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Synthesis of $LiCo_xNi_{1-x}O_2$ cathode materials from electrolysis Co-Ni alloys①

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Abstract: The $LiCo_xNi_{1-x}O_2$ ($x = 0.2$, 0.5 and 0.8) cathode materials were synthesized by sintering the mixtures of lithium salt and $Co_xNi_{1-x}(OH)_2$ ($x = 0.2$, 0.5 and 0.8) which were achieved from corresponding Co_xNi_{1-x} alloys by electrolysis technique. The structure and electrochemical characteristics of the obtained $LiCo_xNi_{1-x}O_2$ were studied by XRD, SEM, PSCA and charge-discharge cycling test. The results show that the electrochemical capacities of the $LiCo_xNi_{1-x}O_2$ ($x = 0.2$, 0.5 and 0.8) materials are improved with the increase of the Ni content. The electrochemical performance of $LiCo_{0.2}Ni_{0.8}O_2$ made in oxygen atmosphere has higher charge-discharge capacity and better cycleability compared with the one made in air atmosphere.

Key words: cathode materials; electrolysis; $LiCo_xNi_{1-x}O_2$; Co-Ni alloys
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1 INTRODUCTION

Lithium ion battery is considered the most promising energy storage device at present because of its high discharge voltage, long cyclic lifetime and lower self-discharge rate[1]. The cathode materials being used now are usually $LiCoO_2$, $LiNiO_2$ and their derivatives with ordered layered structure like α-$NaFeO_2$[2]. Among the materials, $LiCoO_2$ is the one used most widely in commercial products, because its preparation is simple and convenient, and the electrochemical performance is fairly good compared with the others[3]. $LiNiO_2$ is another cathode material candidate and also attracts much attention due to its low cost and the possibility of larger capacity than $LiCoO_2$ in practice ($LiCoO_2$, 140 mA·h/g; $LiNiO_2$, 200 mA·h/g)[4]. But it is well known that the property of $LiNiO_2$ strongly depends on the stoichiometry and structure while the preparation is difficult[5-9]. Moreover, the cyclic stability of the $LiNiO_2$ electrode is not good, because $LiNiO_2$ may decompose and release O_2 during charging, which causes unsafe problems for lithium ion battery, especially at elevated temperatures[10-12].

Since the structures of $LiCoO_2$ and $LiNiO_2$ are similar, which are helpful to form a solid solution in the overall composition domain[13], the compound $LiCo_xNi_{1-x}O_2$ was studied extensively[14-19]. Their performances seem much better than those of $LiNiO_2$ and $LiCoO_2$, such as the thermal stability and capacity density. The capacity density in practice is about 180 mA·h/g. The XAFS analysis results show that the oxidation of the Ni ion in $Li_{1-x}(Ni_{0.5}Co_{0.5})O_2$ occurs immediately when the cell is charged, then stops at x of 0.5, whereas the oxidation of Co continues slowly until x of 0.8[20]. Therefore, the material is identified as one of the most promising cathode materials in lithium ion battery[15-17].

In this paper, cathode materials $LiCo_xNi_{1-x}O_2$ ($x = 0.2$, 0.5, 0.8) were synthesized by means of high-temperature solid-state reactions from relevant reactants $Co_xNi_{1-x}(OH)_2$ ($x = 0.2$, 0.5, 0.8) which were prepared from Co_xNi_{1-x} alloy by electrolysis method. Since cobalt and nickel have similar character and form an intergrowth in the mine, the cobalt and nickel were first mined as Co-Ni alloy, then the alloy was electrolyzed to get pure metal or corresponding salt. So the advantages of this method are: 1) the raw material is not a Ni-Co salt but Ni-Co alloy, so the cost is reduced; 2) the electrolyte can be recycled, which does little pollution to the environment.

2 EXPERIMENTAL

High purity metals with stoichiometrical ratios of Co to Ni (0.2∶0.8; 0.5∶0.5; 0.8∶0.2) were arc-melted in vacuum to get the Co_xNi_{1-x}

