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ORIGINAL PAPER

Ball milled cobalt oxyhydroxide coat on the surface of nickel hydroxide

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Abstract Cobalt oxyhydroxide coat on the surface of nickel hydroxide particles is finished employing a simple ball milling process. The structure, morphology, and surface composition of the coated $Ni(OH)_2$ particles is characterized by using X-ray diffraction, scanning electron microscopy, and energy dispersive spectroscopy tests. The results show that numerous strip-like particles of a mixture of $Ni(OH)_2$ and CoOOH aggregate on the surface of the $Ni(OH)_2$ particles, and a structure of β-$Ni(OH)_2$ is preserved. Compared to the $Ni(OH)_2$ electrodes with a mixed CoO additive, the electrochemical activity of the electrodes with ball milled CoOOH coat can be improved as shown by using electrochemical impedance spectroscopy test, thus resulting in charge–discharge and cycle life performance improvement of the electrodes.

Keywords Nickel hydroxide · Cobalt oxyhydroxide · Ball milling · Surface · Coat

1 Introduction

Pasted nickel hydroxide electrodes are widely used in the nickel-based alkaline secondary batteries such as nickel–cadmium (Ni–Cd), nickel–metal-hydride (Ni–MH), and nickel–zinc (Ni–Zn) batteries. In these $Ni(OH)_2$ electrodes, cobalt monoxide powder is usually used as an additive owning to enhancement of their conductivity [1, 2]. It was reported [3] that CoO could dissolve in an alkaline medium (usually a KOH electrolyte), then precipitate on the surface of nickel hydroxide particles, and be oxidized to a highly conductive β-type cobalt oxyhydroxide (β-CoOOH) during the first charge of the electrodes, thus resulting in a higher utilization of nickel hydroxide.

Usually, the battery manufacturers add just a few percentages of CoO into the $Ni(OH)_2$ electrodes to reduce cost. With a small amount of the additive, it is difficult to achieve uniform distribution among nickel hydroxide particles. One solution is to introduce a metal cobalt film on the surface of the particles by electroless plating [4, 5]. This process needs not only a reducing agent, and one or two complexing and stabilizing agents in the plating solution, but also $PdCl_2$ as an active agent before the plating, making it more complicated and costlier. An alternative solution is to directly coat a CoOOH film on the surface of the particles by a chemical precipitation/oxidation process [6, 7]. Compared to the metal cobalt coat, this process is simpler, but it has still some shortcomings such as time-consumption and water-consumption.

Recently, a ball milled coating process has been introduced into the preparation of battery materials [8, 9]. Carbon-coated lithium iron phosphate was successfully prepared with a planetary ball mill. It could deliver better battery performance in terms of the discharge capacity, cycling stability, and rate capability than the bare $LiFePO_4$ [8]. In this article, we report a ball milled CoOOH film coated on the surface of nickel hydroxide particles. The electrochemical performance of the coated nickel hydroxide and the bare nickel hydroxide with mixed CoO were investigated and compared.

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2 Experimental

Ball milling was performed using a planetary ball mill with a 50-mL-capacity stainless steel pot and 50-g stainless steel balls. A mixture of commercial β-type spherical $Ni(OH)_2$ 4.73 g, $CoSO_4 \cdot 7H_2O$ 1.15 g, and NaOH 0.37 g was added into the pot. The revolution speed was 450 r min^{-1}, and the milling time was 30 min for the following reaction,

$$CoSO_4 + 2NaOH \rightarrow Co(OH)_2 + Na_2SO_4 \qquad (1)$$

Then, another mixture of $K_2S_2O_8$ 1.38 g and NaOH 0.45 g was added into the above spot. Ball milling was operated again with the same revolution speed and milling time for the oxidation of $Co(OH)_2$,

$$2Co(OH)_2 + K_2S_2O_8 + 2NaOH \\ \rightarrow 2CoOOH + K_2SO_4 + Na_2SO_4 + 2H_2O \qquad (2)$$

The resulting powder was washed repeatedly with distilled water until there was no $BaSO_4$ precipitation in the filtrate with the addition of a $BaCl_2$ solution, then dried at 65 °C for use. The coating amount was controlled to 5 wt%. The morphology and surface composition of the coated nickel hydroxide was tested by using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The powder X-ray diffraction (XRD) was used to analyze the phase structure of the coated nickel hydroxide.

