

Short communication

# Novel hollow PtRu nanospheres supported on multi-walled carbon nanotube for methanol electrooxidation

Dao-Jun Guo<sup>a,b</sup>, Long Zhao<sup>a</sup>, Xin-Ping Qiu<sup>a,\*</sup>, Li-Quan Chen<sup>a</sup>, Wen-Tao Zhu<sup>a</sup>

<sup>a</sup> Key Laboratory of Organic Optoelectronics and Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, PR China

<sup>b</sup> College of Chemistry Science, Qufu Normal University, Qufu, Shandong 273165, PR China

Received 24 October 2007; received in revised form 20 November 2007; accepted 20 November 2007

Available online 4 December 2007

## Abstract

A multi-walled carbon nanotube supported hollow PtRu nanosphere electrocatalysts was prepared at room temperature in a homogeneous solution employing cobalt metal nanoparticles as sacrificial templates. Transmission electron micrograph (TEM) measurements showed that carbon nanotube supported PtRu nanospheres were coreless and composed of discrete PtRu nanoparticles with the crystallite size of about 2.1 nm. X-ray diffraction (XRD) results showed that the hollow PtRu nanospheres had a face-centered cubic structure. Electrochemical measurements demonstrated that the carbon nanotube supported hollow PtRu nanosphere electrocatalysts exhibited enhanced electrocatalytic performance for methanol oxidation compared with carbon nanotube supported solid PtRu nanoparticles and commercial E-TEK PtRu/C (20 wt%) catalysts, which is crucial for anode electrocatalysis in direct methanol fuel cells (DMFCs).

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** PtRu nanospheres; Hollow; Methanol oxidation; Electrocatalyst

## 1. Introduction

Direct methanol fuel cells (DMFCs) have attracted much attention as power sources for portable electronic devices because they are superior to hydrogen/oxygen-type fuel cells in terms of weight, volume energy densities, and so on. However, the further development of DMFCs faces serious problems such as low activity of methanol electrooxidation catalysts [1–3], methanol crossover [4–6] from the anode to the cathode, carbon dioxide gas management, water management [7], and so on. Unlike other fuel cells, the liquid feed DMFC suffers from mass transport limitations predominantly at the anode due to the low diffusion coefficient of methanol in water and the release of carbon dioxide gas bubble [8]. A methanol concentration gradient exists within the thickness of the catalyst layer and results in poor utilization of the catalyst. In addition, a methanol diffusion limiting current is found in DMFC with the low concentration

methanol solution [9], which inhibits getting high power density. Therefore, the conventional anode structure based on the gas diffusion electrodes employed in proton exchange membrane fuel cells is not ideal for the transport of the methanol and carbon dioxide.

Recently, hollow metal nanoparticles have captured the attention of researchers [10,11]. The increased surface area, low density, saving of material and concomitant reduction in cost coupled with the interesting special properties of such structures have potential application in catalysis. Some supported [12] and unsupported [13,14] Pt-based hollow nanospheres are prepared and exhibited enhanced electrocatalytic performance for methanol oxidation. It is well known that the supported metal nanoparticles show a higher electrocatalytic activity and utilization efficiency than unsupported metal particles because of their large surface area on the supports [15]. Zhao et al. [12] reported hollow Pt nanospheres supported on the carbon Vulcan XC-72 that show good electrocatalytic activity for methanol oxidation. But to the best of our knowledge, hollow metal catalysts supported on the carbon nanotubes (CNTs) have not been reported.

\* Corresponding author. Tel.: +86 10 62794234; fax: +86 10 62794234.  
E-mail address: [qiuxp@mail.tsinghua.edu.cn](mailto:qiuxp@mail.tsinghua.edu.cn) (X.-P. Qiu).

In this paper, we synthesized hollow PtRu nanospheres supported on multi-wall carbon nanotubes (MWNTs). The prepared hollow PtRu/MWNT nanospheres demonstrated enhanced electrocatalytic activity for methanol oxidation in comparison to carbon nanotube supported solid PtRu nanoparticle electrocatalysts and commercial E-TEK PtRu/C (20 wt%) catalysts, which is very important to increase the utilization of catalysts and improve the structure of the catalyst layer of the direct methanol fuel cell.

