



Search for Li-electrochemical activity and Li-ion conductivity among lithium bismuth oxides



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ARTICLE INFO

Article history:

Received 16 June 2015

Received in revised form 8 October 2015

Accepted 30 October 2015

Keywords:

Lithium ion batteries

Cathode materials

Lithium bismuth oxides

ABSTRACT

Previously reported lithium bismuth oxides, LiBiO_2 , LiBiO_3 , Li_3BiO_3 , Li_3BiO_4 , Li_5BiO_5 , and Li_7BiO_6 were prepared either via ceramic or hydrothermal synthesis methods, and their feasibility as lithium battery cathode materials was tested. None of the oxides showed any desirable electrochemical activity at higher potentials, except for the limited capacity observed during the first discharge in LiBiO_3 . In contrast, these phases uptake large amounts of Li^+ via conversion reactions when cycled down to zero volt, but the reversibility is poor. The transformation of LiBiO_3 to LiBiO_2 and Li_3BiO_3 to Li_3BiO_4 observed via X-ray diffraction showed absence of intermediate phases with mixed $\text{Bi}^{3+}/\text{Bi}^{5+}$ oxidation states. Among the materials studied, the highest ionic conductivity of 3.8×10^{-8} S/cm at 25 °C was measured for LiBiO_2 . The Li^+ conduction pathways deduced from bond valence energy landscape approach suggest the best Li diffusion characteristics in Li_7BiO_6 among the Li-Bi-O phases studied.

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Efficient energy production, storage, and distribution are major global challenges, and Li-ion batteries with their wide range of applications are a promising solution [1]. However, the ability of Li-ion batteries to successfully address the growing energy storage demands relies on the development of new and efficient electrode materials. Such new materials must have high power and energy densities, while simultaneously being inexpensive and sustainable. Further, candidates for Li-ion electrodes must have sufficient electronic and ionic conductivities as well as an open structure for the insertion-extraction of Li-ions [2].

Currently available Li-ion batteries use transition metal oxide-based cathodes; either layered (LiMO_2) or spinel (LiM_2O_4) with $\text{M} = \text{Co}, \text{Ni}, \text{Mn}$. While these materials have the advantage of high redox voltages, they are plagued by high cost (Ni and Co) and limited chemical stability. Hence, there is a need for stable yet inexpensive alternatives. In fact, the search for such materials over the years has led to the discovery of a large number of Fe-based polyanionic compounds, including LiFePO_4 , which is now commercially used. Although these polyanionic materials are desirable for their low costs, their low capacities due to high

molecular weight makes them less ideal. Therefore, there still exists a need for new and affordable high energy density electrode materials.

The energy density of electrode materials can be enhanced either by increasing their voltage or specific capacity. The latter of which can be achieved by designing low molecular weight insertion compounds or compounds with the ability to accept more than $1e^-$ per 3d metal. While significant efforts have been dedicated to increasing capacities by decreasing molecular weight, literature search suggests very little exploration of materials with more than $1e^-$ per 3d metal. Among those previously explored are vanadium- and manganese-based compounds, which exhibit a wide range of oxidation states ($\text{V}^{5+} \rightarrow \text{V}^{2+}$, $\text{Mn}^{4+} \rightarrow \text{Mn}^{2+}$) [3]. One such example is $\text{Li}_2\text{MnSiO}_4$ phases with $\text{Mn}^{2+}/\text{Mn}^{4+}$ redox couple that have been shown to remove 2 Li^+ , but the inability to form MnSiO_4 (in agreement with DFT calculations) has limited their pursuit [4]. In contrast, although LiVPO_4F has been successfully shown to display a two electron process, the large voltage interaction domain (> 2 V) associated with successive $\text{V}^{2+}/\text{V}^{3+}$ and $\text{V}^{3+}/\text{V}^{4+}$ redox couples has made it less suitable for battery applications [5,6]. We are therefore interested in identifying new compounds within which a $2e^-$ process can occur at a single voltage as a result of the favorable electronic configuration of constituent elements.

