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ScienceDirect
Trans. Nonferrous Met. Soc. China 24(2014) 3551−3555
Transactions of Nonferrous Metals Society of China
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Effects of additives on performance of zinc electrode

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Received 8 January 2014; accepted 5 March 2014

Abstract: In order to improve the properties of the nickel−zinc battery and study the effects of the additives on performance of zinc electrode, 3 levels and 4 factors (acetylene black, Bi_2O_3, PbO, $Ca[Zn(OH)_3]_2{\cdot}2H_2O$ coated by $La(OH)_3$) that affect the zinc electrode were tested with orthogonal design experiments. The charge−discharge experiments of zinc electrode made up of only zinc oxide were done in 20% KOH solution to investigate the function of the additive. In order to better understand the discharge capability attenuation of electrode, the ratios of zinc to calcium in the worst sample and the best sample of the orthogonal design test were analyzed. The samples were characterized by charge−discharge cycling, phase structure analysis, cyclic voltammetry and X-ray diffraction. Experimental evidences indicate that the optimum ratio of electrode additive is as follows: 0.02 g acetylene black, 0.5 g Bi_2O_3, 0.3 g PbO and 0.2 g $Ca[Zn(OH)_3]_2{\cdot}2H_2O$ coated with $La(OH)_3$ in 5 g sample.
Key words: additive; nickel−zinc battery; orthogonal design experiments; zinc electrode

1 Introduction

There is a wide variety of applications for zinc metal as high capacity anodic material in the secondary alkaline batteries due to its high specific energy, good reversible property, environmental friendliness, low equilibrium potential, low cost and no-toxicity [1−3]. Despite so many good performances, the commercial applications of Zn−Ni alkaline secondary batteries are severely hindered by poor cycle lifetime, which mainly results from the drawbacks of zinc electrode, such as shape change, zinc dendrite formation, surface passivation, zinc self-corrosion and self-discharge [4−6]. These problems derive from a high solubility of the discharge products of zinc electrode in alkaline electrolyte and non-uniform deposition of zinc active material during charging [5,7,8]. Over the years, many attempts have been made to eliminate or minimize the effects of these phenomena [9−11]. Although the cycle life and properties of zinc electrodes are improved to some extent, the problem still remains elusive [6,7]. An effective approach is to incorporate additives in either the electrode or the electrolyte [12−14]. Additives, such as Bi_2O_3 [15], V_2O_5 [16], In_2O_3 [17] and quaternary ammonium compounds [18], have beneficial effect on the performance of zinc electrodes.

In this work, the orthogonal experimental design was used to study the effects of the additives on performance of zinc electrode for the optimum ratio of electrode additives. Meanwhile, the capacity fading mechanism was also preliminarily analyzed.

2 Experimental

2.1 Experimental schemes

Experiment was divided into the following parts: the preparation of $Ca[Zn(OH)_3]_2{\cdot}2H_2O$ coated with $La(OH)_3$; the preparation of the electrode; charging and discharging experiments; cycling voltametry. The product of the early stage preparation is $Ca[Zn(OH)_3]_2{\cdot}2H_2O$, and it is the main material to make zinc electrode; orthogonal experiment with 4 factors and 3 levels was designed, the amount of additives in the electrode material of every 5 g is listed in Table 1.

2.2 Preparation of $Ca[Zn(OH)_3]_2{\cdot}2H_2O$ coated with $La(OH)_3$

According to the experimental conditions, the experiment scheme was designed as follows: putting

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DOI: 10.1016/S1003-6326(14)63500-7

Table 1 Orthogonal experimental design

Serial No.	Mass of additive/g			
	Acetylene black (A)	Bi_2O_3 (B)	PbO (C)	$Ca[Zn(OH)_3]_2·2H_2O$ coated by $La(OH)_3$ (D)
1	0.02	0.1	0.7	0.2
2	0.04	0.1	0.3	0
3	0.06	0.1	0.5	0.4
4	0.02	0.3	0.5	0
5	0.04	0.3	0.7	0.4
6	0.06	0.3	0.3	0.2
7	0.02	0.5	0.3	0.4
8	0.04	0.5	0.5	0.2
9	0.06	0.5	0.7	0

5.0 g $Ca[Zn(OH)_3]_2·2H_2O$ powders into 100 mL 10% KOH solution (mass fraction) and stirring fully to form suspension. The suspension was sprayed into the continuously stirring 100 mL 5.5% $La(NO_3)_3$ solution so that the surface of $Ca[Zn(OH)_3]_2·2H_2O$ can be coated by reaction product $La(OH)_3$. The reaction product was precipitated, filtered and dried at 80 °C, and finally $Ca[Zn(OH)_3]_2·2H_2O$ coated with $La(NO_3)_3$ can be obtained.

