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Research on high density and safety $LiCoO_2$ as cathode materials for lithium ion batteries

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Abstract: Three $LiCoO_2$ samples of different specifications were synthesized using different Co_3O_4s as starting material, and characterized in physical, electrochemical and safety properties. There demonstrates clear dependence of $LiCoO_2$ on Co_3O_4 in particle size and density. The main difference among the three $LiCoO_2$ samples lies in physical, rate capability and safety properties, the sample with larger particle size, higher density (accordingly smaller surface area) demonstrates better safety but lower rate capability, while there is little difference among them in terms of capacity and cycling stability despite of the variation in physical properties.

Key words: cathode material; $LiCoO_2$; Co_3O_4; lithium ion battery

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1 Introduction

Lithium ion batteries are largely adopted for potable electronic devices due to its high capacity, high voltage and good safety attributes. The advancement of lithium battery requires new type of cathode materials with high energy density, as well as good safety and low cost. Accordingly the cathode materials are being developed in two directions[1]. One way is to increase the gravimetric capacity of the materials, e.g. by preparing $LiNi_{1-y}Co_yO_2$ with higher capacity but poor thermal stability[2] and rate capability; the other way is to increase the volumetric capacity, e.g. by making $LiCoO_2$ with higher density, larger particle size and small surface area, thus increasing the energy density and safety properties of the battery. Up to now, $LiCoO_2$ is the only cathode material commercialized successfully, so the improvement and upgrade of $LiCoO_2$ is practically one of the most important tasks of the lithium battery industry.

In this paper, three samples of $LiCoO_2$ with different specifications were synthesized and tested. There demonstrates clear dependence of $LiCoO_2$ on Co_3O_4 in particle size and density. The main difference among them lies in the safety and physical properties. The sample with larger particle size, higher density (accordingly smaller surface area) demonstrates better safety, while there is little difference among them in terms of electrochemical properties.

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2 Experimental

Three $LiCoO_2$ samples, denoted as $LiCoO_2$-6#, $LiCoO_2$-8# and $LiCoO_2$-10#, were synthesized in a solid state reaction of Li_2CO_3 with Co_3O_4 of 3 specifications, correspondingly named as Co_3O_4-6#, Co_3O_4-8# and Co_3O_4-10#. In order to compensate the loss of Li-source, extra Li_2CO_3 were added for preparing large-sized $LiCoO_2$.

To examine the correlation of the products and raw materials, the XRD patterns of the raw material of Co_3O_4s and the product $LiCoO_2$s were tested by using Rigaku 20/2 diffractometer, of which CuKα with a wavelength of 1.5406 angstrom was used as a ray source, and tube voltage and current are of 40 kV, 40 mA, respectively. Besides, all the samples are characterized in terms of physical properties, e.g. SEM, particle size distribution, surface area, apparent density and tap density.

To compare the electrochemical properties of the $LiCoO_2$ samples, prismatic batteries 053048 with a nominal capacity of 700 mAh were fabricated using the $LiCoO_2$ samples as cathode active material, artificial graphite as anode, 1M LiPF6/EC+DMC+EMC as electrolyte, and some properties were tested including charging-discharging, cycling, rate capability and thermal shock at 150℃ of fully charged battery.

3 Results and discussion

To examine the dependence of $LiCoO_2$ on Co_3O_4, XRD of the raw materials and the products were tested using a diffractometer of Rigaku, with a scanning step of 0.02°, Fig. 1 shows the X-ray diffraction profiles of Co_3O_4 of different specifications. All the Co_3O_4 mainly have the spinel-type of structure, although Co_3O_4-10# contains little impurity phase of CoO, which is indicated by the line at ca. 42.4°. Bear in mind that Co_3O_4-10# has the largest particle size of all these three Co_3O_4 samples, it suggests that it is difficult to fully oxidize cobalt oxide with larger particle size due to the diffusion of oxygen. Fig. 2 shows the XRD profiles of the samples of $LiCoO_2$, all the $LiCoO_2$ samples have a rock-salt structure of α-$NaFeO_2$, concluding no impurity phase. This means the little content of impurity CoO phase in Co_3O_4 doesn't affect the crystallization of $LiCoO_2$. By comparison of XRD of the $LiCoO_2$ samples, the diffraction peak moves to larger angle with the increase in particle size of the samples, implying that the lattice constant decreases with the increase in particle size, e.g. $LiCoO_2$-10# with the largest particle size while having the smallest lattice constant. Besides the effect of larger size of Co_3O_4 was adopted, higher Li/Co was used to benefit the crystallization for making large-sized $LiCoO_2$, which may be one of the reasons for the lattice contraction.

