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## The relationship of spherical nano-Ni(OH)<sub>2</sub> microstructure with its voltammetric behavior

Received: 13 January 2005 / Revised: 3 June 2005 / Accepted: 9 June 2005 / Published online: 2 August 2005  
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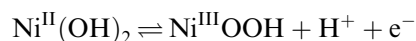
**Abstract** The spherical nano-Ni(OH)<sub>2</sub> has been characterized by a series of spectra methods such as the scanning electron microscope (SEM), the transmission electron microscope (TEM) and the X-ray diffraction (XRD). The electrochemical behavior of spherical nano-Ni(OH)<sub>2</sub>, attached to a graphite electrode and adjacent to an aqueous KOH-KCl electrolyte solution, has been studied by cyclic voltammetry. Spherical nano-Ni(OH)<sub>2</sub> exhibits a pair of quasi-reversible redox peaks. The relationship of the granularity and the potential was investigated, as well as the effect of different pH conditions. Moreover, the cycling experiments have been set up using spherical nano-Ni(OH)<sub>2</sub> and traditional analytical grade Ni(OH)<sub>2</sub>, respectively, and their cycling performances were evaluated as well. The capacity of spherical nano-Ni(OH)<sub>2</sub> is ca. ten times higher than the one with the traditional material under the same conditions, which shows its better electrochemical properties.

**Keywords** Voltammetry · Spherical nano-Ni(OH)<sub>2</sub> · Graphite electrode

### Introduction

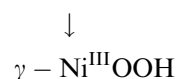
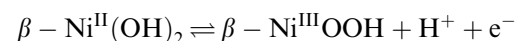
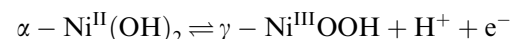
Nickel hydroxide is widely used as an active material of the cathodes of rechargeable alkaline batteries. The high power density, very good cyclicality, and high specific energy of these electrodes make them very competitive for an extended range of applications. The most recent application of nickel electrodes is in nickel–metal hydride (Ni-MH) batteries [1]. Increasing the energy density of the nickel hydroxide electrode is essential to raise

the whole energy density of such batteries. The charge/discharge process of nickel hydroxide involves a release/uptake of proton:



It is generally recognized that both the charge and discharge processes are mainly controlled by the solid-state diffusion of protons in the active material [2–4]. Recently, a dual structure model is proposed to interpret the featuring that proton diffusion is slow within densely packed grains while being fast within inter-grain matrix [5, 6].

It is reported that there are four phases produced over the lifetime of a nickel hydroxide electrode [7].



The formation of  $\gamma$ -Ni<sup>III</sup>OOH is associated with the volume expansion or swelling of the nickel hydroxide electrode [8]. To improve the characteristics of the nickel hydroxide electrode and to suppress the formation of  $\gamma$ -Ni<sup>III</sup>OOH, much work has been focused on the following two directions: one is modifying the nickel hydroxide by adding some compound inside it, the other is the direct application of spherical Ni(OH)<sub>2</sub> powder.

The addition of aluminium compound [9–14] is very useful to improve the charging efficiency of the nickel electrodes. Adding several percent of Cd, Zn, Co [15–22], or other elements [9, 23–25] as solid solutions to the nickel hydroxide is a very effective method of suppressing the formation of  $\gamma$ -Ni<sup>III</sup>OOH, and it can improve the charging efficiency as well. Although there are numerous studies on these topics, the results are still not complete. Furthermore, the presence of the additives descends the density, obstructs the increase of specific energy and has negative effect on the cyclicality as well.

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Spherical nano-Ni(OH)<sub>2</sub>, which suppresses the development of the inner pore volume, makes it possible to increase the density of the active material itself [26, 27]. The pores and the crannies in spherical particles can shorten the proton transmission distance and speed its velocity, which may bring about the local polarization being lowered. Moreover, the electrochemical performances of the spherical Ni(OH)<sub>2</sub> are improved by enhancing the conducting properties of the crystalline lattice due to its fast proton transmission. Using spherical nano-Ni(OH)<sub>2</sub> as anode active material, higher energy density and longer cyclic life will be realized. In this paper, the relationship of spherical nano-Ni(OH)<sub>2</sub> microstructure with its voltammetric behavior was investigated.