2.3 Preparation of electrode

The floc that PTFE boiled with alcohol was used for electrode forming binder.

According to Table 1, the addictives were added into 5 g zinc powders, respectively. Then they were mixed with 0.2 mL poly tetra fluoro ethylene (PTFE) binder. The mixtures were boiled with alcohol for 5 min so that PTFE can become floc. The mixtures were rolled into thin slices after the excrescent alcohol was filtered. The density of the thin slices was calculated. Then the thin slices were cut into electrode slice with the dimensions of 1 cm×1 cm, meanwhile, copper mesh was cut into several pieces with the dimensions of 4 cm×1 cm, and was used as current collector.

The electrode slice and current collector were placed, as shown in Fig. 1. Then zinc electrode was manufactured under the pressure of 10 MPa for 2 min.

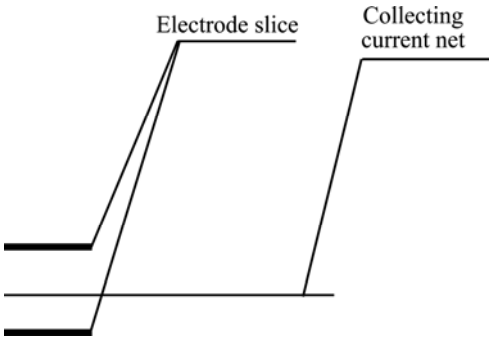

Fig. 1 Relative position diagram of electrode slice and collecting current net

2.4 Charge−discharge experiments of electrodes

Hg/HgO was selected as reference electrode and porous nickel was selected as counter electrode. Zinc electrode and porous nickel were inserted in the homemade electrolytic cell with 20% KOH solution. So, a three-electrode system was formed, as shown in Fig. 2.

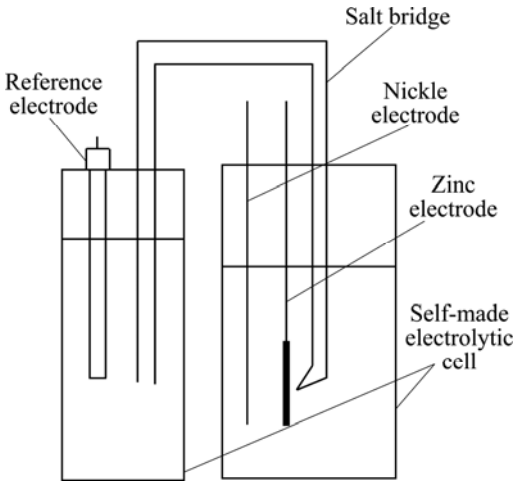

Fig. 2 Schematic diagram of three-electrode system

The test scheme of the zinc electrode made from orthogonal experiment was designed as follows: 1) constant-current charge in 150 mA for 8 min; 2) constant-current discharge in 100 mA until the voltage was 30 mV; 3) the experiment was cycled for 100 times.

2.5 Cyclic voltammetry curve test of electrode

In order to carry on the preliminary study of the charge and discharge mechanisms of electrode, the cyclic voltammetry curve of each electrode was tested. In order to reduce the discharge area of electrodes, electrode device was used, as shown in Fig. 3. The electrode slice made from orthogonal experiment was put in the packed hole of electrode material (the diameter was 2.36 mm,

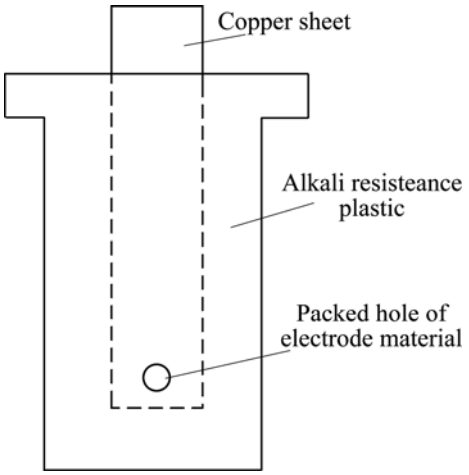

Fig. 3 Self-made electrode device for cyclic voltammetry curve test

the depth was 0.72 mm), and it contacted with the copper sheet that coated with alkali resistance plastic, so the alkaline solution can only interact with a small piece of electrode material. The cyclic voltammetry curve was tested using three-electrode system.

