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Syntheses of $LiCoO_2$ for cathode materials of secondary batteries at low temperature

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Abstract: *In this paper, it acquired an important discovery that the new Co_3O_4 fine particles include more O than the traditional Co_3O_4 particles. Synthesized $LiCoO_2$ by the LT- solid state reaction. Experimented the factor affect the process. $LiCoO_2$ have well-crystallized with the layered structure as proved by powder X-ray diffraction(XRD). The particles have a smaller size distribution around 100-300nm(SEM).*

Key words : tricobalt tetraoxygen, fine particles ,the low temperature synthesis reactions

1. INTRODUCTION

$LiCoO_2$ have been studied as cathode materials in lithium secondary batteries because of their high operating voltage and energy density, large capacity, and long cycle life. Despite the highest cost among the candidate materials,$LiCoO_2$ is used most widely for its better thermal and structural stability during electrochemical operations.

$LiCoO_2$ powders are synthesized by solid state reactions about at high temperatures(HT) of 800^{o}C. The structure of $LiCoO_2$ is the Li+ implanting in the Co_3O_4 crystal. However, the structure of Co_3O_4 crystal is key factor for the $LiCoO_2$ crystal. The low temperature synthesis reactions can acquire more uniform fine particles, it is a useful feature for the battery electrode materials. In order to realize syntheses of $LiCoO_2$ by the LT-solid state reaction, the Co_3O_4 particles size need smaller than the HT process, we acquired an important discover that the new Co_3O_4 particles include more O than the traditional Co_3O_4 particles.

In this paper, we report the solid state reaction mixing the Co_3O_4 fine particles and $LiCoO_3$ powders at temperature 400-500^{o}C. The consequences in terms of the phase purity, crystallization, and particle sizes are described. The electrochemical charging and discharging characteristics of a representative sample is also presented.

2. EXPERIMENTAL

2.1 Raw material Co_3O_4 characterization

The raw material were identified by X-ray powder diffractometry(D/Max-Ra, Cu-K$_\alpha$, 40kv,40ma)Fig1. The particles size distribution was identified by the SEISHIN LMS-30. Fig2 is the SEM photography of Co_3O_4 fine particles Fig3 is traditional Co_3O_4 particles size distribution, D50 is about 27μ. Fig4 is the Co_3O_4 fine particles size distribution, D50 is 2.3μ. The experiment is base on the Co_3O_4 fine particles as the original material. The density of Co_3O_4 fine particles is only 1/8-1/10 of traditional Co_3O_4 particles.

2.2 Synthesis

In a LT-solid state reaction, Co_3O_4 fine particles and $LiCoO_3$ particles mole ratio 1:1.5 were mixed with alcohol (99%), grinding 4 hours, drying the mixture at 80^{o}C, the grinding time is decreased notably and the mixture is more homogeneous than the traditional Co_3O_4 particles. It is only spend 1/5 time of traditional Co_3O_4 particles acquired homogeneous state. The next step, rising the oven temperature at 450^{o}C, the mixture was put

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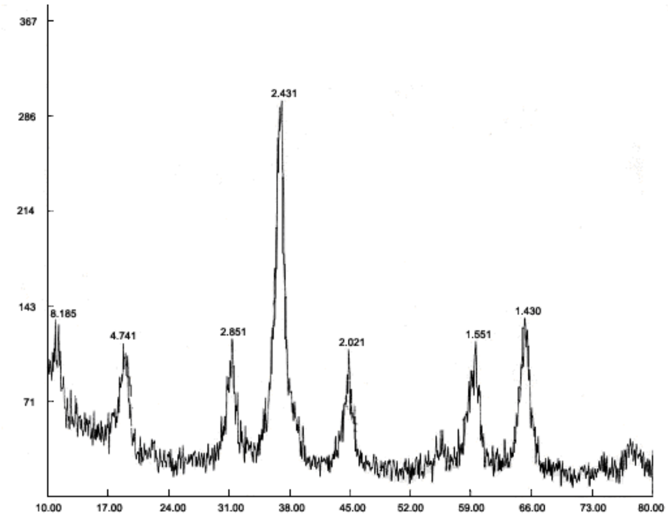

Figure 1: X-ray powder patterns of Co_3O_4.

