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Synthesis and electrochemical properties of porous Pt wire electrodes for methanol electro-oxidation

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ABSTRACT

We have fabricated macroporous Pt wire electrodes via electroplating by using polycarbonate membranes with the pores filled with polystyrene colloidal crystals. The macroporous structure of the resulting Pt wire electrodes is the inverse replica of the colloidal crystal templates. Scanning electron microscopy, Transmission electron microscopy, and X-ray diffraction analysis show the successful formation of macroporous Pt wire electrodes. The catalytic activity of methanol electro-oxidation on the resulting macroporous Pt-wire electrodes due to the three dimensional continuous porous structures is 21.0 mA/cm² at 0.718 V, which is 3.8 times higher than of the dense Pt wire electrodes, 5.4 mA/cm², obtained without use of the colloidal crystals as templates. The chronoamperometry results demonstrate that the macroporous Pt wire electrodes exhibit superior catalytic stability as compared with the dense Pt wire electrode and the commercial Pt/C catalyst.

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1. Introduction

Direct methanol fuel cells (DMFCs) have received considerable attention for use in high-power electronic devices because of several advantages such as high energy density of methanol fuel, relatively low operating temperatures, and easy storage [1–3]. The success of DMFCs is determined by the catalytic activity at the anode, methanol penetration into the polymer electrolyte membrane, and water management at the cathode [4]. Up to now, much effort has been devoted to modify the structures of the catalysts to enhance the catalytic activity at the anode for methanol electro-oxidation by for instance using alloy-based binary, ternary, and multiple catalysts [5,6], using catalyst nanoparticles supported by C-based (GNFs, Vulcan XC-72, and CNT) or metal oxide-based (RuO₂, SnO₂, and CeO₂) matrices [7–12], using one-dimensional nanostructured catalysts such as nanowires [13,14]. Recently, one-dimensional nanostructured catalysts receive growing attention due to their unique electrochemical behaviors and better mechanical and physical properties [14,15].

Pt is one of the most commonly used catalysts in DMFCs. However, the commercial use of Pt as the catalyst for DMFCs is

largely limited by its high price and limited supply. The solution for that is to enhance Pt utilization, namely, to reduce the loading amount of Pt catalysts and, at the same time, increase their catalytic activity. In this scenario, macroporous Pt wire electrodes should be promising as the porous structures can not only lower the Pt amount used but also increase the active surface area for catalysis. Pt wire electrodes are usually produced by electrochemical deposition using porous membranes as templates. Till now, however, this strategy is mainly used to produce the dense (possibly microporous in some cases) wires and tubes with tens of microns in length and hundreds of nanometer in diameter [16–18]. Colloidal crystals, three dimensional hexagonally closely packed arrays of sub- or micron-sized beads spheres, have been extensively used as templates to grow ordered macroporous materials. Herein, we succeeded in fabrication of macroporous Pt wires by combining porous membrane-assisted electroplating and colloidal crystal templating growth of porous materials. Therefore, Pt wire electrocatalysts having uniform diameter and ordered channel structures give superior catalytic activity due to increased surface area and electrolyte/electrode contact area, leading to the improvement of performance in DMFCs.

2. Experimental method

Fig. 1 schematically illustrates our strategy to fabricate macroporous Pt wire electrodes. Polycarbonate (PCTE) membranes