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alloy. The Co_xNi_{1-x} alloy was galvanostatically electrolyzed in 100 g/L NaCl solution, then the electrolysis product was rinsed by water to remove Cl^- anion, dried at 80 ℃ to obtain corresponding $Co_xNi_{1-x}(OH)_2$. The $Co_xNi_{1-x}(OH)_2$ (x= 0.2, 0.5, 0.8) were mixed with LiOH (AR grade) by stoichiometric ratio 1∶1.05. The mixtures were ground in an agate mortar and pre-heated at 600 ℃ for 6 h, then quenched to the room temperature and grounded again, followed by heat-treating in the range of 700 - 800 ℃ for 12 h to get the $LiCo_xNi_{1-x}O_2$ (x = 0.2, 0.5 and 0.8). The structures of Co_xNi_{1-x} alloys and $Co_xNi_{1-x}(OH)_2$ were determined by XRD (D-max/2500 Rigaku, Cu K_α radiation). The particle morphology of the powders was observed by a scanning electron microscopy (SEM, Hitachi S-3500N). The compositions of Co_xNi_{1-x} alloys and $Co_xNi_{1-x}(OH)_2$ were determined by atomic absorption spectrometry (AAS).

Positive electrode for the electrochemical test was fabricated with active material, acetylene black as conducting additive and PTFE as binder mixed together in mass ratio of 80∶15∶5. Then the electrodes were dried at 120 ℃ for 24 h. The coin cells for test were assembled in the Ar-filled glove box with the prepared positive electrode and lithium foil as the negative electrode, 1 mol/L $LiPF_6$/EC (ethylene carbonate) + DEC (diethylene carbonate) (1∶1, volume ratio) as the electrolyte (Battery-grade, Merck Germany), and Celgard 2 400 (polypropylene) films as the separator. The charged-discharged cycling was galvanostatically performed between 4.2 - 3.0 V at a current of 30 mA/g. To study the diffusion coefficient of Li^+ through the electrodes, potential step chronoamperometry measurements were performed using a Solartron 1 287 potentiostat.

3 RESULTS AND DISCUSSION

3.1 Preparation of $Co_xNi_{1-x}(OH)_2$ and $LiCo_xNi_{1-x}O_2$

The mechanism of electrochemical preparation for $Co_xNi_{1-x}(OH)_2$ can be expressed as

Anodic reaction:

$$Co \longrightarrow CO^{2+} + 2e,\ Ni \longrightarrow Ni^{2+} + 2e \qquad (1)$$

Cathodic reaction:

$$2H_2O + 2e \longrightarrow H_2\uparrow + 2OH^- \qquad (2)$$

pH value of the solution near cathode increased during the electrolysis process, and the precipitation of Ni^{2+}, CO^{2+} with OH^- took place:

$$xCO^{2+} + (1-x)Ni^{2+} + 2OH^- \longrightarrow Co_xNi_{1-x}(OH)_2\downarrow \qquad (3)$$

After being rinsed and dried, the Co-Ni hydroxide precipitation was mixed with LiOH by molar ratio of Li to Co_xNi_{1-x} of 1.05/1.00. The mixture was calcined to obtain the cathode material $LiCo_xNi_{1-x}O_2$. The contents of Ni and Co in the alloys and the electrolysis products are listed in Table 1. As can be seen, the ratio of Ni to Co in the $Co_xNi_{1-x}(OH)_2$ keeps accordant with that in the alloys, which means the preparation method is convenient.

Table 1 Molar ratio of Co to Ni in Co_xNi_{1-x} alloy and $Co_xNi_{1-x}(OH)_2$

Co_xNi_{1-x} alloy	Molar ratio of Co to Ni
$Co_{0.2}Ni_{0.8}$	0.199∶0.801
$Co_{0.5}Ni_{0.5}$	0.510∶0.490
$Co_{0.8}Ni_{0.2}$	0.800∶0.200
$Co_xNi_{1-x}(OH)_2$	Molar ratio of Co to Ni
$Co_{0.2}Ni_{0.8}(OH)_2$	0.207∶0.793
$Co_{0.5}Ni_{0.5}(OH)_2$	0.502∶0.498
$Co_{0.8}Ni_{0.2}(OH)_2$	0.802∶0.198

The XRD characterizations of Co, Ni and the Co_xNi_{1-x} alloy were investigated. All the XRD peaks for $Co_{0.2}Ni_{0.8}$ alloy are indexed as a single phase with a Ni fcc structure, indicating that the Ni and Co can be co-melted completely to form a solid solution alloy. Meanwhile, $Co_{0.5}Ni_{0.5}$ and $Co_{0.8}Ni_{0.2}$ alloys have the identical crystalline phase with a Co hexagonal structure. Fig. 1 shows the XRD patterns of $Co_xNi_{1-x}(OH)_2$ (x= 0.2, 0.5 and 0.8) obtained by electrolysis of their corresponding Co_xNi_{1-x} (x= 0.2, 0.5 and 0.8) alloys. It is found that the peaks of $Co_{0.2}Ni_{0.8}(OH)_2$ can be assigned to β-$Ni(OH)_2$ with a hexagonal structure, while $Co_{0.5}Ni_{0.5}(OH)_2$ and $Co_{0.8}Ni_{0.2}(OH)_2$ are detected to mainly have β-$Co(OH)_2$ structure with a little $Ni(OH)_2 \cdot 0.75H_2O$. Therefore, it can be concluded that the hydroxide precipitate can be obtained by electrolysis of Ni-Co alloy, and the structure of the hydroxide depends on the main element content in their corresponding alloys.

