Short communication

Influence of zinc ions in electrolytes on the stability of nickel oxide electrodes for single flow zinc–nickel batteries

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ABSTRACT

The present paper aims at discussing the effect of zinc ions in electrolytes on the cycling stability of nickel oxide electrodes for the zinc/nickel single flow battery. It is shown that the presence of zinc in KOH electrolytes decreases the charging voltage to some extent and inhibits changes in the galvanostatic charging curve vs. cycling number as compared to KOH electrolytes with no zinc present. As a result, the discharge capacity of the electrodes basically does not decay even after 500 charge–discharge cycles. The cycling performance of nickel oxide electrodes is enhanced substantially. It is demonstrated that zinc ions in electrolytes may be incorporated into the lattice structure of nickel hydroxides during the cell cycling, forming a composite where the zinc plays a role as an additive and preventing the formation of γ-phase and overcharge.

1. Introduction

The redox flow battery (RFB) is well suited to large-scale energy storage for stationary applications [1]. Up to date, a single flow battery has received increasing attention due to no separators needed and simplified design of stacks. The zinc/nickel single flow battery was proposed by Cheng et al. [2,3]. In this system, nickel hydroxides are employed as positive electrodes and deposited zinc is employed as negative electrodes. Concentrated solutions of ZnO dissolved in a KOH aqueous medium serve as the electrolyte. Theoretically, the deposition/dissolution of zinc on inert metal current collectors can be cycled endlessly. As a result, the cycle life of the zinc/nickel single flow battery is dependent on the stability of nickel oxide electrodes. Therefore, it is very necessary to explore the factors influencing the cycling performance of nickel oxide electrodes and the ways to enhance their stability.

Nickel hydroxide has been the subject of many studies because of its intensive use as an active material for alkaline batteries. Early in 1994, a study that dealt with the effects of zinc or iron ions added to the electrolytes, showed that some of the negative chemical effects of iron and zinc on nickel electrode performance could be alleviated by the presence of cobalt and lithium [4]. But, addition of zinc to the electrolytes still somewhat lowered the discharging capacity. Besides, several elements are commonly substituted for nickel in the solid state to improve the electrochemical behavior of

nickel oxide electrodes. For Ni/MH or Ni/Cd batteries, the addition of Zn or Cd into nickel hydroxide prevented the volume expansion or swelling of nickel oxide electrodes effectively, prolonging the cycle life [5–8]. Tessier et al. obtained zinc-substituted nickel hydroxides by precipitation [9]. It was shown that an increase of the zinc amount in nickel hydroxides tends to prevent the formation of the γ-phase and to increase the cell voltage during electrochemical cycling. Further, the structural and textural evolution of zinc-substituted α- and β(II)-nickel hydroxides was also investigated by Tessier [10]. It was shown that since a large amount of zinc was lost during strong oxidation of β(II)- and α-phases, octahedral vacancies must remain within the slabs of the resulting β-phase. Their presence leaded to a peculiar charge compensation. Therefore, up to now, one question has been remained open concerning the effects of zinc, added to the electrolyte, on the stability of nickel oxide electrodes during a cell cycling.

It is demonstrated that cobalt and lithium additives improve the charge storage reaction and cycle life of nickel oxide electrodes. Thereby, in our present work, sintered nickel oxide electrodes doped with cobalt and concentrated KOH electrolytes containing $20 \, g \, L^{-1}$ LiOH were applied to deal with the influence of zinc ions in electrolytes on the stability of nickel oxide electrodes during a cell cycling. At the same time, the cycling stability of nickel oxide electrodes was explored directly according to changes in charge–discharge curves with cycling number.

2. Experimental

Reagent grade KOH and ZnO were used and the KOH solutions containing ZnO were prepared using deionised water.

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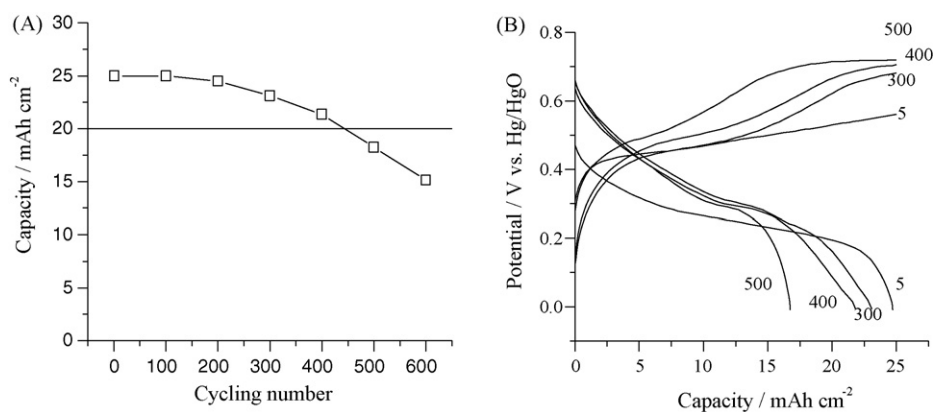E-mail address: wen_yuehua@126.com (Y.-H. Wen).

