

Short communication

# Influence of surface modification with $\text{Sn}_6\text{O}_4(\text{OH})_4$ on electrochemical performance of ZnO in Zn/Ni secondary cells

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## Abstract

The surface-modified ZnO by  $\text{Sn}_6\text{O}_4(\text{OH})_4$  was prepared by a simple hydrolyzation process and the influence of  $\text{Sn}_6\text{O}_4(\text{OH})_4$  on electrochemical performance of ZnO was investigated by charge/discharge cycling test, slow rate cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Compared with the unmodified ZnO, the  $\text{Sn}_6\text{O}_4(\text{OH})_4$ -modified ZnO showed improved electrochemical properties, such as superior electrochemical cycle stability, higher discharge capacity and utilization ratio. The surface modification could suppress the dissolution of ZnO in the alkaline electrolyte and maintain the electrochemical activity of ZnO. When the  $\text{Sn}_6\text{O}_4(\text{OH})_4$  content reached 27 wt.%, the discharge capacity of the modified ZnO hardly declined over 80 cycling test, the average utilization ratio could reach 98.5%, and the modified ZnO electrodes had no obvious weight loss after the cycling tests. However, the charge/discharge plateau voltage with the  $\text{Sn}_6\text{O}_4(\text{OH})_4$ -modified ZnO slightly decreased. For the modified ZnO electrodes, two anodic peaks occurred in the CV curves, and the charge transfer resistance increased from the EIS results, both of which were ascribed to the suppressive effect of surface modification on the electrochemical reactions.

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**Keywords:** ZnO; Surface modification;  $\text{Sn}_6\text{O}_4(\text{OH})_4$ ; Zn/Ni secondary cells

## 1. Introduction

The Zn/Ni electrochemical system is a promising candidate for alkaline storage cells. It exhibits good cell performance: high energy density, high power density, high open-circuit-voltage, low cost and low toxicity. However, cycle life of the system remains relatively low due to shape change of the Zn electrode, Zn dendrite growth and Zn corrosion. Thereby, the Zn/Ni secondary cells have not received serious consideration for application. So far, many attempts have been undertaken to overcome these difficulties and still the problems remain elusive. Various electrode additives, such as  $\text{Ca}(\text{OH})_2$  [1,2],  $\text{Bi}_2\text{O}_3$  [3],  $\text{TiO}_2$  [4],  $\text{PbO}$  [5],  $\text{SnO}_2$  [6], etc., were adopted to minimize these problems. The touted beneficial effects of the additives include: suppression of  $\text{H}_2$  formation, reduction of Zn species solubility, increased electronic conductivity of the ZnO electrode and more-uniform current density distribution [7–11]. Nevertheless, most works focused on the physical mixture of ZnO and

additives. There are two disadvantages about the physical mixture process: (1) the efficiency of the additives is relatively low because it is difficult to achieve sufficient contact between ZnO and additives by the simple physical mixture and (2) the dissolution of ZnO in the alkaline electrolyte is still not enough suppressed. It should be pointed out that the essential reason for the short cycle life of secondary Zn based cells is just the dissolution of ZnO in the alkaline electrolyte. Therefore, the physical mixture of ZnO and the additives is not the most efficient way to utilize the additives.

The surface modification technique has been widely investigated and considered as an alternative method for improvement of the electrochemical performance of electrode materials in lots of electrochemical systems, e.g. Li-ion cell [12,13], Ni-MH cell [14,15]. This method consists in surface treatment of electrode materials with various substances which do not participate in the electrochemical reaction. It has been shown that surface-modified electrode materials display higher capacity retention and cell lifetime [12–15]. It is a pity that similar investigation is seldom carried out in Zn/Ni secondary cells. Compounds of Sn are the important additives for the ZnO electrode and they can suppress  $\text{H}_2$  formation, decrease self-discharge and shape

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change, improve cell lifetimes. The compounds of Sn are usually added to the ZnO electrode by a simple physical mixture method. Our team recently found a very simple process to modify a compound of Sn on the surface of ZnO particles [16]. After surface modification, the electrochemical performance of ZnO showed significant improvements. Nevertheless, the effect of surface modification on electrochemical performance of ZnO was not yet investigated sufficiently and the mechanism that explained the effect was also absent. In this present work, the modified ZnO with different amounts of surface addition was prepared by the same process. The effect of surface modification on electrochemical performance of ZnO was studied in detail. Especially, the mechanism for electrochemical behavior of surface-modified ZnO was discussed.

