Effect of K₂SnO₃ in Electrolyte on the Property of Single-Flow Zinc-Nickel Battery

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The effect of K_2SnO_3 in electrolyte on the single-flow zinc nickel battery was studied in the work. The chemical properties were evaluated using cyclic voltammetry tests. The coulombic efficiency was analyzed by Constant current charge and discharge tests. The morphologies and components of deposited particles were detected by Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectrosopy (EDS). The study found that with the increasing of K_2SnO_3 concentration in electrolyte, the deposition of zinc and tin would inhibit the formation of anode peak and cause the decrease of the dissolution peak. The tin and zinc co-deposited battery with fine and even microstructure was proved in K_2SnO_3 electrolyte. The K_2SnO_3 additive in electrolyte played a role in alleviating the deposition of zinc and promoting the growth of crystal particles. The self-discharge experiment showed that K_2SnO_3 in electrolyte can improve the coulombic efficiency and the battery performance.

Keywords: the single-flow zinc nickel battery, K_2SnO_3 electrolyte, Cyclic voltamme, Self-discharge, Coulombic efficiency

1. INTRODUCTION

Zinc is widely used in various batteries due to their abundant sources, low cost, low toxicity, no environmental pollution, and good reversibility [1] especially in alkaline zinc series batteries [2–5]. Traditional zinc-nickel batteries have disadvantages such as easy passivation of the negative electrode and short-circuit of the battery. The emergence of zinc-nickel single-flow batteries has solved this problem. Compared with zinc-nickel batteries, zinc-nickel single-flow batteries have the advantages of high efficiency, long life and no pollution.

However, the cycle life and the capacity of the battery will be reduced due to the deformation, dendrite growth, corrosion, and passivation during the discharge process of the zinc electrode. In order

to satisfy the demand, it is necessary to improve the performance of the battery. At present, the domestic and foreign studies have found that adding electrode additives to the electrolyte [6-7] could improve the performance of the battery.

Electrolyte additives can also be divided into organic and inorganic additives. The research of inorganic electrolytic additives is mainly focused on finding metal elements (Sn, Bi, In, Cd, Pd) with higher hydrogen evolution overpotential to inhibit the corrosion of zinc electrodes. Y. H. Wen [8] added lead ions and tungstate ions to alkaline zincate and found that these two additives can produce more uniform and dense deposits, thereby reduced the growth of sponge zinc. Yao [9] added Sn^{4+}, Ga^{3+} and Pb^{2+} to the zinc-nickel single-flow battery to investigate the influence on the deposition and dissolution of zinc. The experimental results showed that the additives can be co-deposited with zinc, formed uniform crystal, but Pb^{2+} could pollute the environment.

The organic electrolytic additives could reduce the active sites of corrosion reaction by producing films which were produced by active molecules on the surface of the electrode. In the electrolyte, the electrode made a reducing action [10-11], which increased the activation energy required for the electrode reaction to inhibit the corrosion effect. Liua [12] used DTAB (Dodecyltrimethylammonium Bromide) as an electrolyte additive and found that it can form a protective effect on the surface of the zinc electrode, greatly improving the utilization rate of the zinc electrode. C. J. Lan [13] researched the inhibitory effect of organic additives of quaternary ammonium hydroxide with different structures on zinc dendrites, and investigated the effect of quaternary ammonium salts on the charge-discharge cycle performance of solid secondary batteries. The study had shown that the ability to inhibit zinc dendrites depends on the concentration of additives. Zhan [14] explored the additives in zinc deposition and dissolution by adding NCZA (polyquaternium-2) to the alkaline zincate solution. He found that this additive could have a great inhibition effect on the electrodeposition of zinc and transformed the growth mechanism of zinc into continuous nucleation.

In this study, the influence of the single-flow zinc-nickel battery continued to be investigated, by using cyclic voltammetry, galvanostatic techniques, SEM, EDS and self-discharge. According to previous papers, it can be seen from the above summary that, for the zinc-nickel single-flow battery in alkaline solution, the research on the influence of electrolyte additives on the electrochemical behavior of self-discharge is still very lacking. In this experiment, different concentrations of inorganic electrolyte K_2SnO_3 were added to the electrolyte to characterize the deposition morphology, coulomb efficiency and self-discharge of the zinc anode. The experiment provides a simple and effective way to improve the performance of single-flow zinc-nickel battery.