Fig. 1. Discharge capacity (A) and galvanostatic charge/discharge curves (B) of the nickel oxide electrode as a function of cycling number in a solution containing 8 M KOH + 20 g L^{-1} LiOH.

The charge–discharge cycling experiments of nickel oxide electrodes were carried out in a two-electrode cell. A sintered nickel oxide (thickness: 0.70 mm, area capacity: 25 mAh cm^{-2}) doped with cobalt was employed as the positive electrode. A cadmium electrode was employed as the negative electrode, its capacity strongly exceeding that of the positive electrode, so as not to limit the cycling of the battery. The size of the positive electrode is 2.0 cm × 2.0 cm. Before test, the sintered nickel oxide electrodes were pre-activated [5,7]. The galvanostatic charge–discharge tests were performed with a battery test system CT2000A (Jinnuo Wuhan Corp., China). The applied current density was 20 mA cm^{-2}.

The capacity of sintered nickel oxide electrodes was determined one time per 100 charge–discharge cycles. This test was performed in a three-electrode cell, which comprised a sintered nickel electrode as working electrode, with a sintered cadmium and Hg/HgO as counter and reference electrodes. In a galvanostatic mode, the working electrode was charged to the rated capacity (25 mAh cm^{-2}), and then discharged down to 0.0 V vs. Hg/HgO cut-off. This single electrode charge–discharge experiment was conducted using an electrochemical station (Solartron 1280Z).

All above experiments were performed at room temperature and under the conditions of magnetic stirring.

After charge–discharge cycles, the nickel oxide electrodes were rinsed in concentrated KOH solutions and washed fully with deionised water. Zinc elemental analysis of the electrodes rinsed was carried out by X-ray photoelectron spectroscopy (XPS) by using a PHI 5300 X-ray Photoelectron Spectrometer. The XPS analysis was performed with a monochromatic Mg Kα source operating at 250 W with a pass energy of 20 eV. To reveal bulk electrode properties, the powder X-ray diffractometry (D/max2500VB2+/PC X, Rigaku) was used to characterize the nickel oxide electrodes rinsed.

3. Results and discussion

Due to a good solubility of ZnO in concentrated KOH solutions, a 8 M KOH solution was selected as the electrolyte. In order to compare with the effect of zinc in electrolytes on the cycling stability of nickel oxide electrodes, firstly the cycling performance of nickel oxide electrodes in 8 M KOH solutions with no zinc present was investigated. Fig. 1 shows the variation of the discharge capacity of nickel oxide electrodes as a function of cycling number in 8 M KOH + 20 g L^{-1} LiOH electrolytes and its corresponding charge/discharge curves. As can be seen, with an increase in the cycling number, the discharge capacity of the electrode decays more rapidly during the cell cycling. The electrode just

retains 80% of its initial capacity after 400 charge–discharge cycles. Correspondingly, it is shown in Fig. 1B that with the increase of cycling number, the charging potential is continually shifted to more positive values. As a result, a high charging potential plateau appears close to the end of charge. Moreover, this plateau becomes longer with the increase of cycling number. It means that the overcharge and oxygen evolution take place on the electrodes, causing a mechanical deformation which results in an irreversible damage to nickel oxide electrodes [5–7]. After 400 charge/discharge cycles, a charge-of-end potential plateau starts to appear. Up to 500 charge/discharge cycles, a long charge-of-end potential plateau could be observed, indicating that oxygen evolution occurs so seriously that the capacity of the electrode drops dramatically.

