

Short communication

# Effect of platinum amount in carbon supported platinum catalyst on performance of polymer electrolyte membrane fuel cell

Yong-Hun Cho, Hyun-Seo Park, Yoon-Hwan Cho, Dae-Sik Jung,  
Hee-Young Park, Yung-Eun Sung\*

*School of Chemical & Biological Engineering & Research Center for Energy Conversion and Storage, Seoul National University,  
Seoul 151-744, Republic of Korea*

Received 30 October 2006; received in revised form 21 December 2006; accepted 24 January 2007

Available online 2 February 2007

## Abstract

The performance of polymer electrolyte membrane fuel cells fabricated with different catalyst loadings (20, 40 and 60 wt.% on a carbon support) was examined. The membrane electrode assembly (MEA) of the catalyst coated membrane (CCM) type was fabricated without a hot-pressing process using a spray coating method with a Pt loading of  $0.2 \text{ mg cm}^{-2}$ . The surface was examined using scanning electron microscopy. The catalysts with different loadings were characterized by X-ray diffraction and cyclic voltammetry. The single cell performance with the fabricated MEAs was evaluated and electrochemical impedance spectroscopy was used to characterize the fuel cell. The best performance of  $742 \text{ mA cm}^{-2}$  at a cell voltage of 0.6 V was obtained using 40 wt.% Pt/C in both the anode and cathode.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Polymer electrolyte membrane fuel cell; Catalyst coated membrane; Membrane electrode assembly; Spray coating; Platinum loading

## 1. Introduction

Fuel cells are a promising energy source on account of their high efficiency and low pollutant emission. Polymer electrolyte membrane fuel cells (PEMFC) have attracted considerable attention as a transport and portable power source for low operation temperature and rapid start-up [1]. However, it is believed that PEMFC are not competitive enough to rechargeable lithium ion battery with respect to the cost price because of the expense of the rare metals used such as platinum in PEMFC. Therefore, reducing the amount of platinum used in fuel cells is very important for their commercialization [2].

Generally, there are two approaches to reduce the amount of platinum in fuel cell. One method is to develop an alloyed catalyst based on platinum, which has a better catalytic activity, or to discover a new catalyst [3–5]. The other is to invent a new catalyst layer fabrication method such as pulse electrodeposition, electrospray technique, sputter deposition, pulsed

laser deposition and ion-beam deposition [6–10]. With respect to the thin catalyst film formation in a fuel cell, supported catalysts and polymer ionomers within the catalyst layer has been used to reduce the amount of catalyst from  $4 \text{ mg cm}^{-2}$  to approximately  $0.4 \text{ mg cm}^{-2}$ . A supported catalyst has a much larger surface area compared with an unsupported catalyst, and a mixed polymer ionomer containing catalyst within the catalyst layer has tremendously increased the number of electrochemical reaction sites, so-called three-phase boundary [11].

It was reported that the catalyst particle size increases and the electrochemical active area (ECA) decreases with increased loadings of the supported catalyst [12]. When the supported platinum loading was increased from 20 to 40 and 60 wt.%, the amount of carbon particles for given amount of platinum was lower, and the structure of the catalyst layer with the polymer ionomer was changed. Structural modification affects the mass transport of the reactant gas and water produced during the reaction. The ion and electron transfer was also affected and the single cell performance was changed in the end. Then, catalysts with several different platinum loadings (20, 40, and 60 wt.%) were used to investigate the effects of

\* Corresponding author. Tel.: +82 2 880 1889; fax: +82 2 888 1604.  
E-mail address: [ysung@snu.ac.kr](mailto:ysung@snu.ac.kr) (Y.-E. Sung).

the loading on the performance of a fuel cell. The MEAs were examined by scanning electron microscopy (SEM) and single-cell test. The electrochemical properties were also studied using electrochemical impedance spectroscopy.