## 2. Experimental

Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>-modified ZnO was prepared as follows. The starting materials were commercial zinc oxide and tin chloride dihydrate. 0.5 g, 1.0 g, 2.0 g and 2.5 g SnCl<sub>2</sub>·2H<sub>2</sub>O was dissolved in the concentrated HCl solution, respectively, and then diluted into 250 ml solution with distilled water. ZnO was added into the solution under constant mechanical stirring and ultrasonic vibration. After 10 min, the powder was filtrated and washed with distilled water, dried at 90 °C for 60 min in vacuum. The as-prepared powder was then characterized using transmission electron microscopy (TEM, JEM200CX; HRTEM, JEM2010), X-ray diffractometer (XRD, D/max-rA). The Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> content was calculated according to the results of energy dispersive X-ray spectrum (EDS, GENESIS4000).

The ZnO electrodes were prepared by incorporating slurries containing as-prepared ZnO, CMC and PTFE to a Ni foam substrate (2 cm × 2 cm in size). The weight ratio of ZnO, CMC and PTFE was 80:15:5. The theoretic capacity of each ZnO electrode was about 100 mAh. The ZnO electrodes were dried at 50 °C and pressed to a thickness of 0.3 mm for improving the adherence of the electrode material onto the Ni foam substrate. For comparison, the unmodified ZnO electrodes with the same composition were prepared, too. A solution of 4 M KOH, 1.6 M K<sub>2</sub>BO<sub>3</sub>, 0.9 M KF and 0.1 M LiOH, saturated with ZnO, was used as the electrolyte. Separators were used in the Zn/Ni cell to retard Zn dendrite penetration and also to prevent the electrodes from shorting. Cellulose triacetate microporous membranes were chosen to enwrap ZnO electrodes for above purposes. The ZnO electrode and Ni(OH)<sub>2</sub> electrode were assembled into a cell and placed in a simple cell container made of perspex. The capacity of the Ni(OH)<sub>2</sub> electrode was far more than that of the ZnO electrode.

The galvanostatic charge–discharge tests were performed on a DC-5 battery-testing instrument. During the cycling procedure, the cells were charged at 0.1 C for 10.5 h and discharged at 0.2 C down to 1.2 V cutoff voltage. At the end of cycling tests, some ZnO electrodes were taken out from Zn/Ni cells to evaluate the weight loss of the ZnO electrodes. At the sixth cycling tests, some Zn/Ni cells discharged down to the 1.0 V (the potential of the ZnO electrode was –0.7 V). The ZnO electrodes were taken out, washed repeatedly in distilled water, rinsed with ethanol, air-dried and then analyzed by XRD.

Cyclic voltammetry was carried out using an electrochemical workstation (CHI640B, China) at a scanning rate of 0.1 mV s<sup>–1</sup> shifting from –0.8 V to –1.45 V. A three electrode cell assembly was used in cyclic voltammetry with a Hg/HgO electrode as the reference electrode, a pasted Ni(OH)<sub>2</sub> electrode as the counter electrode and a ZnO electrode as the working electrode. Electrochemical impedance spectroscopy (EIS) measurements were performed on CHI640B, too. The frequency range was between 0.01 Hz and 100 KHz. The amplitude of AC signal was 10 mV. The cell assembly used was the same as that in cyclic voltammetry.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of the as-prepared ZnO powder. It can be seen that the sample only contained two phases, ZnO and Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> after the treatment with SnCl<sub>2</sub> solution. Fig. 2 displays the morphologies of the unmodified ZnO and surface-modified ZnO. From Fig. 2a, the surface of the unmodified ZnO particles is smooth and clear. After the ZnO treated in the SnCl<sub>2</sub> solution, lots of nanosized particles appear on the surface of ZnO particles and the average particle size is about 15 nm, as shown in Fig. 2b. According to the XRD results, the nanoparticles on ZnO particles must be Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>. Fig. 2c shows the HRTEM image of the selected area in Fig. 2b. The lattice image can be seen on some Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> nanoparticles and an amorphous layer with the thickness of about 1 nm appears on the exterior surface of Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> nanoparticles. The Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> content in the modified ZnO in Fig. 2b is 22 wt.% and the corresponding amount of SnCl<sub>2</sub> is 2.0 g. In the present work, the modified ZnO with various Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> content is prepared by changing the amount of SnCl<sub>2</sub> in the process. Fig. 3 shows the relationship between Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> content and amount of SnCl<sub>2</sub>. With increasing the amount of SnCl<sub>2</sub>, the Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> content approximately linearly rises.