2. EXPERIMENTAL

2.2 Assemble the battery

As is shown in Fig. 1 the three-electrode system. The anode material was a nickel-plated steel strip, which was cut into 2cm×2cm square pieces, and the metal strip was used as the counter electrode. The sintered nickel sheet was cut into small pieces of 2cm×2.5cm and welded together by a spot welder which was cathode material.

The electrode material needed to be cleaned after the battery was charged. First, in order to eliminate the electrolyte on the surface, the electrode must be cleaned in a beaker filled with distilled water until the distilled water is completely clear. Then wash it with alcohol, and put it into constant temperature oven for drying which can make the drying speed faster. The default temperature was 60°C.

The basic electrolyte was composed of 8mol/L KOH, 0.5mol/L ZnO and 10g/L LiOH which was labelled as S. In addition, the other electrolytes were prepared based on the addition of different concentrations of K_2SnO_3 to the basic electrolyte. These electrolytes were labeled as S+X (x = 0.03, 0.05, 0.08, 0.1 mol/L) according to the weight of dilute potassium.
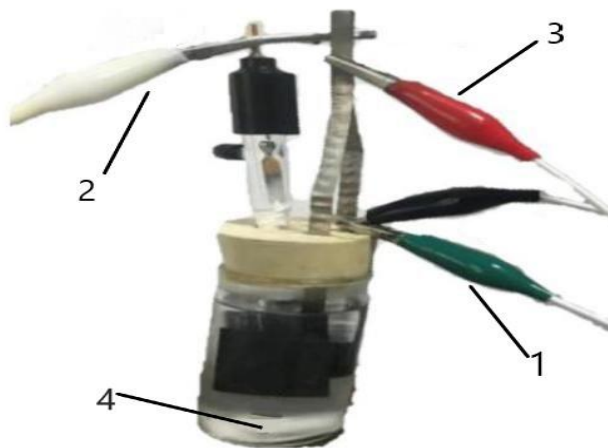

Figure 1. The three-electrode system, (1) anode electrode; (2) reference electrode; (3) cathode electrode; (4) magneton.

2.2 Experimental part

The cyclic voltammetry was carried out by CS150 electrochemical workstation. The scanning rates and voltage range were 1mV/s and -1.6V to -0.6V (the ending voltage was -0.6V). Stopped the experiment after 20 cycles until the curves coincided.

Constant current charge and discharge tests were carried out with the three-electrode system. The current density of charge and discharge was 10mA/cm^2 for 6 hours. The constant current charge and discharge were 10 cycles. The potential range was -0.6V to -1.6V (the cut-off voltage was -0.6V).

The self-discharge performance of single-flow zinc-nickel batteries is characterized by the capacity retention rate after the battery has been left for a period of time, in which solution flow is maintained during the stationery process. Firstly, the battery was charged at a constant current of 10mA/cm^2 to 150mAh. After being rested for 24 hours, the battery was discharged at a constant current. The discharge was stopped at the potential of 1.2V. Then the coulomb efficiency was calculated at last.

The scanning electron microscope (ZEISS MERLIN COMPACT) and energy dispersive X-ray spectrometer (EDS) were used to detect the morphology and composition of the deposited particles.

3. RESULTS and DISCISSION

3.1 Analysis of Cyclic voltammetry

Fig. 2 shows the steel strip electrodes obtained from nickel-plated in different concentrations of potassium stannate with 1mV/s cyclic voltammetry curve. The dissolution peak and the interval of the dissolution peak gradually decrease with the concentration of K_2SnO_3 increasing. There is a small anode peak at -0.88V (as shown in Fig.2), it only exists in the basic electrolyte where the zinc is oxidized on the surface of the nickel-plated steel strip [15]. However, with the potassium stannate adding to the electrolyte the anode peak disappears, which may be related to the deposition of potassium stannate. This is the co-deposition of zinc and tin, which will form a relatively stable alloy composition and inhibit the anode peak.