## Experimental

### Apparatus

Cyclic voltammetric experiments were performed with an EG&G PAR Model 273 potentiostat/galvanostat (Princeton Applied Research, USA) and a Model 270 electrochemical software in a three-electrode cell. The working electrode was a paraffin-impregnated graphite electrode (PIGE) or a modified PIGE electrode, the auxiliary and reference electrodes were platinum wire and saturated calomel electrode (SCE), respectively. The scanning electron microscope (SEM) image was obtained using JSM-5600LV (Jeol, Japan). The transmission electron microscope (TEM) image was obtained using JEM-2000FX (Rigaku, Japan). The X-ray diffraction (XRD) image was obtained using D/max-RA (Rigaku, Japan).

### Reagents and solutions

The spherical nano-Ni(OH)<sub>2</sub> was provided by Changsha Research Institute of Mining and Metallurgy (China). All other reagents were of analytical grade. Water was triply distilled from an all-quartz still.

The buffer and sample solutions were purged with highly purified nitrogen for at least 5 min prior to the experiments. Nitrogen atmosphere was maintained over the solutions during the experiments. All experiments were carried out at room temperature (18 ± 2°C).

### Fabrication of the modified electrode

The procedure of mechanically immobilizing Ni(OH)<sub>2</sub> on the surface of a paraffin-impregnated graphite electrode (PIGE) has been described elsewhere [28–30] and is used here in the same way. We denote this electrode as Ni(OH)<sub>2</sub>-PIGE.

### Cycling procedure of the anode material

The cycling performance of the anode material was evaluated in laboratory cells [19] that comprised: Ni(OH)<sub>2</sub> | 1 M KOH aqueous solution | Zn. The anode consisted of 0.1 g of Ni(OH)<sub>2</sub> and 0.005 g of polytetrafluoroethylene (PTFE) powder as a binder. The mixture was pressed onto a nickel screen at 20 MPa. The cells were cycled at a current density of 2 mA/cm<sup>2</sup>.

## Results and discussion

### Characterization of the spherical nano-Ni(OH)<sub>2</sub>

The correlated parameters of the six spherical nano-Ni(OH)<sub>2</sub> samples are listed in Tables 1, 2 and 3.

The six spherical nano-Ni(OH)<sub>2</sub> samples are all characterized by the SEM, TEM and XRD. Here we show the typical figures of one sample, as they have similar properties from each other (The same situations are described in the electrochemical investigation of the Ni(OH)<sub>2</sub>-PIGE and the effect of the pH value). They are based on a bimodal size distribution: spherical particles of ca. 10 micron consisting of nanoparticles lumped together. Figure 1 shows the typical SEM image of the spherical nano-Ni(OH)<sub>2</sub> sample when being magnified

**Table 1** Appearance and density

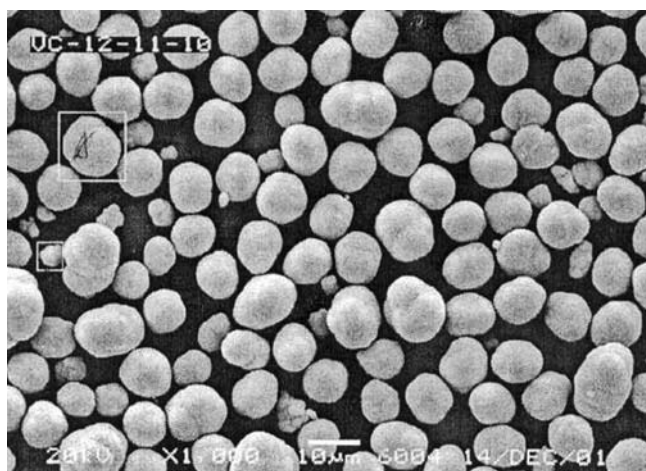
Samples	Appearance	Loose density (g/cm <sup>3</sup> )	Tight density (g/cm <sup>3</sup> )
1#	Green	1.73	2.12
2#	Green	1.88	2.08
3#	Reseda	1.51	2.08
4#	Emerald	1.64	2.4
5#	Green	1.57	2.04
6#	Emerald		2.38