## 2. Experimental

### 2.1. Preparation of PtRu/MWNT composites

Hollow PtRu/MWNT catalysts (HN-PtRu/MWNT) were prepared by a two-step method described in detail in previous paper [16]. In a typical process, a HN-PtRu/MWNT catalyst with a nominal molar Pt/Ru ratio of 1/1, denoted as Pt<sub>50</sub>Ru<sub>50</sub>/MWNT, was prepared as follows. Carbon nanotube (48 mg) was pretreated with 5 M HCl and concentrated HNO<sub>3</sub> solution before being suspended in 20 mL of deionized water. Hundred milliliters of 0.4 mM CoCl<sub>2</sub>·6H<sub>2</sub>O was mixed with 0.4 mM citric acid solution, which was used as a stabilizer. MWNT supports were then added to the above solution, sonicated for 15 min. Then the solution was purged with N<sub>2</sub> for 15 min. A freshly prepared solution of NaBH<sub>4</sub> (10 mg in 20 mL of H<sub>2</sub>O) was added drop wise into the above solution under vigorous stirring giving rise to a Co hydrosol. The Co hydrosol was aged for 1 h to decompose the residual NaBH<sub>4</sub>. Afterwards, appropriate amounts of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O and RuCl<sub>3</sub> aqueous solutions were added drop wise under vigorous stirring, during which high purity argon gas was passed through the reaction system to remove the dissolved oxygen. After 30 min, the product is collected by centrifugation, washed several times with H<sub>2</sub>O and ethanol, the obtained catalyst was dried in a vacuum oven at 70 °C overnight and then the hollow PtRu/MWNT (20 wt% PtRu) catalysts were obtained. For comparison, Pt<sub>50</sub>Ru<sub>50</sub>/MWNT nanoparticle catalysts (SN-PtRu/MWNT) were also obtained directly by co-reducing the Pt and Ru precursors in a carbon nanotube suspension using the drop wise addition of NaBH<sub>4</sub> at room temperature with stirring.

### 2.2. Measurement

Electrochemical reactivity of the catalysts was measured by cyclic voltammetry (CV) using a three-electrode cell at the PAR-STAT 2273 potentiostat controlled by PowerSuite<sup>®</sup> software (Princeton Applied Research). The working electrode was a gold plate covered with a thin layer of Nafion-impregnated catalyst. As a typical process, the catalyst ink was prepared by ultrasonically dispersed about 1 mg catalyst in the 25 μL mixture of Nafion solution (20% Nafion and 80% ethylene glycol) for 30 min. After casting the catalysts ink onto a polished planar gold patch (1.0 cm × 1.0 cm), the electrodes were air-dried at 80 °C for 1 h. Pt gauze and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. All potentials in this report are quoted versus SCE. Cycle voltammetry (CV) test was conducted at 50 mV s<sup>-1</sup> in a solution of 1 M HClO<sub>4</sub> with 1 M CH<sub>3</sub>OH, potential ranging from -0.2 to 1.0 V. CO stripping experiments were performed as follows: after purging the solution with N<sub>2</sub> gas for 20 min, gaseous CO was bubbled for 20 min to allow adsorption of CO onto the electro-catalysts while maintaining a constant voltage of 0.1 V versus SCE. Excess CO dissolved in solution was purged out with N<sub>2</sub> for 20 min and CO stripping voltammetry was recorded in 1 M HClO<sub>4</sub> solution at a scan rate of 20 mV s<sup>-1</sup>. The electrochemical measurements were conducted under 25 °C.

The morphology of PtRu/MWNT composites were investigated using transmission electron microscopy (TEM, JEOL model JEM-2011) operated at 200 keV and equipped with an energy-dispersive spectrometer (EDS). The X-ray diffraction (XRD) analysis was performed using the Rigaku X-ray diffractometer with Cu Kα radiation source.

## 3. Results and discussion

### 3.1. TEM analysis and elemental composition of the HN-PtRu/MWNT composites

Transmission electron microscope (TEM) images of the HN-PtRu/MWNT catalysts are shown in Fig. 1. The reaction appears to form hollow spheres with average diameters of 10–20 nm. The individual PtRu nanospheres are consistent with a hollow

