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Preparation of nanoparticle size $LiBiO_2$ by combustion method and its electrochemical studies for lithium secondary cells

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Abstract. A simple combustion method has been tried for the preparation of nanoparticle-sized $LiBiO_2$ powder with urea as the igniter and glycerol as the binding material. Nitrates of Li^+ and Bi^{3+} were mixed together to form a uniform mixture. Required quantities of urea and glycerol were added to this mixture to form a paste. This paste was carefully heated to 100°C initially and finally heated to 460°C for 5 h. The product obtained was subjected to TG/DTA and XRD analysis. The particle size of the cathode material was roughly calculated from the X-ray data using Scherer equation. However, SEM and EDAX analysis were carried out in detail to confirm the particle size and the composition of $LiBiO_2$ respectively. A 2016 coin type button cell was assembled with $LiBiO_2$ as cathode and graphite as anode containing polypropylene separator and a solution of 1 M $LiClO_4$ dissolved in 1 : 1 (EC+DEC) mixture as the electrolyte. Charge/discharge studies were conducted to establish viability of the reversible cell.

Keywords. Nanoparticle; $LiBiO_2$; X-ray diffraction studies; scanning electron micrograph; combustion method; lithium-ion batteries.

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1. Introduction

Transition metal oxides, such as $LiCoO_2$, $LiNiO_2$ and $LiMnO_2$ have been proposed as cathode materials for Li-ion batteries [1–11]. Among these compounds $LiNiO_2$ is a good compromise between electrochemical performance and materials cost when compared with the poorer cyclability of $LiMnO_2$ and the higher cost of $LiCoO_2$. But $LiNiO_2$ is difficult to obtain, because a high-temperature treatment of $LiNiO_2$ leads to the decomposition of $LiNiO_2$ to $Li_{1-x}Ni_{1+x}O_2$ ($x > 0$), which has a partially disordered cation leading to poorer electrochemical property [1,12–14].

To overcome the drawbacks of $LiCoO_2$, $LiNiO_2$ and $LiMnO_2$, in the present work, a new cathode material $LiBiO_2$ has been synthesized by combustion method using urea as fuel and glycerol as the binding material. We report the structural

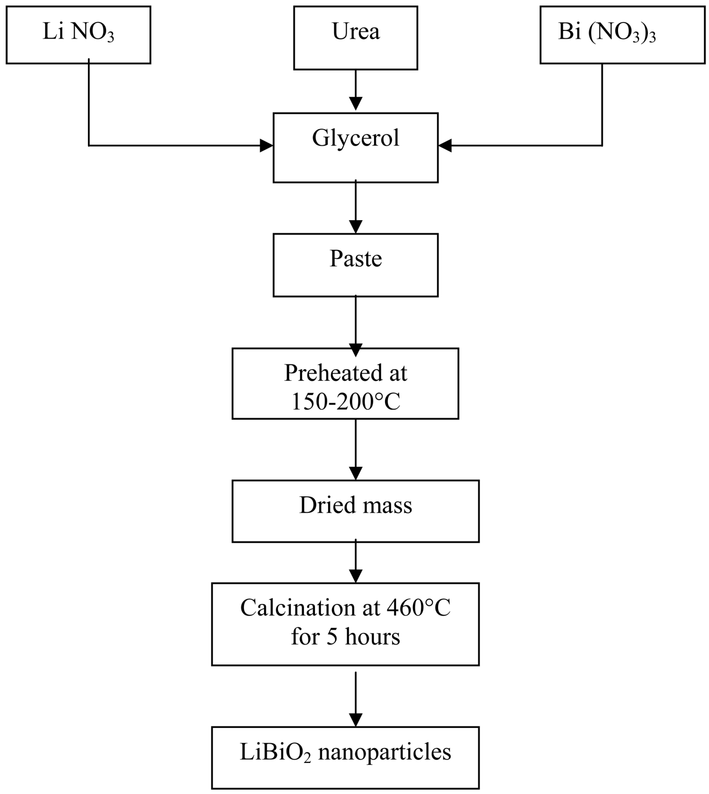

Figure 1. Preparation procedure of $LiBiO_2$ nanoparticles by a simple combustion route.

study of the synthesized $LiBiO_2$ powder and also the effect of calcination on the crystallization of the synthesized $LiBiO_2$.