**Table 2** Granularity distribution and BET analysis result

Samples	Diameter at 10% (μm)	Diameter at 50% (μm)	Diameter at 90% (μm)	Average diameter (μm)	BET (m <sup>2</sup> /g)
1#	1.16	6.74	14.23	7.72	8.75
2#	2.32	9.88	13.22	9.29	4.57
3#	0.44	4.73	10.89	5.42	10.73
4#	1.62	10.01	16.76	9.93	7.74
5#	0.50	7.13	11.24	6.63	7.85
6#	1.21	8.56	16.26	8.98	10.74

**Table 3** X-ray analysis result

Samples	D001	FWHM001	FWHM101	I001	I101	I001/I101
1#	4.6786	0.858	0.794	1755.3	1619.6	1.08
2#	4.6543	0.822	0.691	1706.6	1714.2	0.99
3#	4.6733	0.799	1.001	1933.9	1651.5	1.17
4#	4.6782	0.664	0.895	2026.7	1602.0	1.265
5#	4.6676	0.703	0.870	1930.5	1708.4	1.13
6#	4.6708	0.667	0.878	1899.1	1404.0	1.35

**Fig. 1** SEM image of spherical nano-Ni(OH)<sub>2</sub> (1,000 times magnified)**Fig. 3** SEM image of the smaller granule in Fig.1 (30,000 times magnified)**Fig. 2** SEM image of the larger granule in Fig.1 (30,000 times magnified)

1,000 times. It can be found that spherical nano-Ni(OH)<sub>2</sub> have smooth surface appearance. When magnified 30,000 times (Figs. 2, 3), the cavity surface appearance and the spiculate structure can be observed. The same appearance is observed clearly as well in the TEM image (Fig. 4). The XRD pattern showed in Fig. 5 is consistent with hexagonal Ni(OH)<sub>2</sub> (JCPDS card No.:14-0117).

#### Electrochemical investigation of the Ni(OH)<sub>2</sub>-PIGE

Cyclic voltammograms (CVs) of Ni(OH)<sub>2</sub>-PIGE exhibit a pair of cathodic peak and anodic counterpeak in the 0.1 M KOH-KCl electrolyte solution (pH 11.0). The peak separation is 0.32 V at the scan rate of 0.05 V/s and does not change with the scan rate, which indicates here a quasi-reversible redox process. The anodic peak currents increase linearly with the square root of the scan rate in the range of 0.05–0.3 V/s, which shows the electrode reaction is controlled by the diffusion (Fig. 6).

The thickness of the modified layer has great impact on the electrochemical properties of the electrode. The charging currents are getting much larger, as the modified gel being got heavier. Despite that the peak potential has little relation to the amount of material at the surface in our investigation the amount of modified material was still carefully controlled to be consistent as about 0.1 mg.

Comparing with traditional analytical grade Ni(OH)<sub>2</sub>, spherical nano-Ni(OH)<sub>2</sub> illustrates larger redox potential difference and more positively anodic potential (Fig. 7). The electrochemical characteristics of the spherical nano-Ni(OH)<sub>2</sub> are affected especially by its microstructure complications. Our samples have many differences from each other at various factors, such as the chemical component, granularity distribution and diameter, density, surface configuration and structure,

