

Effects of erbium additions on high temperature performance of high power Ni-MH batteries

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Abstract: The Co(III)-coated spherical nickel hydroxide powder is optimum as positive electrode of high power Ni-MH battery because of its excellent property. But the performances at high temperature (above 50 °C) is still not satisfied. In the present paper, the effect of element erbium, used as additive by different methods to prepare positive electrode, on the high temperature performances of the Ni-MH batteries is studied. It is found that the charge acceptance ability of the spherical Ni(OH)₂ electrode with element erbium as additive is improved. The discharge capacities of Ni(OH)₂ coated with 1% (atomic fraction) Er(OH)₃ and mechanically added with 1% (atomic fraction) Er₂O₃ at 1C are 12.6% and 11.7%, respectively, higher than those of the samples without erbium at 70 °C.

Key words: Ni-MH battery; nickel hydroxide electrode; Er-coating; high temperature performance

1 Introduction

Nickel metal hydride (Ni-MH) battery has become one of the most dominant batteries due to its excellent application performance, such as high energy density, well charge/discharge endurance, long cycle life, especially the safe property and high-rate discharge performance[1–3]. However, its high temperature (above 50 °C) performance is still not satisfied[4].

Being aimed at improving the high temperature performances, many studies were conducted by additions of cobalt oxide[5–6], zinc oxide[7], cadmium oxide[8] and rare earth oxides[9–11] to the nickel hydroxide electrode. It has been found that these methods can increase the utilizing efficiencies of the active materials, and suppress the formation of γ -NiOOH during the charge/discharge processes[12]. The surface modification method, such as coating the surface with metallic cobalt, Co(II) or Co(III)[13–15], can greatly increase the utilization efficiency, improve the charge/discharge reversibility, elevate the oxygen evolution potential of the nickel hydroxide electrode. However, its high temperature performance is still necessary to be

improved[16].

It has been found that the addition of heavy lanthanide oxides is particularly effective for improving the charge acceptance of positive electrodes at the elevated temperatures[9], especially for the chemical compositions (3.5%, mass fraction) of the oxides of erbium(Er), thulium(Tm), ytterbium(Yb) and lutetium(Lu). However, most rare earth oxide additives have negative influence on the electrochemical performances, especially for the high rate charge/discharge ability at low temperature because of its poor conductivity.

In this work, the effects of erbium element added by mechanically mixture and chemical deposition on the high temperature performance are investigated.

2 Experimental

2.1 Powder preparation and characterization

The commercial Co(III)-coated β -type spherical nickel hydroxide powder and erbium hydroxide powder were used to prepare the following samples.

Sample A: It is made of commercial Co(III)-coated Ni(OH)₂ powder without any additive used as comparison.

Sample B: A part of the sample A was mechanically mixed with Er_2O_3 , its molar ratio of elements erbium and nickel was controlled to be 1:100.

Sample C: Er_2O_3 was dissolved in hydrochloric acid to form a 0.5 mol/L ErCl_3 solution. $\text{Ni}(\text{OH})_2$ was added into a container with de-ionized water under agitation, forming suspension solution. Then the ErCl_3 hydroxide solution was added into the $\text{Ni}(\text{OH})_2$ suspension solution under agitation, leading $\text{Er}(\text{OH})_3$ to coat on the surface of spherical $\text{Ni}(\text{OH})_2$ (molar ratio of Er to Ni was 1:100). Afterwards, the particles in the suspension solution were filtered and washed with de-ionized water till $\text{pH} < 8$, and dried at 60°C .

The particle morphology of the powders was observed by scanning electron microscopy (SEM). The concentration of element erbium on the surface of the spherical $\text{Ni}(\text{OH})_2$ was surveyed by energy dispersive spectrometry (EDS).

2.2 Electrode preparation and electrochemical property

The powders of sample A, B, C were forced into nickel foam respectively. After mechanical press, electrodes made of samples A, B, C respectively were cut to the size of $2\text{ cm} \times 1.5\text{ cm} \times 0.06\text{ cm}$.