2. Experimental details

2.1 *Powder preparation*

$LiBiO_2$ was prepared by combustion method. The stoichiometric amount of lithium nitrate and bismuth nitrate were taken along with urea as fuel, glycerol as binding material and made into a homogeneous paste. The preparation procedure is described using a flowchart in figure 1.

The stoichiometry of the redox-mixture used for the combustion reaction was calculated based on the total oxidation and reduction valencies of the components, which serve as the numerical coefficient for the stoichiometric balance to equivalence ratio which was maintained at unity (O/F), so that the heat released by the combustion is maximum. According to the concept used in propellant chemistry, the oxidizing valency (O) of $LiNO_3$ is -5, $Bi(NO_3)_3$ is -15 and the reducing valency of urea is $+6$.

The amount of urea required for combustion is calculated using the general empirical formula for the system $LiBiO_2$, i.e.

$$(1x - 5) + (1x - 15) + 6n = 0.$$

$$\therefore n = 20/6 = 3.66 \text{ M}$$

Hence, the required amount of urea is 3.66 M. The above homogeneous mixture was heated to dryness at 200°C and then the dried mass was calcined at 460°C for 5 h to get the nanocrystalline product.

2.2 *Thermal analysis*

Thermal analysis of the precursor sample was made using TG/DTA thermal analyzer (STA-1500 Model) at the heating rate of 10°C/min under ambient atmosphere to find out the optimum temperature for phase formation and/or complete crystallization of the precursor sample.

2.3 *XRD sample*

The purity and structural property of the product was confirmed by JEOL (JDX-8030) X-ray diffraction analysis using Cu-Kα radiation. The diffraction patterns were obtained at 25°C in the range of $10° \leq 2\theta \leq 75°$ in step scans. The step size and scan rate were set at 0.1 and 2°C/min respectively. Finally the particle size of the cathode material was roughly calculated from X-ray data using Scherer equation.

2.4 *SEM analysis*

To analyse the particle nature and size of the synthesized $LiBiO_2$ powder, SEM photographs were taken by JEOL (JSM-840A) scanning electron microscope.

2.5 *Electrochemical characterization*

Charge–discharge studies were conducted to establish the viability of a reversible cell by assembling 2016 coin type button cell with $LiBiO_2$ as cathode and graphite as anode containing polypropylene separator and a solution of 1 M $LiClO_4$ dissolved in 1 : 1 EC+DEC mixture as the electrolyte. The cathode was made by mixing $LiBiO_2$ powder, acetylene black and colloidal teflon binder in the 80 : 10 : 10 weight ratios. The above composite materials were mixed with alcohol and pressed in a die onto an expanded aluminium grid at a pressure of 5 tons/cm^2 using a hydraulic press to yield a circular pellet electrode. The pellets were then dried at 120°C in an oven. The capacity and cyclability of the cathode material were calculated based on the result of charge–discharge studies using WPG-100 pontentiostat/galvanostat, Korea.

3. Results and discussion

3.1 *Properties of synthesized powder*

Phase transformation of the precursor sample ($LiBiO_2$) was studied using TG/DTA measurements and its corresponding TG/DTA curves are shown in figure 2. The complete crystallization/phase formation temperature of $LiBiO_2$ was identified to be 460°C. This temperature was used to obtain highly crystalline $LiBiO_2$ powder.

The observed XRD pattern for the synthesized $LiBiO_2$ powder is shown in figure 3. The diffractogram reveals the formation of highly crystalline-layered hexagonal structured products with high phase purity on calcination at 460°C for 5 h and this is evident from the calculated lattice parameters. The calculated lattice parameters for $LiBiO_2$ are $a = 2.856$ Å and $c = 14.242$ Å. The particle size of the cathode material was roughly calculated from X-ray data using Scherer equation

$$\text{Average particle size } L = \frac{k\lambda}{\beta\cos\theta},$$

where k is the shape factor, β the full-width half-maximum, λ the X-ray wavelength of Cu-Kα radiation and θ the Bragg angle. Using this formula, we have calculated the particle size of $LiBiO_2$ which is in the range of 70 nm. Such excellent

