# **Study of Nickel-Plated Monolithic Porous Carbon as a Substrate for Nickel Hydroxide Electrode**

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Monolithic porous carbon (MPC) is prepared by a simple polymer-blend carbonization, in which phenolic resin, polyvinyl butyral and activated carbon are used to make a polymer blend. MPC is electroplated with nickel, and evaluated as a substrate for a nickel hydroxide electrode. Microstructure characterization results show that the nickel-plated MPC exhibits almost the same pore structure as that of the MPC with an open-cell structure and peak pore size of about 2  $\mu$ m. Cyclic voltammetry and charge-discharge tests show that the nickel-plated MPC has a higher oxygen evolution potential and better contact with Ni(OH)<sub>2</sub> than those of MPC. Charge-discharge results show that the specific capacity of the nickel-plated MPC-Ni(OH)<sub>2</sub> electrodes reaches 130 mAh·g<sup>-1</sup> in terms of the total electrode weight, and the specific capacity of active material reaches 276 mAh·g<sup>-1</sup>. Moreover, the property of capacity degradation of the nickel-plated MPC-Ni(OH)<sub>2</sub> electrode is largely improved than that of the MPC-Ni(OH)<sub>2</sub> electrode. It suggests that the nickel-plated MPC would be a promising lightweight matrix for the nickel hydroxide electrode.

Keywords: monolithic porous carbon; nickel hydroxide electrode; electroplate; nickel

# **1. INTRODUCTION**

Nickel hydroxide material has been extensively used as active material for the positive electrode in rechargeable alkaline batteries, such as Ni-Cd, Ni-Fe, Ni-Zn, or Ni-MH batteries. Nickel hydroxide material is an electronic semiconductor with a large band gap [1]. Therefore, the positive electrode has to include a conductive support. The support has no capacity and contributes to the weight of the electrode, and thus, the specific capacity of the electrode material (SCEM, according to

Ah per g) is much lower than the specific capacity of the active material (SCAM, according to Ah per g). The sintered-nickel porous plaques as conductive supports, are heavy, and constitute nearly 60% of the weight of the positive electrode [2]. To improve the specific energy density, lightweight materials, such as nickel fiber and nickel foam have been widely investigated as the substitutes for the nickel hydroxide electrodes [3–5]. However, the shedding of the active materials and morphological changes of the electrodes occur easily during the charge and discharge cycles when the above mentioned substrates are utilized.

Porous carbons have attracted considerable attention and have emerged as the current collector materials for their favorable properties, such as light weight, large specific surface area, good corrosion resistance and high electric conductivity. Czerwiński *et al.* [6] employed reticulated vitreous carbon (RVC) plated with nickel as the substrate to prepare nickel hydroxide electrode by chemical impregnation. It was shown that the SCEM of the Ni/RVC-Ni(OH)<sub>2</sub>/NiOOH electrodes reached 88.70 mAh·g<sup>-1</sup>. This value was considerably better than that of the sintered Ni-Ni(OH)<sub>2</sub>/NiOOH electrodes (43.45 mAh·g<sup>-1</sup>, prepared by the same method as the Ni/RVC-Ni(OH)<sub>2</sub>/NiOOH electrodes). In our previous research, phenolic resin-based monolithic porous carbon (MPC) was used as the substrate to prepare nickel hydroxide electrodes by electrochemical impregnation [7]. It was shown that the SCEM of the MPC-Ni(OH)<sub>2</sub>/NiOOH electrodes reached 115 mAh·g<sup>-1</sup>, which is higher than the SCEM of about 100 mAh·g<sup>-1</sup> of commercial sintered nickel hydroxide electrodes. However, the SCAM of the MPC-Ni(OH)<sub>2</sub>/NiOOH electrode was only 238 mAh·g<sup>-1</sup> [7]. Compared with the SCAM of about 289 mAh·g<sup>-1</sup> of sintered nickel hydroxide electrodes [8, 9], the MPC-Ni(OH)<sub>2</sub>/NiOOH electrode has a fairly lower SCAM [7]. On the other hand, the contact resistance between MPC and Ni(OH)<sub>2</sub>/NiOOH is a little higher [7].