XRD patterns of the resulting oxides $LiCo_xNi_{1-x}O_2$ are illustrated in Fig. 2, which show a hexagonal structure with good crystallizability. Taking the pattern of $LiCo_{0.2}Ni_{0.8}O_2$ as an example, the diffraction intensity of (003) plane (2θ= 18.8°) is the strongest, the intensity ratio of I_{003}/I_{104} is about 1.785 7, whereas the intensity ratio of I_{003}/I_{006} is near 25. Therefore, the structure of $LiCo_{0.2}Ni_{0.8}O_2$ can be approved as the layered α-$NaFeO_2$[14]. Moreover, as seen in Table 2, the values of a and c decrease, and the ratio of c/a is raised with the increasing Co content. In addition, the particle size distribution is homogeneous from SEM images as shown in Fig. 3.

3.2 Electrochemical performance

In the galvanostatic charge-discharge cycling

Table 2 Crystallographic parameters of $LiCo_xNi_{1-x}O_2$ cathode materials synthesized in different atmospheres

Material	a/ Å	c/ Å	c/a	V/ Å^3	I_{003}/I_{104}	R-factor
$LiCo_{0.2}Ni_{0.8}O_2$(air)	2.867 4	14.193 9	4.950 1	101.07	1.893 2	0.520 6
$LiCo_{0.5}Ni_{0.5}O_2$(air)	2.845 5	14.132 9	4.966 7	99.1	2.008	0.458
$LiCo_{0.8}Ni_{0.2}O_2$(air)	2.827 2	14.083	4.981 2	94.78	2.056	0.455 9
$LiCo_{0.2}Ni_{0.8}O_2$(O_2)	2.864 3	14.173 8	4.948 4	100.71	2.045	0.416 9

R-factor: $[I_{006}+I_{102}]/I_{101}$

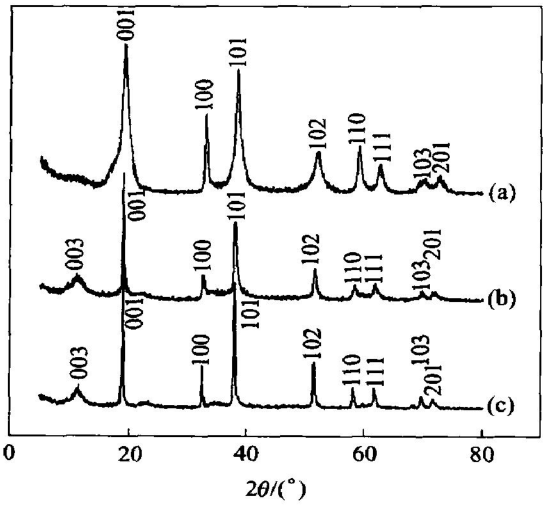

Fig. 1 XRD patterns of $Co_xNi_{1-x}(OH)_2$
(a) —$Co_{0.2}Ni_{0.8}(OH)_2$; (b) —$Co_{0.5}Ni_{0.5}(OH)_2$; (c) —$Co_{0.8}Ni_{0.2}(OH)_2$

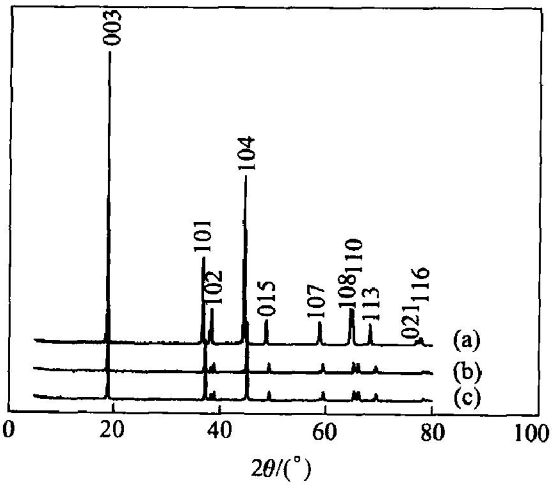

Fig. 2 XRD patterns of $LiCo_xNi_{1-x}O_2$ cathode materials
(a) —$LiCo_{0.2}Ni_{0.8}O_2$; (b) —$LiCo_{0.5}Ni_{0.5}O_2$; (c) —$LiCo_{0.8}Ni_{0.2}O_2$