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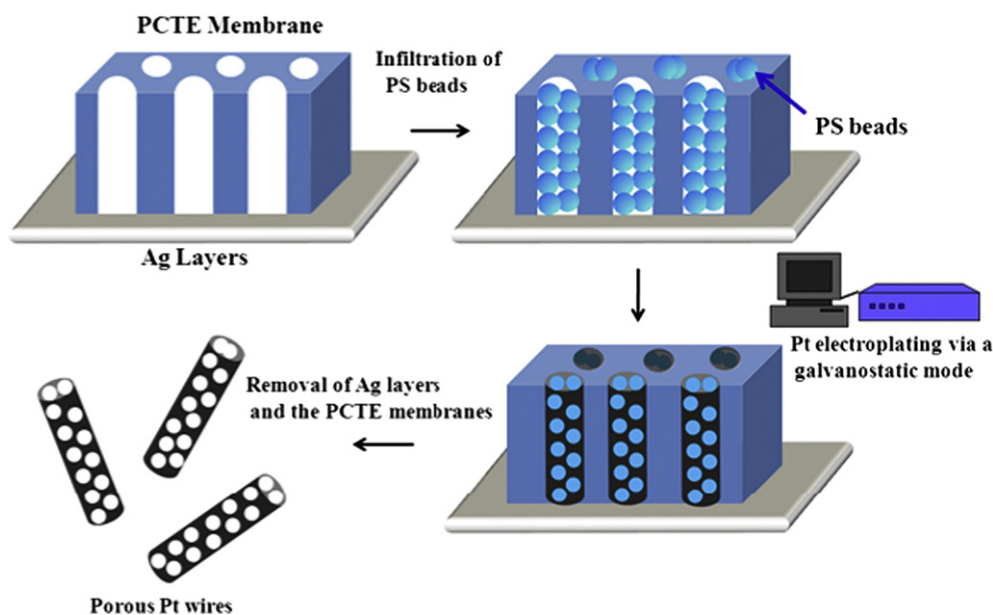


Fig. 1. Schematic illustration of fabrication of macroporous Pt wire electrodes via electroplating by templating PCTE membranes with the pores filled with colloidal crystals.

(Whatman Inc.) containing cylindrical pores of 1 μm in diameter were employed as the templates for Pt electroplating [18–21]. Ag layers were deposited onto the branched side of PCTE membranes to serve as the working electrode using resistance evaporation systems (Edward Auto 306). PS beads (2 wt%) of ca. 200 nm in diameter (Microparticles GmbH, Germany) were diluted to 0.2 wt%. After Ag deposition, polystyrene (PS) beads of ca. 200 nm in diameter were infiltrated into the pores of the PCTE membranes, followed by ultrasonication for 1 h and heat treatment in a convection oven at 65 $^{\circ}\text{C}$ for 2 h. Afterward, the PCTE membranes filled with the PS beads were used as templates for Pt electroplating by means of galvanostatic mode at $-199 \text{ mC}/\text{cm}^2$ and at 50 $^{\circ}\text{C}$. The PCTE membranes filled with PS beads, Pt wires, and Ag/AgCl (sat. KCl) electrodes were used as the working, counter, and reference electrodes. The electroplating solutions contained 0.01 M H_2PtCl_6 and 0.2 M H_2SO_4 . After electroplating, the Ag layers were dissolved by immersion of the membranes in 5 M HNO_3 . The decomposition of the PCTE membranes and the PS beads by dichloromethane yielded macroporous Pt wires. The dense Pt wires were fabricated by using PCTE membranes without filling by PS beads as templates for electroplating under the same condition. The resulting Pt wires were immersed into aqua regia (33 wt%, $\text{HNO}_3:\text{HCl} = 1:3$ in a volume) for 15 min prior to further use.

Scanning electron microscopy (SEM) images were obtained using a Gemini LEO 1550 instrument operated at 3 kV. Transmission electron microscopy (TEM) images were obtained using a TECHANI-F20 microscope (FEI COMPANY), operating at an accelerating voltage of 200 kV. X-ray diffraction (XRD) analysis was implemented using a Bruker D8 Advance diffractometer equipped with a CuK_α source.

Electrochemical activity measurements of all the samples prepared were conducted by using a three-electrode system. The Pt electrode, Ag/AgCl (in 3 M KCl), and glassy carbon (0.07 cm^2) were used as the counter, reference, and working electrodes, respectively. Catalyst inks of equivalent weight (0.02 $\text{mg}_{\text{metal}} = 0.286 \text{ mg}_{\text{metal}} \text{ cm}^{-2}$) that contain the catalyst and Nafion (9 : 1 wt%) were loaded onto the working electrode by micropipette, followed by drying in an oven at 70 $^{\circ}\text{C}$ for 1 h. A mixture of aqueous solutions of 2 M CH_3OH and 0.5 M H_2SO_4 was used as an electrolyte. The test cells were stirred constantly and purged continuously with

nitrogen gas for 1 h before electrochemical testing. The catalytic activity of the electrodes was evaluated by a cyclic voltammetry (AUTOLAB by Eco Chemie) at a scan rate of 50 mV s^{-1} in the range of -0.2 to 1.0 V. Chronoamperometry tests were examined in a mixture of 2.0 M CH_3OH and 0.5 M H_2SO_4 at 0.5 V for 600 s. For the comparison, the electrochemical measurements of the commercial Pt/C catalyst (E-TEK, 20 wt%) were carried out under the same experimental conditions.