In the present study, nickel was electroplated on MPC, and the Ni/MPC was used as the substrate to improve MPC more suitably for nickel hydroxide electrode in nickel-based alkaline batteries. The effect of the Ni/MPC on the electrochemical performance of nickel hydroxide electrodes was evaluated by cyclic voltammetry and galvanostatic charge-discharge tests in conjunction with scanning electron microscope (SEM), mercury porosimetry test and X-ray diffraction (XRD).

### 2. EXPERIMENTAL

#### 2.1 Preparation of MPC

The phenolic resin-based MPCs were prepared as follows. Novolac-type phenolic resin (Tianjin Resin Factory, Tianjin, China) was mixed with hexamethylene tetramine (analytical grade purity, Shantou Xilong Chemical Factory, Shantou, China). The mixing ratio was set at 10:1 by weight. The mixture was hardened in an oven at a temperature of 185°C for 1 hour. The cured resin was crushed into fine particles with a grinding machine for 1 hour. The resin powder was then mixed with poly(vinyl butyral) (analytical grade purity, Shantou Xilong Chemical Factory, Shantou, China) and activated carbon powder (provided by Xinhua Activated Carbon Factory, Taiyuan, China; the specific surface area is about 1020 m<sup>2</sup>·g<sup>-1</sup> and the electrical conductivity is about 5 S·cm<sup>-1</sup>) also with a

grinding machine for 1 hour. The mixing ratio was set at 4:2:1 by weight. The mixed powder was compacted into a disc (about 19 mm in diameter, 1.5 mm in thickness) under a compacting stress of 30 MPa. The compacted resin discs were then subjected to carbonization in nitrogen at a temperature of 1000°C for 1 hour at a heating rate of 5°C min<sup>-1</sup>. Thus, MPCs were obtained (average weight: 0.18 g, about 17 mm in diameter, 1.2 mm in thickness).

#### 2.2 Preparation of Ni/MPC substrates

Cathodic plating of Ni on MPC was accomplished in a borate bath (280 g·L<sup>-1</sup> NiSO<sub>4</sub>·6H<sub>2</sub>O; 26 g·L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>; 20 g·L<sup>-1</sup> NaCl; 45 g·L<sup>-1</sup> H<sub>3</sub>BO<sub>3</sub>; 0.02 g·L<sup>-1</sup> sodium laurgl sulphate) by pulsing squarewave electrodeposition at room temperature, as described in the literature [10]. The MPC was adhered to a slide of nickel-coated iron mesh with electric agglutinant to accomplish a substrate electrode. Here, the nickel-coated iron mesh was used as a current collector. The weight of the substrate electrode was determined on a balance. Then, the nickel was electroplated on the MPC by using pulsing current under constant stirring with respect to a nickel plated anode. The current density was 7 mA·cm<sup>-2</sup> based on the geometric area of the MPC. The current pulse lasted 1 second with "on" and "off" times set at 1:9. The total time of cathodic plating was 10 hours (i.e., the current lasted 1 hour). Subsequent to the plating, the resulting Ni/MPC electrode was thoroughly washed in deionized water. Next, it was dried to a constant weight at 120°C to estimate the weight gain. The weight gain is about 0.05 g, i.e., about 0.05 g of nickel was coated on MPC. Then, the Ni/MPC electrode was used for electrochemical impregnation.