Fig. 4 presents the variation of specific discharge capacity with cycle number of the unmodified ZnO and Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>-

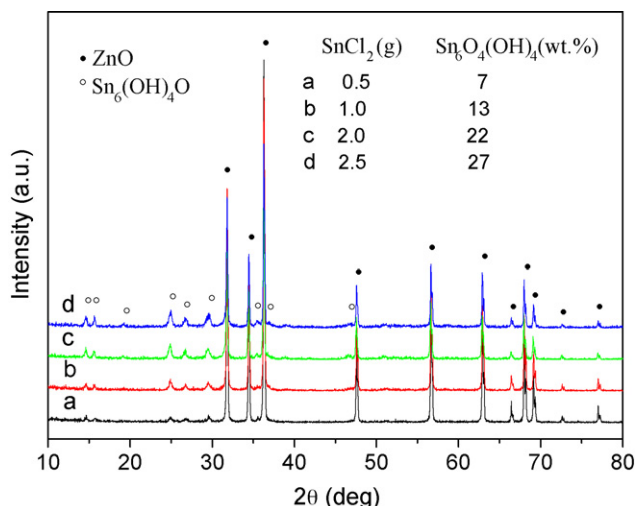


Fig. 1. XRD patterns of as-prepared ZnO powders.

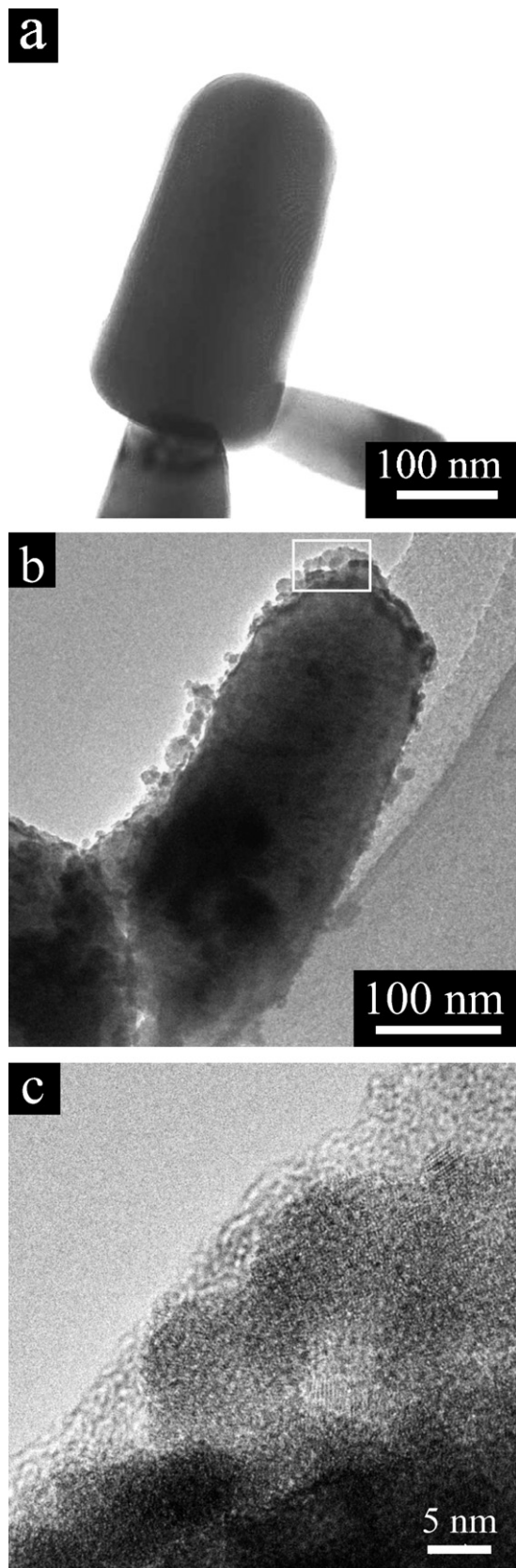


Fig. 2. TEM images of: (a) unmodified ZnO, (b) surface-modified ZnO with 22 wt.%  $\text{Sn}_6\text{O}_4(\text{OH})_4$  and (c) HRTEM image of the selected area in (b).

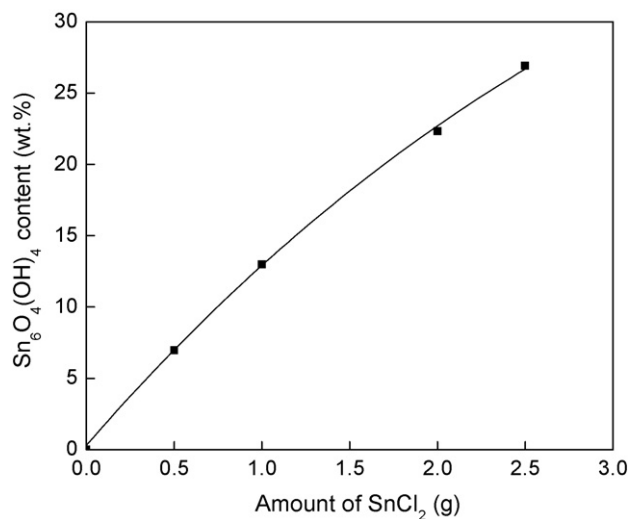


Fig. 3. Relation of  $\text{Sn}_6\text{O}_4(\text{OH})_4$  content in surface-modified ZnO to the amount of  $\text{SnCl}_2$  in the preparation process.

