Hydrothermal Synthesis of Cathode Materials for Lithium-ion Batteries

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Introduction

Lithiated transition metal oxides, such as $LiCoO_2$, $LiMnO_2$ (orthorhombic or layered) and $LiMn_2O_4$, have been studied widely as cathode materials for lithium-ion batteries because of their high operating voltage and energy density, large capacity and long cycle life. Despite of highest cost among candidate materials, $LiCoO_2$ is produced and used most widely due to its good thermal and structural stability during electrochemical operations. Commercial $LiCoO_2$ is synthesized by solid state reactions at high temperatures of 800 °C to 1000 °C, usually requiring a pretreatment step at lower temperatures. In order to reduce the production cost there was many attempts to find new synthetic methods at lower temperatures. Generally, low temperature synthesis result in fine powdery samples, which can be additional useful feature for battery materials as long as the cristallinity is not affected by small particles sizes. Many of low temperature synthesis methods, besides hydrothermal tehnique, results in low temperature (LT) phase (space group Fd3m) of $LiCoO_2$, with poorer electrochemical performance than the layer type high temperature (HT) (space group R-3m) phase, and requires additional heat treatment at 300 °C to 900 °C. Hidrothermal method appears to be the best alternative to traditional solid state reactions. This poster presents the details on the reaction conditions in the hydrothermal method, phase composition and particle morphology.

Experimental

Parr floor stand reactor

Two syntheses were done under the same conditions of temperature and pressure, but with different composition of precursor materials suspension. Reactant mixture, used for the synthesis of sample 1, was prepared from lithium hydroxide and cobalt (II) nitrate hexahydrate with Li/Co ratio 20:1. 50 ml of 1.2 M aqueous solution of cobalt (II) nitrate was added dropwise under vigorous stirring to 250 ml of lithium hydroxide solution/suspension. This mixture was hydrothermally treated at 200 °C for 4 h in Parr stirred batch reactor of 2000 ml volume made of 316 series stainless steel. Stirring rate was 300 rpm. The filling factor was 0.15 and hating rate to desired temperature was 2 °C/min. The same procedure was used for the synthesis of sample 2, except 50 ml of 50 % hydrogen peroxide was added to 250 ml of starting mixture with same amount of precursor materials. After synthesis the reactor was cooled to room temperature naturally in air. Products of both syntheses were dark brown colloidal suspensions, that were hard to ground. Products were filtrated off and washed repeatedly with distilled water until pH=7 was reached. Filtrates were dried at 150 °C in a drier. X-ray diffraction analysis of prepared samples was performed at Philips diffractometer (Cu $K\alpha_{1,2}$ radiation). X-ray diffraction data were used for structural refinement. Particle morphology was reveald by scanning elecron microscop JEOL JSM-6460LV.

SEM Results

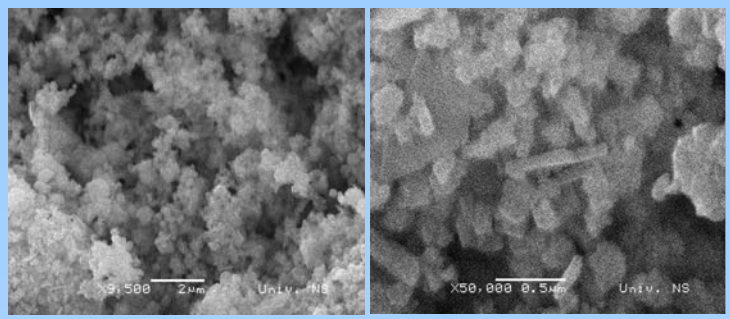

Figure 3 SEM images of $LiCoO_2$ powder sample 1

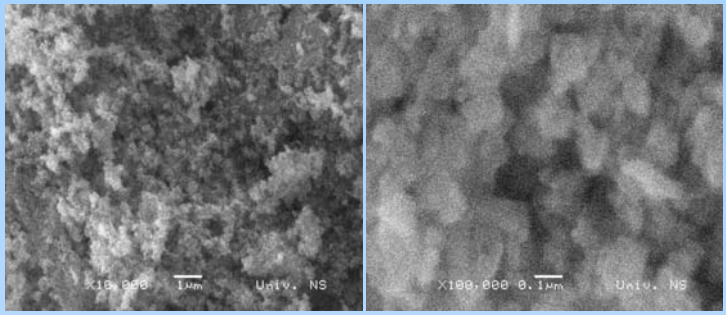

Figure 4 SEM images of $LiCoO_2$ powder sample 2

SEM images show that the particles are agglomerated and have wide size distribution from nano- to sub-micron sizes.

