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Short communication

Ytterbium coating of spherical $Ni(OH)_2$ cathode materials for Ni–MH batteries at elevated temperature

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Abstract

The Yb/Co coated nickel hydroxides were prepared by precipitation of $Yb(OH)_3$ on the surface of spherical nickel hydroxide, followed by precipitation of $Co(OH)_2$ on its surface. The optimum coating content of ytterbium was around 2% (atomic concentration) to obtain high discharge capacity at 60 °C. It was shown that the discharge capacity of nickel hydroxide at high temperatures was improved by coating of ytterbium and cobalt hydroxide. The high temperature performances of the sealed AAA-sized Ni–MH batteries using Yb/Co coated nickel hydroxide as positive electrodes were carried out, showing much better than those using the un-coated and only $Co(OH)_2$ coated nickel hydroxide electrodes. The charge acceptance of the battery using 2% Yb and 2% Co coated nickel hydroxide reached 92% at 60 °C, where the charge acceptances for the un-coated and only cobalt coated ones were only 42 and 46%, respectively. It has shown that the Yb/Co coating is an effective way to improve the high temperature performance of nickel hydroxide for nickel–metal hydride batteries.

Keywords: Spherical nickel hydroxide; Ytterbium; Coating; Elevated temperature performance; Nickel–metal hydride battery

1. Introduction

Rechargeable alkaline nickel–metal hydride (Ni–MH) batteries have been studied intensively due to their good cycleability and charge/discharge kinetics [1–4]. However, as power sources for electric and hybrid electric vehicles (EV and HEV) as well as electric tools, the Ni–MH batteries are required to work at elevated temperature. The high temperature performance of Ni–MH batteries is directly related to the behavior of the nickel hydroxide electrode materials [5]. Because of oxygen evolution readily on positive electrode at elevated temperatures (>50 °C), the charge efficiency of positive electrodes significantly declines, leading to poor performances of Ni–MH batteries at elevated temperatures. In order to enhance the performances, many studies on addition of cobalt oxide (CoO) [6–9], zinc oxide [10], cadmium oxide [11] and lanthanide oxides [12–14] on the positive electrodes were conducted. On the basis of these studies, the addition of cobalt oxide into nickel hydroxide electrode increases the oxygen evolution potential, improves material utilization and suppresses γ-NiOOH formation during charge–discharge cycling [6,7]. The utilization, charge–discharge reversibility and oxygen evaluation potential of the nickel hydroxide electrode have been further improved after surface modification with metallic cobalt or addition of cobalt hydroxide [9,15,16]. However, this modification takes a little effect for its performance at elevated temperature. The addition of heavy lanthanide oxides was found to be particularly attractive for improving charge acceptance of positive electrodes at elevated temperatures as reported in the literature [13]. The doping of yttrium can significantly improve the performance of nickel hydroxide at elevated temperature [5]. After doping of yttrium, the charge acceptance of the doped nickel hydroxide increases from 41 to 82% at 60 °C, not good enough for high temperature performance.

In this study, the spherical nickel hydroxides were coated with ytterbium hydroxides by precipitation. It was found that the coated materials showed excellent performance at elevated temperature.

2. Experimental

The spherical $Ni(OH)_2$ powders were prepared as reported in [5], and added into a container with deionized water under

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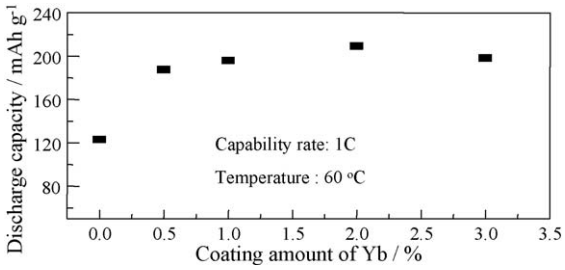

Fig. 1. The effect of ytterbium coating amount on the discharge capacity of nickel hydroxide electrodes at 60 °C at 1 C.