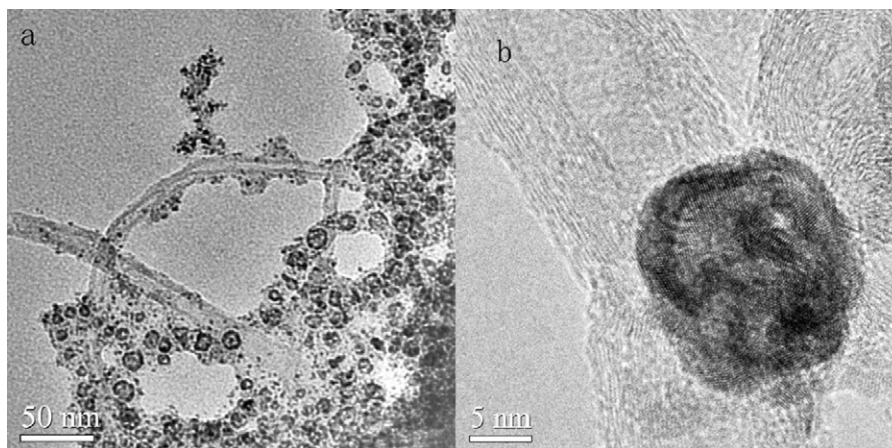


Fig. 1. TEM image of HN-PtRu/MWNT composites.

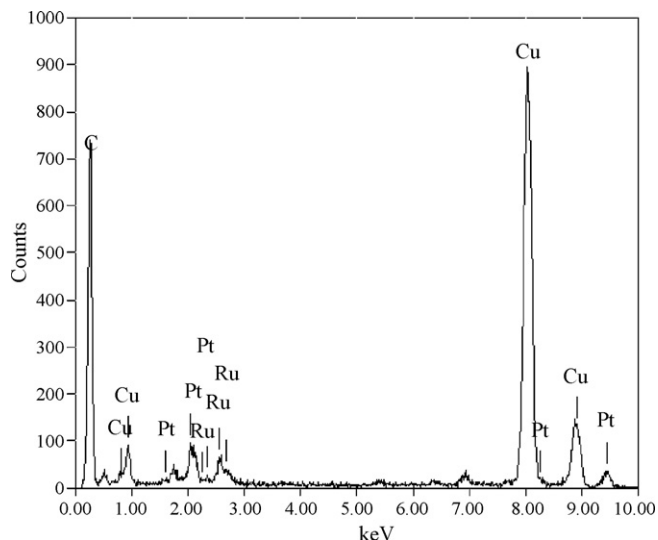


Fig. 2. EDS spectrum of HN-PtRu/MWNT composites.

structure. Another feature is that the shell is incomplete and porous, not solid. The shells of the PtRu hollow nanospheres seem to be rough and consist of discrete small PtRu nanoparticles. This feature endows the hollow PtRu nanospheres with a high active surface area. Energy-dispersive X-ray spectroscopy data for many spheres indicate that the hollow spheres contain both Pt and Ru and confirm an average stoichiometry of Pt<sub>50</sub>Ru<sub>50</sub> (Fig. 2).

### 3.2. XRD analysis of HN-PtRu/MWNT composites

The XRD patterns of the HN-PtRu/MWNT composites described above are shown in Fig. 3, together with the patterns of the SN-PtRu/MWNT composites. The formation of sharp diffraction peaks (002) around a  $2\theta$  value at  $26.2^\circ$  indicate the crystalline nature of graphitic structure of the MWNTs. Clearly, the PtRu composites displayed the similar characteristic patterns of Pt(0) face-centered cubic (fcc) diffraction, and no patterns of

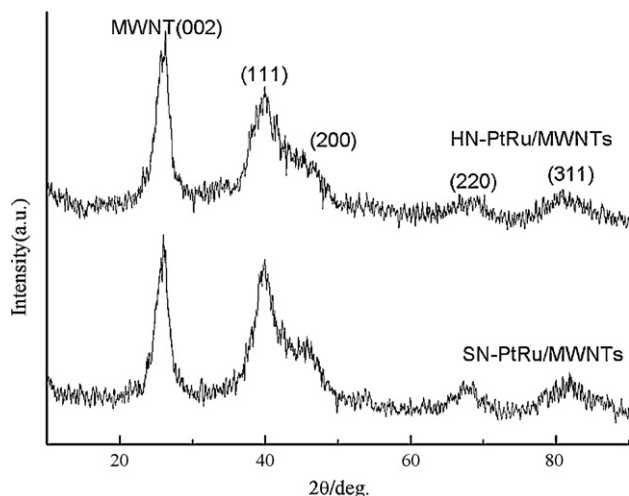


Fig. 3. Powder X-ray diffraction (XRD) pattern of HN-PtRu/MWNT composites.

the Pt and/or Ru oxides were detectable. This means that the precursor mainly converted into metallic PtRu. The breadth of the XRD peaks also indicated that small PtRu crystallites were obtained. The average particle sizes of the catalysts were calculated from broadening of the (220) diffraction peaks using Scherrer's equation; and they are found to be in the range of 2.1 and 2.8 nm, respectively, for hollow PtRu nanospheres and solid PtRu nanoparticles. These results also show that the hollow PtRu nanospheres consist of small PtRu nanoparticles consistent with the TEM results.