3 Results and discussion

3.1 Surface appearance analysis of $Ca[Zn(OH)_3]_2{\cdot}2H_2O$ coated with $La(OH)_3$

In Fig. 4, the white $La(OH)_3$ is not simply mechanically mixed but attached on the surface of $Ca[Zn(OH)_3]_2{\cdot}2H_2O$. The white dots appear in some areas because of less $La(OH)_3$ coated, and the background of $Ca[Zn(OH)_3]_2{\cdot}2H_2O$ is covered by large $La(OH)_3$ in some areas. The main reason is that the manipulation of spray is artificial in the process of experience, so the flow of spraying cannot be controlled accurately, meanwhile, the concentration of $La(NO_3)_3$ continuously decreases with increasing the reaction time, which is also a large factor of effect.

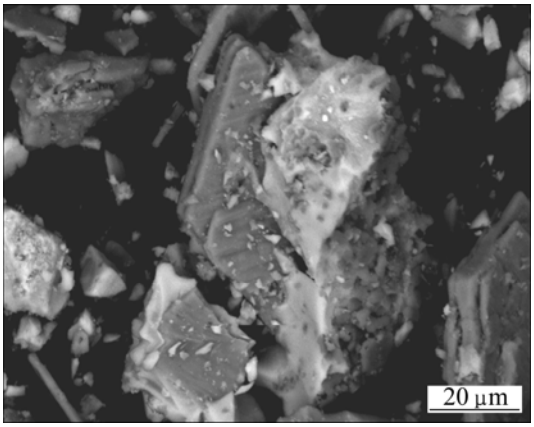

Fig. 4 SEM image of surface of $Ca[Zn(OH)_3]_2{\cdot}2H_2O$ coated with $La(OH)_3$

3.2 Discharge capacity of electrode analysis and optimization of electrodes formula

Unit mass discharge capacity data of 9 samples are listed in Table 2. The cycle numbers are 1, 11, 31, 41, 51, 61, 71, 81, 91, 100, respectively. Cyclic discharge curves of the optimal sample (sample 8) are shown in Fig. 5, and cyclic discharge curves of the worst sample (sample 3) are shown in Fig. 6.

It is found that the capacity of sample 8 is the best among these samples for 100 cycles, so it is marked as 100 points. According to the ratios of other samples except sample 8, the corresponding scores can be gotten. Sample 3 does not maintain 10 cycles among these samples, so its score is 0. The ratio of the 21st discharge capacity and the 1st discharge capacity is served as the attenuation rate. If the attenuation rate is lower, the performance of electrode is better, so the reciprocal attenuation rate serves as the reference standard: the highest score is the maximum value of reciprocal attenuation rate. Likewise, the scores of the others can also be gotten. The mass of the discharge capacity is 0.7, and the mass of decay rate is 0.3, then the comprehensive score can be gotten.

According to the intuitive analysis method, it is found that sample 8 is the best.

With an application of numerical analysis method to the experiment, the results are listed in Table 3.

According to the result, it is found that the order is B>D>C>A. Among them, the major factor is Bi_2O_3. Based on the chart, the optional proportion is $A_1B_3C_1D_2$, that is 0.02 g acetylene black, 0.5 g Bi_2O_3, 0.3 g PbO, 0.2 g $Ca[Zn(OH)_3]_2{\cdot}2H_2O$ coated with $La(OH)_3$ in 5 g sample.

3.3 Cyclic voltammetric analysis of electrode

Figures 7 and 8 show the 6th and 26th cyclic voltammetry curves of the optimal electrode, respectively.