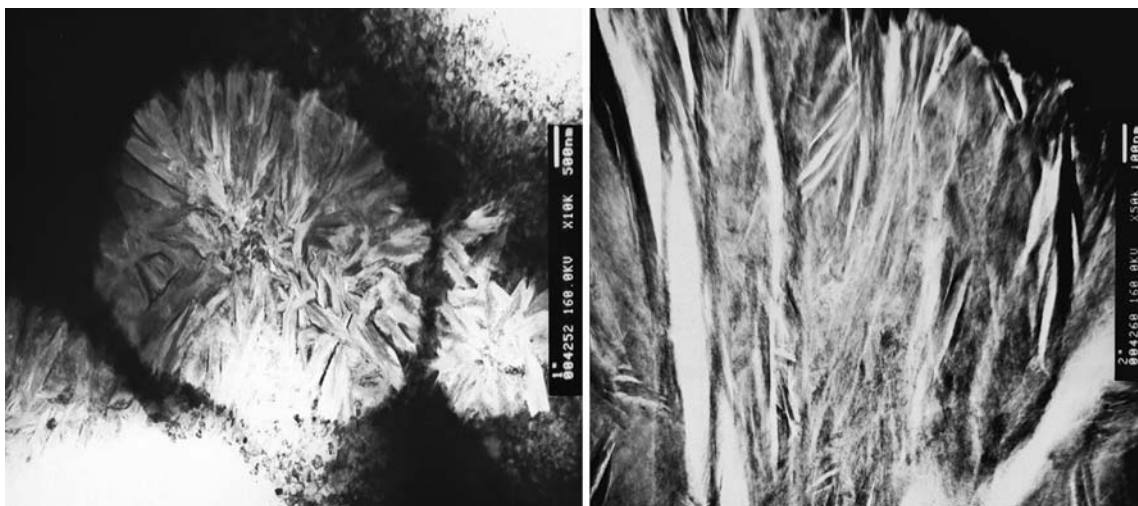


Fig. 4 TEM image of spherical nano-Ni(OH)<sub>2</sub>

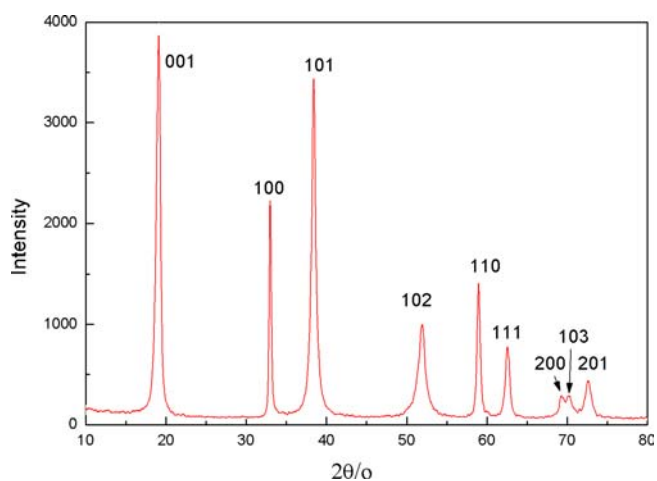


Fig. 5 XRD image of spherical nano-Ni(OH)<sub>2</sub>

crystal inner layer minute crystal dimension and disfigurement and so on. Figure 8 describes the relationship between the loose density of the spherical nano-Ni(OH)<sub>2</sub> and the potentials ( $E_{p_a}$ ,  $E_{p_c}$  and  $\Delta E$ ). The  $E_{p_a}$  and  $E_{p_c}$