The positive electrode was placed in the middle of two metal hydride electrodes. The positive and negative electrodes were separated by two pieces of separator, and two stainless steel sheets were used to fix those electrodes. Then the cells were immersed into 6 mol/L $\text{KOH} + 15\text{ g/L LiOH}$ aqueous solution for 24 h.

After activation, the experimental cells were tested at temperature range of $25\text{--}70^\circ\text{C}$ controlled by water bath. The charge/discharge tests were conducted using a Land battery testing equipment (CT2001A). The positive electrodes were: 1) charged at $0.2C$ for 6 h and discharged at $0.2C$, $1C$, $2C$, $3C$ to a cut-off voltage of 1.0 V at room temperature; 2) charged at $1C$ for 1 h and discharged at $1C$ to 1.0 V at the temperatures ranging from room temperature to 70°C .

3 Results and discussion

3.1 Structure and surface morphology of particles

Fig.1 shows SEM images of the three $\text{Ni}(\text{OH})_2$ powder samples. A high-resolution SEM image is inserted in each picture to give a more detailed observation of the surface microstructure.

Fig.2 and Table 1 show the EDS analysis results of samples B and C. It can be seen that the distribution and the concentration of element erbium on the surface of spherical nickel hydroxide of the two erbium-added $\text{Ni}(\text{OH})_2$ powders are quite different. On the surface of sample B, the element erbium is hardly found. While for sample C, the atom ratio of Er to Ni was about 1:50.

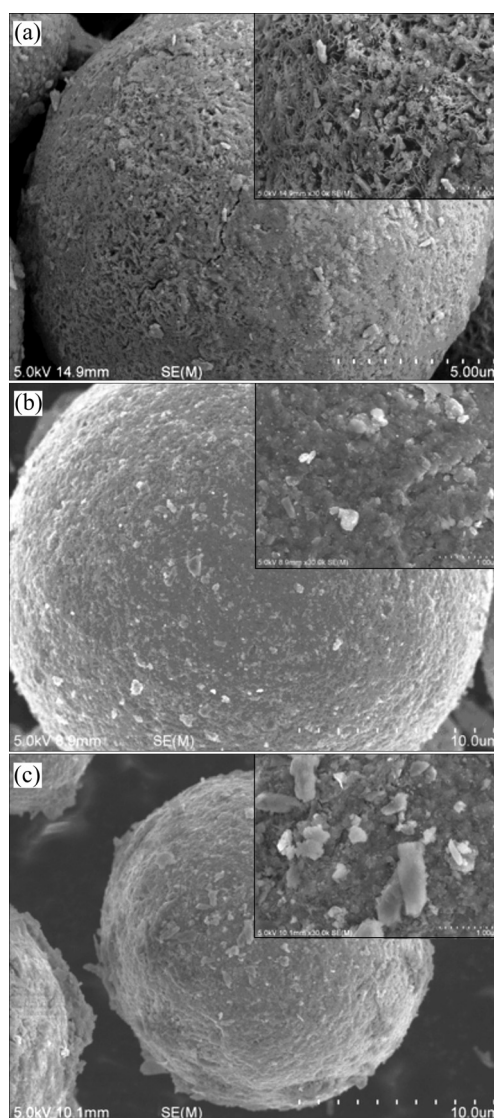


Fig.1 SEM micrographs of particles of samples A (a), B (b) and C (c) (Inserts: high-resolution SEM images of corresponding samples)

Table 1 Compositions of samples B and C

Element	Sample B		Sample C	
	Mass fraction/%	Molar fraction/%	Mass fraction/%	Molar fraction/%
O	43.26	73.81	37.80	69.85
Co	4.38	2.03	5.89	2.96
Ni	48.45	22.53	49.04	24.69
Zn	3.91	1.63	4.42	2.00
Er	0.00	0.00	2.85	0.50

3.2 Charge/discharge performances at room temperature

In order to evaluate the effects of the different addition methods of erbium on the high temperature performances of nickel hydroxide electrode, the charge/discharge capacities of the three electrode

samples at room temperature were measured from 0.2C to 3C after activation. The 0.2C charge/discharge curves are shown in Fig.3, and the discharge capacities data from 0.2C to 3C are summarized in Table 2.

