Study on the preparation of LiCoO$_2$ by multiphase redox method

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ARTICLE INFO

ABSTRACT

We report a new method, which is called multiphase redox method, to prepare LiCoO$_2$ cathode material. The SEM results of precursors show that the secondary particles are dispersed well. The effects of process conditions on the preparation of precursors for LiCoO$_2$ have been studied and the best conditions for synthesis of the precursors have been obtained. The reaction temperature is 75–85 °C; the reaction time is 6–8 h and the Li$^+$ concentration is 20–30 g L^{-1}. Under these conditions, the precursors have been obtained, in which specific surface area (BET) is 20–50 m^2 g^{-1}; the particle size is about 100 nm and n(Li)/n(Co) is 0.8 to 1.0. The best sintering process is as follows. The heating rate is 165 °C h^{-1}; the sintering temperature is 850 °C and the retention time is 5 h. Sintered products present good electrochemical performance. The results indicate that the initial discharge capacity is above 150 mAh g^{-1} and the average decay rate of each cycle is only 0.04% in the initial eight cycles.

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1. Introduction

LiCoO$_2$ is the most widely used cathode material for commercial secondary lithium batteries due to its advantages, including easy preparation and good cyclability [1–3]. Numerous researches on LiCoO$_2$ have been carried out to find out the novel preparation method [4–9]. In this paper, a new method to prepare LiCoO$_2$, which is called multiphase redox method, is introduced.

The process of preparation of LiCoO$_2$ by multiphase redox method is as follows. First, the cobalt sulfate (CoSO$_4$·7H$_2$O) or cobalt chloride (CoCl$_2$·6H$_2$O) was used as the raw material to generate the precipitation of cobalt hydroxide (Co(OH)$_2$). Then by adding lithium hydroxide (LiOH·H$_2$O) or lithium chloride, cobalt hydroxide was oxidized to the precursors for LiCoO$_2$. After the precursors were dried in drying equipment and sintered in a certain temperature and treated appropriately, the product of LiCoO$_2$ was obtained. The most important feature of the method is that the layered structure of LiCoO$_2$ is obtained directly in water solution, improving greatly the uniformity of the material. Compared with other method reported in Refs. [10,11], multiphase redox method to prepare the LiCoO$_2$ had greater advantages in both technology and cost. From a technical perspective, by making use of the new theory of multiphase reaction, the reaction of embedding lithium was fulfilled in water solution and the ultrafine precursors with the structure of LiCoO$_2$ could be obtained. With BET of 20–50 m^2 g^{-1} and particle size of about 100 nm, the precursors not only were very uniform in chemical composition, but also had good sintering activity, which could reduce the sintering temperature, shorten the sintering time and provide a reliable guarantee for LiCoO$_2$ with high quality. Meanwhile, from a cost perspective, the raw materials to prepare

LiCoO$_2$ by multiphase redox method were not the costly Co$_3$O$_4$ or CoO, but cobalt salt with relatively low price. So the production costs could reduce greatly, improving the competitiveness of this product.

This paper studies the preparation of LiCoO$_2$ by multiphase redox method, including the process conditions to prepare the precursors, the reaction mechanism, the sintering and the electrochemical performance of the sintered products.

2. Experimental

After CoSO$_4$·7H$_2$O or CoCl$_2$·6H$_2$O was dissolved and purified, the qualified solution containing cobalt salt was obtained. Followed by adding the excessive solution of sodium hydroxide, the different oxidants were fed into the solution, and then the precipitation of Co(OH)$_2$ was obtained. When the reaction temperature was 50–90 °C; the reaction time was 1–10 h and the concentration of Li$^+$ in the solution was 5–28 g L^{-1}, the reaction of embedding lithium was fulfilled. After filtering the reaction product, the precursors were obtained. The dried precursors were sintered at the heating rate of 165 °C h^{-1}, at the temperature range of 650–900 °C and in different retention time, followed by appropriate treatment to obtain the product of LiCoO$_2$.

The phase structure of the precursors was tested by X-ray diffraction (Rigaku, D/Max-rA). The XRD data were collected between 10° and 70° of the 2θ angles with a step size of 0.01° under monochromatized Cu Kα radiation (50 kV and 100 mA). The morphology of sample was checked using a scanning electron microscope (SEM, JSM-5600LV).