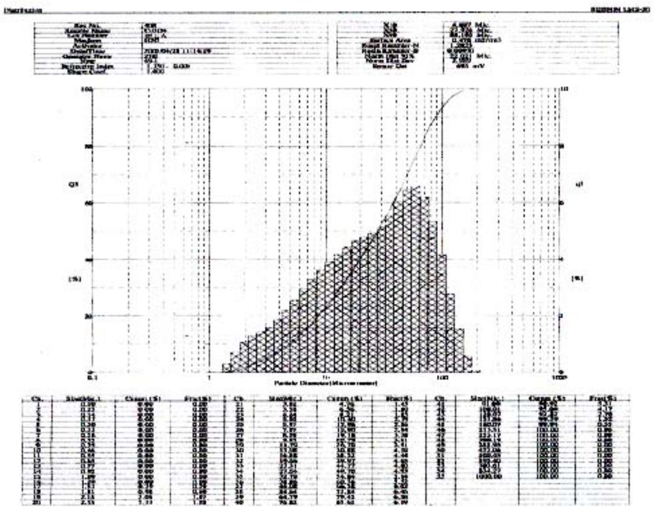

Figure 3: Traditional Co_3O_4particles size distribution.

Figure 2: the SEM photography of Co_3O_4 intermediate fine particles

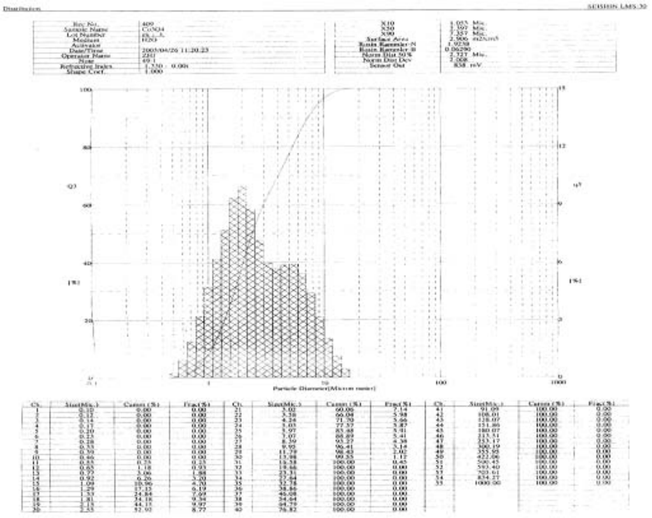

Figure 4: Co_3O_4 fine particles size distribution.

in the oven. The reaction is carried out at the temperature for 144 hours. The product was washed by the high-purity water for 15 times. Then it acquired the $LiCoO_2$ particles. The characteristic of $LiCoO_2$ was studied.

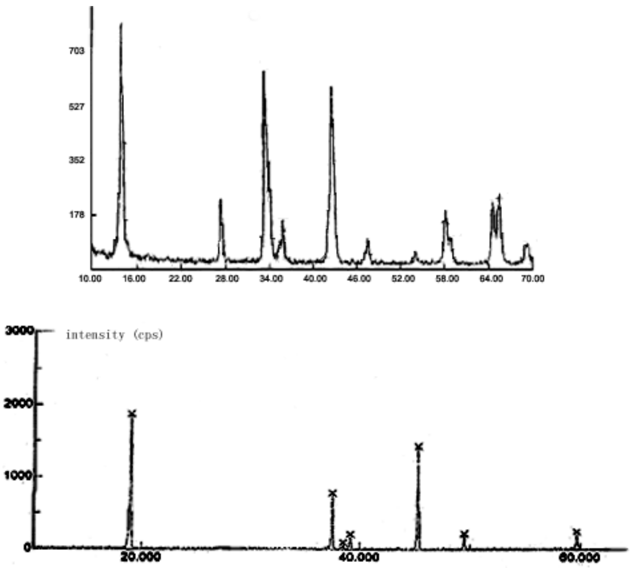

Figure 5: XRD patterns of $LiCoO_2$ powders at different reaction time

The fig5 shows XRD patterns of $LiCoO_2$ powders reaction time at 72hours and 144hours. Reaction time 144hours can acquire more purity $LiCoO_2$ powders. The average particle size is 1-3μ. $LiCoO_2$ is the Li+ implanting in the Co_3O_4crystal. The structure of $LiCoO_2$ is more uniform and the particle sizes is more small fig7, it can implant more Li+ than the traditional materials. The initiative capability of charging and discharging of $LiCoO_2$ electrode is better than the market selling battery. The initiative capability was improved about 14-20mAh/g notably. But the cycle efficiency of charging and discharging decreased rapidly, because the post-treatment of new $LiCoO_2$ electrode need more time to stabilize fig6.