The Ni(OH)<sub>2</sub> materials were impregnated into the Ni/MPC substrate from the nickel nitrate solution. This was performed by galvanostatic electrodeposition at 80°C, as described in the literature [11]. The Ni/MPC substrate was vacuum immersed in the nickel nitrate solutions (2 mol·L<sup>-1</sup> Ni(NO<sub>3</sub>)<sub>2</sub>; 0.1 mol·L<sup>-1</sup> Co(NO<sub>3</sub>)<sub>2</sub>; 0.1 mol·L<sup>-1</sup> NaNO<sub>2</sub> dissolved in deionized water mixed with ethanol in a 70:30 volume ratio) for 20 min. Then, the nickel hydroxides were electrodeposited into the Ni/MPC substrate by using galvanostatic current under constant stirring with respect to a nickel-plated anode. The deposition current density was 80 mA·cm<sup>-2</sup> based on the geometric area of the Ni/MPC substrate. The time of impregnation was 3 hours. Subsequent to the deposition, the resulting Ni/MPC-Ni(OH)<sub>2</sub> electrode was thoroughly washed in deionized water. Next, it was dried to a constant weight at 120°C to estimate the weight gain. Then, the Ni/MPC-Ni(OH)<sub>2</sub> electrode was used for electrochemical performance studies with about 0.20 g of nickel hydroxide loaded. For comparison, the MPC-Ni(OH)<sub>2</sub> electrode was prepared by the same method from the MPC without plating, and about 0.2 g of nickel hydroxide materials was loaded into the MPC substrate.

## 2.3 Performance tests

Electrochemical performance tests were performed in a three-electrode cell at an ambient temperature (about 25°C) using a CHI608D electrochemical workstation. The above mentioned three-electrode cell consisted of the as-fabricated positive electrode, a sintered cadmium counter electrode (2

× 2 cm<sup>2</sup>) and an Hg/HgO reference electrode (8 mol·L<sup>-1</sup> KOH aqueous electrolyte). The electrolyte was 8 mol·L<sup>-1</sup> KOH with 20 g·L<sup>-1</sup> LiOH aqueous solution. Prior to the electrochemical performance tests, the as-fabricated electrodes were immersed in the electrolyte for over 10 hours. For activation, the as-fabricated electrodes were activated by cyclic voltammetry (CV) in a potential window from 0.0 to 0.6 V versus Hg/HgO for 50, 25 and 10 cycles at scan rates of 1, 5 and 10 mV·s<sup>-1</sup>, respectively. The electrochemical performance was evaluated by using CV and galvanostatic technique. The CV measurements were performed at a scan rate of 10 mV·s<sup>-1</sup>. In the subsequent constant current charge–discharge tests, the electrodes were charged to 0.58 V versus Hg/HgO (or cut-off after 6 hours) and discharged to 0 V versus Hg/HgO at 7.5 mA·cm<sup>-2</sup> (based on the geometric area of the substrate, about 85 mA·g<sup>-1</sup>).

The substrates were characterized by X-ray diffraction (RIGAKUD/MAX-RB diffractometer using Cu Kα radiation). Scanning electron micrographs of substrates were obtained using a S4800 field emission electron microscope. Mercury porosimetry test (Autopore IV 9500 porosimeter) was used to investigate the macropore structure of the substrates.

### **3. RESULTS AND DISCUSSION**

## 3.1 Microstructure of MPC and Ni/MPC substrates



Figure 1. X-ray structural analysis: (a) pure MPC substrates; (b) Ni/MPC substrates

X-ray structural analysis results of pure MPC and Ni/MPC are shown in Figure 1. The obtained result demonstrates that the MPC mainly shows amorphous phase with little graphitic phase. The

distinct diffraction peaks of the MPC are consistent with those of graphite (such as JCPDF card 75-1621). The graphitic phase is from the activated carbon powder added during the preparation of the MPC. It can be observed that the typical peaks of nickel crystallites (such as JCPDF card 4-850) are present on Ni/MPC. This indicates that the MPC substrates have been coated with nickel after the plating process.