modified ZnO. For the unmodified ZnO, the discharge capacity declines rapidly after 20 cycles. At the 50th cycle, the discharge capacity decreases to  $172 \text{ mAh g}^{-1}$  with retention of 26%. The electrochemical stability of  $\text{Sn}_6\text{O}_4(\text{OH})_4$ -modified ZnO is remarkably superior to that of the unmodified ZnO. After the 30th cycle, the discharge capacity of the modified ZnO with 7 wt.%  $\text{Sn}_6\text{O}_4(\text{OH})_4$  is always  $200 \text{ mAh g}^{-1}$  higher than that of unmodified ZnO (the calculation of discharge capacity excludes the mass of  $\text{Sn}_6\text{O}_4(\text{OH})_4$ ). The modified ZnO with a higher  $\text{Sn}_6\text{O}_4(\text{OH})_4$  content delivers a higher discharge capacity. The discharge capacity of the modified ZnO with 27 wt.%  $\text{Sn}_6\text{O}_4(\text{OH})_4$  is the most stable throughout 80 cycles with capacity retention rate of 98%. The weight of each ZnO electrode was examined at the end of cycling test. The weight loss of the unmodified ZnO electrode was 64%. For the surface-modified ZnO with 7 wt.%  $\text{Sn}_6\text{O}_4(\text{OH})_4$ , the weight loss of electrode was just 8%. The modified ZnO electrodes with more than 7 wt.%  $\text{Sn}_6\text{O}_4(\text{OH})_4$  did not observe the obvious weight loss. The above

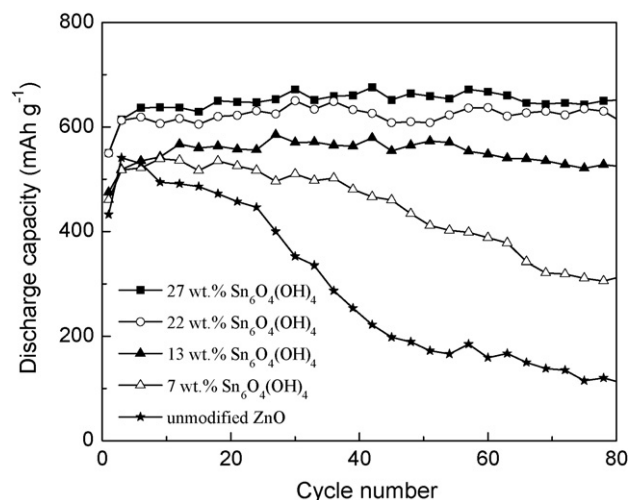


Fig. 4. Electrochemical cycle behavior of the surface-modified ZnO and unmodified ZnO.

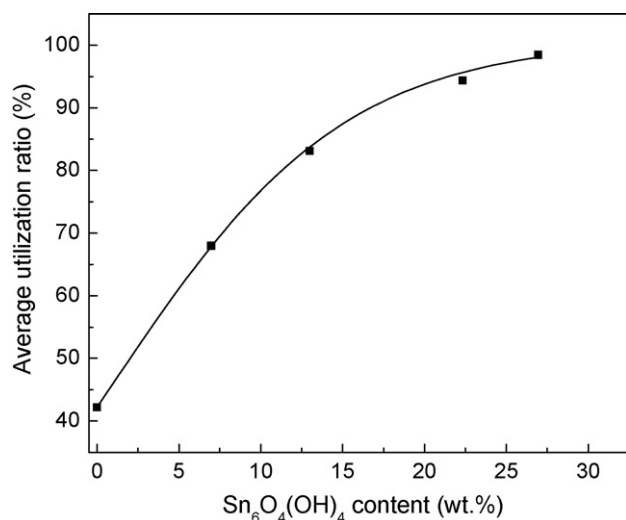


Fig. 5. Variation of average utilization ratio of the surface-modified ZnO and Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> content.

results demonstrate that Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>-modified ZnO has a good reversible cycling behavior. The capacity fade of ZnO is generally attributed to (i) high solubility of ZnO in the concentrated KOH electrolyte and (ii) rapid electrochemical kinetics [17]. Hence, any approach to improve the capacity retention of ZnO should be directed to the retainment of ZnO at the electrode. For the modified ZnO, Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> on the surface of ZnO particles may prohibit the direct contact of the active core material with the alkaline electrolyte, and further suppress the dissolution of ZnO in the electrolyte. Since the ZnO is retained at the electrode, the electrochemical stability is accordingly improved. Fig. 5 shows the variation of average utilization ratio (average discharge capacity/theoretic capacity (659 mAh g<sup>-1</sup>)) of the modified ZnO and the Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> content. The average utilization ratio of the unmodified ZnO is only 42%. While the modified ZnO with 7 wt.% Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> has an average utilization ratio 68%. When the Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> content exceeds 18 wt.%, the average utilization of the modified ZnO can exceed 90%. It can be concluded that the surface modification with Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> is an effective way to improve the electrochemical stability and utilization of ZnO.