## 2. Experimental

### 2.1. Characterization of the catalysts and catalyst layer

The size of the platinum particles in the catalyst powder was examined by X-ray diffraction (XRD) (D/MAX2500PC, Rigaku Corp.) before applying them to the membrane electrode. Catalyst ink was prepared by mixing the catalyst powder (20, 40 and 60 wt.% platinum on carbon) with an ionomer (5 wt.% Nafion solution, DuPont) in de-ionized water and isopropyl alcohol. The Nafion loading in both electrodes was 30 wt.%, and the ink was ultrasonicated.

Cyclic voltammetry (CV) (Autolab PGSTAT 30, Eco Chemie. Co.) measurements were carried out to calculate the electrochemical active area of the catalyst [13]. A saturated calomel electrode (SCE) was used as the reference electrode and platinum wire was used as the counter electrode. The catalyst ink was dropped onto glassy carbon as the working electrode. The electrodes were immersed in an argon purged  $\text{H}_2\text{SO}_4$  solution at room temperature and the measurement was carried out at a scan rate of 10 mV per second.

A Nafion 112 membrane (DuPont) was used as the polymer electrolyte membrane. The membrane was treated with 3 wt.%  $\text{H}_2\text{O}_2$  (Junsei Chemical Co. Ltd.) for 1 h and boiled in de-ionized water for another 1 h. The above process was repeated twice. The treated membrane was immersed in 0.5 M  $\text{H}_2\text{SO}_4$  (Sigma–Aldrich, 95–98%, A.C.S. reagent grade) at 100 °C for 1 h and washed in de-ionized water for 1 h [14].

### 2.2. Fabrication of MEA with different platinum loading on electrodes

The membrane electrode assembly was fabricated via the catalyst-coated membrane by spraying the platinum catalyst on both sides of the polymer membrane. This was followed by just physically placing GDLs without the need for a hot-pressing process. A treated Nafion 112 membrane was fixed on a proper plate during fabrication of the catalyst coated membrane by the spraying method. The amount of platinum catalyst used in the spraying method was  $0.2 \text{ mg cm}^{-2}$ , which is approximately a half of the conventional platinum usage (ca.  $0.4 \text{ mg cm}^{-2}$ ) in a PEM fuel cell [18]. The fabricated catalyst coated membrane was dried for approximately 1 h [15].

The effect of different supported platinum loadings on the anode electrode performance was investigated by fixing the catalyst loading on the cathode electrode to 20 and 40 wt.% for various anode-supported catalyst loadings. The anode catalyst loading used was 20, 40 and 60 wt.%. The effect of the different catalyst loading on the cathode electrode was investigated by fixing the amount of the catalyst loading on the anode and varying the cathode catalyst loading.

### 2.3. Single cell performance measurements

The performance of the fabricated MEA with the different catalyst loading was evaluated using a single cell (CNL-PEM005-01, CNL Energy) and electronic loader. The active area of the MEA was  $5 \text{ cm}^{-2}$  and the MEA was placed between the graphite plates with serpentine flow-field. Two GDLs were also placed between the graphite plate and MEA, and the whole unit was tightened between the metal plates with the proper pressure. The single cell performance was characterized using humidified hydrogen gas at 75 °C on an anode electrode and humidified air gas at 70 °C on a cathode electrode with a stoichiometric ratio of 1.5/2 for the anode and cathode. The cell temperature during the single cell test was maintained at 70 °C and ambient pressure [16]. The current–voltage characteristics were measured using an electronic loader (WFCTS, WonATech Co., Ltd.).

The electrochemical properties of the prepared MEA were examined by electrochemical impedance spectroscopy (Gamry Instruments). The DC current of the single-cell was set to 1 A, and the AC current was maintained at 0.1 A root-mean-square during the impedance measurement. The measurement was carried out at frequencies ranging from 10 kHz to 1 Hz and ten points per logarithmic decade were recorded.

## 3. Results and discussion

### 3.1. XRD, CV, and SEM measurements

X-ray diffraction was used to show the changes in particle size as a function of the catalyst loading on carbon. From Fig. 1, the particle size of the platinum catalyst was calculated to 3.4, 4.0 and 5.4 nm at a catalyst loading 20, 40 and 60 wt.% on the carbon support, respectively.