The electrochemical properties of the uncoated and coated nickel hydroxide electrodes were investigated in a half-cell system containing a 7 mol L^{-1} KOH solution at 25 °C. A hydrogen absorbing alloy (a commercial $MmNi_{3.55}Co_{0.75}Al_{0.2}Mn_{0.5}$ alloy, where Mm is misch metal) electrode with a large capacity was used as the counter electrode, and a Hg/HgO (7 mol L^{-1} KOH) electrode was employed as the reference electrode. Two kinds of pasted positive $Ni(OH)_2$ electrodes were separately made by filling a nickel foam substrate with a mixture of 2 wt% polytetrafluoroethylene (PTFE) binder, 5 wt% CoO, and 93 wt% $Ni(OH)_2$, or a mixture of 2 wt% PTFE binder and 98 wt% CoOOH coated $Ni(OH)_2$. The pasted electrodes were then dried at 65 °C and pressed to a thickness of 0.65 mm.

The $Ni(OH)_2$ electrodes were charged initially at a 0.05 C rate for 5 h, followed with a 0.1 C rate for 12 h, and discharged at a 0.2 C rate to a cut-off potential 0.1 V (versus Hg/HgO). Here, C corresponds to the current needed to discharge the total capacity of the electrodes in 1 h. Afterward, a cycling test was performed on the electrodes by charging at a 0.2 C rate for 7 h and discharging at the same rate to a cut-off potential 0.1 V for stabilizing their capacity. The electrodes were then charged at a 0.2 C rate for 7 h and discharged separately at a 1 C (or 5 C) rate to a cut-off potential 0.1 V for high-power performance tests. Electrochemical impedance spectroscopy (EIS) tests were performed on the electrodes by using a Solartron Electrochemical Interface model SI1287. Cycle life tests of the $Ni(OH)_2$ electrodes were performed as follows: the electrodes were charged at a 1 C rate for 1.2 h, rested for 10 min, then discharged at the same rate to a cut-off potential 0.1 V.

3 Results and discussion

Figure 1 shows SEM images of three kinds of nickel hydroxide particles. A higher resolution SEM image is inserted in each case to further observe the surface morphology. As shown in Fig. 1a, before ball milling, the surface of spherical $Ni(OH)_2$ particles seems smooth. After ball milling, the $Ni(OH)_2$ particles become smaller and irregular in shape (Fig. 1b); numerous strip-like particles aggregate on their surface. However, for the $Ni(OH)_2$ particles with mixed CoO (Fig. 1c), after the initial charge (0.05 C rate for 5 h), they can be kept spherical, and some sheet-like particles spread partially on their surface. These results indicate that compared to the common CoO additive, the ball milling process used in this article is more effective to modify the surface structure and properties of the $Ni(OH)_2$ particles. In addition, this coating process does not need the complexing, active, reducing, and stabilizing agents, nor does it need to prepare any solution, and can be finished in 1 h, thus lowering the coating cost.

Figure 2 shows the initial charge curves of the $Ni(OH)_2$ electrodes. For the electrode with mixed CoO (Fig. 2b), the charge plateau at about 0.12 V corresponds to the formation of CoOOH. On the contrary, for the electrode with ball milled CoOOH (Fig. 2a), this plateau disappears since the cobalt additive has been chemically oxidized to Co(III) by $K_2S_2O_8$ before the initial charge.

Figure 3 presents XRD patterns of three kinds of nickel hydroxide. It shows that whatever method is used for the introduction of CoOOH on the surface of $Ni(OH)_2$ particles, only a structure of β-$Ni(OH)_2$ is observed on them. The diffraction peaks at 19.0°, 33.1°, and 38.5° correspond to {001}, {100}, and {101} crystal planes, respectively. It should be noticed that there is 5 wt% cobalt additive added into nickel hydroxide. Thus, it seems that as CoOOH spreads on the surface of $Ni(OH)_2$ particles either by ball milling or dissolution–precipitation, its structure may be similar to $Ni(OH)_2$.