The typical charge/discharge curves of Zn/Ni cells with the modified and unmodified ZnO tested at the 12th cycle are displayed in Fig. 6. For the Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> modified ZnO, the Zn/Ni cells show more lower charge plateau voltage and discharge plateau voltage. When the Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> content reaches 27 wt.%, the charge and discharge plateau voltages of the corresponding Zn/Ni cells are 29 mV, 79 mV lower than those of the unmodified ZnO, respectively, and both the lowest in all tested cells. This decrease in plateau voltage indicates that surface modification has an impeditive effect on the electrochemical reactions of ZnO/Zn. The impeditive effect should be associated with the decrease in the direct contact between core ZnO with the electrolyte. Although the plateau voltage decreases, the discharge capacity of ZnO is not influenced. It suggests that surface modification only influences electrochemical reaction rate and leads to a lower electrochemical kinetics. This decrease in elec-

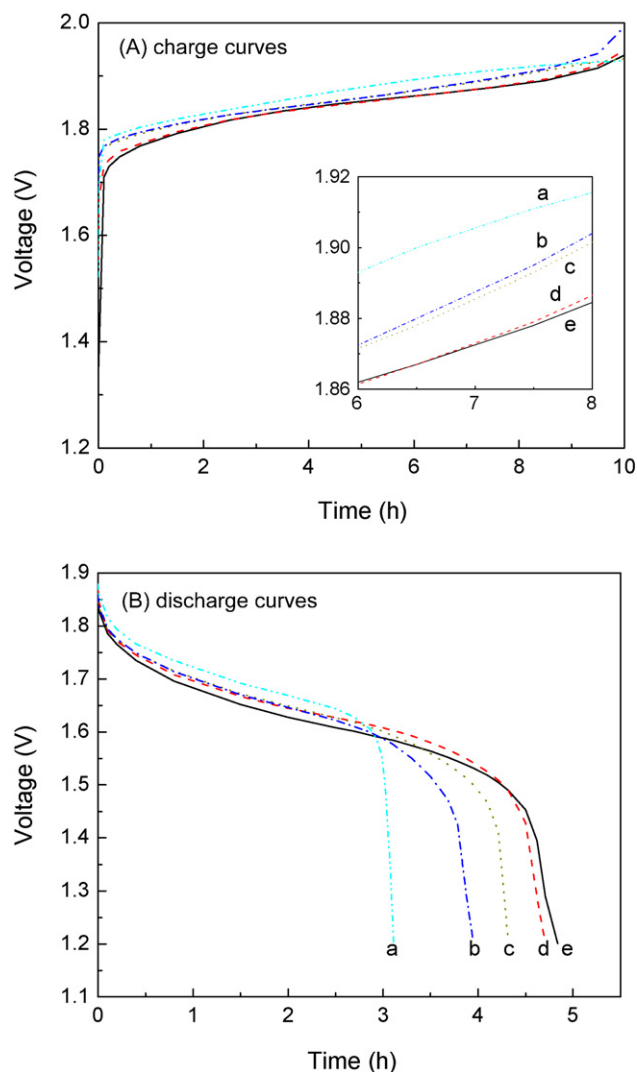


Fig. 6. Typical charge/discharge curves of Zn/Ni cells tested at the 12th cycle: (a) unmodified ZnO, (b) 7 wt.% Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>, (c) 13 wt.% Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>, (d) 22 wt.% Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> and (e) 27 wt.% Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>.

trochemical kinetics is a favorable phenomenon for improving electrochemical stability of ZnO.

Fig. 7 shows the XRD patterns of the surface-modified ZnO electrode after the sixth charge–discharge cycling test. In this case, the Sn appeared, while Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> disappeared. For active material and other substance in the ZnO electrode, a charge process is a reduction process and a discharge process is an oxidation process. After Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> is reduced into Sn at charging, Sn is not oxidized at discharging, as shown in Fig. 7. That is to say, the surface modifying addition all the time exists as the form of Sn metal after Sn<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> is reduced to Sn metal. Sn metal modified on the ZnO particles can produce a good electrical contact between ZnO/ZnO and ZnO/Ni foam, facilitate electron transfer in the ZnO electrodes; serve as a substrate that promotes the formation of compact Zn deposits via electro-deposition; suppresses H<sub>2</sub> formation and decreases self-discharge. The Ni peaks in Fig. 7 are derived from the foam Ni substrate.