Members of column V in the periodic table (Bi, Sb, As) with s^2 lone pair electrons open up the possibility of having oxidation state changes

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in steps of two. In fact, Bi-based oxides are extensively studied for high T_c superconductors [7,8], and several compounds (e.g. BaBiO_3) with mixed $\text{Bi}^{3+}/\text{Bi}^{5+}$ oxidation states have been reported [9,10]. These mixed-valence compounds could present disproportionation reactions and consequently prove to be good candidates for understanding $2e^-$ redox processes. However, little is known regarding their electrochemical behavior, especially with respect to Li-ion batteries.

Recent work by Sathiyamoorthi et al. [11] on layered LiBiO_2 showed complete removal of Li from the structure and a capacity of 110 mAh/g. While the authors do not discuss the oxidation mechanism responsible for such high capacities in the Bi-based material, one of the possibilities is a $2e^-$ transfer resulting from a disproportionation reaction ($2 \text{LiBiO}_2 \rightarrow 2 \text{Li} + \text{Bi}^{3+}\text{Bi}^{5+}\text{O}_4$). Such an observation motivates the study of other Li-Bi-oxides, which have Bi in +3 oxidation state. Among them, oxides that can reversibly exchange 2Li^+ during the $2e^-$ redox process would be of particular interest. Accordingly, Li_3BiO_3 with the removal of 2Li^+ to promote the oxidation of Bi^{3+} to Bi^{5+} would have a theoretical capacity of 192.9 mAh/g, which is comparable to that of commercially available LiFePO_4 (170 mAh/g). Hence, we studied all the reported Li-Bi-oxide phases (LiBiO_2 [12,13], LiBiO_3 [14], Li_3BiO_3 [15], Li_3BiO_4 [16], Li_5BiO_5 [17,18], and Li_7BiO_6 [19]) for Li-ion battery cathode applications. Here we discuss their synthesis, electrochemical activity, and Li-ion conductivity. We also include a short discussion on some of the corresponding Li-Sb oxide phases to provide an insight into their feasibility as cathode materials.

1. Synthesis

A 5 g intimate mixture of $\text{Bi}_2\text{O}_3:\text{Li}_2\text{O}$ in a molar ratio corresponding to the Bi:Li ratio of the desired final oxide phase with 10 mol% excess of Li_2O was prepared by ball milling for 30 min on a Spex Miller®. The stainless steel milling jars were filled and emptied in an Ar-filled glove box. The milled mixture was pressed into a pellet (diameter 13 mm \times 3 mm thickness) and heated in a quartz crucible in air for 24 h at 525 °C to make LiBiO_2 and Li_3BiO_4 , and at 650 °C to make Li_5BiO_5 and Li_7BiO_6 samples. Li_3BiO_3 was prepared by heating under Ar flow for 16 h at 450 °C.

The LiBiO_3 samples were prepared *via* hydrothermal methods using a slight variation of the procedure described by Kumada et al. [14]. A 0.5 g mixture of 1:12 molar ratio of $\text{NaBiO}_3 \cdot n\text{H}_2\text{O}$ to LiOH was added to 15 mL of distilled water and heated to 120 °C for 48 h in a Teflon-lined Parr bomb. The resulting mixture was washed with water and dried at 80 °C in a vacuum oven for 2 h.

Similar to the Li-Bi-O materials, several of the reported Li-Sb-O phases (LiSbO_2 , Li_3SbO_4 , LiSbO_3 , Li_5SbO_5) were prepared by ceramic process starting from Li_2O and Sb_2O_3 precursors and heating in air at a rate of 100 °C/h to between 450 °C and 600 °C overnight.

2. Characterization

2.1. X-ray powder diffraction

X-ray powder diffraction measurements (XRD) were conducted using Bruker D8 diffractometers with either a Co-K α ($\lambda_1 = 1.78897 \text{ \AA}$, $\lambda_2 = 1.79285 \text{ \AA}$) or Cu-K α ($\lambda_1 = 1.54056 \text{ \AA}$, $\lambda_2 = 1.54439 \text{ \AA}$) radiation source. The phase purity of the samples was confirmed by a Le Bail fit of the resulting patterns conducted using the FullProf program [20].