Fig. 2 shows cyclic voltammetry measurements of the surface areas of the 20, 40 and 60 wt.% carbon supported platinum. The results indicate that the surface area decreases with increasing platinum loading. The surface area of the 20, 40 and 60 wt.% of the carbon supported platinum was calculated to be 42.09, 33.40 and  $28.02 \text{ m}^2 \text{ g}^{-1}$ .

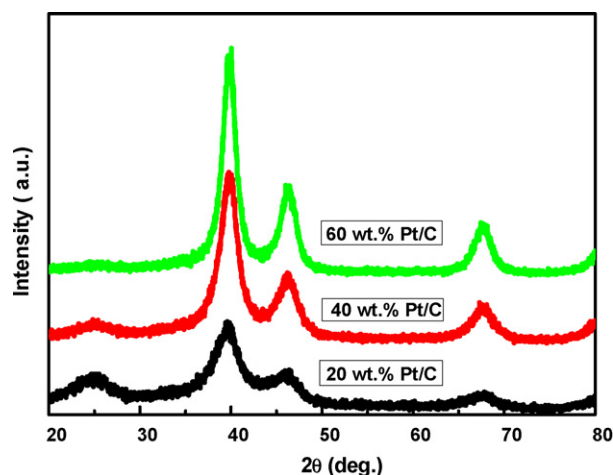


Fig. 1. X-ray diffraction (XRD) patterns of 20, 40, and 60 wt.% Pt/C catalysts.

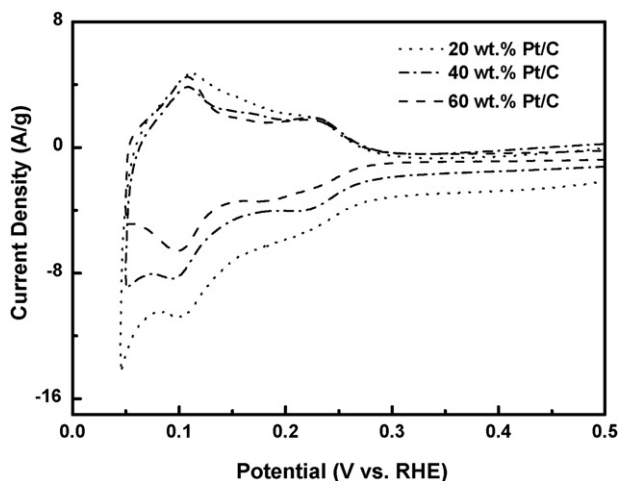


Fig. 2. Cyclic voltammetry (CV) curves for 20, 40 and 60 wt.% Pt/C catalysts.

The MEAs prepared with the 30 wt.% Nafion solution were characterized by scanning electron microscopy. Fig. 3 (a) and (b) in show the SEM images of the electrode surface with 20 and 40 wt.% platinum loading catalysts. The images show that there are many pores with a diameter larger than one hundred nanometers and a few pores in the micrometer range. How-

ever, the electrode containing 60 wt.% platinum loading catalyst contained well distributed pores without any large pore in the micrometer range (see Fig. 3(c)). The amount of carbon support decreased with increasing platinum loading in the supported catalyst particles. This suggests that electrode should contain more of the Nafion ionomer for the same amount of carbon support as the platinum loading is increased. According to reports, the specific pore volume of micrometer size decreased with increasing ionomer content within the electrode [17]. This explanation is consistent with our results.