Energy dispersive spectroscopy spectrum for the surface of the ball milling-coated nickel hydroxide particles is shown in Fig. 4 and the element contents are shown in Table 1. Obviously, the strip-like particles (Fig. 1b) on the surface of the $Ni(OH)_2$ particles are composed of cobalt oxyhydroxide and nickel hydroxide. The latter originates

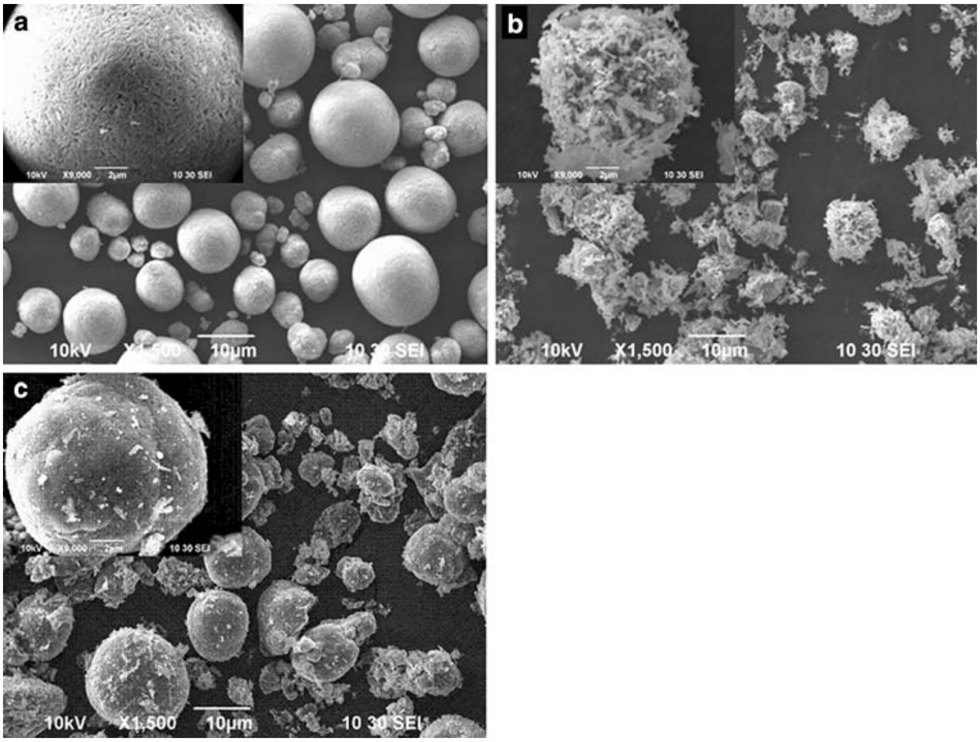

Fig. 1 SEM images of nickel hydroxide particles **a** uncoated, **b** with ball milled CoOOH and **c** with mixed CoO after the initial charge. *Inset*: higher-resolution images of them

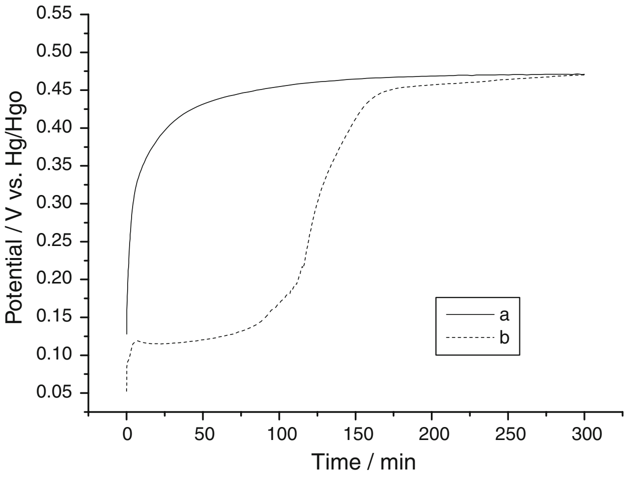

Fig. 2 Typical initial charge curves of pasted $Ni(OH)_2$ electrodes at a 0.05 C rate: (*a*) with ball milled CoOOH and (*b*) with mixed CoO