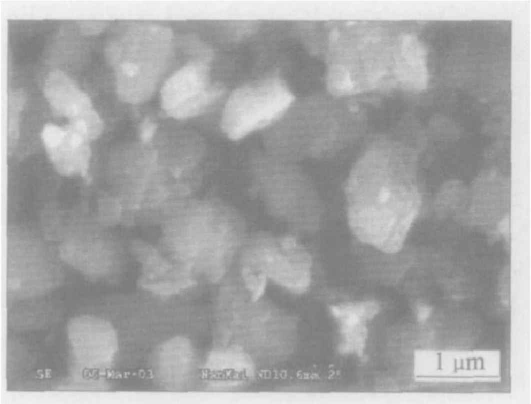

Fig. 3 SEM images of $LiCo_{0.2}Ni_{0.8}O_2$ synthesized in air atmosphere

test, the first charge/discharge capacity of the $LiCo_xNi_{1-x}O_2$ ($x=0.2$, 0.5 and 0.8) cathode is 199/156, 180/146 and 168/146 (mA • h/g), respectively. After 20 charge/discharge cycles, the charge/discharge capacity of the $LiCo_xNi_{1-x}O_2$ ($x=0.2$, 0.5 and 0.8) cathode is 150/146, 142/138 and 130/127 (mA • h/g), respectively. It's clear that the $LiCo_{0.2}Ni_{0.8}O_2$ cathode material exhibits highest electrochemical charge/discharge capacity and best cycle stability. The higher Ni content in the oxide is beneficial to increasing discharge capacity and improving cycle stability of the electrodes.

In order to investigate the effect of the atmosphere during heat-treatment on the properties of $LiCo_xNi_{1-x}O_2$, $LiCo_{0.2}Ni_{0.8}O_2$ was prepared under air and oxygen flow respectively. The crystallographic parameters of $LiCo_{0.2}Ni_{0.8}O_2$ cathode synthesized in different atmosphere are shown in Table 2. Compared with the $LiCo_{0.2}Ni_{0.8}O_2$ prepared in air, the ratio of I_{003}/I_{004} is higher and R-factor ($[I_{006}+I_{102}]/I_{101}$) is lower for the material prepared in O_2, which means that the crystallizability of the latter is better[21]. Fig. 4 shows the charge-discharge cycle performance of $LiCo_{0.2}Ni_{0.8}O_2$ cathode synthesized in different atmospheres. The capacity of the $LiCo_{0.2}Ni_{0.8}O_2$ prepared in O_2 atmosphere at the first charge-discharge cycle is 224 mA • h/g for charging and 175 mA • h/g for discharging, thus the efficiency is 78.1%. The charging/discharging capacity decreases gradually down to 170/164 (mA • h/g) after 40 cycles. The reversible capacity of the oxide made in air is relatively lower, and the reversibility seems stable for both samples.

The diffusion coefficients D of Li^+ in the $LiCo_{0.2}Ni_{0.8}O_2$ cathode prepared in different atmospheres were studied by PSCA (potential step chro-

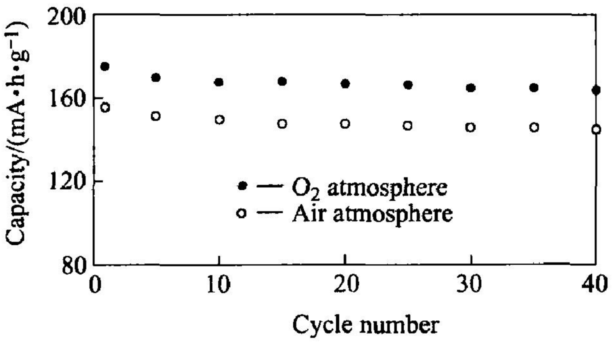

Fig. 4 Charge-discharge cycle performance of $LiCo_{0.2}Ni_{0.8}O_2$ cathode synthesized in air and O_2 atmosphere at current rate of 0.2C