### 3.2. Effects of different anode platinum loading on single cell performance

In order to examine the effect of the different supported platinum loading on the anode electrode performance, the catalyst loading on the cathode electrode was fixed and the anode catalyst loading was varied. Fig. 4(a) shows the single cell performances as a function of the anode catalyst loading (20, 40 and 60 wt.%) when the cathode catalyst loading was fixed to 20 wt.%. The performances of the 20 and 40 wt.% anode catalysts were similar but the single cell containing the 60 wt.% anode catalyst showed an inferior performance. The experiments with the 40 wt.% cathode catalyst showed similar results to those

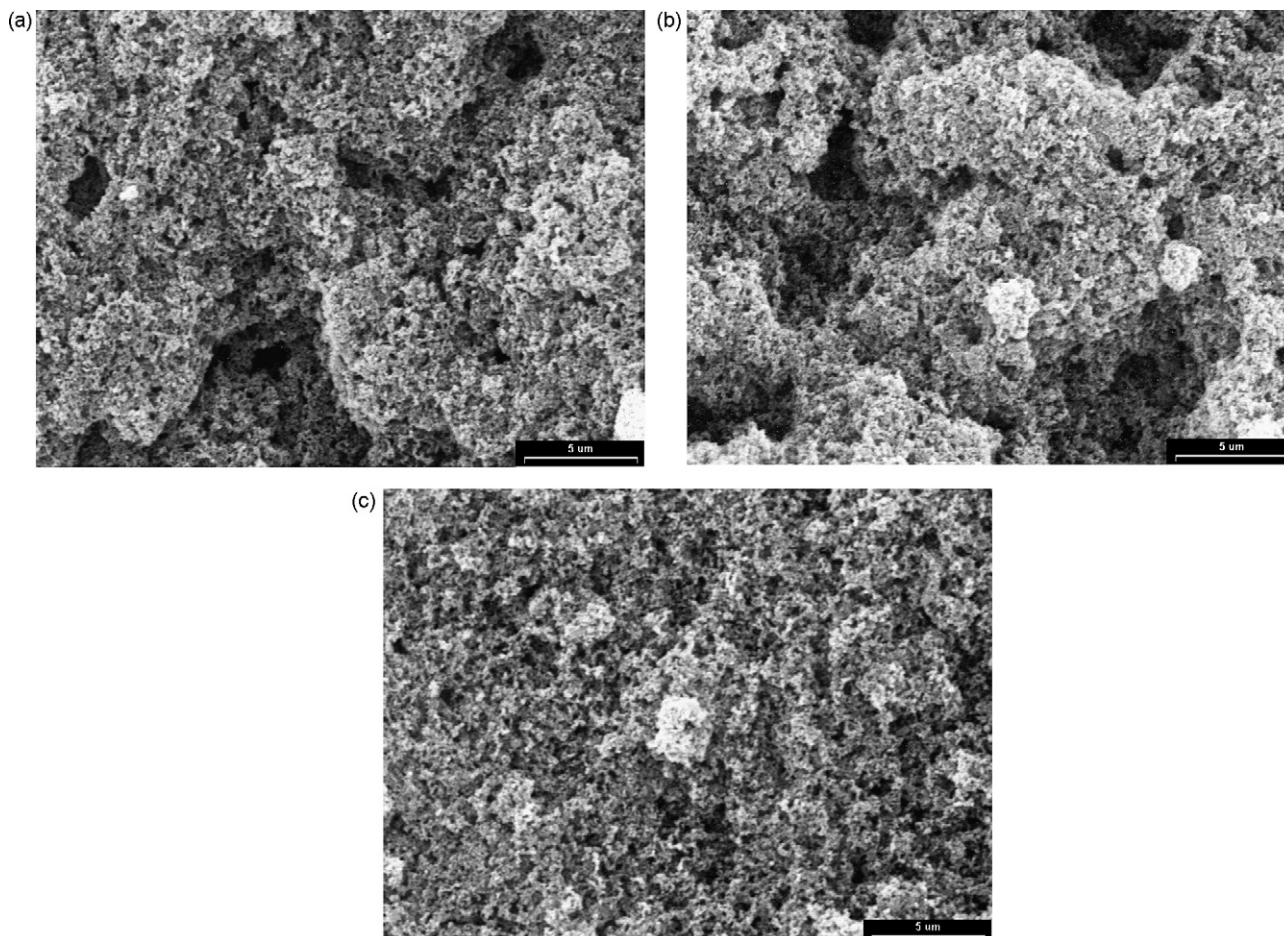


Fig. 3. Scanning electron micrograph (SEM) images of (a) 20 wt.%, (b) 40 wt., and (c) 60 wt.% Pt/C catalysts.