Table 2 Discharge capacity of orthogonal experimental samples

Number of cycle	Discharge capacity/(mA·h·g^{-1})								
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9
1	96.68	74.83	89.84	76.29	52.9	147.32	116.01	95.66	88.63
11	44.49	54.12	42.88	40.79	23.49	19.05	22.65	65.48	35.55
21	27.24	43.94	55	36.78	11.13	11.71	21.4	76.11	32.84
31	25.5	51.48	36.6	37.66	7.46	9.52	16.73	83.76	33.07
41	22.89	29.21	4.85	47.93	6.33	9.62	17.3	87.59	39.31
51	25.72	26.46	−	47.05	4.9	7.34	21.63	87.16	55.2
61	26.8	22.03	−	44.11	3.68	9.33	36.32	86.45	56.14
71	28.43	22.03	−	41.47	2.96	12	55.56	84.89	59.56
81	38.63	21.67	−	36.19	2.55	14.38	48.61	84.18	58.5
91	68.14	20.95	−	30.32	2.14	18.35	48.84	85.03	58.15
100	41.78	24.9	−	26.21	2.25	24.21	45.42	86.17	57.44

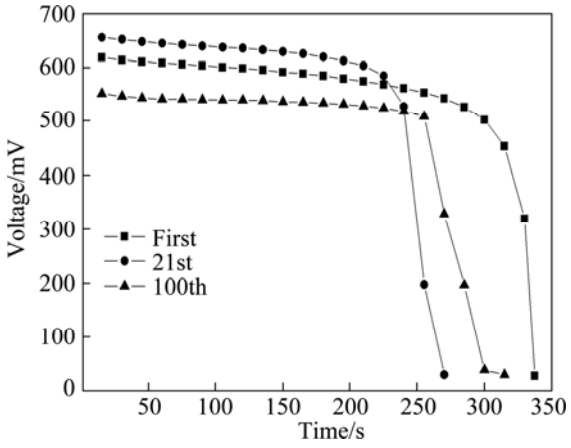

Fig. 5 Cyclic discharge curves of sample 8

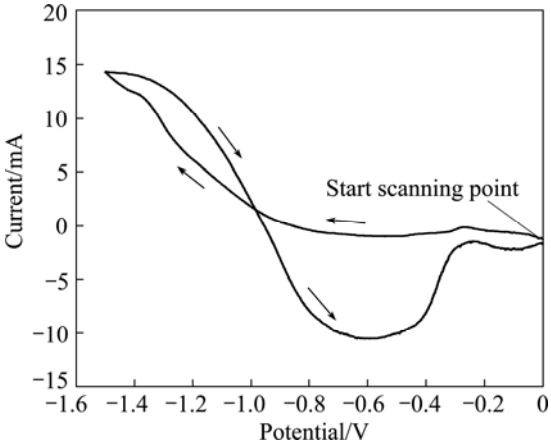

Fig. 7 6th cyclic voltammetry curve of optimal electrode

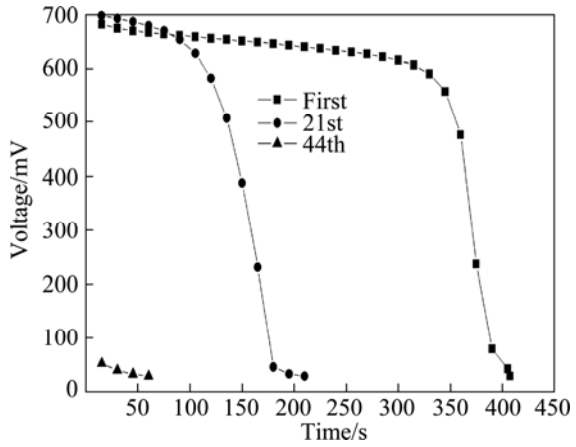

Fig. 6 Cyclic discharge curves of sample 3

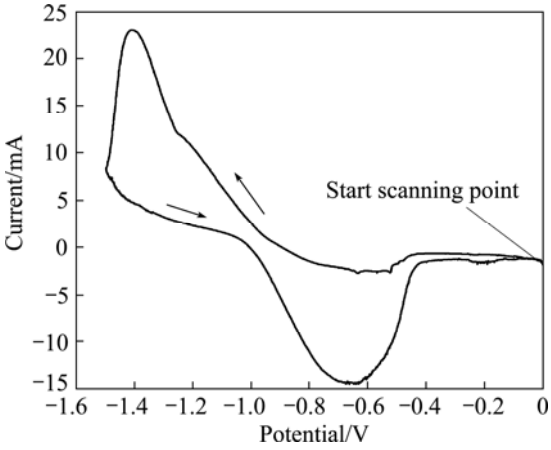

Fig. 8 26th cyclic voltammetry curve of optimal electrode

Table 3 Numerical analysis of orthogonal experiment

Number	Acetylene black (A)	Bi_2O_3 (B)	PbO (C)	$Ca[Zn(OH)_3]_2·2H_2O$ coated with $La(OH)_3$ (D)	Total score
1	0.02(1)	0.1(1)	0.7(3)	0.2(2)	42.4
2	0.04(2)	0.1(1)	0.3(1)	0(1)	24.3
3	0.06(3)	0.1(1)	0.5(2)	0.4(3)	3.9
4	0.02(1)	0.3(2)	0.5(2)	0(1)	26.2
5	0.04(2)	0.3(2)	0.7(3)	0.4(3)	13.2
6	0.06(3)	0.3(2)	0.3(1)	0.2(2)	49.7
7	0.02(1)	0.5(3)	0.3(1)	0.4(3)	49.8
8	0.04(2)	0.5(3)	0.5(2)	0.2(2)	73
9	0.06(3)	0.5(3)	0.7(3)	0(1)	53.1
*K*1’	118.4	70.6	123.8	103.6	−
*K*2’	110.5	89.1	103.1	165.1	−
*K*3’	106.7	175.9	108.7	66.9	−
*K*1	39.5	23.5	41.3	34.5	−
*K*2	36.8	29.7	34.4	55	−
*K*3	35.6	58.6	36.2	22.3	−
R	3.9	35.1	6.9	32.7	−

According to Fig. 7, cyclic voltammetry curve intersects in voltage of −0.98 V can be seen, and the figure is made up of one positive current loop and one negative current loop. The positive current loop is nucleation process, and the negative current loop is diffusion process. So, in the previous cyclic process, the charge−discharge process of the sample is combinedly controlled by nucleation process and diffusion process.