Electrochemical performances were evaluated with coin cells. Cathodes were prepared by mixing 85 wt.% active material with 10 wt.% acetylene black and 5 wt.% poly (tetrafluoroethylene) binder, rolling the mixture into thin sheets below 0.2 mm thick. Coin cells were assembled with the cathodes, lithium anode, 1 mol L^{-1} LiPF$_6$ in
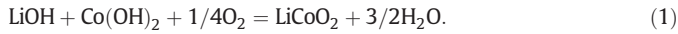
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ethylene carbonate/diethyl carbonate electrolyte, and Celgard polyethylene separator.

3. Results and discussion

The reaction of $Co(OH)_2$ with LiOH and O_2 is as follows.

$$LiOH + Co(OH)_2 + 1/4O_2 = LiCoO_2 + 3/2H_2O. \tag{1}$$

The free enthalpy variation of this chemical reaction at 298 K is -69.295 kJ mol^{-1}, so Eq. (1) is feasible in thermodynamics.

The condition that the reaction of multiphase redox can run smoothly is that the volume of the product V(P) is smaller than that of the reactant V(R). The expression of PBR is as follows. PBR = V(P)/V(R) = M(P)d(R)/M(R)d(P), where M(P) and M(R) are the molecular weights of products and reactants, and d(P) and d(R) are the densities of products and reactants, respectively.

When PBR > 1, the layer of products covers completely the surface of reactants. But when PBR < 1, the product layer is loose and porous, and cannot cover the surface of reaction, which means that the new unreacted surface will be exposed during reaction and the product layer will peel off the substrate. So the necessary condition that the product layer of multiphase redox reaction will be peel is PBR < 1.

The value of PBR for Eq. (1) is PBR = V(LiCoO$_2$)/V(Co(OH)$_2$) = (97.87/5.1)/(92.93/3.6) = 0.74 < 1. So LiCoO$_2$ cannot form a complete covering layer on the reactant of Co(OH)$_2$, which means that LiCoO$_2$ can continually grow.

In addition, the chemical bond on solid surface is asymmetry and the chemical bond is open during the reaction of multiphase redox, which makes it possible that the lithium ion may be involved in the reaction to generate the LiCoO$_2$. The above analysis shows that Eq. (1) is also feasible in dynamic.

The molar ratio of Li/Co of synthetic product can be calculated by n(Li)/n(Co) = 8.49 × (w(Li)/w(Co)), where w(Li) and w(Co) are the mass fractions of lithium and cobalt in the product, respectively. The purity of LiCoO$_2$ can be expressed by n(Li)/n(Co) which is 1.0 in pure LiCoO$_2$. The more the LiCoO$_2$ will be produced, the more the value of n(Li)/n(Co) is close to 1. In fact, the value of n(Li)/n(Co) in synthetic product is less than 1.

Combined with the previous experiment, it is proposed that the surplus cobalt that did not generate LiCoO$_2$ actually generated Co$_3$O$_4$, which means that, beside Eq. (1), Eq. (2) also occurred when the cobalt hydroxide was oxidized.

$$3Co(OH)_2 + 1/2O_2 = Co_3O_4 + 3H_2O \tag{2}$$
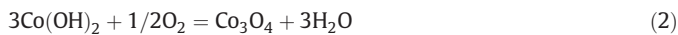
The relationship of E-pH at different ion concentration in the system of Li–Co–H$_2$O was drawn by Wen et al. [12]. When Li$^+$ does not exist in the system, Co element, Co^{2+}, Co(OH)$_2$, HCoO$_2^-$, Co$_3$O$_4$ and Co(OH)$_3$ can exist stably in the thermodynamics within a large range. But after the lithium salt was added (in fact in the alkaline solution), the stability regions of each cobalt compound were influenced by Li$^+$, and the stability region of Co(OH)$_3$, Co$_3$O$_4$, Co(OH)$_2$ and HCoO$_2^-$ compounds was mostly engulfed by LiCoO$_2$ stable region. When the concentration of Li$^+$ increased to 1 mol L^{-1}, the stable region of Co$_3$O$_4$ had been engulfed completely; Co(OH)$_3$ stable zone had been moved mostly above the O$_2$ line, and the stable region of HCoO$_2-$ had been moved to the region of pH > 18.

During the synthesis reaction of the precursors, the concentration of Li$^+$ was usually above 1 mol L^{-1}. According to the experimental phenomenon and E-pH diagram in Li–Co–H$_2$O system, it could be concluded that, in the presence of an oxidant, there could be three mechanisms for the synthesis of LiCoO$_2$ in Li–Co(OH)$_2$–H$_2$O system.