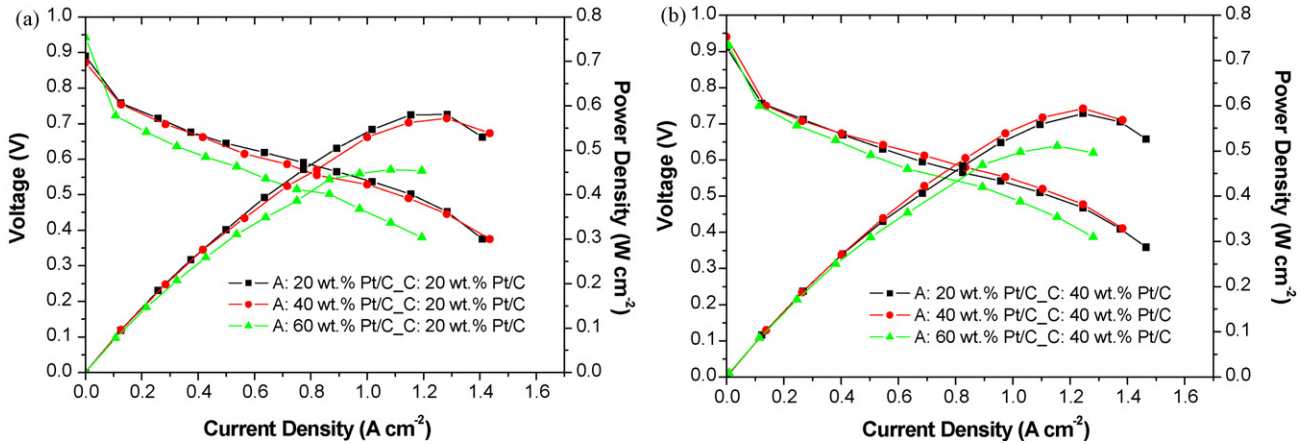


Fig. 4. Polarization curves of single cells with varying anode catalyst loading and fixed cathode catalyst loading at: (a) 20 wt.% and (b) 40 wt.%.