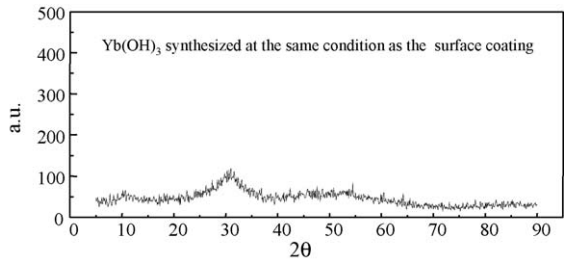

Fig. 2. XRD pattern of $Yb(OH)_3$ precipitate prepared under absence of $Ni(OH)_2$ as the same process of the coating.

agitation, forming suspension solution. The $YbCl_3$ and sodium hydroxide solutions were added into the above suspension solution under agitation, leading to $Yb(OH)_3$ coating on the surface of spherical $Ni(OH)_2$. Successively, $CoSO_4$ and sodium hydroxide solutions were added in to above suspension solution to form $Co(OH)_2$ coating on the surface of $Yb(OH)_3$ coated particles.

Finally, the particles in suspension solution were washed with deionized water, filtered and dried at 80 °C.

Crystal phase of powders were characterized by powder X-ray diffraction (XRD, D/max-rB) using Cu Kα, 40 kV × 120 mA radiation with step of 0.02° at 6° min^{-1}. The particle morphology of the powders was observed using scanning electron microscopy (SEM, JSM6301F).

The un-coated and coated nickel hydroxide powders were, respectively, mixed with graphite and acetylene black in a weight ratio of 10:1:0.25 together with a small amount (2 wt.%) of polytetrafluoroethylene (PTFE) aqueous solution as a binder and then the mixture was forced into a nickel foam to form a 2 cm × 2 cm electrode. After drying at 60 °C for 1 h, the foamed nickel hydroxide electrode was pressed at a pressure of 30 MPa for 1 min. The electrolyte used was a 6 M KOH aqueous solution. The experimental cells were set up in a temperature-controlling water bath and the cells were tested at temperatures in the range of 20–60 °C. The charge/discharge tests of the experimental cells were conducted using a land battery testing equipment (CT2001A). The positive electrodes were charged and discharged at 0.2 C at room temperature for the stable capacity. Then, the electrodes were tested at 1 C to a cut-off voltage of 1.0 V at 20 and 60 °C.

The AAA-size Ni–MH batteries with $MmNi_5$-type alloys as negative electrodes and un-coated or Yb/Co coated nickel hydroxides as positive electrodes were manufactured. The capacity utilization of AAA-size Ni–MH batteries was measured at 1 C rate with a cut-off voltage of 1.0 V at different temperatures.

3. Results and discussion

To evaluate the effect of the ytterbium coating amount on the high temperature performances of nickel hydroxide electrodes, the discharge capacities of nickel hydroxide electrodes with different coating amount at 60 °C were measured at 1 C as shown in Fig. 1. It was found that the optimum ytterbium amount (atomic concentration) was near 2% to obtain higher discharge capacity at 60 °C. The electrochemical properties of the ytterbium coated nickel hydroxide electrode with the amount of 2% were investigated in detail hereafter.

Fig. 2 shows X-ray diffraction patterns of the $Yb(OH)_3$ precipitate prepared under absence of $Ni(OH)_2$ as the same process of the coating. It is found that the ytterbium hydroxide presents very low crystallinity.

The SEM analysis of coated $Ni(OH)_2$ have shown that the coating layer of ytterbium and cobalt hydroxides uniformly covers the surface of spherical nickel hydroxide, as shown in Fig. 3.

The charge/discharge curves of the un-coated and 2% Yb and 2% Co coated nickel hydroxide at 1 C at 20 °C are shown in Fig. 4. It indicates that the un-coated nickel hydroxide presents a little higher discharge capacity than the coated nickel hydroxide at 20 °C. Because the coating materials are electrochemically inactive, it has no contribution to the capacity. However, cobalt hydroxide coating increases the discharge capacity of Yb-coated nickel hydroxide. The reason is as follows. The surface modification of spherical nickel hydroxide by cobalt hydroxide can enhance the electrochemical performance of nickel hydroxide. Due to the high conductivity phase of the formed CoOOH, the conductive networks among nickel hydroxide particles were