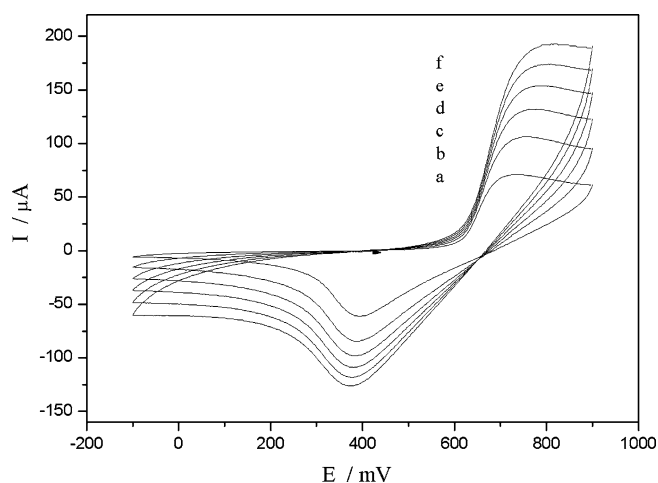


Fig. 6 Cyclic voltammograms of Ni(OH)<sub>2</sub>-PIGE in the 0.1 mol/L KOH-KCl electrolyte solution (pH 11.0), scan rate a 50 mV/s; b 100 mV/s; c 150 mV/s; d 200 mV/s; e 250 mV/s; f 300 mV/s

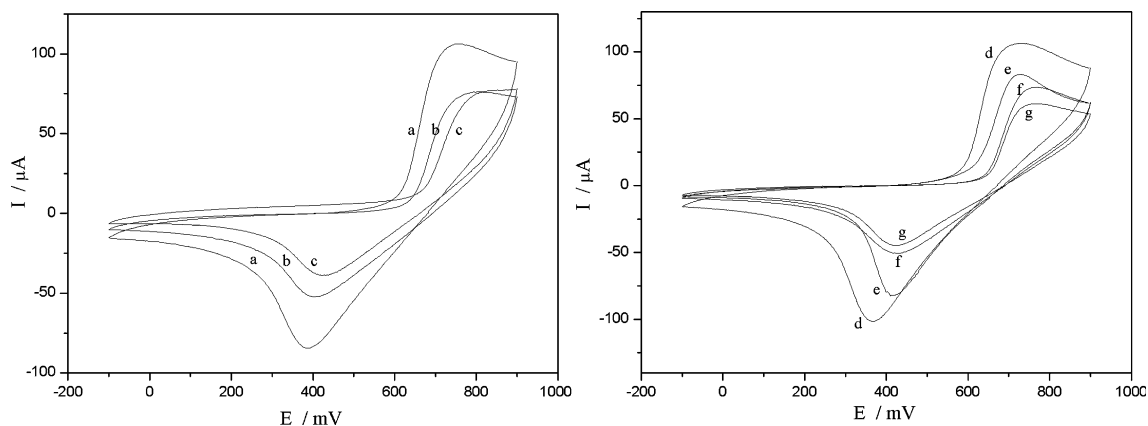
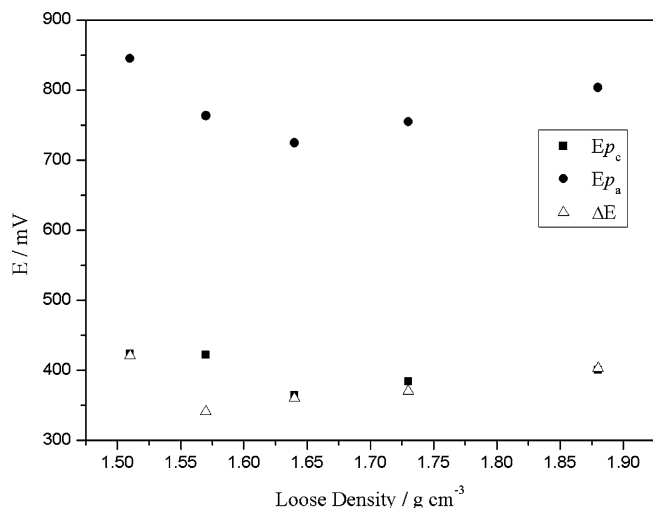


Fig. 7 Cyclic voltammograms of Ni(OH)<sub>2</sub>-PIGE for different samples in the 0.1 mol/L KOH-KCl electrolyte solution (pH 11.0), scan rate 100 mV/s. a 1#; b 2#; c 3#; d 4#; e traditional Ni(OH)<sub>2</sub>; f 5#; g 6#