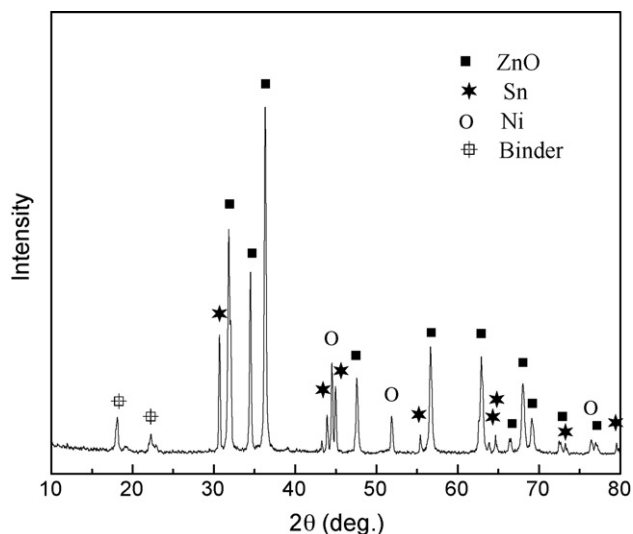


Fig. 7. XRD pattern of the surface-modified ZnO electrode with 13 wt.%  $\text{Sn}_6\text{O}_4(\text{OH})_4$  discharged to down to the 1.0 V cut-off voltage (corresponding potential of the ZnO electrode is  $-0.7$  V).

In order to further understand the influence of surface modification on electrochemical reactions of ZnO, cyclic voltammetry studies are performed and cyclic voltammograms recording the unmodified ZnO as well as  $\text{Sn}_6\text{O}_4(\text{OH})_4$ -modified ZnO are presented in Fig. 8. The characteristic of the cathodic peaks in the cyclic voltammetry lies in the fact that any modified ZnO shows lower inflexion current than the unmodified ZnO, indicating that the reduction reaction of the modified ZnO is suppressed to some extent. The two anodic peaks are an important characteristic for anodic process, which presents two processes of anodic dissolution occurring at the ZnO electrodes. Overlap of two anodic peaks indicates that both processes might proceed simultaneously. It has been clearly established that the reaction at the equilibrium potential leads to the zincate ion,  $\text{Zn}(\text{OH})_4^{2-}$ , by a probable three-step process represented by the over-all reaction [18,19]

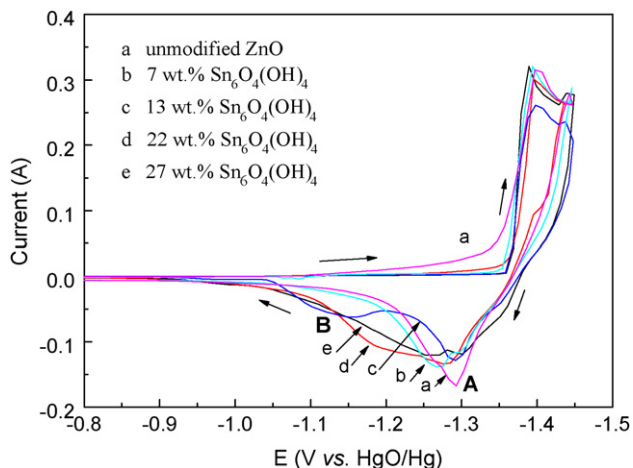
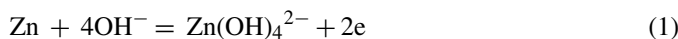
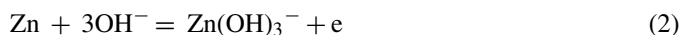


Fig. 8. Slow scanned cyclic voltammetry curves of the surface-modified ZnO and unmodified ZnO with a scanning rate of  $0.1 \text{ mV s}^{-1}$ .

and this reaction must be the one occurring in the first peak A.