3. Results and discussion

After electroplating, the consecutive removal of the Ag layers by nitric acid and PCTE membranes and the PS beads by dichloromethane led to macroporous Pt wires. Distinct from those obtained without use of PS colloidal crystals as templates (Fig. 2(a)), the Pt wires obtained with the use of the PS colloidal crystals as templates have a macroporous structure as shown in Fig. 2(b). Fig. 2(c) and (d) shows that the pores with the sizes of ca. 175 nm, which were calculated by using Lince software (Tu Darmstadt, Germany), are arranged in a hexagonal close-packing array and, at the same time, they are connected by the small opening due to the complete infiltration of Pt in the contact area of neighboring PS beads during electrochemical deposition.

Fig. 3 shows that the TEM image further confirmed the macroporous structures of the Pt wires derived from the colloidal crystal templating. The TEM image shows that relative bright contrast regions having macroporous structures are uniformly dispersed within relative dark contrast regions relative to Pt catalysts. All these data confirm that the macroporous structure of the resulting Pt wires is the inverted replica of the colloidal crystal template. In addition, the XRD patterns of the macroporous Pt wires reveal two characteristic diffraction peaks at $2\theta = 39.8$ and 46.2° (the inset of Fig. 3), which corresponding the (111) and (200) planes [JCPDS 04-0802]. This implies that the macroporous Pt wire electrodes have face-centered-cubic crystalline Pt with space group, $fm3m$. The SEM, TEM, and XRD results are indicative of the successful formation of the macroporous Pt wire structure.

According to their hexagonal close-packing structural character, the resulting macroporous Pt wires have the Pt volume fraction of 26% and the void volume fraction of 74%. That is, polystyrene

