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The synergistic effect of Al/Mg/Co on the crystalline phase and electrochemical performance for nickel hydroxide

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ABSTRACT

Nano-sized α-$Ni(OH)_2$ has been synthesized via doping, which can keep alpha phase structure after being soaked in alkaline solution for 30 days. The influence of Al/Co, Al/Mg, Mg/Co and Al/Mg/Co multiple doping on crystal phase, stability and electrochemical performance of $Ni(OH)_2$ have been systematically investigated. The optimization formula of the doping elements and their doping ratio have been studied according to the synergistic effect of the doping elements.

I. INTRODUCTION

Nanometre nickel hydroxide($Ni(OH)_2$) as the cathode energy storage material for the secondary batteries, because of its environment friendly protection, excellent safety performance, low cost, high power, has been received wide attention. Because of low density and poor stability in alkali solution, α-$Ni(OH)_2$ which has higher theoretical capacity has not been applied on the commercial alkaline batteries. In this work, nano-sized α-$Ni(OH)_2$ doped with various ratio of Al/Mg/Co was synthesized by means of ultrasonic-assisted precipitation. The effect of the Al/Mg/Co ratio on the crystal structure, particle size distribution, structural stability and electrochemical performance of all samples were investigated. In particular, the synergistic effect of Al/Mg/Co on the crystalline phase and electrochemical performance for α-$Ni(OH)_2$.

II. EXPERIMENTAL

Table 1 The preparation conditions of samples.

Samples	Ni^{2+}:Al^{3+}:Mg^{2+}:Co^{2+}	Aged 10 days	Aged N days
a	1: 0:0.1:0.1	a_{10}	a_N
b	1:0.1:0.1:0	b_{10}	b_N
c	1:0.1:0:0.1	c_{10}	c_N
d	1:0.05:0.05:0.10	d_{10}	d_N
e	1:0.05:0.05:0.15	e_0	e_N

Preparation of α-$Ni(OH)_2$ doped with various ratio of Al/Mg/Co was performed by the method reported in our group previous paper [1] and the samples were noted as followed.

III. RESULTS AND DISCUSSION

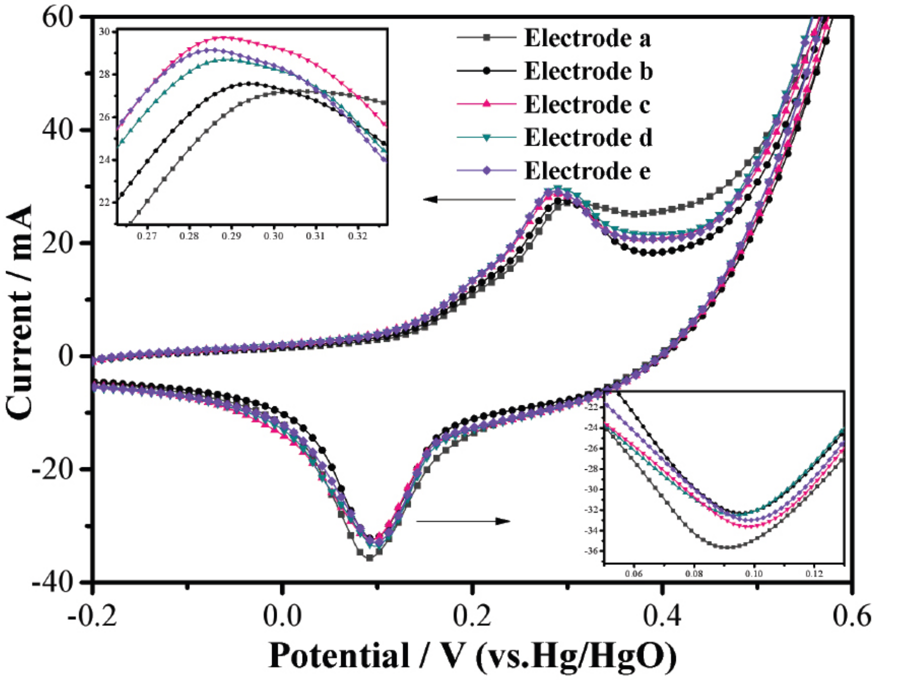

Figure 1 CV curves of electrodes a-e at a scanning rate of 0.10V/s.

Table 2 CV date of electrodes tested at 0.1 V/s.

Electrodes (Ni^{2+}:Al^{3+}:Mg^{2+}:Co^{2+})	E_R (mV)	E_O (mV)	E_{OER} (mV)	$\Delta E_{R,O}$ (mV)	$\Delta E_{O,OE}$ (mV)
a (1:0:0.1:0.1)	306	91	370	215	64
b (1:0.1:0.1:0)	294	95	388	199	94
c (1:0.1:0:0.1)	289	94	381	195	92
d (1:0.05:0.05:0.1)	288	98	384	190	96
e (1:0.05:0.05:0.15)	285	99	386	186	101

Fig.1 presents the CV curves of electrodes and the results of CV measurements are tabulated in Table 2 in detail. According to the test results, Al^{3+} has a good effect on the formation of α-$Ni(OH)_2$ and the maintenance of its structural stability. Relative to Mg^{2+}, Co^{2+} is more favorable to improve the reversibility of electrode. The increase of Co^{2+} content, to a certain extent, not only improves the nickel hydroxide crystal phase, but also improves the stability of structure and physical properties, cyclic voltammetric behavior of the electrode has been also improved.

Mg^{2+} is more conducive to improve the relative efficiency of charging electrode than Co^{2+}. Synergistic effect of Al^{3+}/Mg^{2+} is better than that of Al^{3+}/Mg^{2+}. The synergistic effects between different doping ions is different. Therefore, choosing appropriate doping ions, can play the greatest degree of synergy and improve the electrochemical behavior of electrodes.

Table 3 Proton diffusion coefficient of electrodes.

Electrodes	a	b	c	d	e
K/(×10^{-2})	7.19	7.81	8.37	8.68	8.87
D'/(×$10^{-12}$$cm^2s^{-1}$)	4.59	5.42	6.23	6.69	7.00

According to Randlee-Sevcik equation [2,3], the proton diffusion coefficient of each electrode can be calculated. The proton diffusion coefficients of electrode a, b, c and e are shown in Table 3. The increase in the proton diffusion coefficient accelerates the electrode reaction, favors the fast ionic transportation and decreases the electrode polarization during the charge/discharge process. Clearly, electrode e has the highest proton diffusion coefficient, indicating a higher electrochemical activity and faster reaction kinetics due to the fast ionic transportation.

IV. CONCLUSIONS

In summary, the Al/Mg/Co ratio not only play a significant role in the crystal structure and structural stability, but also markedly affect the electrochemical performance of α-$Ni(OH)_2$. The results demonstrate that reasonable molar ratio of doped elements ions can produce synergic effect of lattice distortion, which can improve electrochemical performance by enhancing the structural stability, proton diffusion coefficient and decreasing electron transfer resistance.

V. REFERENCES

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