### 3.3. Electrochemical properties of HN-PtRu/MWNT composites

The electrocatalytic activity of the HN-PtRu/MWNT composites toward the oxidation of methanol was tested and the results were compared with those obtained on SN-PtRu/MWNT composites and commercial PtRu/C catalysts. The measurements were carried out in a 1M HClO<sub>4</sub> aqueous solution containing 1.0M methanol shown in Fig. 4. Although all samples show catalytic activities toward the methanol oxidation, the peak currents catalyzed by the HN-PtRu/MWNT nanospheres are much larger than those for SN-PtRu/MWNT composites and commercial E-TEK PtRu/C catalysts due to the ideal surface structure for methanol adsorption on the catalyst surface. The remarkably high oxidation current for the hollow-sphere catalysts is directly related to the high surface area. Since PtRu hollow nanospheres are coreless, a larger number of PtRu nanospheres were obtained relative to that found with the same loading of solid PtRu nanoparticles. Theoretically, the curvature radii of the inner surface of PtRu hollow structure are smaller than that of the outer surface, so the inner surface should have much higher activity than the outer surface. This is another reason that the catalytic activity of PtRu nanosphere for methanol oxidation is much higher. Another feature is that the potential for methanol oxidation in the forward scan on HN-PtRu/MWNT and SN-PtRu/MWNT is the almost the same as 0.63 V, much lower than that on commercial PtRu/C catalysts as 0.70 V. This indi-

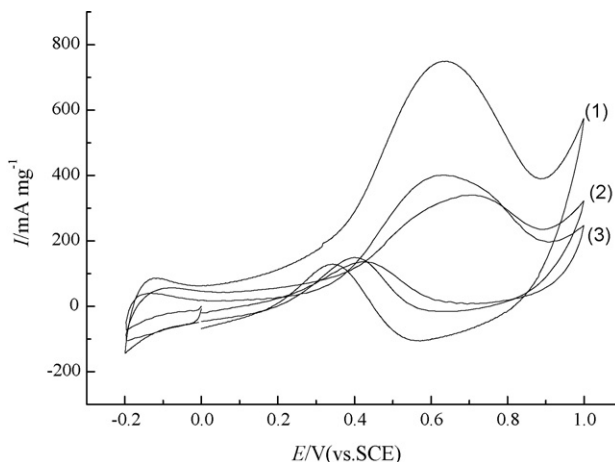


Fig. 4. Cyclic voltammograms of 1M CH<sub>3</sub>OH in 1M HClO<sub>4</sub> at HN-PtRu/MWNT (1), SN-PtRu/MWNT (2) and PtRu/C (3). Scan rate: 50 mV s<sup>-1</sup>.

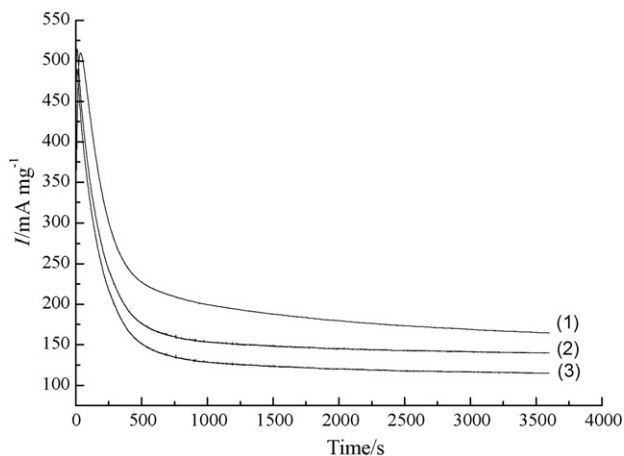


Fig. 5. Chronoamperometry curves for HN-PtRu/MWNT (1), SN-PtRu/MWNT (2) and PtRu/C (3) in 1 M HClO<sub>4</sub> + 1 M CH<sub>3</sub>OH at 0.45 V.

states that the PtRu nanoparticles supported on MWNT are able to significantly reduce the overpotential in methanol oxidation.