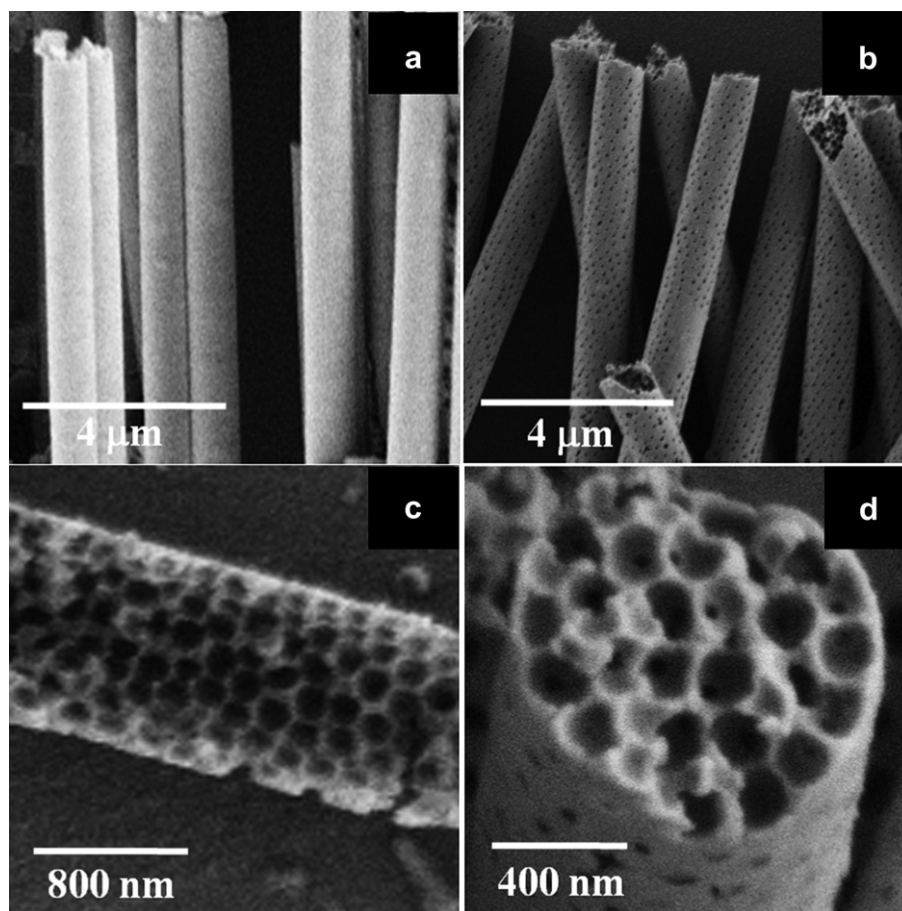


Fig. 2. SEM images of dense Pt wires obtained without use of PS colloidal crystals as templates (a) and macroporous Pt wires obtained with the use of PS colloidal crystals as templates (b). SEM image of the broken part (c) and the cross-section (d) of macroporous Pt wires.

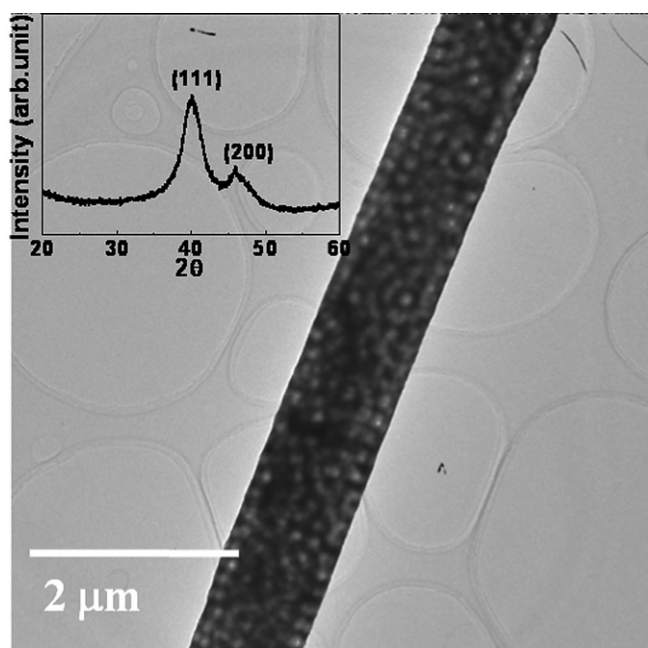


Fig. 3. A TEM image obtained from macroporous Pt wires. A XRD pattern of macroporous Pt wires is shown in the inset.

colloidal crystals have close-packing fraction of about 74% into pores of polycarbonate membranes. Because we grow Pt wires via electroplating in void spaces besides colloidal crystals, the Pt volume fraction is about 26% due to the inverse replica of the colloidal crystals. This should provide the high catalytic active surface area for the resulting macroporous Pt wires. Here we used them as anodes for catalysis of methanol electro-oxidation. Methanol at the anode can be hydrolyzed to carbon dioxide, 6 protons and 6 electrons based on the reaction; $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$ [3]. As shown in Fig. 4(a), the cyclic voltammograms (CVs) of the Pt catalysts for methanol electro-oxidation show the typical two different current peaks, the forward peak corresponds to the methanol oxidation and the backward scan peak to reactions of intermediate species such as CH_2OH , CHO , HCOOH and CO . The forward peak is the anodic current density, which represents the efficiency of the electro-oxidation of methanol at the anode, namely, the high anodic current density suggests a high efficiency. Fig. 4(a) shows that the macroporous Pt wire electrodes have an anodic current density of 21.0 mA/cm^2 and the dense Pt wire electrodes have an anodic current density of 5.4 mA/cm^2 at 0.718 V ; the former is 3.8 times larger than the latter. In addition, an anodic current density of the macroporous Pt wire electrodes is higher than that of the commercial Pt/C catalysts (E-TEK), which exhibit an anodic current density of 16.4 mA/cm^2 at 0.718 V . This underlines a high catalytic activity of macroporous Pt wires as anodes for methanol electro-oxidation. This should arise from the fact that the macroporous Pt wires have a higher surface area as compared with the dense Pt wires. Here we measured the electrochemically active surface (EAS) area of macroporous and