2.2. Thermogravimetric analysis

TGA analysis was conducted using a Netzsch STA 449C apparatus (TGA-DSC) and heating samples in alumina crucibles either under Ar or O_2 flow at 10 °C/min from room temperature to 600 °C.

2.3. Electrochemical testing

The working electrode was prepared by mixing the active electrode material with 25 wt% SP carbon and ball milling for 20 min on a Spex® miller. The material was then tested in Swagelok®-type half cells vs. Li^+/Li^0 using Whatman GF/D borosilicate glass fiber separator and LP30 electrolyte. The cells were assembled in an Ar-filled glove box and generally contained 8–10 mg of active material per cell. Galvanostatic charge–discharge tests were conducted at room temperature (20 °C) using a “Mac-Pile” or a VMP system (Biologic S.A., Claix, France).

2.4. Ionic conductivity measurements

Impedance spectroscopy was used to evaluate ionic conductivity of the Li-Bi-O phases. Samples were pressed into pellets (13 mm diameter \times 1.5 mm thickness) and sintered for 10 h at 450 °C either in air or under Ar (Li_3BiO_3), and carbon paper discs were used to make electrical contact (the contact between C and the pellet was ensured by pressure). Measurements were conducted over a range of frequencies (1 MHz to 1 Hz, using 11 points per frequency decade) as a function of temperature (every 25 °C from 250 °C to 450 °C), in an in-house conductivity setup. The linearity of the system was checked by modifying AC amplitude from 50 to 350 mV before conducting *in situ* measurements. Under the conditions of the experiment, the pellet contribution is described by a semi-circle, and the total resistance of the pellet is attributed to the diameter of the measured semi-circle. Using the measured resistance (R) and dimensions of the pellet [surface area (S) and thickness (e)], the conductivity (σ) values at different temperatures was calculated using the $\sigma = \frac{1}{R} \times \frac{e}{S}$ relationship.

3. Results and discussion

Our study was originally motivated by a report from Sathiyamoorthi et al. [11] showing good electrochemical cycling for LiBiO_2 , but their published procedure for combustion synthesis was not reproducible. In fact, none of the X-ray powder patterns of samples prepared using their synthesis procedure matched those reported for LiBiO_2 , thereby raising doubts about the structure and composition of the material used in their study. However, LiBiO_2 is a well-characterized material and was easily prepared using standard ceramic synthesis [13].

Expanding to other reported Li-Bi-oxides, Li_3BiO_3 , Li_3BiO_4 , Li_5BiO_5 , and Li_7BiO_6 phases were prepared *via* ceramic synthesis. Both LiBiO_2 and Li_3BiO_4 were prepared at 500 °C while Li_5BiO_5 and Li_7BiO_6 required heating to 650 °C in air. The Li_3BiO_3 phase was obtained by heating to 450 °C under Ar flow, while LiBiO_3 was made using hydrothermal methods. The quality of each sample was ascertained by a Le Bail fit to their X-ray powder diffraction patterns (Fig. 1). The resulting lattice parameters along with relevant crystal structure information are provided in Table 1, and a crystal structure representation for each phase is shown in Fig. 2.

We began our study by examining the electrochemical properties of LiBiO_2 , which has a layered structure suitable for Li insertion/extraction. However, when LiBiO_2 was cycled in Swagelok-type Li-half cells, there was no electrochemical activity observed (Fig. 3a). Even with optimizing the carbon loading and cycling conditions, we did not see any electrochemical activity and hence failed to reproduce the electrochemical cycling previously reported by Sathiyamoorthi et al. [11]. However, our results do not come as a complete surprise when we take a closer look at the structure of LiBiO_2 where Li atoms are trapped between layers of Bi-O tetrahedra. This is unlike Li atoms in Li-3d transition metal-based layered oxides, where the Li atoms sit within the van der Waals gap of the M-O layers.

Surveying the other Li-Bi-O compounds, the only other phase containing Bi^{3+} is Li_3BiO_3 , and unlike LiBiO_2 , it has multiple Li^+ per formula unit, which could enable a reversible $2e^-$ redox process. However, it

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