3. ANALYSIS

450^{o}C LT- solid state reaction is possible because the special TGA-DTA characteristic of Co_3O_4 fine particles. The special exothermic at 350.94^{o}C can be detected. It is show in the fig8. The 350.94^{o}C peak form lead to the LT-solid state reaction realization. It shows that Co_3O_4 fine particles have a special crystal structure. From the fig8, It can observe that the new Co_3O_4 fine particles include about 3.085% O more than the traditional Co_3O_4 particles. More O including in the Co_3O_4 help the low temperature reaction process, it can make the LT reaction possible.

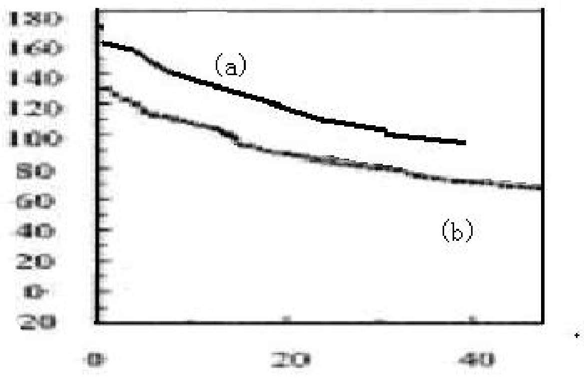

Figure 6: specific discharge capacity (a) LT-reaction syntheses (b) Reference reported[2].

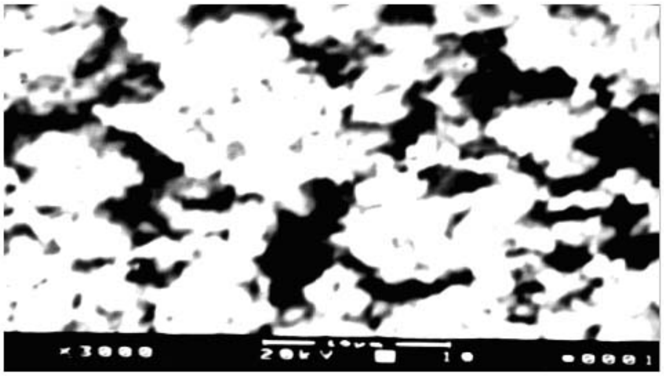

Figure 7: SEM patterns of $LiCoO_2$ powders

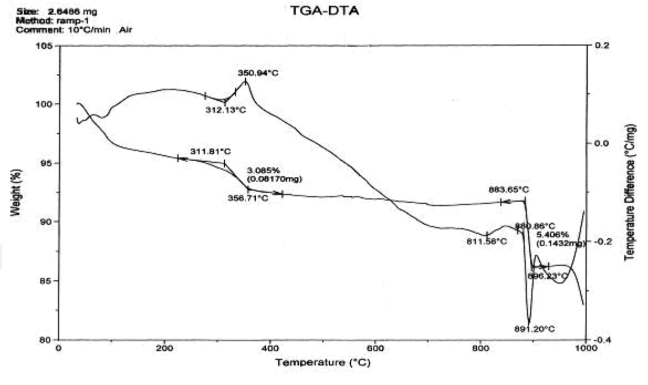

Figure 8: TGA-DTA curve of Co_3O_4 fine particles

It has not reported by other author before. The peak is benefit to the process temperature control, it acquired more uniform $LiCoO_2$ powders in a single phase.

4. CONCLUSION

Co_3O_4 fine particles is beneficial to the mixing process of LT- solid state reaction. It supplied the possibility for the LT- solid state reaction. The phase purity, crystallization, and particle sizes of $LiCoO_2$ powders are more uniform and small. It improves the original capability of charging and discharging of $LiCoO_2$ electrode. But the discharge-charge cycle capability of new $LiCoO_2$ electrode need to study more time.

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