Figure 2. SEM micrographs of (a) MPC substrate and (b) Ni/MPC substrate

The SEM image of the MPC is shown in Figure 2a. It can be observed that pores with various widths formed by cracks between the carbon particles are distributed on the carbon surface. The opencell structure can be clearly seen. The SEM picture of the MPC surface covered with nickel at the same magnification is shown in Figure 2b. The nickel coated on the carbon surface is clearly demonstrated. It seems that the nickel coating has little influence on the macropores of submicron/micron size. Owing to large pores, which will benefit the Ni(OH)<sub>2</sub> deposited at the intersurface of the pores [12, 13], it is implied that the pore volume of Ni/MPC substrates for impregnating has only a slight decrease. This result is supported by a mercury porosimetry test, as shown in Figure 3. The mercury porosimetry tests are used to clarify the macropore size distribution of MPC. The pore volume and specific surface area obtained by mercury porosimetry tests are 0.8293 cm<sup>3</sup>·g<sup>-1</sup> and 3.5 m<sup>2</sup>·g<sup>-1</sup> for MPC substrates, and 0.6362 cm<sup>3</sup>·g<sup>-1</sup> and 3.1 m<sup>2</sup>·g<sup>-1</sup> for Ni/MPC substrates, respectively. As shown in Figure 3, the pore size distribution curves of the MPC and Ni/MPC substrates are basically similar, and exhibit a high peak with a mean pore width of about 2.4 µm and 2.1 µm, respectively. The slight decrease in the mean pore width is due to nickel coated on the pore surface. And the macropore structure of the MPC after plating has been almost unaffected. This indicates that there will be little influence on Ni(OH)<sub>2</sub> impregnation, and almost no change occurring in the macropore structure.



Figure 3. Pore size distribution curves of MPC (a) and Ni/MPC (b), and the inset shows the enlarged pore size distribution curves

## 3.2 Electrochemical performance of the Ni/MPC-Ni(OH)<sub>2</sub> electrodes

The CV curves of the MPC and Ni/MPC electrodes are shown in Figure 4. In the potential range, the bare MPC is characterized with a rectangular capacitive voltammogram. A slight oxygen

evolution seems to occur at above 0.5 V versus Hg/HgO, and the reaction will become vehement, and carbon oxidation might also occur as the potential increases. Based on curve b, it can be seen that there are two current peaks at 0.517 V and 0. 312 V corresponding to the redox couple of Ni(II)/Ni(III), which is from oxidization of the nickel on the surface of MPC. Also, the oxygen evolution potential of Ni/MPC electrodes shifts to a more positive value of above 0.55 V versus Hg/HgO, comparing with that of MPC. This indicates that the plating of nickel on MPC will significantly degrade the undesirable oxygen evolution reaction.



**Figure 4.** Cyclic voltammogram curves of MPC (a) and Ni/MPC electrode (b) between 0 and 0.6 V versus Hg/HgO in 8 mol·L<sup>-1</sup> KOH + 20 g·L<sup>-1</sup> LiOH aqueous solution at a scan rate of 1 mV·s<sup>-1</sup>

After activation, galvanostatic technique and CV were used to analyze the electrochemical properties of the Ni/MPC-Ni(OH)<sub>2</sub> electrodes. The CV curves of the MPC-Ni(OH)<sub>2</sub> and Ni/MPC-Ni(OH)<sub>2</sub> electrodes are shown in Figure 5. It can be seen that there are basically no visible oxidation peaks appearing on the MPC-Ni(OH)<sub>2</sub> electrodes, and oxidation wave of Ni(II)/Ni(III) strongly overlaps and obscures the potential of oxygen evolution. However, one distorted oxidation wave was recorded on Ni/MPC-Ni(OH)<sub>2</sub> electrodes at about 0.55 V versus Hg/HgO. That is because the oxygen evolution reaction was degraded by the plating of nickel. In addition, the reduction wave at about 0.180 V of the MPC-Ni(OH)<sub>2</sub> electrodes shifts to a more positive value of 0.283 V of the Ni/MPC-Ni(OH)<sub>2</sub> electrodes. It is implied that Ni/MPC-Ni(OH)<sub>2</sub> electrodes show a better reversible behavior.