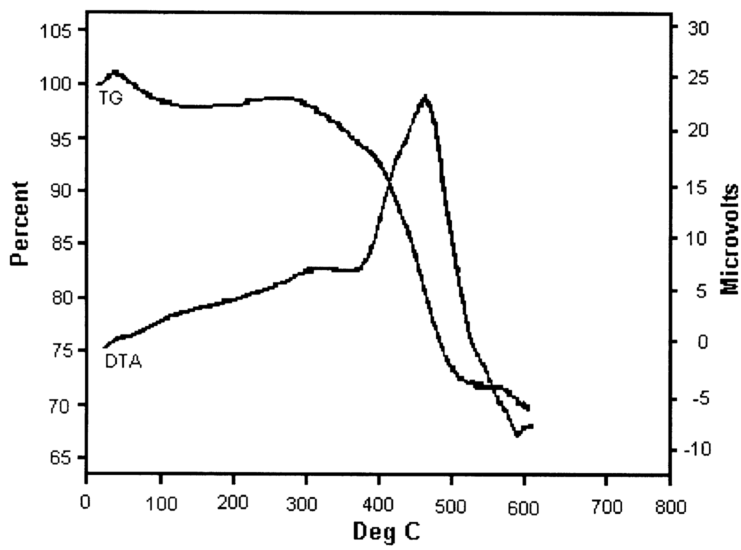

Figure 2. TG/DTA curve for the precursor sample of $LiBiO_2$.

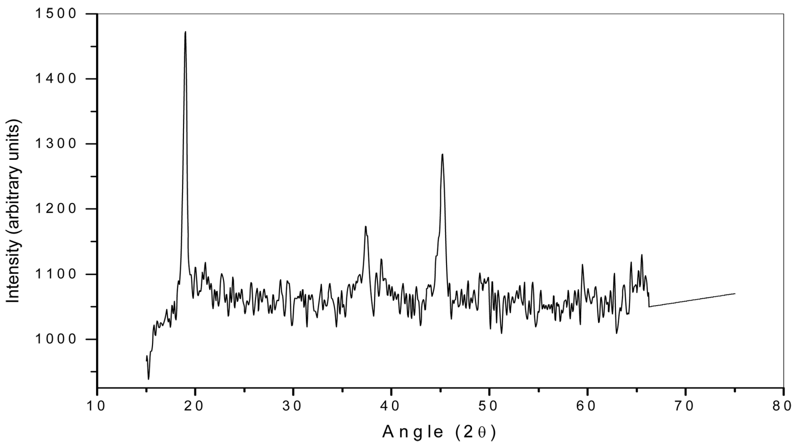

Figure 3. XRD pattern of $LiBiO_2$.

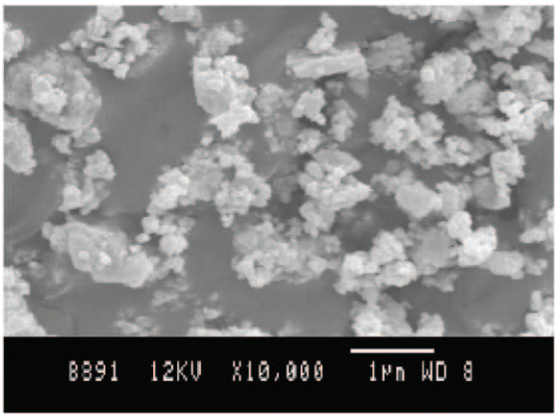

Figure 4. SEM photograph of $LiBiO_2$.

nanoparticles will provide excellent cycle performance for C/$LiBiO_2$ cell. XRD result indicates that combustion method could result in pure $LiBiO_2$ phase at lower temperature.

The scanning electron micrograph of $LiBiO_2$ sample is presented in figure 4. The particles are found to be crystalline with well-defined facets that have a wide range of distribution. Spot EDAX taken for crystalline $LiBiO_2$ powder confirms the exact composition of Bi in the material (figure 5).