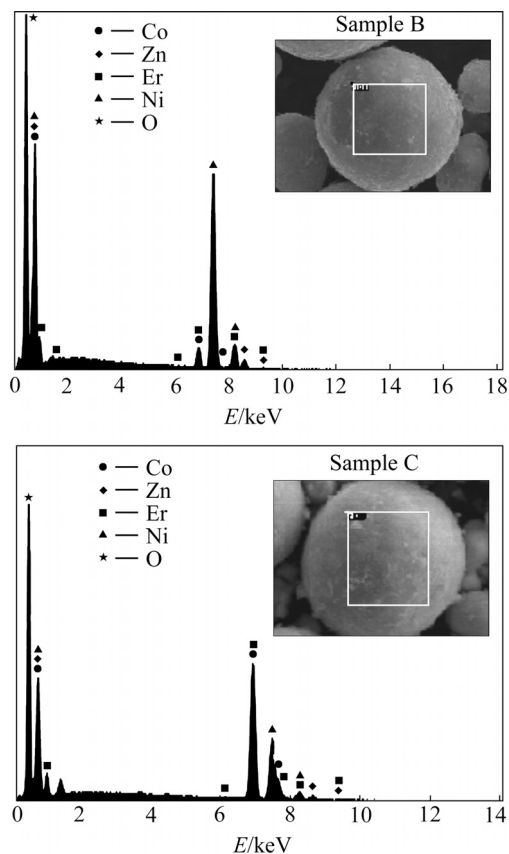


Fig.2 EDS analysis of particles of samples B and C (Inserts: SEM images of corresponding samples ($\times 5\,000$))

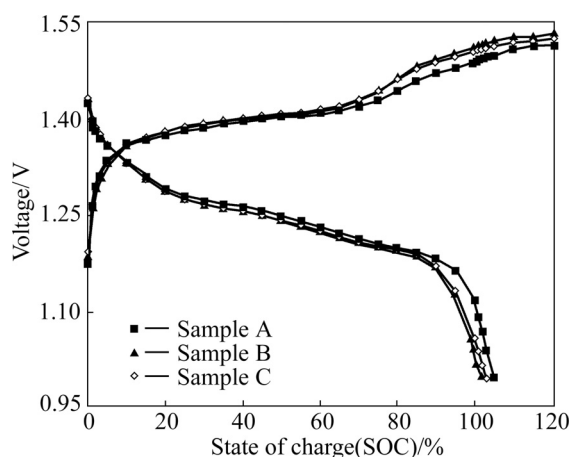


Fig.3 0.2C charge/discharge curves of three electrode samples at room temperature

It is found that the regular Co(III)-coated $\text{Ni}(\text{OH})_2$ electrode has a slightly higher discharge capacity than that of erbium addition at room temperature. With increasing the discharge rate, the discharge capacities of

Table 2 Discharge capacities of three electrode samples at different discharge rates at room temperature

Sample	0.2C	1C	2C	3C
A	93.7	80.7	71.2	64.3
B	91.5	71.3	61.5	52.7
C	92.3	74.7	63.8	55.0

both two erbium-added electrodes decrease much more than that of the un-mixing sample. Meanwhile, the discharge capacity of the $\text{Er}(\text{OH})_3$ -coated electrode is slightly lower than that of the Er_2O_3 -mechanical mixing sample.

3.3 Charge/discharge performances at high temperature

Fig.4 shows the 0.2C charge/discharge curves at 60 °C. The temperature dependence of discharge capacities of the three electrode samples at 1C charge/discharge is illustrated in Fig.5.