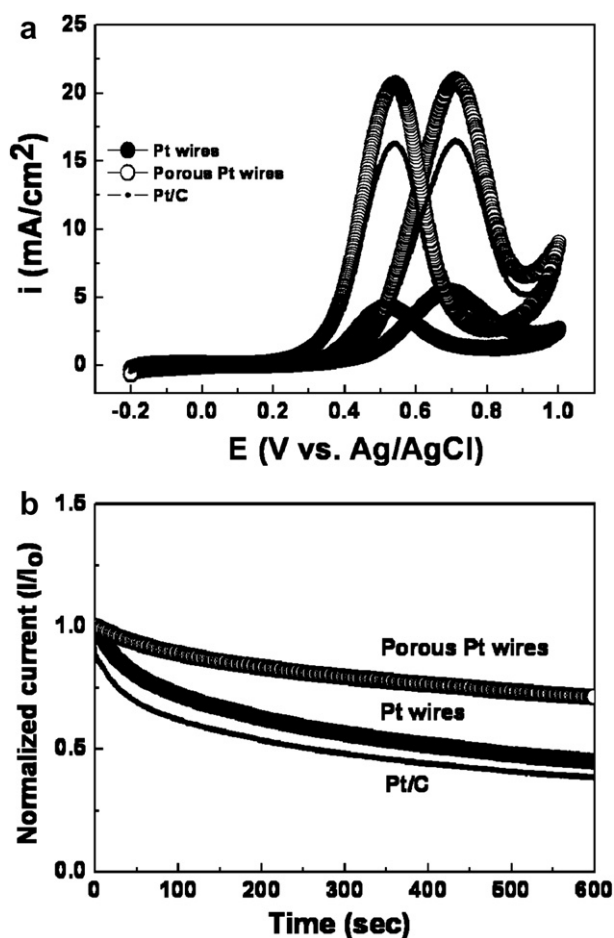


Fig. 4. (a) CVs of the methanol electro-oxidation of macroporous Pt wires, dense Pt wires, and the commercial Pt/C catalyst (E-TEK, 20 wt%). (b) Chronoamperometry on the macroporous Pt wires, dense Pt wires, and the commercial Pt/C catalyst (E-TEK, 20 wt%) characterized at 0.5 V for 600 s in a mixture of aqueous solution of 2 M CH₃OH and 0.5 M H₂SO₄.

dense Pt wire electrodes by cyclic voltammetry in a 0.5 M H₂SO₄ solution (not shown). The EAS area can be calculated from hydrogen desorption peak as follows: $\text{Pt} - \text{H} + \text{OH} \rightarrow \text{Pt} + \text{H}_2\text{O} + \text{e}^-$. The area of hydrogen desorption in the range of -0.2 to 0.0 V after the deduction of the double layer region in the CV curves represents the amount of the charge (Q_H) required for hydrogen desorption. The EAS area (S_{EAS}) of the electro-catalysts can be calculated by using the Q_H as reported previously [22]. Thus, the Q_H values of the macroporous and dense Pt wire electrodes are 5.00×10^{-6} C and 2.05×10^{-6} C, respectively. The EAS areas of the macroporous and dense Pt wire electrodes are calculated as 0.0238 cm² and 0.00976 cm², namely, EAS area of the macroporous Pt wires is 2.4 times as high as that of dense Pt wires. To investigate stability of electrodes, we analyzed the temporal evolution of the oxidation current at the macroporous Pt wire, dense Pt wire, and the commercial Pt/C catalyst by chronoamperometry in a mixture of 2 M CH₃OH and 0.5 M H₂SO₄ solutions at 0.5 V for 600 s (Fig. 4(b)). All the samples exhibit a current decay during the methanol electro-oxidation. As compared with the dense Pt wire and the commercial Pt/C catalyst, however, the macroporous Pt wire electrodes show a much slower current decay. After

600 s, the oxidation current of the macroporous, the dense, and the commercial electrode was reduced by 29%, 56%, and 62%, respectively. This implies that slow current reduction over time underlines the high catalytic activity of the macroporous Pt wire electrodes during methanol electro-oxidation process. All these characters make the present macroporous Pt wires promising candidates as anodes for high performance DMFCs.