1) Mechanism 1 Co(OH)$_2$ was directly oxidated to synthesize the LiCoO$_2$.

$$Co(OH)_2 + Li^+ - e^- = LiCoO_2 + 2H^+ \tag{3}$$

2) Mechanism 2 Co(OH)$_2$ was hydrolyzed firstly to HCoO$_2^-$ which then was oxidated to synthesize the LiCoO$_2$.

$$Co(OH)_2 = HCoO_2{}^- + H^+ \tag{4}$$

$$HCoO_2{}^- + Li^+ - e^- = LiCoO_2 + H^+ \tag{5}$$

3) Mechanism 3 Co(OH)$_2$ was oxidated firstly to Co$_3$O$_4$ which then was oxidated to synthesize the LiCoO$_2$.

$$3Co(OH)_2 - 2e^- = Co_3O_4 + 2H_2O + 2H^+ \tag{6}$$

$$Co_3O_4 + 2H_2O + 3Li^+ - e^- = 3LiCoO_2 + 4H^+ \tag{7}$$
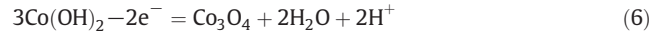
The above three possible mechanisms might exist at the same time when the precursors of LiCoO$_2$ were synthetized by multiphase redox method. When the ionic concentration increased, the stability region of Co$_3$O$_4$ tended to be close to the O$_2$ line and be smaller, so that Eq. (7) became more difficult. So Eq. (6) should try to be restrained during the synthesis of the precursors of LiCoO$_2$, and the reaction to synthetize the precursors of LiCoO$_2$ should be encouraged to occur according to the Mechanism 2.

According to the experimental phenomenon, the filtrate was blue, so it could be concluded that the precursors were synthesized mainly according to Mechanisms 1 and 2. The blue filtrate should be contributed to HCoO$_2$ or [Co(OH)$_4$]$^{2-}$. When the color of blue disappeared, the reaction to generate LiCoO$_2$ became very slow. So the reaction of Mechanism 2 should disappear, and the reaction of Mechanism 3 could exist in the system of LiCoO$_2$ synthesis reaction.

It was also mentioned in the Ref. [12] that the direct synthesis of LiCoO$_2$ could be possible according to the thermodynamics in the non-alkaline solution at low pH values, which means that Co^{2+} could be used to synthesize the LiCoO$_2$ directly in the solution containing Li$^+$. According to the E-pH diagram, when [Li$^+$] = 1 mol L^{-1}; 2.68 < pH < 6.80 and 0.798 V > E > 0.533 V, if Co^{2-} was chosen as one of the raw materials, the LiCoO$_2$ could be synthesized directly in an aqueous solution containing Li$^+$. The reaction is more prone to occur with the increase of the concentration of Li$^+$.

The authors tried to synthesize the LiCoO$_2$ in the range of 2.68 < pH < 6.80, but did not succeed. Using the mixed solution of Co(NO$_3$)$_2$·6H$_2$O, LiOH·H$_2$O and H$_2$O$_2$ (50%), the LiCoO$_2$ was synthesized successfully by hydrothermal method by Burukhin et al. [13]. But there is still a question as to whether the solution system could be made sure to be non-alkaline after adding the LiOH·H$_2$O. It was likely to be that Co(NO$_3$)$_2$·6H$_2$O reacted with the LiOH·H$_2$O to generate Co(OH)$_2$ which then was oxidized to synthesize the LiCoO$_2$.

The SEM of the precursors is shown in Fig. 1 which indicates that the secondary particles with particle size of about 100 nm are very uniform and dispersed well.

3.1. The effect of different oxidants on the synthesis of the precursors

The authors tried to synthesize LiCoO$_2$ by using air, oxygen, H$_2$O$_2$ or NaClO$_3$ as different oxidants at 90 °C with reaction time of 10 h when the concentration of LiOH was 3.7 mol L^{-1}; the concentration of CoSO$_4$ was 30 g L^{-1} and the concentration of NaOH was 80 g L^{-1}. The n(Li)/n(Co) in the precursors is shown in Table 1.

The results in Table 1 indicate that, the value of n(Li)/n(Co) in the precursors is very close when the air and oxygen are used as the oxidant, and less lithium is embedded in the precursors by using H$_2$O$_2$ as the oxidant. H$_2$O$_2$ should be the same effect as the air and oxygen,