noamperometry) method in the potential step of 4.100 V and 4.105 V, as shown in Fig. 5. It can be seen that the materials' particle size is only about 1 μm, the amount of PTFE binder is little, and the oxide powders can contact with each other very well. So the diffusion coefficient D can be calculated from the Cottrell region according to the follow formula[22]:

$$D = \frac{l^2 \cdot \pi (It^{1/2})^2}{Q^2}$$

where Q is the total charge capacity involved in the potential step, l is the diffusion length which is considered a half of the average size of the particle. The diffusion coefficient D of Li^+ in $LiCo_{0.2}Ni_{0.8}O_2$ cathode synthesized in air and O_2 atmosphere is calculated to be 0.78×10^{-12} cm^2/s and 1.69×10^{-12} cm^2/s, respectively. After 40 charge-discharge cycles, the value of D for the latter reduces to be 1.36×10^{-12} cm^2/s. Obviously, the D values for the material prepared in O_2 are larger than the one prepared in air atmosphere, indicating that the reaction polarization of the material synthesized in O_2 atmosphere is lower and Li^+ diffusion efficiency is higher. After 40 cycles, the diffusion coefficient of Li^+ in the $LiCo_{0.2}Ni_{0.8}O_2$ synthesized in O_2 atmosphere can still be kept at a fairly high value, which means that the speed of Li^+ insert/desert is still rapid.

Therefore, the atmosphere for preparing the oxide from the electrolysis product is important. Oxygen is favorable for the oxides preparation, because it is somewhat difficult for Ni^{2+} to be oxidized to Ni^{3+} [23], while oxygen can promote the transformation and reduce the content of Ni^{2+} in the resulting oxide[24]. Based on the results of Rietveld refinement, some Ni^{2+} exists at Li^+ site in $LiNiO_2$[9]. As some nonstoichiometric $LiNiO_2$ can be formed and there are several phase transitions during the charging-discharging process, the electrochemical capacity fading of the electrode will be serious. Based on the results, Ni^{2+} can be oxidized to Ni^{3+} in the material prepared in O_2 atmosphere, so the content of Ni^{2+} can be reduced evidently[24], and the electrochemical properties are improved.

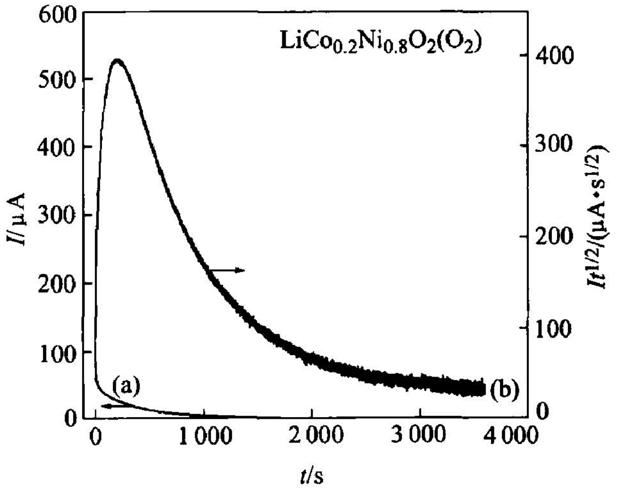

Fig. 5 Relationship between $I - t$(a) and $It^{1/2} - t$ (b) of $LiCo_{0.2}Ni_{0.8}O_2$ cathode synthesized in O_2 atmosphere before charge-discharge cycle

4 CONCLUSIONS

A new method was investigated to prepare the cathode materials $LiCo_xNi_{1-x}O_2$ (x = 0.2, 0.5 and 0.8) from the reactant $Co_{1-x}Ni_x(OH)_2$ by electrolysis of Co_xNi_{1-x} alloy. $Co_{1-x}Ni_x(OH)_2$ can be conveniently attained by electrolysis of corresponding alloy in the same stoichiometry. This method is more economical with less pollution compared with conventional method. The electrochemical performance of $LiCo_xNi_{1-x}O_2$ (x = 0.2, 0.5 and 0.8) materials is improved with the increase of the Ni content. Among them the $LiCo_{0.2}Ni_{0.8}O_2$ exhibits the highest capacity and the best cycleability. The atmosphere in sintering process plays an important role in the performance of the cathode material. Compared with that sintered in air atmosphere, $LiCo_{0.2}Ni_{0.8}O_2$ with better crystallizability, electrochemical character and higher Li^+ diffusion rate can be achieved in oxygen atmosphere.

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