The second peak B does not appear at the unmodified ZnO electrode, indicating that the peak B should be associated with surface modification. The peak B occurs when the reaction (1) has been proceeding for some time at a lower overpotential and consequently when there has been an inadequate contact between ZnO and  $\text{OH}^-$  ion from the reaction layer. The two anodic peaks caused by the inadequate contact were ever reported [18,19]. A probable reaction corresponding to this peak B is



After the bare region on the modified ZnO first reacts according to Eq. (1), the core ZnO covered with  $\text{Sn}_6\text{O}_4(\text{OH})_4$  and reacted region cannot contact  $\text{OH}^-$  ion enough, and therefore, can only react according to Eq. (2). The electrochemical reaction (2) occurs at a higher potential than the reaction (1), which can result in the decrease in discharge voltage of Zn/Ni cells. With the increase of the  $\text{Sn}_6\text{O}_4(\text{OH})_4$  content, the covered region on ZnO increases, the peak B goes more remarkable, and the peak potential of the peak B shifts in the more negative direction. When the amount of  $\text{Sn}_6\text{O}_4(\text{OH})_4$  is 27 wt.%, both the intensity and potential of peak B approximate to those of peak A.

AC impedance measurements are carried out to investigate the influence of surface modification on the resistance. Fig. 9 shows the Nyquist plots of the electrode with the modified and unmodified ZnO at 100% state-of-charging. It can be seen that the AC Nyquist plots contain one depressed semicircle and one slope. The semicircle in the high frequency region is attributed to the charge transfer resistance, and the slope in the low frequency region is caused by the diffusion of zincate in the ZnO electrode. It can be seen from Fig. 9 that surface modification increases the impedance of the ZnO electrode and the modified ZnO with 27 wt.%  $\text{Sn}_6\text{O}_4(\text{OH})_4$  has the largest impedance among these electrodes. The equivalent circuit used to fit the impedance spectra is also shown in Fig. 9, where Q designates

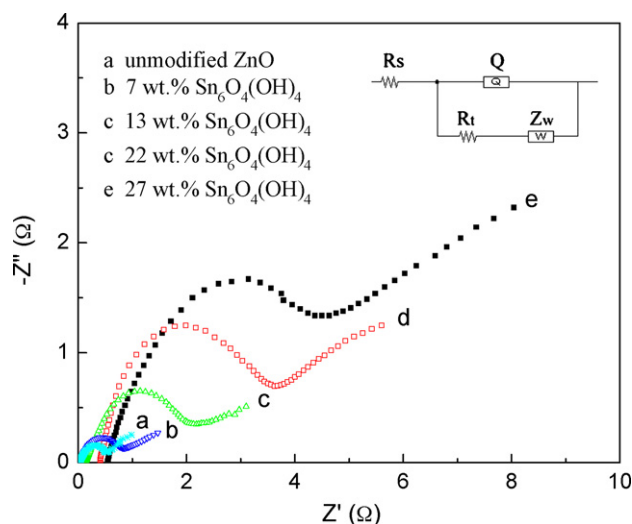


Fig. 9. Nyquist plots of the ZnO electrodes with the modified and unmodified ZnO at 100% state-of-charging and equivalent circuit for the ZnO electrode.

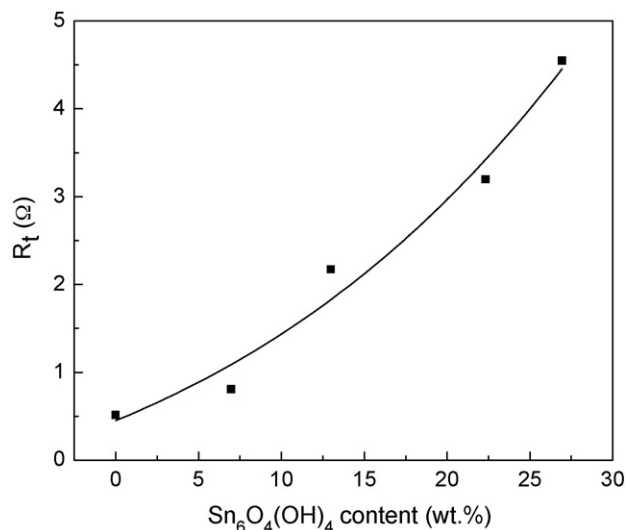


Fig. 10. Plot of charge-transfer resistance ( $R_t$ ) of the ZnO electrodes against  $\text{Sn}_6\text{O}_4(\text{OH})_4$  content.

the constant-phase element,  $R_s$  is the total ohmic resistance, which includes the resistance of the electrolyte, current collector, leads, etc.,  $R_t$  is the charge-transfer resistance and  $Z_w$  is the Warburg impedance.