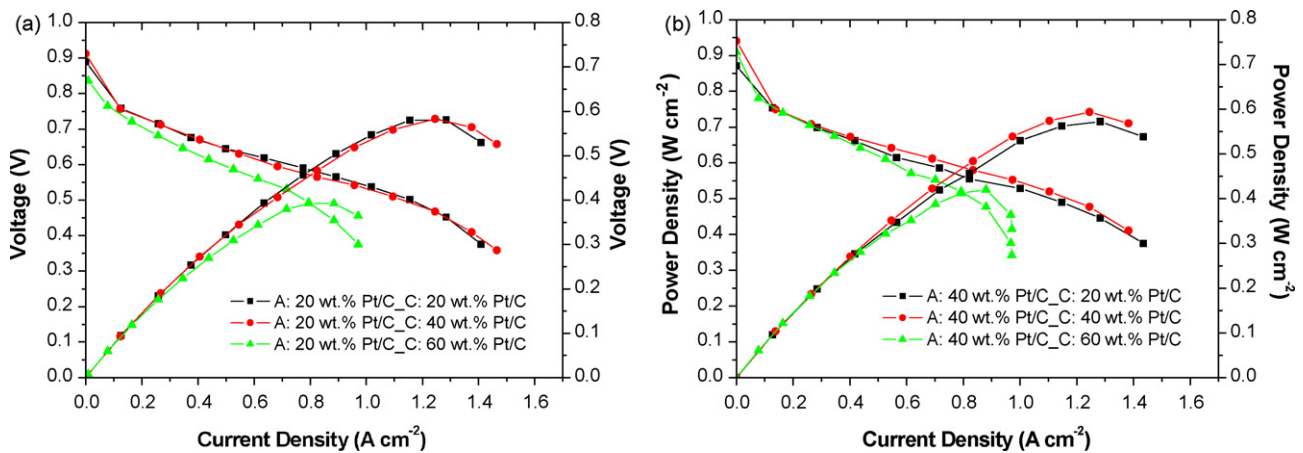


Fig. 5. Polarization curves of single cells with varying cathode catalyst loading and fixed anode catalyst loading at: (a) 20 wt.% and (b) 40 wt.%.

of the 20 wt.% cathode catalyst, as shown in Fig. 4(b). Overall, the single cell containing the 60 wt.% cathode catalyst showed inferior performance to that of the 20 and 40 wt.% cathode catalysts. The cell performances with respect to the different cathode catalyst loading (20 and 40 wt.%) were similar for same anode electrode.

### 3.3. Effects of different cathode platinum loading on single cell performance

In order to determine the effect of the different supported platinum loading on the cathode electrode performance, the catalyst loading on the anode electrode was fixed and the cathode catalyst loading was varied. Fig. 5 shows the single cell performances with the cathode catalyst loading of 20, 40 and 60 wt.% at a fixed the anode catalyst loading of 20 and 40 wt.%. The performances of the 20 and 40 wt.% cathode catalysts were similar but the single cell power density with 60 wt.% cathode catalyst decrease suddenly at the voltage region <0.6 V. The current density at 0.4 V was approximately 1400 mA cm<sup>-2</sup> for the 20 and 40 wt.% cathode electrode but 950 mA cm<sup>-2</sup> for the 60 wt.%. As indicated by the XRD and CV measurements, the surface area of the platinum particle decreased and the particle size increased with increasing the catalyst loading from 20

to 60 wt.%. However, the SEM images of the 20 and 40 wt.% catalyst show a similar porous structure of electrodes and comparable single-cell performance. This indicates that the porosity of the electrode has a larger effect on the performance of the MEA than either the particle size or surface area of the catalyst. In particular, the inferior performance of the 60 wt.% cathode electrode appears to be caused by the increasing resistance to mass transfer.

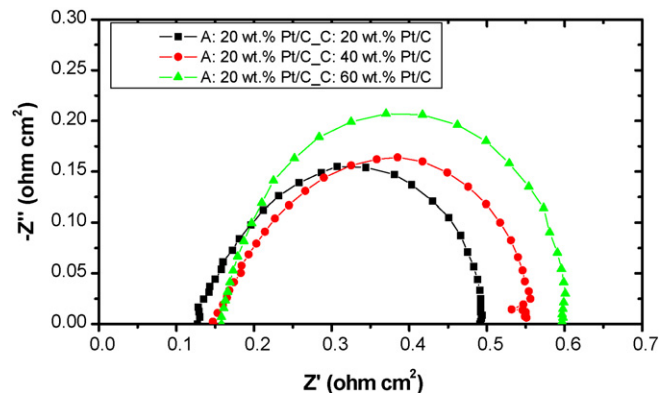


Fig. 6. Cathode impedance plot with varying cathode Pt/C loading (20, 40 and 60 wt.%).

The increasing resistance to mass transfer was confirmed by electrochemical impedance analysis. Fig. 6 shows Nyquist plot of the single cells with the 20 wt.% anode catalyst as a function of the cathode catalyst loading. The ohmic resistances were almost unchanged for the cells but the charge transfer resistance increased from 0.182 to 0.220  $\Omega$  with increasing the cathode catalyst loading from 20 to 60 wt.%. This increasing charge transfer resistance might be caused by flooding at the 60 wt.% cathode electrode that did not contain micrometer sized pores. The cell performance with respect to the different anode catalyst loadings (20 and 40 wt.%) was similar at the same cathode electrode.