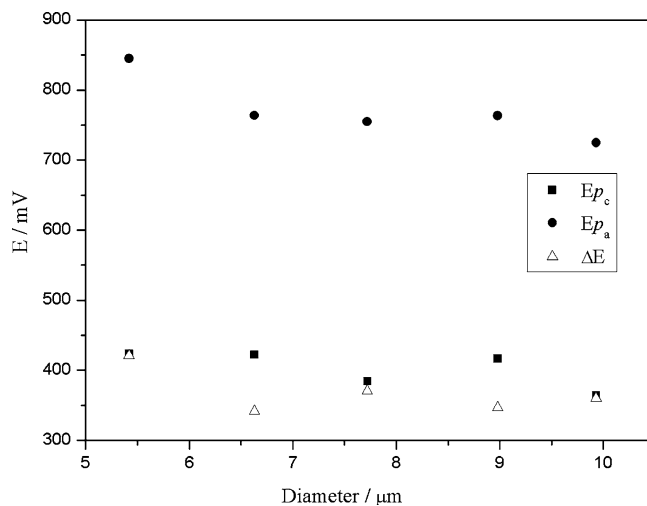


**Fig. 8** Relationship between the loose density of the spherical nano-Ni(OH)<sub>2</sub> and the potentials ( $E_{p_a}$ ,  $E_{p_c}$  and  $\Delta E$ )

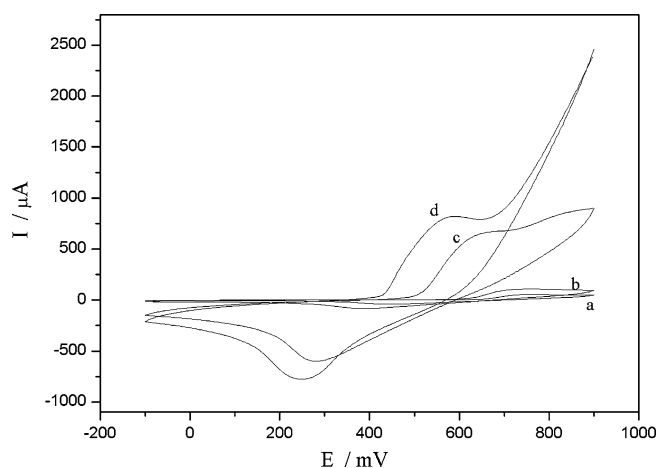
have minimal values at 1.64 g/cm<sup>3</sup>, while the minimal  $\Delta E$  is at 1.57 g/cm<sup>3</sup>. On the other hand, the relationship between the average diameter of the spherical nano-Ni(OH)<sub>2</sub> and the potentials ( $E_{p_a}$ ,  $E_{p_c}$  and  $\Delta E$ ) is showed in Fig. 9. The  $E_{p_a}$  is negatively shifted with the increase of the average diameter. Meanwhile, considering all those factors which make prominent and complicated influences on the electrochemical behaviors of the spherical nano-Ni(OH)<sub>2</sub>, the research of the relationship and rule between the microstructure and the electrochemical behavior needs further systematical investigation.

#### Effect of the pH influence

Figure 10 illustrates the cyclic voltammograms of Ni(OH)<sub>2</sub>-PIGE at different pH values. The cathodic and anodic peak currents aggrandize rapidly as the alkalinescence of the solutions is enhanced. This may be explained by a “self-inhibition” process: when oxidation occurs, protons are produced. In such a low hydroxide environment, the pH will change massively (pores become acidic) and the process might trend to be shut down. There is a regression equation of the peak potential vs pH of the solution for  $E^{0'} = 1.161 - 0.070 \text{ pH}$  ( $E^{0'}$ , V; correlation coefficient,  $r = 0.9945$ ), which shows that the uptake of electrons is accompanied by an equal number of protons.