**Figure 5.** Cyclic voltammogram curves of MPC-Ni(OH)<sub>2</sub> (a) and Ni/MPC-Ni(OH)<sub>2</sub> electrode (b) between 0 and 0.6 V versus Hg/HgO in 8 mol·L<sup>-1</sup> KOH + 20 g·L<sup>-1</sup> LiOH aqueous solution at a scan rate of 10 mV·s<sup>-1</sup>

Figure 6 shows the typical charge/discharge profiles of the MPC-Ni(OH)<sub>2</sub> and Ni/MPC-Ni(OH)<sub>2</sub> electrodes at a current density of 85 mA $\cdot$ g<sup>-1</sup>. It seems that the last potion of the charge curve of both electrodes is controlled by the oxygen evolution potential [13], i.e., a large part of the charging capacity is consumed by oxygen evolution at the potential plateau. As shown in Figure 6, the potential of charge curve of the Ni/MPC-Ni(OH)<sub>2</sub> electrodes is higher than that of the MPC-Ni(OH)<sub>2</sub> electrodes. This means that the oxygen evolution overpotential is improved by the coated nickel. On the other hand, the discharge potential is also obviously improved. The average charge and discharge potentials of the MPC-Ni(OH)<sub>2</sub> electrodes are 0.470 V and 0.323 V versus Hg/HgO, respectively. The average charge and discharge potentials of the Ni/MPC-Ni(OH)<sub>2</sub> electrodes are 0.487 V and 0.343 V versus Hg/HgO, respectively. This indicates that plating nickel on MPC induces the ohmic resistance of the electrodes. The electrical conductivity of the MPC can be enhanced by the coating of nickel, and the contact of particles of substrates and Ni(OH)<sub>2</sub> can be improved by the plating of nickel film. From the charge/discharge plot, the SCAM and SCEM of the MPC-Ni(OH)<sub>2</sub> electrodes were obtained as 253 mAh·g<sup>-1</sup> and 136 mAh·g<sup>-1</sup>, respectively; The SCAM and SCEM of the Ni/MPC-Ni(OH)<sub>2</sub> electrodes were obtained as 276 mAh·g<sup>-1</sup> and 130 mAh·g<sup>-1</sup>, respectively. The above mentioned SCEM value is about 30% higher than that of commercial sintered nickel hydroxide electrodes, of which the SCEM is about 100 mAh·g<sup>-1</sup> [8]. The slight drop in the SCEM of the latter electrodes is due to the added weight of the nickel. However, the SCEM of the latter electrodes is higher, and the Ni/MPC-Ni(OH)<sub>2</sub> electrodes show a more stable cycle life, as shown in Figure 7. After 30 cycles, the discharge capacity

of the Ni/MPC-Ni(OH)<sub>2</sub> electrodes still keeps about 90% of the maximum discharge capacity; However, the discharge capacity of the MPC-Ni(OH)<sub>2</sub> electrodes almost reaches up to 10%.



**Figure 6.** Charge-discharge curves of MPC-Ni(OH)<sub>2</sub> (a) and Ni/MPC-Ni(OH)<sub>2</sub> (b) electrodes on the third cycle after activation. The charging process was held at 85 mA·g<sup>-1</sup> to 0.58 V versus Hg/HgO, or finished at 6 hours. The discharge process was held at 85 mA·g<sup>-1</sup> and finished at a potential of 0.0 V versus Hg/HgO



Figure 7. Charge-discharge cycle curves of the MPC-Ni(OH)<sub>2</sub> (a) and Ni/MPC-Ni(OH)<sub>2</sub> (b) electrodes after activation. The charging process was held at 85 mA·g<sup>-1</sup> to 0.58 V versus Hg/HgO, or finished at 6 hours. The discharge process was held at 85 mA·g<sup>-1</sup> and finished at a potential of 0 V versus Hg/HgO