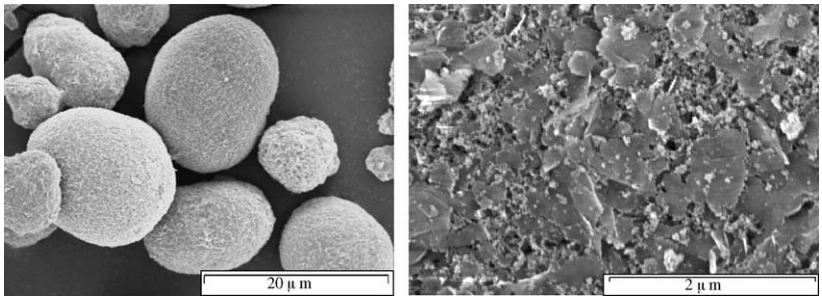

Fig. 3. SEM images of 2% Yb and 2% Co coated $Ni(OH)_2$.

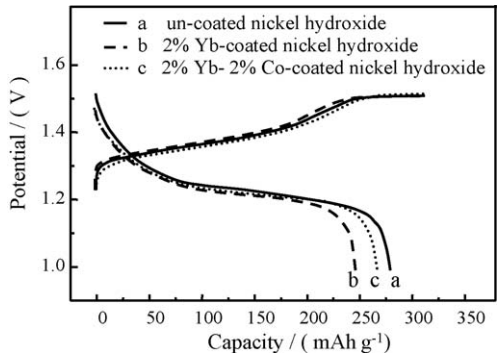

Fig. 4. Charge/discharge curves of un-coated and 2% Yb and 2% Co coated nickel hydroxide at 1 C rate at 20 °C.

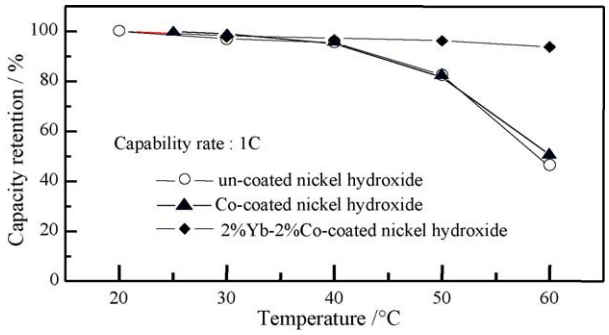

Fig. 6. Capacity retention of AAA-size Ni–MH batteries using un-coated and 2% Yb/2% Co coated nickel hydroxide as active electrode materials at different temperatures at 1 C rate.

considered to be enhanced, leading to improvement of discharge capacity [14].

As shown in Fig. 5, the discharge capacity of Yb/Co coated nickel hydroxide is much higher than that of the regular nickel hydroxide at 60 °C. The ratio of the discharge capacity of coated nickel hydroxide at 60 and 20 °C can reach 92%. In contrast, the ratio of the discharge capacity of the regular nickel hydroxide at 60 and 20 °C is only 42%. This indicates that the Yb/Co coating significantly improves the performance of nickel hydroxide at 60 °C.

The performances improvement of the coated nickel hydroxide positive electrode at high temperatures is caused by the increase of oxygen over-voltage. The coating layer of Yb/Co hydroxide on the surface of nickel hydroxides is beneficial to control the oxygen evolution of nickel hydroxide electrodes at high temperature. As shown in Fig. 5, the charge voltage of coated sample is much higher than that of un-coated sample at the end of the charge process.

Two types of AAA-size Ni–MH batteries were manufactured using the un-coated nickel hydroxide and 2% Yb and 2% Co coated nickel hydroxide as positive electrodes, respectively. As shown in Fig. 6, the capacity retention of the battery using the un-coated or only cobalt coated nickel hydroxide as electrode materials decreases while temperature increases. Especially, it decreases rapidly above 40 °C. However, the charge acceptance of the battery using 2% Yb and 2% Co coated nickel hydroxide is much higher than those of the batteries using the un-coated and only $Co(OH)_2$ coated nickel hydroxide at temperatures of over 40 °C. It reaches 92% even at 60 °C, where the charge acceptances for the un-coated and only cobalt coated ones are only 42 and 46%, respectively. The reason is mainly attributed to the improvement of the charge and discharge performances of Yb/Co coated nickel hydroxide electrode at high temperatures.