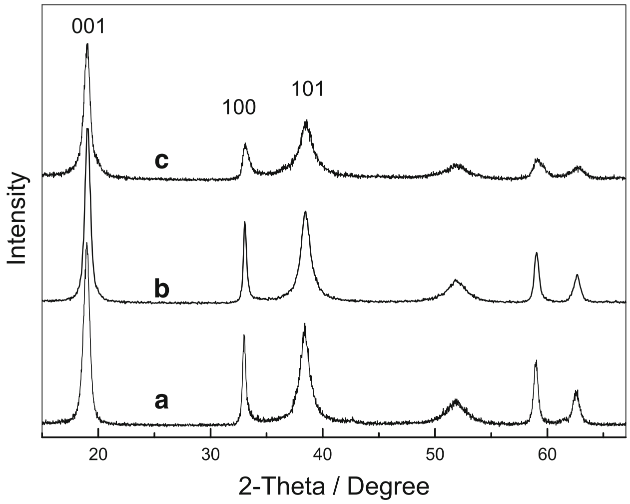

Fig. 3 XRD patterns of nickel hydroxide particles (*a*) uncoated, (*b*) with ball milled CoOOH and (*c*) with mixed CoO after the initial charge

from the chips of nickel hydroxide generating during the ball milling. It agrees with the fact that the nickel hydroxide particles cannot be full coated with only 5 wt% cobalt oxyhydroxide. In addition, no S element is detected on the surface of the coated nickel hydroxide, which indicates that the sulfates are removed completely after washing. However, C and Na elements are residual in it because of CO_2 in the air and the raw material NaOH.

Figure 5 shows impedance plots of the $Ni(OH)_2$ electrodes discharged to 100% depth of discharge (DOD) in the KOH electrolyte. Clearly, the plots exhibit two arcs in the whole frequency range. It is known that the semicircle at high frequency regions corresponds to the charge transfer resistance (R_{ct}) in parallel connection with the double layer capacitance (C_{dl}), and the line at low frequency regions corresponds to the Warburg impedance (Z_w) of proton diffusion [10]. A proposed equivalent circuit for the frequency response of the $Ni(OH)_2$ electrode is given in Fig. 6, where R_s corresponds to the solution resistance. The results of a curve fitting according to the equivalent circuit

Fig. 4 EDS spectrum for the surface of the ball milling-coated nickel hydroxide particles

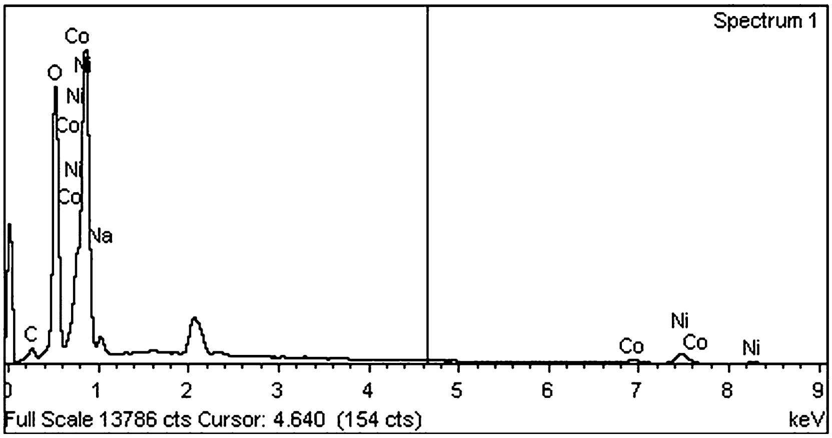

Table 1 Result of EDS analysis for the surface composition of the coated nickel hydroxide

Element	Weight (%)	Atomic (%)
C (K)	1.70	4.12
O (K)	34.95	63.54
Na (K)	1.26	1.59
Co (L)	13.96	6.89
Ni (L)	48.13	23.85
Total	100.00	99.99

show a decrease in R_{ct} and increase in C_{dl} (Table 2). Thus, compared to the electrode with mixed CoO, the surface electrochemical activity of nickel hydroxide can be effectively improved by the ball milled CoOOH coat.

The typical charge–discharge curves of the $Ni(OH)_2$ electrodes at 0.2, 1, and 3 C rates are shown in Figs. 7, 8, and 9, respectively. Compared to the electrodes with mixed CoO, the electrodes with ball milled CoOOH have lower charge potential and higher discharge potential, especially when the discharge current increases to a 5 C rate, the discharge capacity and potential of the electrodes is effectively improved. It is known that CoOOH can provide a good electrical path between the nickel hydroxide particles [3]. Ball milled CoOOH is coated more uniformly on the surface of nickel hydroxide particles than the one converted from mixed CoO (Fig. 1), thus resulting in an effective improvement of the charge–discharge performance of the $Ni(OH)_2$ electrodes especially at large current.