4. Conclusion

Macroporous Pt wire electrodes for DMFCs have been fabricated by using PCTE membranes with the pores filled with PS colloidal crystals as templates for electroplating. The macroporous structure of the resulting Pt wires not only lowers the amount of Pt used for catalysis but also dramatically increases the catalytically active surface area. Among the macroporous wire, the dense wire, and the commercial Pt/C catalyst, therefore, the resulting macroporous Pt wire electrodes showed a best electrocatalytic activity for methanol electro-oxidation with 21.0 mA/cm² at 0.718 V and superior catalytic stability at 0.5 V for 600 s. The results indicate that the macroporous Pt wire electrode could effectively improve the catalytic activity, leading to the fabrication of high-performance DMFCs.

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References

- [1] E. Reddington, A. Sapienza, B. Gurau, R. Viswanathan, S. Sarangapani, E.S. Smotkin, T.E. Mallouk, *Science* 280 (1998) 1735–1737.
- [2] F.J. Liu, L.M. Huang, T.C. Wen, C.F. Li, S.L. Huang, A. Gopalan, *Synth. Met.* 158 (2008) 767–774.
- [3] H.-J. Ahn, W.J. Moon, T.-Y. Seong, D. Wang, *Electrochem. Commun.* 11 (2009) 635–638.
- [4] H.B. Yu, J.-H. Kim, H.-I. Lee, M.A. Scibioh, J. Lee, J. Han, S.P. Yoon, H.Y. Ha, *J. Power Sources* 140 (2005) 59–65.
- [5] F. Colmati, E. Antolini, E.R. Gonzalez, *Electrochim. Acta* 50 (2005) 5496–5503.
- [6] K.W. Park, J.H. Choi, B.K. Kwon, S.A. Lee, H.Y. Ha, S.A. Hong, Y.E. Sung, H. Kim, A. Wieckowski, *J. Phys. Chem. B* 106 (2002) 1869–1877.
- [7] C.A. Bessel, K. Laubernds, N.M. Rodriquez, R.T.K. Baker, *J. Phys. Chem. B* 105 (2001) 1115–1118.
- [8] Y.M. Liang, H.M. Zhang, B.L. Yi, Z.H. Zhang, Z.C. Tan, *Carbon* 43 (2005) 3144–3152.
- [9] H.B. Suffredini, V. Tricoli, L.A. Avaca, N. Vattistas, *Electrochem. Commun.* 6 (2004) 1025–1028.
- [10] A.L. Santos, D. Profeti, P. Olivi, *Electrochim. Acta* 50 (2005) 2615–2621.
- [11] H.-J. Ahn, J.S. Jang, Y.S. Sung, T.-Y. Seong, *J. Alloys Compd.* 473 (2009) L28–L32.
- [12] B. Qu, Y.T. Xu, S.J. Lin, Y.F. Zheng, L.Z. Dai, *Synth. Met.* 160 (2010) 732–742.
- [13] G.Y. Zhao, C.L. Xu, D.J. Guo, H. Li, H.L. Li, *J. Power Source* 162 (2006) 492–496.
- [14] Y.S. Kim, S.H. Nam, H.-S. Shim, H.-J. Ahn, M. Anand, W.B. Kim, *Electrochem. Commun.* 10 (2008) 1016–1019.
- [15] W.C. Choi, S.I. Woo, *J. Power Source* 124 (2003) 420–425.
- [16] S.J. Hurst, E.K. Payne, L. Qin, C.A. Mirkin, *Angew. Chem. Int. Ed.* 45 (2006) 2672–2692.
- [17] Y.-J. Song, S.-B. Han, K.-W. Park, *Mater. Lett.* 64 (2010) 1981–1984.
- [18] C.R. Martin, *Chem. Mater.* 8 (1996) 1739–1746.
- [19] S.R. Nicewarner-Peña, R.G. Freeman, B.D. Reiss, L. He, D.J. Peña, L.D. Walton, R. Cromer, C.D. Keating, M.J. Natan, *Science* 294 (2001) 137–141.
- [20] S. Park, J.-H. Lim, S.-W. Chung, C.A. Mirkin, *Science* 303 (2004) 348–351.
- [21] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, H. Yan, *Adv. Mater.* 15 (2003) 353–389.
- [22] A. Pozio, M. De Francesco, A. Cemmi, F. Cardellini, L. Giorgi, *J. Power Sources* 105 (2002) 13–19.