Fig. 10 compares the simulation results of charge-transfer resistance  $R_t$  of the electrodes with the modified and unmodified ZnO. After surface modification, the charge transfer resistance  $R_t$  increases. A larger  $R_t$  means that the electrochemical reaction is more difficult.  $\text{Sn}_6\text{O}_4(\text{OH})_4$  modified on ZnO decreases the direct contact between the active core ZnO with the electrolyte, and suppresses the charge transfer between core ZnO and the electrolyte, thereby leads to this increase in  $R_t$ . The higher the  $\text{Sn}_6\text{O}_4(\text{OH})_4$  content, the larger the covered ZnO surface, the more remarkable the suppressive effect, the higher the charge transfer resistance. For example, the  $R_t$  value of the modified ZnO electrode with 27 wt.%  $\text{Sn}_6\text{O}_4(\text{OH})_4$  is 4.5  $\Omega$ , and the  $R_t$  value of the modified ZnO electrode with 13.0 wt.%  $\text{Sn}_6\text{O}_4(\text{OH})_4$  is 2.1  $\Omega$ , much more than the  $R_t$  value (0.5  $\Omega$ ) of the unmodified ZnO. The increase in  $R_t$  value can explain the decrease in charge/discharge plateau voltage of Zn/Ni cells. However, the discharge capacity of the modified ZnO does not decline on the cycling test. It is the reason that  $\text{Sn}_6\text{O}_4(\text{OH})_4$  can also simultaneously suppress the dissolution of ZnO in the electrolyte. In comparison with the electrochemical performances of the modified and unmodified ZnO, it can be concluded that the suppressive effect on the dissolution is more significant than

the suppressive effect on the electrochemical reaction. Over all, the suppressive effect of  $\text{Sn}_6\text{O}_4(\text{OH})_4$  is beneficial to a certain extent.

#### 4. Conclusions

Surface modification with  $\text{Sn}_6\text{O}_4(\text{OH})_4$  is a new effective approach to utilize the electrode additives and improve the electrochemical performance of ZnO. With increasing the  $\text{Sn}_6\text{O}_4(\text{OH})_4$  content, the electrochemical cycle stability of ZnO is enhanced, the average utilization ratio of ZnO increases, the weight loss of the ZnO electrodes decreases. The improvement in the electrochemical properties results from the fact that  $\text{Sn}_6\text{O}_4(\text{OH})_4$  modified on ZnO decreases the direct contact of core ZnO with electrolyte, therefore, suppresses the dissolution of ZnO in the electrolyte and retains ZnO at the electrode. The  $\text{Sn}_6\text{O}_4(\text{OH})_4$  also changes the discharge reaction mechanism of ZnO and increases the charge transfer resistance of the ZnO electrode, as analyzed from the cyclic voltammogram and EIS results. Thereby, the charge/discharge plateau voltage of the modified ZnO reduces in comparison with those of the unmodified ZnO.

#### References

- [1] D. Coates, E. Ferreira, A. Charkey, J. Power Sources 65 (1997) 109.
- [2] J.X. Yu, H. Yang, X.P. Ai, X.M. Zhu, J. Power Sources 103 (2001) 93.
- [3] J. McBreen, E. Gannon, J. Power Sources 15 (1985) 169.
- [4] R. Shivkumar, G. Paruthimal Kalaignan, T. Vasudevan, J. Power Sources 75 (1998) 90.
- [5] R. Shivkumar, G. Paruthimal Kalaignan, T. Vasudevan, J. Power Sources 55 (1995) 53.
- [6] J. McBreen, E. Gannon, Electrochim. Acta 26 (1981) 1439.
- [7] J. Jindra, J. Power Sources 66 (1997) 15.
- [8] Y.F. Yuan, J.P. Tu, H.M. Wu, Y.Z. Yang, D.Q. Shi, X.B. Zhao, J. Power Sources 159 (2006) 357.
- [9] R.E.F. Einerhand, W. Visscher, J. Electrochem. Soc. 138 (1) (1991) 7.
- [10] K. Bass, P.J. Mitchell, G.D. Wilcox, J. Smith, J. Power Sources 35 (1991) 333.
- [11] J. Jindra, J. Power Sources 88 (2000) 202.
- [12] S.S. Zhang, K. Xu, T.R. Jow, J. Power Sources 129 (2004) 275.
- [13] P. Suresh, A.K. Shukla, N. Munichandraiah, Mater. Lett. 59 (2005) 953.
- [14] F. Feng, D.O. Northwood, Int. J. Hydrogen Energy 29 (2004) 955.
- [15] Z.R. Chang, H.W. Tang, J.G. Chen, Electrochem. Commun. 1 (1999) 513.
- [16] Y.F. Yuan, J.P. Tu, H.M. Wu, B. Zhang, X.H. Huang, X.B. Zhao, Electrochem. Commun. 8 (2006) 653.
- [17] F.R. McLarnon, E.J. Cairns, J. Electrochem. Soc. 138 (1991) 645.
- [18] J.P.G. Farr, N.A. Hampson, J. Electroanal. Chem. 13 (1967) 433.
- [19] R.W. Powers, M.W. Breiter, J. Electrochem. Soc. 116 (1969) 719.