The poor cyclic performance of the MPC-Ni(OH)<sub>2</sub> electrodes can be attributed to the high overcharge capacity of each cycle. Because the oxygen evolution not only continuously weakens the contact of particles of substrates and activates materials, but it also results in the oxidization of carbon, which can cause structural damages and rapid performance reduction of the electrode. As coated nickel can resist oxidation and protect the carbon particles from oxidation, so the discharge capacity of the Ni/MPC-Ni(OH)<sub>2</sub> electrodes can keep low attenuation during many cycles. If the overcharge capacity is controlled and kept at a small value, the cycling performance of both electrodes will be better.

In general, the above results demonstrate that the Ni/MPC matrix is better than the MPC matrix as a substrate for a nickel hydroxide electrode.

## 4. CONCLUSIONS

Phenolic resin-based MPC which is plated with nickel, is evaluated as a substrate for the nickel hydroxide electrode. Microstructure characterization of the Ni/MPC substrates shows that the Ni/MPC substrates retains the pore structure of the MPC and exhibits an open-cell structure with pores of about 2  $\mu$ m in diameter. The cyclic voltammetry tests show that the Ni/MPC substrates give a higher oxygen evolution overpotential. The charge-discharge characterization of the Ni/MPC-Ni(OH)<sub>2</sub> electrodes shows that the SCAM and SCEM of the Ni/MPC-Ni(OH)<sub>2</sub> electrodes reaches 276 mAh·g<sup>-1</sup> and 130 mAh·g<sup>-1</sup>. The above mentioned SCEM value is about 30% higher than that of commercial sintered nickel hydroxide electrodes, and the cycling performance is highly improved. Thus, the existence of nickel on the MPC surface contributed a substantial effect on the improvement of electrochemical performance. It can be suggested that the Ni/MPC substrate is a promising lightweight matrix for the nickel hydroxide electrode, with a focus on acquiring high weight specific energy for nickel-based alkaline batteries.

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#### References

- 1. P. Oliva, J. Leonardi, J. F. Laurent, C. Delmas, J. J. Braconnier, M. Figlarz, F. Fievet, A. de Guibert, *J. Power Sources*, 8 (1982) 229
- M. Dixit, P. V. Kamath, V. G. Kumar, N. Munichandraiah, A. K. Shukla, J. Power Sources, 63(1996) 167
- 3. K. Watanabe, T. Kikuoka, N. Kumagai, J. Appl. Electrochem., 25 (1995) 219
- 4. M. Oshitani, H. Yufu, K. Takashima, D. Tsuji, Y. Matsumaru, J. Electrochem. Soc., 136 (1989) 1590
- 5. Li Hui, Ding Yunchang, Yuan Jiongliang, Wang Zeyun, J. Power Sources, 57 (1995) 137

- 6. A. Czerwiński, M. Elazowska, J. Power Sources, 64 (1997): 29
- 7. Dong Chen, Jie Cheng, Yuehua Wen, Junqing Pan, Gaoping Cao, Yusheng Yang, *Journal of The Electrochemical Society*, 158 (2011) A1303
- 8. W. K. Zhang, X. H. Xia, H. Huang, Y. P. Gan, J. B. Wu, J. P. Tu, *J. Power Sources*, 184 (2008) 646
- 9. Masahiko Oshitani, Yukio Sasaki, Koichiro Takashima, J. Power Sources, 12 (1984) 219
- 10. M.S. Chandrasekar, Malathy Pushpavanam, Electrochimica Acta, 53 (2008) 3313
- 11. M.W. Earl, T.F. Noble, J Power Sources, 12 (1984) 277
- 12. D. Carmier, C. Vix-Guterl, J. Lahaye, Carbon, 39 (2001) 2181
- 13. Graeme A. Snook, Noel W. Duffy, Anthony G. Pandolfo, J. Power Sources, 168 (2007) 513

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