Variation of the discharge capacity of nickel oxide electrodes with cycling number in electrolytes containing ZnO with different concentrations is listed in Table 1. It is shown that almost no decline in the discharging capacity of the electrodes is presented after 400 charge–discharge cycles. In the electrolytes with 0.3 M ZnO, the electrode only exhibits a decay of around 5% in the discharge capacity after 500 charge–discharge cycles. The excellent cycling stability is achieved for the electrode in the electrolyte with 0.7 M ZnO. Compared with the cycling performance of nickel oxide electrodes in the absence of zinc, the cycling stability of the nickel oxide electrodes are enhanced remarkably attributed to the addition of ZnO into electrolytes. It suggests that the cycle life of nickel oxide electrodes can also be prolonged by zinc ions added into electrolytes. Fig. 2 gives the corresponding charge/discharge curve vs. cycling number of nickel oxide electrodes in electrolytes containing 0.4 M ZnO and 0.6 M ZnO, respectively. It can be seen that in electrolytes with 0.4 M ZnO, although the charging voltage rises obviously with the increase of cycling number, no charge-of-end potential plateau appears after 500 charge/discharge cycles. As the concentration of ZnO in electrolytes is increased to 0.6 M, the charging curves are nearly overlapped even if the cycling

Table 1
Variation of the discharge capacity of nickel oxide electrodes with cycling number in electrolytes containing ZnO with different concentrations.

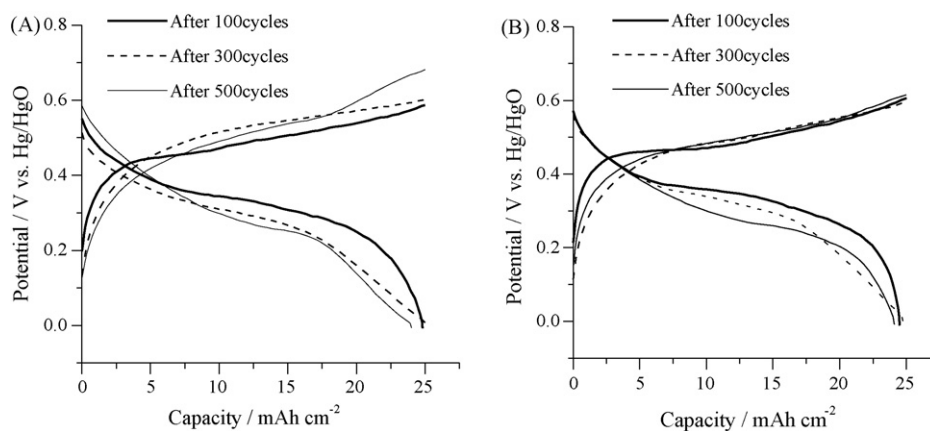| Cycling number	Discharge capacity (mAh)				
	0.3 M ZnO	0.4 M ZnO	0.5 M ZnO	0.6 M ZnO	0.7 M ZnO
5	100	100	100	100	100
100	100	99.31	98.19	97.75	98.02
200	99.23	98.52	98.91	98.72	96.83
300	100	100	99.44	99.67	99.34
400	99.24	99.17	99.22	99.17	99.32
500	95.67	96.07	98.45	96.40	99.88

Fig. 2. Galvanostatic charge/discharge curve vs. cycling number of nickel oxide electrodes in 8 M KOH + 20 g/L LiOH electrolytes containing 0.4 M ZnO (A) and 0.6 M ZnO (B), respectively. Current density: 20 mA cm^{-2}.

number reaches 500. Moreover, compared with the electrolytes without zinc present, the charging voltage is decreased to a certain degree owing to the addition of ZnO in electrolytes. The higher the concentration of ZnO in electrolytes, the more significantly decreases the charging voltage. This indicates that the addition of ZnO in electrolytes attenuates considerably the extent of oxygen evolution and inhibits the transformation of the β(III)-nickel hydroxides to the γ-one during a cell cycling.

As should be expected, a certain amount of zinc ions may be incorporated in the active material, nickel hydroxide lattice and consequently formation of a composite where the zinc plays a role as an additive during charge and discharge. It could result in some stacking faults within the active materials. Fig. 3 presents the XPS patterns of the nickel oxide electrodes before and after 100 charge discharge cycles. Compared with the original nickel oxide electrode, a significant zinc peak appears on the XPS patterns of nickel oxide electrodes after 100 charge–discharge cycles in KOH electrolytes containing either 0.3 M ZnO or 0.6 M ZnO. XRD spectra in Fig. 4 show that no typical diffraction peaks of pure Zn or ZnO are observed. Also, there is no obvious change in structure of nickel oxide electrodes even after 400 charge–discharge cycles in KOH electrolytes containing ZnO. This may be attributed to the intercalation of zinc ions in the Ni(OH)$_2$ lattice. Thus, the presence of zinc and its incorporation in the matrix of nickel hydroxide is confirmed. This suggests that zinc ions can also insert into the slabs of nickel hydroxides from a solution, preventing the formation of γ-phase and overcharge.
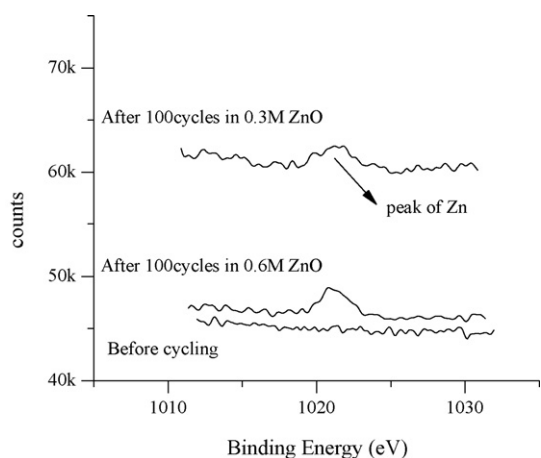