Another method to benchmark the catalyst performance is to compare the ratio of peak current associated with the anodic peaks in the forward ( $I_f$ ) and reverse ( $I_b$ ) scans [17]. Such a ratio has been used to infer the CO tolerance of the catalysts [18]. A lower  $I_f/I_b$  value indicates poor oxidation of methanol to CO during the anodic scan and excessive accumulation of residual carbon species on the catalyst surface. Hence, a higher  $I_f/I_b$  value is indicative of improved CO tolerance. The  $I_f/I_b$  value of the HN-PtRu/MWNT catalysts is 5.8, higher than that of SN-PtRu/MWNT catalysts having a value of 2.9, and commercial E-TEK PtRu/C catalysts having a value of 2.3, indicating the best CO resistance.

In order to compare the performance of the HN-PtRu/MWNT catalysts towards the methanol oxidation reaction, we conducted chronoamperometry tests in 1.0 M HClO<sub>4</sub> solution containing 1 M methanol at 0.45 V for 3600 s, as shown in Fig. 5. In the initial period of time, the potentiostatic current decreases rapidly for both the PtRu catalysts, perhaps due to the formation of intermediate species, such as CO<sub>ads</sub>, CH<sub>3</sub>OH<sub>ads</sub>, and CHO<sub>ads</sub> during the methanol oxidation reaction [19]. After long time operation, although the current is gradually decayed for both the catalysts, but the initial and limiting currents of HN-PtRu/MWNT composites keep higher than those of the other two composites throughout all the ranges up to 3600 s, indicating that the former is more active than the latter for methanol electro-oxidation, as is consistent with the CV results.

Since CO species are the main poisoning intermediate, a good catalyst for methanol electro-oxidation should possess excellent CO electro-oxidizing ability, which can be reflected from CO stripping test. We compared the three catalysts in terms of CO eliminating ability. The CO stripping voltammogram curves were shown in Fig. 6. For both catalysts, a broad peak appears during the first scan and disappears in the subsequent scan, indicating that the adsorbed CO is completely oxidized during the first forward scan. But significant differences in the onset potential and peak potential for CO oxidation between the catalysts

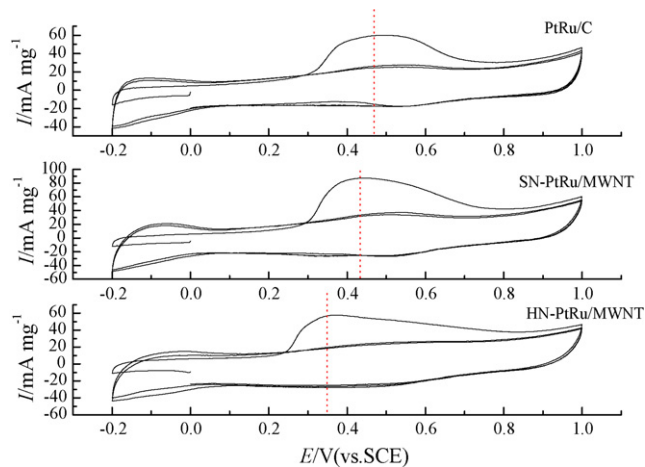


Fig. 6. CO stripping curves for HN-PtRu/MWNT, SN-PtRu/MWNT and PtRu/C in 1 M HClO<sub>4</sub>.

can be observed. The onset potential of CO oxidation on HN-PtRu/MWNTs was at 0.26 V, which was about 10 mV lower than that measured on SN-PtRu/MWNTs and 70 mV lower for E-TEK PtRu/C catalysts, thus illustrating the beneficial role of hollow spheres for CO oxidation. The peak potential of CO oxidation in the forward scan on HN-PtRu/MWNTs was 0.34 V, which decreased to 0.09 V and 0.12 V compared with 0.43 V for SN-PtRu/MWNTs and 0.46 V for E-TEK PtRu/C, respectively. These facts show that the HN-PtRu/MWNT catalysts possess a good electrocatalytic activity for CO oxidation. According to the previous works [20,21], the Ru sites at the PtRu boundaries facilitate the nucleation of oxygen-containing species, thus oxidizing the adsorbed CO at a lower electrode potential, and the maximum activity towards CO oxidation is achieved when the number of PtRu neighbours is maximized resulting in more nucleation sites. For HN-PtRu/MWNT nanospheres, the PtRu can be well neighbored during the Pt and Ru co-formation reduced by the Co nanoparticles, a well distributed rather than aggregated PtRu nanoparticle array can be achieved. So the HN-PtRu/MWNT can significantly shift the peak potential and the onset potential of CO oxidation to a lower electrode potential compared with the SN-PtRu/MWNT and the commercial PtRu/C catalysts.