#### 4. Conclusions

Polymer electrolyte membrane fuel cells with different catalyst loadings (20, 40 and 60 wt.% on carbon) were fabricated and their performance was examined. The CCM type of MEA was fabricated. The single cell performance with the fabricated MEAs was examined using an electrochemical loader. Despite the different particle size and electrochemical active area of the 20 and 40 wt.% Pt/C catalysts, the effects of the different catalyst loading on the single cell performance was not significant. With the 60 wt.% Pt/C applied to any electrode of the MEA, the cell performance decreased particularly in the high current density region. This is because the electrode structure containing 60 wt.% Pt/C, which did not contain a significant amount of large micrometer-sized pores, as shown in the SEM image, was unsuitable for removing the product water at the cathode and transporting the reactant gases at both electrodes. The increased mass transfer resistance was also shown in the impedance spectra. In conclusion, the catalyst loading and Nafion solution ratio relative to the carbon support and the loading of platinum particles affect the microstructure and fuel cell performance.

#### Acknowledgments

This work was financially supported by Korea Research Foundation (Grant # KRF-2004-005-D00064), KOSEF through the Research Center for Energy Conversion and Storage, and National RD&D Organization for Hydrogen & Fuel Cell & Ministry of Commerce, Industry and Energy.

#### References

- [1] T.R. Ralph, G.A. Hards, *Chem. Ind.* (9) (1998) 337.
- [2] E.A. Ticianelle, C.R. Derouin, A. Redondo, S. Srinivasan, *J. Electrochem. Soc.* 135 (1988) 2209.
- [3] H.A. Gasteiger, S.S. Kocha, B. Sompalli, F.T. Wagner, *Appl. Catal. B: Environ.* 59 (2005) 10.
- [4] K. Sawai, N. Suzuki, *J. Electrochem. Soc.* 151 (12) (2004) 2132.
- [5] H. Zhong, H. Zhang, G. Liu, Y. Liang, J. Hu, B. Yi, *Electrochem. Commun.* 8 (2006) 707.
- [6] E.J. Taylor, E.B. Anderson, N.R.K. Vilambi, *J. Electrochem. Soc.* 139 (1992) L45.
- [7] S. Hirano, J. Kim, S. Srinivasan, *Electrochim. Acta* 42 (1997) 1587.
- [8] N. Cunningham, E. Irissou, M. Lefevre, M.C. Denis, D. Guay, J.P. Dodelet, *Electrochem. Solid-State Lett.* 3 (2003) A125.
- [9] M.K. Debe, T.N. Pham, A.J. Steinbach, US Patent 97,948,851 (1999).
- [10] R. Benitez, J. Soler, L. Daza, *J. Power Sources* 151 (2005) 108.
- [11] A.J. Appleby, *J. Power Sources* 37 (1992) 223.
- [12] T.R. Ralph, M.P. Horgath, *Platinum Metals Rev.* 46 (1) (2002) 4.
- [13] J.-H. Choi, K.-W. Park, B.-K. Kwon, Y.-E. Sung, *J. Electrochem. Soc.* 150 (2003) 973.
- [14] J.-H. Choi, K.-W. Park, H.-K. Lee, Y.-M. Kim, J.-S. Lee, Y.-E. Sung, *Electrochim. Acta* 48 (2003) 2784.
- [15] M. Prasanna, H.Y. Ha, E.A. Cho, S.-A. Hong, I.-H. Oh, *J. Power Sources* 137 (2004) 2.
- [16] K.-W. Park, B.-K. Kwon, J.-H. Choi, I.-S. Park, Y.-M. Kim, Y.-E. Sung, *J. Power Sources* 109 (2002) 440.
- [17] M. Uchida, Y. Fujioka, Y. Sugawara, N. Eda, A. Otha, *J. Electrochem. Soc.* 143 (1996) 2247.
- [18] W.-M. Yan, S.-C. Mei, C.-Y. Soong, Z.-S. Liu, D. Song, *J. Power Sources* 160 (2006) 119.