The capacity of the $Ni(OH)_2$ electrodes during 300 cycles at a 1 C rate is shown in Fig. 10. Compared to the electrodes with mixed CoO, the electrodes with ball milled CoOOH show better cycling durability. Their capacity after 300 cycles decreases by 3.1% for the latter but 14.8% for the former. These results indicate that the cycle performance of the $Ni(OH)_2$ electrodes can be considerably improved by ball milled CoOOH as the better surface modification than the one converted from mixed CoO.

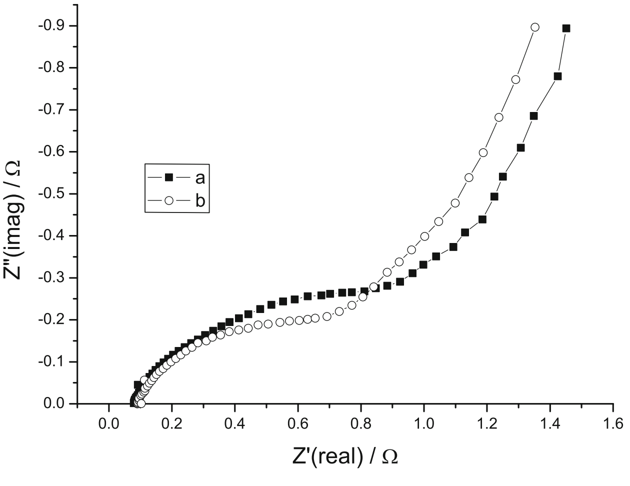

Fig. 5 Impedance plots of pasted $Ni(OH)_2$ electrodes (area = 1 cm^2, loading = 150 mg cm^{-2}, discharged to 100% depth of discharge) in 7 mol L^{-1} KOH electrolyte at a frequency range from 10^5 to 10^{-2} Hz: (*a*) with mixed CoO and (*b*) with ball milled CoOOH

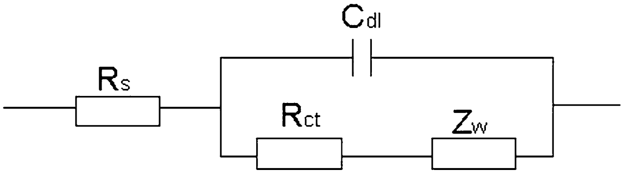

Fig. 6 Proposed equivalent circuit for $Ni(OH)_2$ electrode

Table 2 Impedance parameters of pasted $Ni(OH)_2$ electrodes in 7 mol L^{-1} KOH electrolyte

	R_{ct} (Ω)	C_{dl} (F)
Electrode with mixed CoO	0.515	0.309
Electrode with ball milled CoOOH coat	0.438	0.363

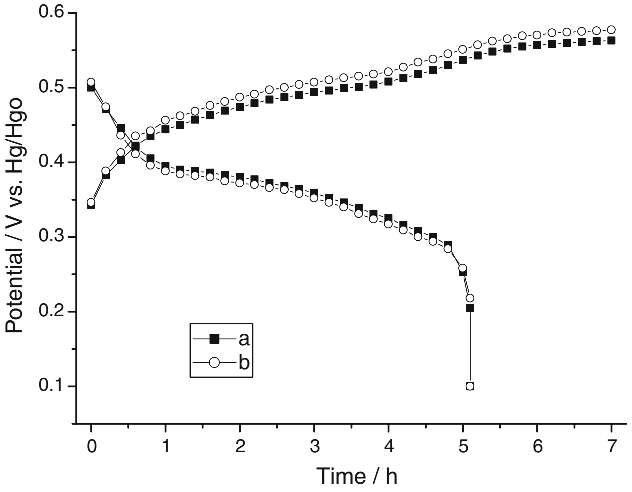

Fig. 7 Typical charge–discharge curves of pasted $Ni(OH)_2$ electrodes at a 0.2 C rate: (*a*) with ball milled CoOOH and (*b*) with mixed CoO