Fig. 3. XPS (Zn 2p3) patterns of nickel oxide electrodes in electrolytes containing ZnO with different concentrations before and after charge–discharge cycles.
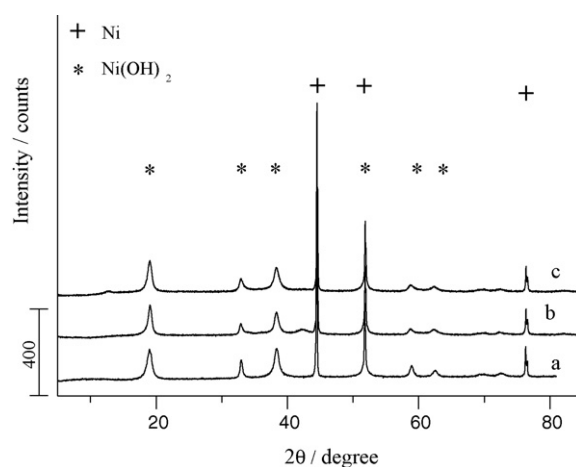

Fig. 4. XRD spectra of nickel oxide electrodes in electrolytes containing ZnO with different concentrations before and after charge–discharge cycles, (a) before cycling; (b) after 400 cycles in 0.3 M ZnO; (c) after 400 cycles in 0.6 M ZnO.

4. Conclusion

Effect of zinc ions in electrolytes on the cycling stability of nickel oxide electrodes for the zinc/nickel single flow battery was investigated. It is shown that the addition of ZnO in KOH solutions causes a significant enhancement in the cycling performance of nickel oxide electrodes. In electrolytes with no zinc present, a reduction in the discharge capacity of the electrodes is accelerated continuously with the increase of cycling number. After 500 charge/discharge cycles, a long end-of-charge potential plateau could be observed, indicating the occurrence of serious oxygen evolution. In electrolytes containing ZnO, the discharge capacity of the electrodes basically does not decay even after 500 charge–discharge cycles. With an increase in the ZnO concentration, the charging voltage drops to some extent and a change in the charging curve vs. cycling number is restrained gradually. This may result from the intercalation of zinc ions in electrolytes into the nickel hydroxide lattice during the cell cycling, preventing the formation of γ-type nickel hydroxides and overcharge.

References

[1] C. Ponce de Leĭon, A. Frĭias-Ferrer, J. Gonzĭalez-Garcĭıa, J. Power Sources 160 (2006) 716–732.
[2] J. Cheng, L. Zhang, Y.-S. Yang, Y.-H. Wen, G.-P. Cao, Electrochem. Commun. 9 (2007) 2639–2642.
[3] L. Zhang, J. Cheng, Y.-S. Yang, Y.-H. Wen, J. Power Sources 179 (2008) 381–387.
[4] I. Krejci, P. Vanysek, J. Power Sources 47 (1994) 79–88.
[5] X.X. Yuan, M.D. Wang, Chin. J. Power Sources 24 (4) (2000) 192–196.
[6] R. Barnard, C.F. Randell, F.L. Tye, J. Appl. Electrochem. 10 (1980) 109.
[7] J.Y. Xie, S.Q. Wang, B.J. Xia, Q.S. Zhang, Chin. J. Power Sources 21 (1) (1997) 22–27.
[8] M. Dixit, P.V. Kamath, J. Gopalakrishnan, J. Electrochem. Soc. 146 (1) (1999) 79–82.
[9] C. Tessier, L. Guerlou-Demourgues, C. Faure, Solid State Ionics 133 (2000) 11–23.
[10] C. Tessier, L. Guerlou-Demourgues, B. Delatouche, J. Power Sources 102 (2001) 105–111.