The curve of the base solution is still stable on the reference line at -1.134V approximately. The reduction reaction does not start until -1.405V, and deviates from -1.516V, and the reaction ended at the final potential of -1.6V. Fig.2 illustrates that the electrolyte with K_2SnO_3 addition has an earlier reaction time and a slower decay, while the basic electrolyte has a relatively late reaction time and a faster decay.
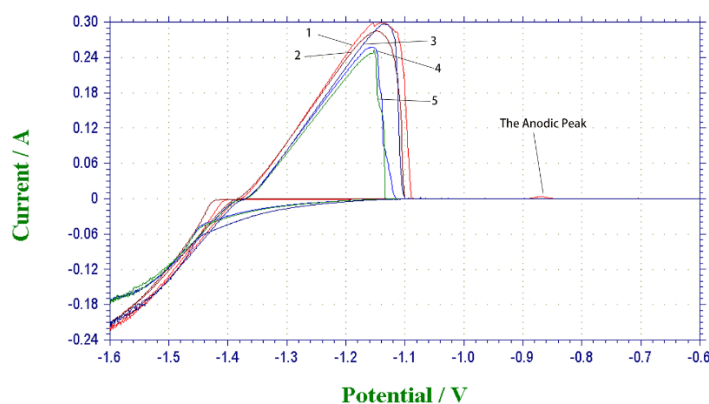

Figure 2. The cyclic voltammetry curve of eighth cycle at scan rate of 1mV/s on the nickel-planted steel strip in different electrolytes, (1) S; (2) S+0.03mol/L K_2SnO_3; (3) S+0.05mol/L K_2SnO_3; **)**4) S+0.08mol/L K_2SnO_3; (5)S+0.1mol/L K_2SnO_3.

3.2 Constant current charge and discharge test

Constant current charge and discharge analysis was carried out on the battery, and the results are shown in Fig.3. The base electrolyte charge and discharge voltage are higher than those electrolytes which add K_2SnO_3 at the same current densities, and this phenomenon continues until the end of the 21000s cycle. Fig.3(b) illustrates that as the number of cycles increases, the phenomenon of negative shift of the charge discharge voltage plateau in the solution with potassium stannate is always stable. Coulomb efficiency can evaluate the performance of zinc nickel single liquid battery, which is the specific capacity of discharge capacity and charging capacity. Therefore, the coulomb efficiency of the basic electrolyte is the lowest, which also demonstrates that the effect of tin is effective for a long time, and the existence of tin zinc deposits inhibits the growth of dendrites. It can be seen from Fig.3(b) that

as the concentration of potassium stannate increases, the charge-discharge voltage decreases, and the coulombic efficiency becomes higher. The coulombic efficiency is the highest when the 0.1mol/L potassium stannate solution is added. The nucleation overpotential also increases with the increase of the concentration of K_2SnO_3, and is the smallest in the basic electrolyte.
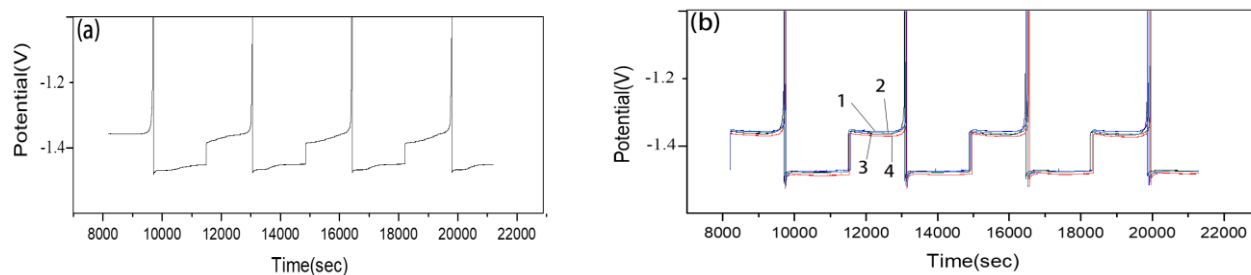

Figure 3. Charge-discharge curves of nickel-plated steel strip in different electrolytes, (a) the basic electrolyte S; (b) the electrolytes with different concentration K_2SnO_3, (1)S+0.03mol/L K_2SnO_3; (2)S+0.05mol/L K_2SnO_3; (3)S+0.08mol/L K_2SnO_3; (4)S+0.1mol/L K_2SnO_3.