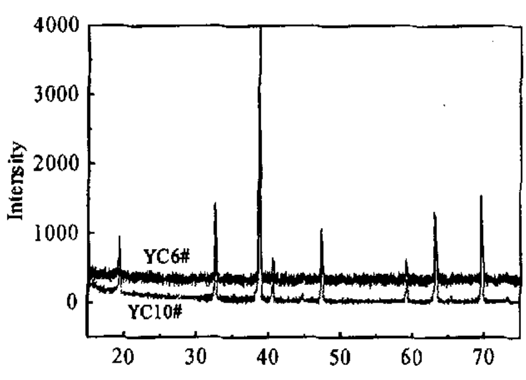

Fig. 1 XRD profiles of Co_3O_4

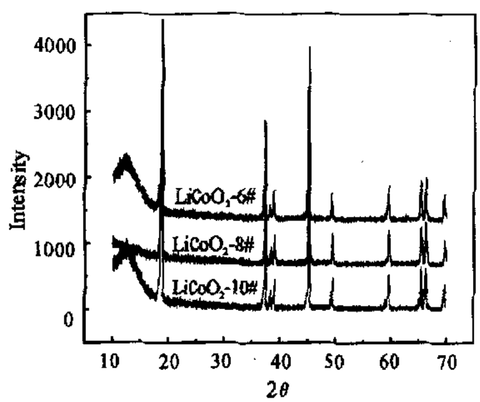

Fig. 2 XRD profiles of $LiCoO_2$

Fig. 3 shows the SEM images of $LiCoO_2$ samples, along with the corresponding raw material of Co_3O_4. These pictures show that: the larger particle size is the Co_3O_4, the larger size and better sphericity is the $LiCoO_2$. Table 1 also gives out the physical properties in terms of medium particle size (D50), tap density, apparent density and surface area of the Co_3O_4s and $LiCoO_2$s. There shows clear dependence of $LiCoO_2$ on Co_3O_4 in such physical properties. The larger is the particle size and density of Co_3O_4, the larger is the particle size, higher density and smaller surface area of $LiCoO_2$.

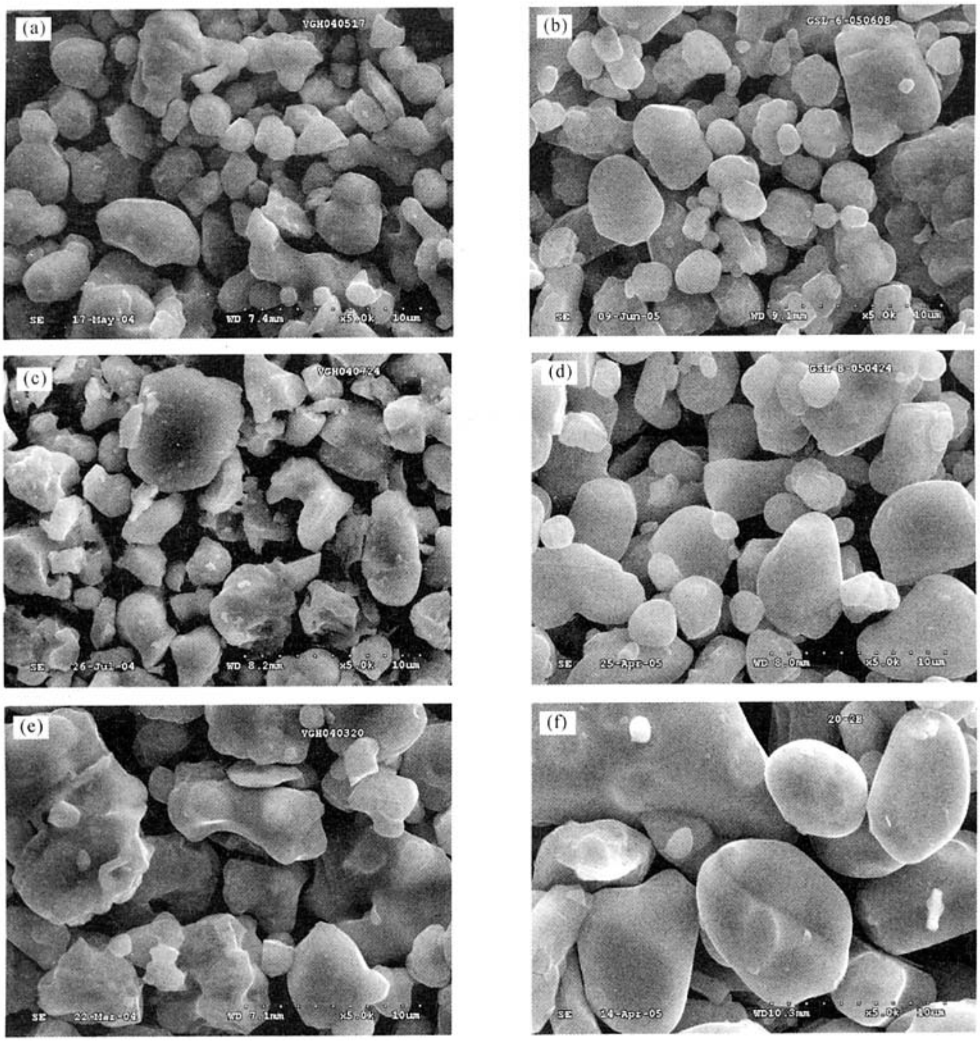

Fig. 3 SEM of $LiCoO_2$s and Co_3O_4s

(a)—Co_3O_4-6#; (b)—$LiCoO_2$-6#; (c)—Co_3O_4-8#; (d)—$LiCoO_2$-8#;
(e)—Co_3O_4-10#; (f)—$LiCoO_2$-10#