Above results have shown that the Yb/Co coating is an effective way to improve the high temperature performance of nickel hydroxide for nickel–metal hydride batteries. The Yb/Co coated spherical nickel hydroxide is a promising cathode material of Ni–MH hydride batteries for EV applications.

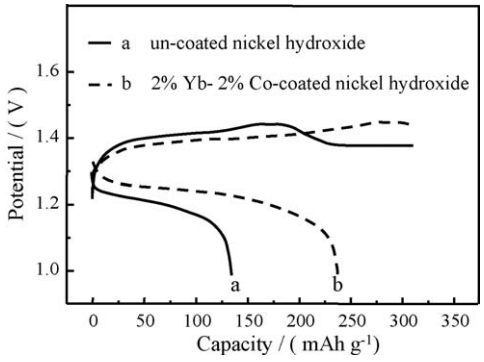

Fig. 5. Charge/discharge curves of un-coated and 2% Yb and 2% Co coated nickel hydroxide at 1 C rate at 60 °C.

4. Conclusions

The Yb/Co coated nickel hydroxides can be prepared by precipitation of $Yb(OH)_3$ on the surface of spherical nickel hydroxide, followed by precipitation of $Co(OH)_2$ on its surface. The optimum coating content is shown to be around 2% to obtain higher discharge capacity at 60 °C. It is demonstrated that the discharge capacity of nickel hydroxide at high temperatures is improved by coating of ytterbium and cobalt hydroxide. The former improves the voltage of oxygen evolution, and the latter improves the conductivity of active material. The high temperature performances of the sealed AAA-sized Ni–MH batteries using Yb/Co coated nickel hydroxide as positive electrodes are much better than those using the un-coated and only $Co(OH)_2$ coated nickel hydroxide electrodes. The charge acceptance of the battery using 2% Yb and 2% Co coated nickel hydroxide reaches 92% at 60 °C, where the charge acceptances for the un-coated and only cobalt coated ones are only 42 and 46%, respectively.

Acknowledgment

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References

[1] C. Faure, C. Delmas, M. Fouassier, J. Power Sources 35 (1991) 279.
[2] M.S. Wu, C.M. Huang, Y.Y. Wang, C.C. Wan, Electrochim. Acta 44 (1999) 4007.
[3] M. Dixit, R.S. Jayashree, P.V. Kamath, A.K. Shukla, V.G. Kumar, N. Munichandraiah, Eletrochem. Solid State Lett. 2 (1999) 170.

[4] W.K. Hu, D. Noreus, Chem. Mater. 15 (2003) 974.
[5] X. Mi, X.P. Gao, C.Y. Jiang, M.M. Geng, J. Yan, C.R. Wan, Electrochim. Acta 49 (2004) 3361.
[6] R.D. Armstrong, G.W.D. Griggs, E.A. Charles, J. Appl. Electrochem. 18 (1988) 215.
[7] A.K. Sood, J. Appl. Electrochem. 16 (1986) 274.
[8] K. Watanabe, M. Koseki, N. Kumagai, J. Power Sources 58 (1996) 23.
[9] V. Pralong, A. Delahaye-Vidal, B. Beaudoin, J.B. Leriche, J.M. Tarascon, J. Electrochem. Soc. 147 (2000) 1306.
[10] C. Tessier, C. Faure, L.G. Demourgues, C. Denage, G. Nabias, C. Delmas, J. Electrochem. Soc. 149 (2002) A1136.
[11] M. Oshitani, Y. Sasaki, K. Takashima, J. Power Sources 21 (1984) 219.
[12] Y. Morioka, S. Narukawa, T. Itou, J. Power Sources 100 (2001) 107.
[13] M. Oshitani, M. Watada, K. Shodai, M. Kodama, J. Electrochem. Soc. 148 (2001) A67.
[14] V. Pralong, A. Delahaye-Vidal, B. Beaudoin, B. Gerand, J.M. Tarascon, J. Mater. Chem. 9 (1999) 955.
[15] X.Y. Wang, J. Yan, H.T. Yuan, Z. Zhou, D.Y. Song, Y.S. Zhang, L.G. Zhu, J. Power Sources 72 (1998) 221.
[16] F. Lichtenberg, K. Kleinsorgen, J. Power Sources 62 (1996) 207.