3.2 *Charge–discharge studies*

Figure 6 shows the charge–discharge curves for C/$LiBiO_2$. During charging, the lithium ion was extracted from the material and when discharged it got inserted back into position. It was observed that the material $LiBiO_2$ synthesized from

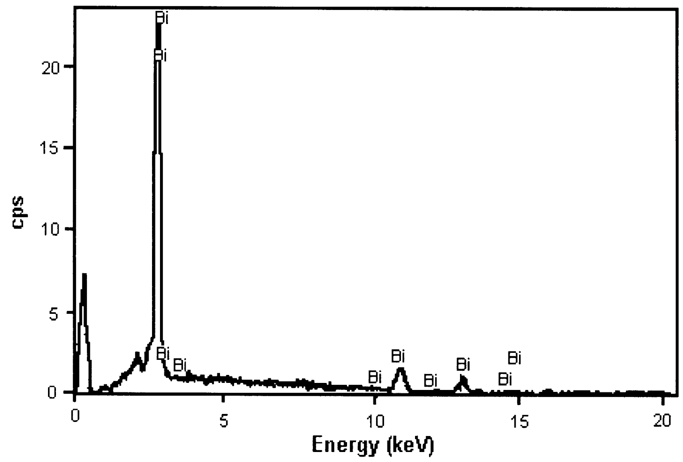

Figure 5. EDAX pattern of $LiBiO_2$.

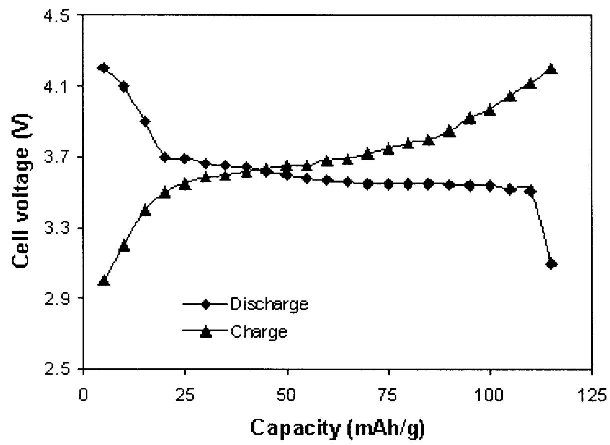

Figure 6. The charge–discharge curves of $LiBiO_2$ synthesized by a simple combustion route.

combustion method, had the initial discharge capacity value of 108 mAh/g and this was maintained even after 50th cycle and retained for more than 97% of its initial capacity (figure 7).

4. Conclusions

The layered $LiBiO_2$ powders can be synthesized by a simple combustion method using urea as the fuel and glycerol as the binding material at low temperature. The X-ray diffraction patterns showed the formation of layered hexagonal powder and its lattice parameters a and c were calculated. The SEM analysis confirmed the formation of sub-micron particle nature of $LiBiO_2$ powder. Spot EDAX taken for

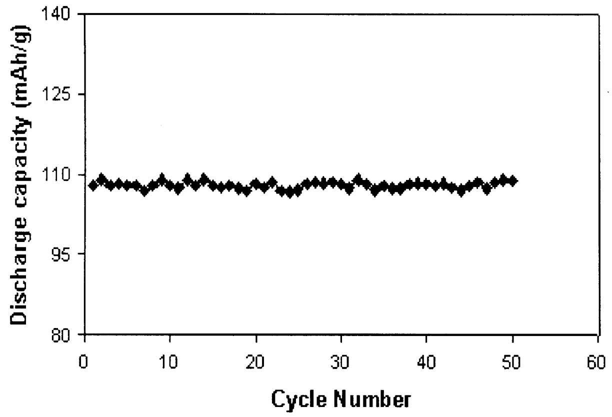

Figure 7. Relationship between the discharge capacity and cycle number of C/$LiBiO_2$ in the voltage range of 3.0 to 4.2 V at a current density of 0.1 $mAcm^{-2}$.

crystalline $LiBiO_2$ powder reveals a uniform composition of Bi and it has an overall discharge capacity of 108 mAh/g with a good cycling performance and retention of almost 97% of its theoretical capacity even after the 50th cycle and hence can be used as an effective cathode material. Therefore, this combustion method could be a promising method for synthesizing $LiBiO_2$ powder.

The experimental conditions will be fine-tuned to obtain reduced particles and further electrochemical studies could be carried out to establish the best cathode material for Li-ion battery applications.

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