Table 1 Physical properties of Co_3O_4s and $LiCoO_2$s

Raw materials	D50 /μm	Tap density /(g·cm^{-3})	Apparent density (/g·cm^{-3})	Products	D50 /μm	Tap density /(g·cm^{-3})	Apparent density /(g·cm^{-3})	Surface area /(m^2·g^{-1})
Co_3O_4-6#	4.52	3.20	1.20	$LiCoO_2$-6#	7.58	2.34	0.93	0.45
Co_3O_4-8#	5.47	3.38	1.40	$LiCoO_2$-8#	7.93	2.57	1.21	0.39
Co_3O_4-10#	7.17	3.34	1.20	$LiCoO_2$-10#	11.12	2.63	1.42	0.27

Fig. 4 shows the cycling properties of the 3 $LiCoO_2$s-based batteries at 1.0C charge-discharge. These materials have very good cycling stability, generally keeping 96% of their initial capacity after 100 cycling. The capacity to 2.75 V, and the cycling stability of these materials are in the same level. While there is a little difference in the capacity above 3.6 V of the $LiCoO_2$ samples, which is readily related to difference in the rate capability of them at 1.0C.

To compare the rate capability of batteries using the 3 $LiCoO_2$ as cathode material, the batteries were firstly fully charged to 4.2 V, and then discharged to 2.75 V at various currents of 0.2C, 0.5C, 1.0C and 2.0C. The test results in Table 2 and Fig. 5 clearly show that the rate capability of $LiCoO_2$-6# is the best of the 3 samples, and the capacity ratio of 2.0C/0.2C can be 96.59%, while the capacity ratio of 2.0C/0.2C for $LiCoO_2$-10# is only 94%, although it has a similarly high capacity as other samples at low current.

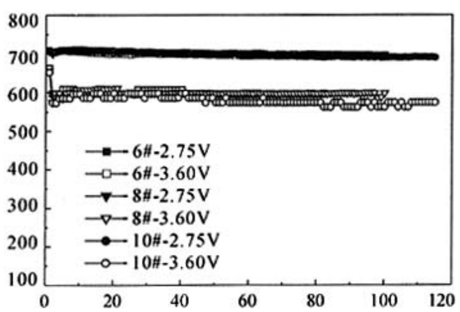

Fig. 4 Cycling stability of $LiCoO_2$-6#, $LiCoO_2$-8# and $LiCoO_2$-10#

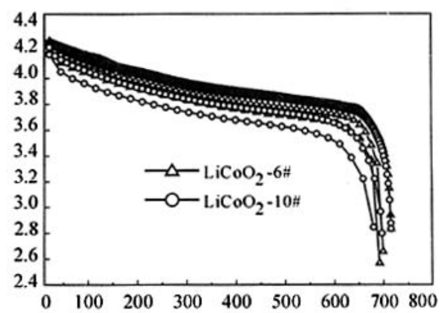

Fig. 5 Comparison of rate capability of $LiCoO_2$-6# and 10#

The safety properties of lithium ion battery attract much concern of the industry[3]. In this research, the batteries using the $LiCoO_2$ samples as cathode materials were stored in the thermal box of 150℃ at fully charged state of 4.2 V[4], and checking the time duration before explosion of the battery. The results are shown in the last column of Table 2, $LiCoO_2$-10# goes through the longest time, and enjoys the best safety.

Table 2 Rate capability and thermal shock of $LiCoO_2$-6#, $LiCoO_2$-8# and $LiCoO_2$-10#

Sample	0.2C/0.2C	0.5C/0.2C	1.0C/0.2C	2.0C/0.2C	Thermal shock (150℃)
$LiCoO_2$-6#	100%	98.53%	97.65%	96.59%	22 min
$LiCoO_2$-8#	100%	99.14%	98.25%	95.73%	43 min
$LiCoO_2$-10#	100%	98.82%	97.33%	94.84%	>60 min

4 Conclusion

The above data and discussion can readily lead to the conclusion. There are clear effects of the specification of the raw material Co_3O_4 on $LiCoO_2$ in the structure, physical properties, electrochemical properties and safety aspects. And large particle size and high density of Co_3O_4 are quite beneficial to prepare $LiCoO_2$ with large particle size, high density and small surface area. These will in turn affect the electrochemical and safety properties of the battery. The $LiCoO_2$ material with large particle size enjoys good safety properties, while small-sized $LiCoO_2$ takes an advantage in rate capability.

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