XRD Results

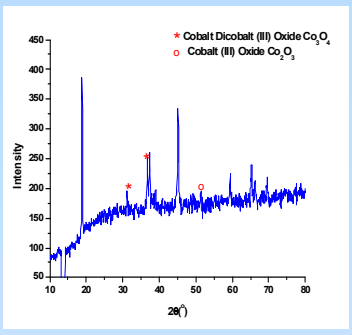

Figure 1 X-diffraction pattern of $LiCoO_2$ powder sample 1

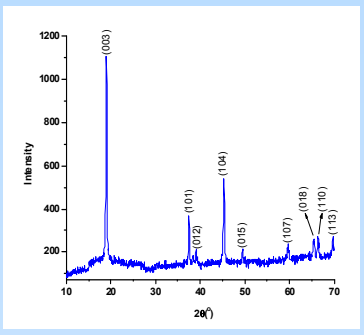

Figure 2 X-diffraction pattern of $LiCoO_2$ powder sample 2

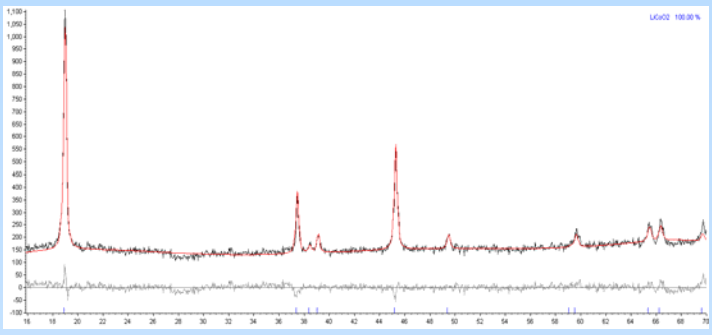

Figure 3 The observed (--), calculated (--) and difference (--) X-ray diffraction data of $LiCoO_2$ powder sample 2

Figs. 1 and 2 show XRD patterns of synthesized powders. First synthesis yields a mixture of $LiCoO_2$, Co_2O_3 and Co_3O_4. The presence of Co_3O_4 impurity is probably because of insufficient amount of O_2 available to fully oxidize Co^{2+} ion. Also, it is known that high oxidation state of metal ion is stabilized by high pH value, but in our case required pH value wasn't achieved because of low solubility of LiOH. The presence of Co_2O_3 is maybe because of a lack of time for subsequent formation of $LiCoO_2$ after oxidation reaction. X-ray pattern of sample 2 shows the presence of $LiCoO_2$ only, with no impurity phases. Phase purity was obtained due to oxidation of reactant mixture with hydrogen peroxide. Therefore, Rietveld based profile refinement was performed on sample 2, Fig. 3. The calculated cell parameters are a=2.81926 Å and c=14.0689 Å, while the c/a ratio is equal to 4.99, which is typical for HT-$LiCoO_2$. Increased intensity ratio of 003/104 indicates higher crystallinity of obtained phase structure. Average crystallite size of 40 nm was calculated from the half-width at the full maximum (β1,2) of (003) plane by using the Scherrer's equation.

Conclusion

- **Hydrothermal method was successfully used for the synthesis of $LiCoO_2$.**
- **Presence of oxidizer is required for obtaining the single-phased sample.**
- **The structure of $LiCoO_2$ powder has been refined in the space group R-3m.**
- **The particle morphology is the same for both synthesized powders and particles are agglomerated with wide size distribution from nano- to sub-micron sizes.**

References

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