According to Fig. 8, after electrode materials cycle for several times, both the cross points and negative current loop disappear, and there is only one positive current loop, indicating that the charge−discharge process of the sample is mainly controlled by nucleation process. Based on the above two figures, the possible reason may be that a portion of the active substance loses activity, so it cannot transform to Zn or $Ca[Zn(OH)_3]_2·2H_2O$, and there is only a small amount of active material to be left. Meanwhile, the electrolyte fully infiltrates into the internal electrode after the repeatedly charge−discharge cycling, so nucleation process becomes the main factor of controlling the charge−discharge process of electrode, and the diffusion process becomes the secondary factor.

4 Conclusions

1) Under the experimental conditions, Bi_2O_3 is the most important factor in improving the performance of electrode among the four factors (Bi_2O_3, PbO, acetylene black and $Ca[Zn(OH)_3]_2·2H_2O$ coated with $La(OH)_3$); moderate $Ca[Zn(OH)_3]_2·2H_2O$ coating with $La(OH)_3$ also has a certain influence on improving the performance of electrode, while excessive addition of acetylene black makes the performance degrade.

2) The optimum ratio of electrode additive is as follows: 0.02 g acetylene black, 0.5 g Bi_2O_3, 0.3 g PbO and 0.2 g $Ca[Zn(OH)_3]_2·2H_2O$ coated with $La(OH)_3$ in 5 g sample.

3) During the cyclic voltammetry tests of electrode, the beginning of the cathode process is controlled by the nucleation process and diffusion process, while as the reaction proceeds, the later stage is controlled by nucleation process.

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添加剂对锌电极性能的影响

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摘 要：为了改善镍锌电池的性能，同时研究电极中添加剂对锌电极性能的影响，选用正交设计对影响锌电极的4个因素(乙炔黑、Bi_2O_3、PbO、包覆 $La(OH)_3$ 的 $Ca[Zn(OH)_3]_2·2H_2O$)选择3个水平进行测试。对没有任何添加剂的氧化锌在20% KOH电解液中进行充放电循环实验，研究添加剂的作用。为了更好地解释锌电极放电容量衰减的原因，对正交实验的最差样品和最优样品放电产物所含的Zn和Ca的比例进行分析。通过表征，得出了在该实验条件下的电极添加剂的最优配比方案为：在5 g样品中，乙炔黑0.02 g，Bi_2O_3 0.5 g，PbO 0.3 g，包覆 $La(OH)_3$ 的 $Ca[Zn(OH)_3]_2·2H_2O$) 0.2 g。

关键词：添加剂；镍锌电池；正交实验；锌电极

(Edited by Chao WANG)