**Fig. 9** Relationship between the average diameter of the spherical nano-Ni(OH)<sub>2</sub> and the potentials ( $E_{p_a}$ ,  $E_{p_c}$  and  $\Delta E$ )



**Fig. 10** Cyclic voltammograms of Ni(OH)<sub>2</sub>-PIGE in the 0.1 mol/L KOH-KCl electrolyte solution, at different pH values of **a** 10.2; **b** 11.0; **c** 12.3; **d** 13.1, scan rate 100 mV/s

#### Investigation of the stability and reproducibility of the Ni(OH)<sub>2</sub>-PIGE

The same PIGE was modified by Ni(OH)<sub>2</sub> five times in the same way, and tested in the same KOH-KCl solution (0.1 mol/L), the relative standard deviation (RSD) of peak currents is 5.1%. The same Ni(OH)<sub>2</sub>-PIGE was tested in five KOH-KCl solutions (0.1 mol/L), and the

**Table 4** The cycling performance of spherical nano-Ni(OH)<sub>2</sub> and traditional analytical grade Ni(OH)<sub>2</sub>, current density 2 mA/cm<sup>2</sup>

Cyclic times	Traditional Ni(OH) <sub>2</sub>				Spherical nano-Ni(OH) <sub>2</sub> samples			
	$E_{\text{charge}} / \text{V}$	$E_{\text{discharge}} / \text{V}$	$C_{\text{charge}} / \text{mAh}$	$C_{\text{discharge}} / \text{mAh}$	$E_{\text{charge}} / \text{V}$	$E_{\text{discharge}} / \text{V}$	$C_{\text{charge}} / \text{mAh}$	$C_{\text{discharge}} / \text{mAh}$
1	1.8699	1.6732	0.15	0.11	1.8699	1.6838	0.88	0.93
2	1.8699	1.6732	0.12	0.09	1.8693	1.6839	0.79	0.88
3	1.8707	1.6780	0.10	0.07	1.8719	1.6820	0.76	0.86
4	1.8707	1.6668	0.09	0.06	1.8702	1.6813	0.74	0.82
5	1.8692	1.6778	0.08	0.06	1.8697	1.6812	0.71	0.79

reproducibility of peak currents is 2.7% (RSD). Therefore, the Ni(OH)<sub>2</sub>-PIGE has good stability and reproducibility.

#### Investigation of the cycling performance of the spherical nano-Ni(OH)<sub>2</sub>

The cycling performance of spherical nano-Ni(OH)<sub>2</sub> and traditional analytical grade Ni(OH)<sub>2</sub> is shown in Table 4. That the discharge capacity of spherical nano-Ni(OH)<sub>2</sub> in the cyclic processes is less than the theoretical capacity of 289 mAh/g results from the quite thick Ni(OH)<sub>2</sub> layer on the nickel screen, which leads to the inner layer not taking in for reaction. However, the capacity of spherical nano-Ni(OH)<sub>2</sub> is higher than the one with the traditional material under the same conditions, which indicates better electrochemical properties of spherical nano-Ni(OH)<sub>2</sub>.

#### Conclusions

In this paper, we have studied the electrochemical properties of spherical nano-Ni(OH)<sub>2</sub> by solid state electrochemical method as well as cycling performance experiments. The redox reaction is a quasi-reversible redox process dominated by diffusion. Spherical nano-Ni(OH)<sub>2</sub> shows excellent electrochemical properties comparing with traditional material. The capacity of spherical nano-Ni(OH)<sub>2</sub> is ca. ten times higher than the one with the traditional material under the same conditions. It is believed that using spherical nano-Ni(OH)<sub>2</sub> as anode active material, the Ni-MH battery will get much higher energy density and longer cyclic life. Meanwhile, considering all the chemical component, granularity distribution and diameter, density, surface configuration and structure, as well as the crystal inner layer minute crystal dimension and disfigurement factors, which make prominent and complicated influences on the electrochemical behaviors of the spherical nano-Ni(OH)<sub>2</sub>, the research of the relationship and rule between the microstructure and the electrochemical behavior needs further systematical investigation.

**Acknowledgements** This work was supported by the National Natural Science Foundation of China (No. 50134020). We also appreciate Changsha Research Institute of Mining and Metallurgy for providing the spherical nano-Ni(OH)<sub>2</sub> samples.

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