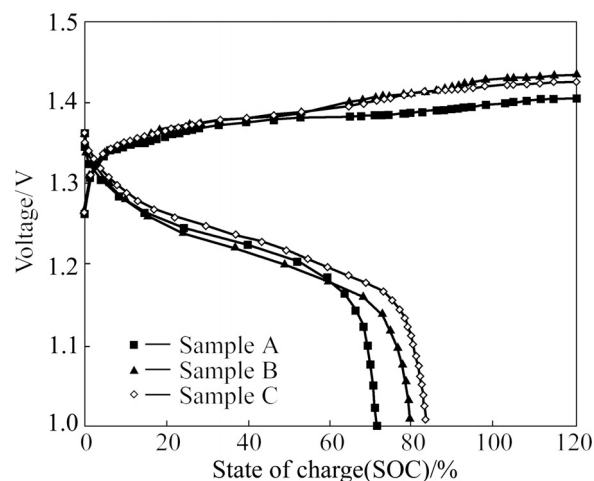


Fig.4 0.2C charge/discharge curves of three electrode samples at 60 °C

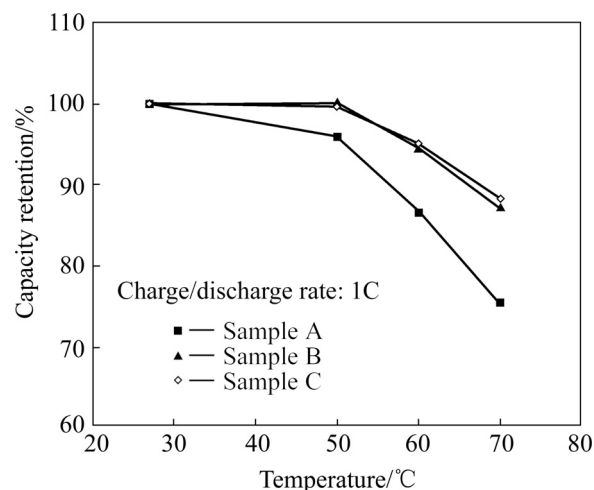


Fig.5 1C capacity retention of three electrode samples at different temperatures

It can be seen from Fig.3, the electrode without erbium presents a slightly higher discharge capacity than those of the erbium-added ones at room temperature. Because the additives are electro-chemically inactive, they have no contribution to the capacity.

However, it can be seen from Figs.4 and 5 that the discharge capacities of the Er-added electrodes are higher than that of the comparing sample above 50 °C. Furthermore, as the temperature increases, the discharge capacity of the comparing electrode decreases more rapidly than those of the two electrodes with erbium. The Er(OH)₃-coated electrode shows slightly higher capacity than that of the mechanical mixing Er₂O₃ sample. The ratio of the discharge capacity of Er(OH)₃-coated electrode at 70 °C reaches 88.1% and the Er₂O₃ mechanical mixing one is 87.2%. However, the ratio of the electrode without Er at 70 °C is 75.5%. This indicates that erbium can improve the performance of nickel hydroxide at high temperature.

The improvement of the performances of the erbium-added nickel hydroxide positive electrodes at the high temperature can be attributed to the increase of oxygen evolution over-potential[9]. At high temperature, the coating layer of Er(OH)₃ is beneficial to the depression of the oxygen evolution.

4 Conclusions

1) The element erbium has been added to Co(III)-coated Ni(OH)₂ powders by different ways. The Er concentration on the surface of the spherical Ni(OH)₂ particles by chemical deposition method is higher than that of the mechanically mixing one. The two methods are effective in improving the elevated temperature performance of nickel hydroxide electrode for the high power Ni-MH battery.

2) The discharge capacity of Ni(OH)₂ with 1% (atom fraction) Er(OH)₃ coating is 12.9% higher at 0.2C in 60 °C and 12.6% higher at 1C in 70 °C than those of the sample without erbium respectively. The discharge capacity of Ni(OH)₂ with 1% (atom fraction) Er₂O₃ mechanically mixture is 12.1% higher than that of the regular sample at 0.2C in 60 °C, and is 11.7% higher at 1C in 70 °C.

3) It is demonstrated that both chemical deposition method and mechanical mixing method can improve the over-potential of oxygen evolution. The chemical deposition method has less influence on the conductivity

of the active material and obvious influence on the performances at high temperature

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