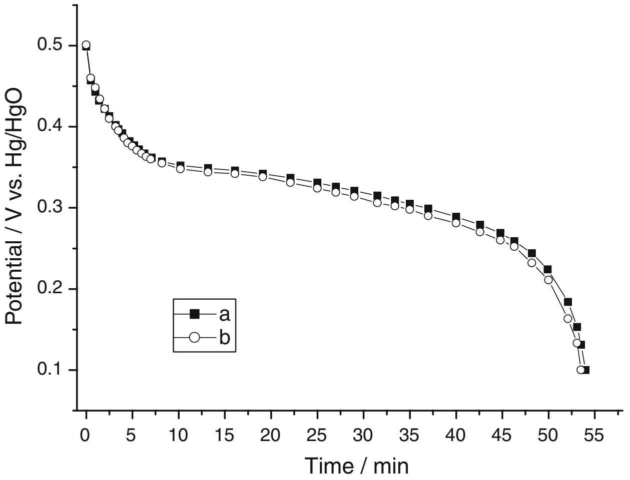

Fig. 8 Typical discharge curves of pasted $Ni(OH)_2$ electrodes at a 1 C rate: (*a*) with ball milled CoOOH and (*b*) with mixed CoO

4 Conclusion

A simple ball milling process is used to directly coat a CoOOH film on the surface of nickel hydroxide particles. Numerous strip-like particles of a mixture of CoOOH and $Ni(OH)_2$ aggregate on the surface of the $Ni(OH)_2$ particles by SEM and EDS observation. XRD analyses show a structure of β-$Ni(OH)_2$ for the coated particles. Compared to the $Ni(OH)_2$ electrodes with the mixed CoO additive, the surface electrochemical activity of the electrodes with the ball milled CoOOH coat can be improved as shown by using EIS tests, thus resulting in charge–discharge and cycle performance improvement of the electrodes.

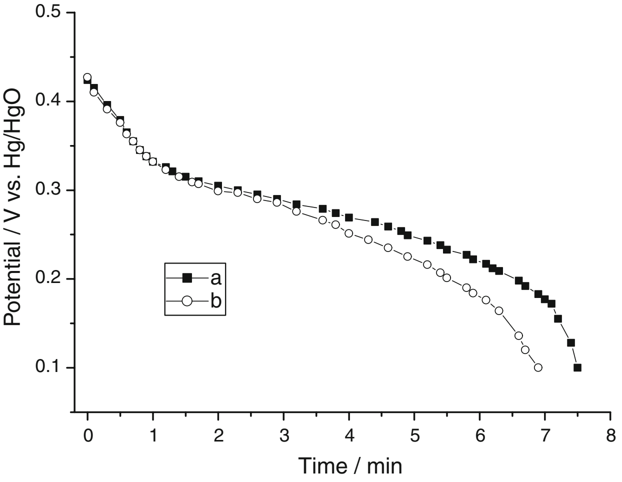

Fig. 9 Typical discharge curves of pasted $Ni(OH)_2$ electrodes at a 5 C rate: (*a*) with ball milled CoOOH and (*b*) with mixed CoO

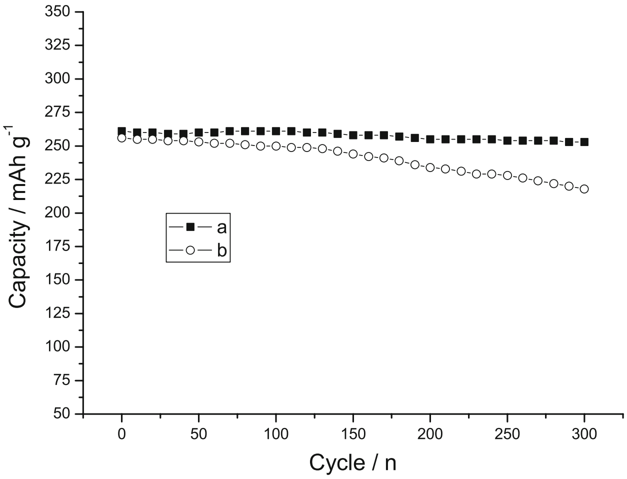

Fig. 10 The capacity of pasted $Ni(OH)_2$ electrodes during 300 cycles at a 1 C rate: (*a*) with ball milled CoOOH and (*b*) with mixed CoO

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