3.3 morphology and component analysis

As shown in Fig.4(a), SEM images of the zinc coating is obtained by charging different electrolytes at 10mA/cm^2 for 20min. It can be seen that the electrodeposited particles on the zinc surface are not uniform, and the speed of crystal grain formation is relatively slow in the electrodeposition of the basic solution. By comparing the SEM image of S+0.03mol/L K_2SnO_3 in Fig. 4(B), it can be seen that after adding potassium stannate, the coating is relatively flat, the formation rate of grains becomes faster [16] and the grains begin to become smaller which is due to the substrate-effect after the addition of K_2SnO_3.

As shown in the Fig. 4 (c) (d), after 0.05mol/L potassium stannate, the deposition area of tin and zinc is relatively uniform, the zinc coating becomes flatter and the adhesion is enhanced to a certain extent. With the concentration of potassium stannate increasing, the size of grain for zinc coating becomes smaller, the formation rate of grain and the growth rate of the dendritic crystal becomes faster [17]. It indicates that the potassium stannate plays a regulatory role in the deposition of zinc.
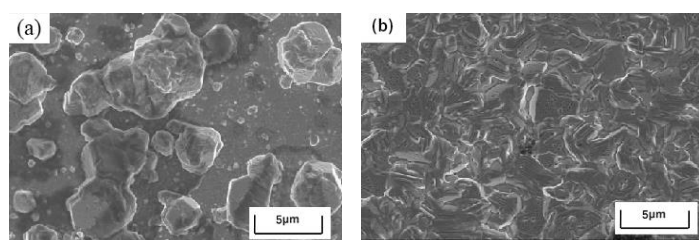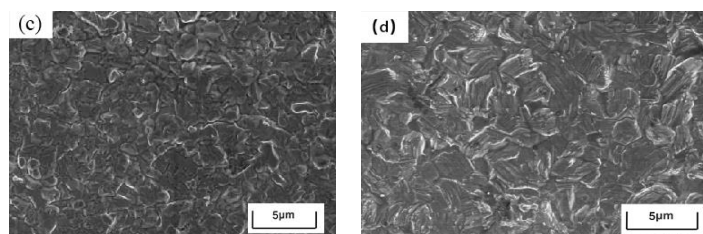
Figure 4. SEM images of the nickel-plated steel strip electrode in different electrolytes, (a) S; (b) S+0.03mol/L K_2SnO_3; (c) S+0.05mol/L K_2SnO_3; (d) S+0.1mol/L K_2SnO_3.

The nickel-plated steel strip was used as the negative electrode to charge the coating in different concentration electrolyte for 20 minutes at 10mA/cm^2 current. Fig.5(a) (b) shows the EDS images of two samples in basic electrolyte and electrolyte which was adding 0.1mol/L K_2SnO_3. According to EDS, Zn only exists in the basic electrolyte, while Zn and Sn are electrodeposited after potassium stannate is added, as shown in Fig. 5(b). The atomic ratio of the two elements is Zn/Sn=97.23/2.77, which can indicate that Sn and Zn have been deposited together during the electrodeposition process.
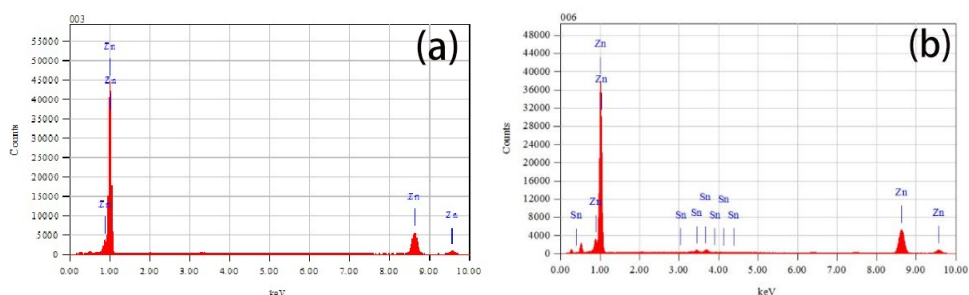

Figure 5. EDS analysis of the nickel-plated steel strip electrode in different electrolytes, (a) S; (b) S+0.1mol/L K_2SnO_3.