#### 4. Conclusion

A facile procedure for the large-scale synthesis of PtRu hollow nanosphere catalysts supported on the MWNTs was developed. The catalysts can be simply prepared at room temperature in a homogeneous solution with Co nanoparticles as sacrificial templates. The incomplete and porous shells of the PtRu hollow nanospheres have a higher surface area and, therefore, exhibit a superior electrocatalytic activity toward the methanol oxidation reaction compared to the solid PtRu nanoparticle catalysts and commercial E-TEK PtRu/C catalysts. These metallic hollow nanospheres could be useful in fuel cell.

## Acknowledgement

This project was supported by China Postdoctoral Science Foundation (project no. 20070410075).

## References

- [1] T. Iwasita, F.C. Nart, *J. Electroanal. Chem.* 317 (1991) 291.
- [2] T.D. Jarvi, S. Sriramulu, E.M. Stuve, *J. Phys. Chem.* 101 (1997) 3646.
- [3] E. Redding, A. Sapienza, E.S. Smotkin, *Science* 280 (1998) 1735.
- [4] P.S. Kauranen, E. Skou, *J. Electroanal. Chem.* 408 (1996) 189.
- [5] X. Ren, S. Zelenay, S. Thomas, J. Davey, S. Gottesfeld, *J. Power Sources* 86 (2000) 111.
- [6] B. Gurau, E.S. Smotkin, *J. Power Sources* 112 (2002) 339.
- [7] G.Q. Lu, F.Q. Liu, C.Y. Wang, *Electrochem. Solid-State Lett.* 8 (2005) A1.
- [8] H. Yang, T.S. Zhao, Q. Ye, *J. Power Sources* 139 (2005) 79.
- [9] K. Scott, W.M. Taama, S. Kramer, P. Argyropoulos, K. Sundmacher, *Electrochim. Acta* 45 (1999) 945.
- [10] S.W. Kim, M. Kim, W.Y. Lee, T. Hyeon, *J. Am. Chem. Soc.* 124 (2002) 7624.
- [11] S.J. Oldenburg, G.D. Hale, J.B. Jackson, N.J. Halas, *Appl. Phys. Lett.* 75 (1999) 1063.
- [12] J. Zhao, W.X. Chen, Y.F. Zheng, X. Li, *J. Power Sources* 162 (2006) 168.
- [13] G. Chen, D.G. Xia, Z.R. Nie, Z.Y. Wang, L. Wang, L. Zhang, J.J. Zhang, *Chem. Mater.* 19 (2007) 1840.
- [14] H. Liang, H. Zhang, J. Hu, Y. Guo, L. Wan, C. Bai, *Angew. Chem. Int. Ed. Engl.* 43 (2004) 1540.
- [15] N. Chakroune, G. Viau, S. Ammar, L. Poul, D. Veautier, M.M. Chehimi, C. Mangeney, F. Villain, F. Fievet, *Langmuir* 21 (2005) 6788.
- [16] Y. Vasquez, A.K. Sra, R.E. Schaak, *J. Am. Chem. Soc.* 127 (2005) 12504.
- [17] Z.L. Liu, X.Y. Ling, X.D. Su, J.Y. Lee, *J. Phys. Chem. B* 108 (2004) 8234.
- [18] Y.Y. Mu, H. Liang, J. Hu, L. Jiang, L.J. Wan, *J. Phys. Chem. B* 109 (2005) 22212.
- [19] A. Kabbabi, R. Faure, R. Durand, B. Beden, F. Hahn, J.M. Leger, C. Lamy, *J. Electroanal. Chem.* 444 (1998) 41.
- [20] H.A. Gasteiger, N. Markovic, P.N. Ross, J.E. Cairns, *J. Phys. Chem.* 98 (1994) 617.
- [21] S. Park, A. Wieckowski, M.J. Weaver, *J. Am. Chem. Soc.* 125 (2003) 2282.