Carbon Combustion Synthesis of Lithium Cobaltate

Y. Mamyrbayeva¹², M.A. Hobosyan¹, S.E. Kumekov², K.S. Martirosyan¹

¹University of Texas at Brownsville, Department of Physics and Astronomy, Brownsville, TX, 78520, USA, e-mail: karen.martirosyan@utb.edu
²Kazakh State Technical University named after K.I. Satpaev, Almaty, Republic of Kazakhstan

ABSTRACT

The crystalline LiCoO₂ nanoparticles were synthesized by carbon combustion synthesis of oxide (CCSO). The thermo-gravimetric analysis was used to identify interaction features in the system LiNO₃ - Co₃O₄ - Carbon to produce LiCoO₂. The major parameters affecting the process are the carbon concentration in the reactant mixture and the ability of the oxygen infiltration to the reaction zone. A stable self-propagating reaction front can be obtained only at carbon and oxygen concentrations exceeding a critical value. We examined effects of process variables such as carbon concentration on the particle size and crystal structure. The average particle diameter increased with an increasing the concentration of carbon and oxygen flow rate. The crystalline nanoparticles synthesized were nearly spherical, and their average particle diameters ranged from 60 to 200 nm. Electrochemical characterization of the synthesized lithium cobaltate was made using 8-channel battery analyzer with multiple charge-discharge cycles under constant voltage-constant current modes. The results are well comparable to best commercial cathode powders available, showing capacity of about 200 mAh/g.

Keywords: Carbon Combustion Synthesis of Oxide, Lithium Cobaltate, Nanoarticles, Li-ion Batteries

1 INTRODUCTION

Intensive research has been performed in solid-state chemistry and electrochemistry to develop new efficient synthesis methods for production of advanced nano and submicron size complex oxides for positive electrodes in Li-ion batteries. The electrochemical performance of lithium ion batteries is strongly dependent on the structure of the cathode material [1]. Understanding the structure and reaction mechanism of synthesis of cathode materials helps to identify how to modify the structure and to design new materials for improvement of battery performance. Therefore, in this area main objectives of research are to develop cathode materials with reduced cost, which have the ability to store much higher specific capacity and energy densities, and remain chemically and mechanically stable during high current transport, operating temperatures, time of storage as well as have reduced irreversible capacity loss [2]. Currently, the market price of cobalt is high and the application of LiCoO₂ for the positive electrode active material is depressed. However, due to several advantages the LiCoO₂ remains one of most widely used cathode materials and the production cost decreasing demand is still strong [3]. Thus, it is necessary to continue the effort to decrease the production expenses of the material and improve its characteristics. The battery performance can be dramatically improved by the reduction of particle size of the intercalation materials used to prepare the electrodes. When large particles are used the capacity is lost because concentration polarization occurs within the particle before the entire capacity can be utilized. The experimental capacity 130mAhg⁻¹ of the LiCoO₂ electrode is significantly lower than the theoretical capacity 300mAhg⁻¹.

The utilization of nano-structured cathode materials has become a very useful method to overcome the problem. It is not only enhancing the rate performance of the batteries but also extends some materials electrochemical activity [4]. The utilization of nano-structured electrode materials leads to improvement of the performance of lithium-ion batteries by reducing diffusion path length for Li⁺ ions and electron transport compared to micron-sized particles. There is an increased contact area between the electrode and the electrolyte that leads to better charge and discharge rates. The volume changes originating from Li⁺ insertion/desertion will be better accommodated by nano-materials compared to bulk materials due to faster stress relaxation, which can extend the battery cycle life [5].

In this paper, the synthesis of nanosized and submicron LiCoO₂ is presented using a novel method named Carbon Combustion Synthesis of Oxides (CCSO) [6-8]. The DSC analysis of synthesis reaction and the electrochemical performance of synthesized product are provided.

2 EXPERIMENTAL

For the synthesis of LiCoO₂, we used LiNO₃ (99%, Sigma Aldrich), Co₃O₄ (99.5%, Sigma Aldrich) and Carbon (particle size <50nm, 99%, Sigma Aldrich). The molar ratio among the reactants was set according to the stoichiometry of the desired product. The reactants were thoroughly mixed with carbon powder (“carbon acetylene”) by ball milling for about 60 min. The combustion synthesis was conducted by loading a loose mixture (relative densities of about 0.3) into a ceramic boat that was placed inside a cylindrical stainless steel vessel (30- mm i.d. and 50- mm length) fed by oxygen at a flow rate at 20 ml/min. To initiate the propagating temperature front the reactant
The local combustion temperature (Tc) was measured by inserting in the center of the sample an S-type (Pt-Rh) thermocouple of about 0.1 mm diameter. The thermocouple readings were recorded and processed by an Omega data acquisition board connected to a PC.

The Differential Scanning Calorimetry (DSC) (Q-600, TA Instrument) was used to test LiNO3-Co3O4-C reactions with linear heating rate 20 °C/min, with resolution of mass changes of 0.1 microgram, which provides opportunity to work with very small amounts of mixtures (~20 mg). The DSC experiments were conducted under air.

