 4). Haug et al. [9] utilized a similar multi-layer sputter deposition technique, but applied on the membrane instead, and a MEA prepared with similar Pt loading and tested under similar oper-

ating conditions. They achieved a current density of  $0.7 \text{ A cm}^{-2}$  at 0.4 V.

#### 4. Conclusion

A high-performance MEA with ultra-low platinum loading has been prepared by a multi-layer Pt sputter approach. For all the substrates studied, the presence of higher Nafion content in EA series has not only increased the ohmic resistance of the MEA, but the presence of a thick layer of Nafion blocked some of the catalyst sites making them inactive. Therefore, the optimal Nafion content for the MEA is 29 wt.%. This value is significantly less than the Nafion used in the anode of standard MEA (50 wt.%). Also, we suggest that the thinness and uniform porous structure of the catalyst layer as a result of multiple layers sputtering may be the crucial factors yielding the high performance in PA3. Single-layer Pt deposition results in thicker Pt films with less porosity increasing mass-transport limitations. Therefore, we concluded that the MEA with 29% Nafion content in the catalyst layer with three-layered Pt sputter deposition showed the best performance by minimizing ohmic and mass-transport limitations. And also, the limiting current density is significantly larger for the anode that is manufactured with four times less Pt than a standard anode. The preparation of MEAs with extremely high activity anodes suggests future study for low-loading cathodes.

#### Acknowledgements

We would like to thank the National Resources and Engineering Research Council of Canada (NSERC), MTACS (Accelerate program) and the *Laboratoire des Technologies de l'Énergie* (LTÉ, Hydro-Québec) for financially supporting this work. Also, we extend our thanks to François Allaire from the LTÉ for the use of the Emitech sputter coater and the useful suggestions in the study.

#### References

- [1] S. Hirano, J. Kim, S. Srinivasan, *Electrochim. Acta* 42 (1997) 1587–1593.
- [2] S. Gamburgzev, A.J. Appleby, *J. Power Sources* 107 (2002) 5–12.
- [3] M.S. Wilson, S. Gottesfeld, *J. Appl. Electrochem.* 22 (1992) 1–7.
- [4] C.K. Witham, W. Chun, T.I. Valdez, S.R. Narayanan, *Electrochem. Solid-State Lett.* 3 (2000) 497–500.
- [5] A. Caillard, C. Coutanceau, P. Brault, J. Mathias, J.M. Léger, *J. Power Sources* 162 (2006) 66–73.
- [6] C.H. Wan, M.T. Lin, Q.H. Zhuang, C.H. Lin, *Surf. Coat. Technol.* 201 (2006) 214–222.
- [7] H.T. Kim, J.K. Lee, J. Kim, *J. Power Sources* 180 (2008) 191–194.
- [8] S.Y. Cha, W.M. Lee, *J. Electrochem. Soc.* 146 (1999) 4055–4060.
- [9] A.T. Haug, R.E. White, J.W. Weidner, W. Huang, S. Shi, T. Stoner, N. Rana, *J. Electrochem. Soc.* 149 (2002) A280–A287.
- [10] S.K. Natarajan, D. Cossement, J. Hamelin, *J. Electrochem. Soc.* 154 (2009) B310–B315.
- [11] S.K. Natarajan, J. Hamelin, *Electrochim. Acta* 52 (2007) 3751–3757.
- [12] H.N. Su, S.J. Liao, T. Shu, H.L. Gao, *J. Power Sources* 195 (2010) 756–761.
- [13] G. Sasikumar, J.W. Ihm, H. Ryu, *J. Power Sources* 132 (2004) 11–17.
- [14] M.S. Saha, A.F. Gullà, R.J. Allen, S. Mukerjee, *Electrochim. Acta* 51 (2006) 4680–4692.