3.4 Self-discharge test

The zinc coating surface could be corroded after the battery is stored for a period of time. The corrosion of zinc coating is the self-discharge of the battery. As shown in Fig.6, the discharge curve of a nickel-plated steel strip in different concentrations of electrolyte for 24 hours. The battery was charged to 150mAh with a constant current of 10mA/cm^2 and discharged to 1.2 V with a constant current of 10mA/cm^2 after 24 hours. Then the battery need to be stored for 24hours. The coulombic efficiency of the basic electrolyte is 48.8%. The coulombic efficiencies are 49.3%, 54.6%, 55.8%, 62.5% after adding different concentration of K_2SnO_3 (As shown in Tab1). These data indicate that the addition of potassium stannate can increase the coulombic efficiency. The self-discharge is obviously inhibited after adding potassium stannate [18]. The highest coulomb efficiency of the battery at the maximum solubility of 0.1mol/L potassium stannate has the greatest inhibition effect on the self-discharge.

Based on the above research results, the mechanism of tin is analyzed. Firstly, the deposition potential of tin is much higher than that of zinc, tin is deposited on the active sites of the nickel-plated

steel strip during charging, and the tin deposits become zinc nucleation crystal grains. On the one hand, when the potential reaches the zinc deposition potential, zinc and tin are deposited together, and the preferential growth direction of zinc crystals is affected by the reduction of tin, thereby changing the electrodeposited particles. When potassium stannate is added to the base solution, the coating becomes smooth and compact, which slows down the self-dissolution of zinc to a certain extent. On the other hand, tin is a metal with a strong overpotential of hydrogen evolution, which can inhibit hydrogen evolution to a certain extent, and can keep the self-dissolution activity of zinc relatively low in the whole range of discharge potential. Therefore, the addition of potassium stannate can improve the self-discharge of zinc anode to a certain extent.
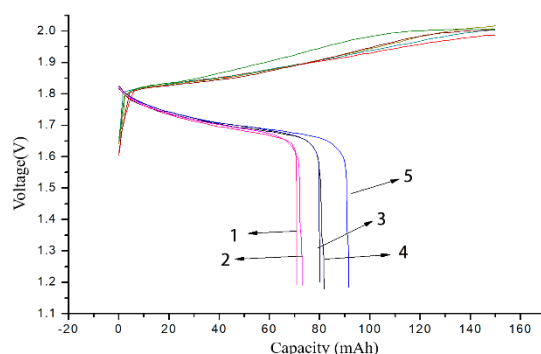

Figure 6. Discharge curve of nickel-plated steel strip in different concentrations of electrolyte for 24h, (1) S; (2) S+0.03mol/L K_2SnO_3; (3) S+0.05mol/L K_2SnO_3; (4) S+0.08mol/L K_2SnO_3;(5) S+0.1mol/L K_2SnO_3.

Table 1. Self-discharge test results of electrolyte in the solution with different K_2SnO_3 concentration

The solution of the electrolyte	The coulombic efficiency (%)
The basis solution (S)	48.8%
S+0.03mol/L K_2SnO_3	49.3%
S+0.05mol/L K_2SnO_3	54.6%
S+0.08mol/L K_2SnO_3	55.8%
S+0.1mol/L K_2SnO_3	62.5%

4. CONCLUSIONS

This study mainly shows the effect of K_2SnO_3 as an electrolyte addition on the performance of zinc anode. The conclusions are as follows.

When the scanning speed is 1m/s, with the K_2SnO_3 concentration increasing, the peak of the

dissolution peak gradually decreases. After K_2SnO_3 is added to the basic electrolyte, the peak is stable and the range of the dissolution peak is narrowed. The reduction reaction proceeds in advance. However, it is indicated that the anode peak only exists in the basic electrolyte.

The SEM and EDS results show that after adding K_2SnO_3, zinc and tin are co-depositing, which inhibits the formation of the anode peak. With the increase of potassium stannate, the surface of the zinc deposition density becomes more and more smooth. The addition of K_2SnO_3 is beneficial to grain refinement and growth.The growth rate of crystal grains and the growth rate of dendrites will also depend on the dissolution of the K_2SnO_3 solution. The addition of potassium stannate is beneficial to the growth of grain, and the growth rate of grain dendrite will also increase with the addition of potassium stannate.

The self-discharge experiment proves that potassium stannate can improve the capacity of the battery and inhibit self-discharge. After adding potassium stannate, the coulombic efficiency increased from 48.8% to 62.5%. This article provides a simple way to improve the performance of single-flow zinc-nickel battery.

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