The electrochemical testing of the lithium cobalt oxide-based nano-composite were prepared consisting of the active powder material (93.5 wt. %), carbon black (4 wt. % as the conductor) and polyvinylidenefluoride (PVDF, <1µm, Sigma Aldrich) dissolved in N-methyl pyrrolidinone (NMP, MTI Company) as the binder (2.5 wt.%). After all components were mixed thoroughly, the cast was coated on an aluminium foil substrate; the coating was followed by pressing and drying at 120 °C for 12 h under a vacuum. Laboratory made pouch-type battery was assembled in glove box using separator membrane with special type of polyethylene: thickness 16~25 µm, Surface Density 10~14 g/m2, Porosity 36 - 44 %, Pore Size 0.03 µm, Penetration (Conductivity 10.5 ± 0.5 ms/cm at 25 oC, MTI Company). LiPF6 was used as electrolyte. The electrochemical characterization was performed using 8-channel battery analyzer. Charge-discharge cycles were carried out in the potential range of 2.7 - 4.2 V. The analyser discharges the battery at constant current until 4.2 V to obtain nominal capacity and the voltage was held constant at 4.2 V until the current dropped till 50 mA. The battery was cycled continuously for 30 cycles.

3 REZULTS AND DISCUSSION

3.1. Synthes of LiCoO2

The first part of this report focused on the synthesis of LiCoO2 by using LiNO3 and Co3O4 precursors with addition of carbon. Typical temporal temperatures at the center of a sample for the carbon concentration at 10 wt. % during the CCSO was ~ 820 °C. The total time of temperature rise and decay for the reaction was about 50 s. The stable front motion generated using 8-20 wt. % of carbon led to maximum temperatures of 600-1100 °C below the melting temperature of the LiCoO2. The morphology of the as-synthesized powder prepared at 10 wt. % carbon shows that the agglomerates contained small nanoparticles 60-200 nm with a smooth surface. The reaction in LiNO3-Co3O4 system is mainly endothermic, as can be seen from Figure 1. The initial 4 wt. % weight loss below 100 °C is due to absorbed water that can be present in the mixture. The heat flow curve shows and endotherm with 42 J/g energy for the complete removal of absorbed water from the system. At 250 °C starts the melting of LiNO3 with 117 J/g energy consumption, during which no weight change is observed. After 380 °C the decomposition of LiNO3 is starting with 37 wt. % weight loss and 541 J/g decomposition energy. At this stage Co3O4 is not undergoing to any change or reacting with other components, and the decomposition of Co3O4 with oxygen release can be expected only after 900 °C [9]. Thus, in the system LiNO3-Co3O4 no exothermic interaction is possible between the reagents below 900 °C.

To initiate exothermic reaction, we introduced 10 wt. % carbon to the initial mixture. To utilize the oxygen releasing from the LiNO3 decomposition at least 8.5 wt. % carbon should be presented in the mixture. Fig. 2 is presenting the DSC analysis results for the 3LiNO3-Co3O4 system with addition of 10 wt. % carbon.

The initial weight loss below 100 °C is almost 7 wt. % probably due to absorbed water. The endotherm is correspondingly greater reaching to 63 J/g. The endotherm at 250 °C is again showing the melting of LiNO3. However, due to presence of nano-sized carbon, the decomposition of LiNO3 is starting earlier at 300 °C and a very strong

![Figure 1. DSC Analysis of the mixture 3LiNO3-Co3O4.](image)

![Figure 2. DSC Analysis of the mixture 3LiNO3-Co3O4 with 10 wt. % carbon.](image)
exotherm peak with 1447 J/g energy release is observed. This indicates that carbon is reacting with the oxygen released from LiNO₃ decomposition. The weight change in this stage is 30 wt. %. After first strong exotherm, occurs the second exotherm with 53 J/g energy and 6.5 wt. % weight loss, which is due to excess amount of carbon that we have in the system. In the case we further increase the amount of carbon at 20 wt. % in initial mixture (Figure 3), the second exotherm is becoming correspondingly higher and even has greater value 1470 J/g than the exotherm originating from the reaction of carbon with decomposition products of LiNO₃. It is interesting to note that carbon is not reacting with air oxygen even at 600 °C.

Thus, the addition of carbon to the initial mixture of 3LiNO₃-Co₃O₄ is transforming the system from endothermic to exothermic interaction. For the reaction product LiCoO₂ we performed electrochemical testing in the following section.

3.2. Electrochemical performance of synthesized LiCoO₂

In order to study the multiple charging-discharging influence on the performance of Li-ion battery made with the synthesized LiCoO₂ as cathode material, the battery was tested over 30 cycles and the current, voltage, capacity and charging-discharging efficiency curves were monitored during the measurement process.

Figure 4 is presenting the cyclic charge-discharge voltage/current/time recordings for the first 5 cycles. In the first stage, the battery was charged with 150 mA/h constant current mode until the voltage raised to 4.2 V. At this point, the charging mode shifted to 4.2 V constant voltage charging mode and charging continued until the current dropped to the 10 % of initial value (15 mA/h). After charging, the battery was relaxed for 1 min and then the constant current discharge with 50 mA/h was applied until the voltage dropped to the cutoff value of 2.7 V. After another 1 minute rest, the cycle repeated from the constant voltage charging mode. The duration of one cycle was about 2 hours.

4 CONCLUSION

LiCoO₂ based materials have been prepared by CCSO using LiNO₃ as Li-precursor. The cathode materials prepared from as synthesised materials shows good performance for lithium-ion batteries. The CCSO is giving submicron and nano-sized particles which are showing excellent consistency of specific capacity and retaining over 90 % of initial capacity after 30 cycles. The as-prepared LiCoO2 has over 200 mAh/g capacity which is more than 66% of theoretical maximum value for LiCoO2. The CCSO is a promising method to produce ultrafine LiCoO₂ cathode materials with improved electrochemical performance.

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