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Bismuth phosphate: A novel cathode material based on conversion reaction for lithium-ion batteries

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ABSTRACT

Here, we provide a new scientific insight in the field of lithium-ion batteries, in which $BiPO_4$ is initially reported as a cathode material based on conversion reaction. $BiPO_4$ exists in three polymorphic phases, which have been synthesized using a room-temperature liquid precipitation route followed by heating treatment. The effects of phase transformation on electrochemical performances of $BiPO_4$ have been investigated. Herein the hexagonal $BiPO_4$ exhibits the best reversibility, rate capability and cycling stability. A conversion reaction has also been proved to occur in $BiPO_4$ with reduction of $BiPO_4$ into a metallic Bi^0 phase and a Li_3PO_4 phase upon lithiation, and the reformation of $BiPO_4$ phase during next charge process. Its theoretical specific capacity and theoretical output voltage are 264.5 mA h g^{-1} and ~3.14 V, respectively. Especially, its theoretical volumetric energy density is as high as 5253.1 Wh L^{-1}, close to twice higher than $LiCoO_2$. Therefore, it is still worthy of further study for lithium-ion batteries.

1. Introduction

Lithium-ion batteries have drawn more attention since their commercialization in 1991. However, in the age of automotive technologies, automotive applications require at least a two-fold improvement in energy and power densities. Nowadays, there are three different Li-storage mechanisms to store capacity for electrode materials of lithium-ion batteries, namely, conventional intercalation of Li ions [1,2], alloying with Li [3,4], and conversion reactions [5–7]. Among the three Li-storage mechanisms, because the reversible conversion reactions can make use of all possible oxidation states of the metal cation thus yielding higher specific capacities for lithium-ion batteries [8], the materials accompanying with conversion reactions will be a good alternative to meet the requirements of higher energy and power densities.

Since Tarascon et al. [9] firstly reported the reversible Li-storage reaction for transition-metal oxides through the heterogeneous conversion, the reversible conversion reactions have been observed in a large number of compounds, such as metal oxides [10,11], chlorides [12,13], sulfides [14–16], nitrides [17,18], fluorides [19–22], and phosphides [23,24]. The overall reaction for the conversion can be summarized as follows:

$$m\mathrm{Li}^+ + me^- + \mathrm{MX}_n \underset{\text{delithiation}}{\overset{\text{lithiation}}{\rightleftarrows}} n\mathrm{Li}_{m/n}\mathrm{X} + \mathrm{M} \tag{1}$$

where M stands for a cation and X an anion [25]. However, for the practical application of the cathode materials, the active materials are required to have the output voltage of more than 2 V. Therefore, for the above compounds, only a few metal oxides [10], chlorides [12,13], sulfides [15,16], and fluorides [19–22] were studied as possible alternatives for the cathode materials of lithium-ion batteries.

In recent years, a few metal oxides (CuO) [10], chlorides ($CoCl_2$, AgCl, and $CuCl_2$) [12,13], and sulfides (CuS and Cu_2S) [15,16] have been reported as positive electrode materials, but the output voltages of metal oxides and sulfides are only about 2 V, thus further studies on metal oxides and sulfides as the cathode materials have rarely been performed. Besides, because most of metal chlorides are hygroscopic and soluble in liquid organic electrolyte, they are also difficultly served as a solid electrode for practical battery applications. Fortunately, metal fluorides, such as FeF_3 [19,21,26], BiF_3 [20,25], CoF_2 [22,27], and NiF_2 [28], have been studied as a promising new class of cathode materials for lithium ion batteries. Among these metal fluorides, FeF_3 has recently become one of the most promising cathode materials because of its high capacity and excellent thermal stability. However, the poor kinetic properties of FeF_3 cathode material hinder its further development. In order to overcome the above problem, morphology control and size reduction to nanoscale dimension are two effective ways. Therefore,

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many recent studies have focused on synthesizing FeF_3 cathode materials with different morphology and particle size, such as three-dimensionally ordered macroporous [26], porous nanospheres [29], highly amorphous and porous microspheres [30], worm-like mesoporous [31]. All these materials exhibited superior electrochemical performances. However, in the age of miniaturization, the portable electronic device needs to further pursue the characteristics of light quality, small size and high specific energy density. There is no denying that the cathode materials of lithium-ion batteries with higher gravimetric energy density and volumetric energy density will play a vital role. Besides, compared with the commercial cathode materials, the output voltage of the FeF_3 cathode materials is not enough ideal. Especially, its volumetric energy density is much lower. Therefore, to develop new cathode materials based on conversion reaction will be a very significant work.

Bismuth phosphate ($BiPO_4$) is a typical non-transition metal phosphate, which exists in three polymorphic phases, namely hexagonal, low temperature monoclinic and high temperature monoclinic $BiPO_4$ [32–35]. The hexagonal form is generally associated with water of hydration, namely hexagonal $BiPO_4$ (HBP), which can be synthesized at room temperature through a wet chemical method [32]. The most stable form is the low temperature monoclinic monazite-type (LTMBP). The third phase is the high temperature monoclinic structure (HTMBP) which can be obtained via heating HBP or LTMBP at high temperature [32,36]. The crystal structure and the phase transformation of $BiPO_4$ have been studied by many researchers [32,33,37]. Moreover, $BiPO_4$ enables extensive applications in various fields such as separation of radioactive elements [34], microwave dielectric [37], orthophosphate ion sensor [38], and photocatalyst [39]. However, to the best of our knowledge, the study on $BiPO_4$ as positive electrode of lithium ion battery has not been reported. For $BiPO_4$, due to the presence of the polyanion (PO_4^{3-}), P–O covalent bond of PO_4^{3-} can stabilize Bi^{3+} by the inductive effect of Bi–O–P bond. Thus, $BiPO_4$ will have a higher theoretical output voltage (3.14 V) compared with the corresponding metal oxide (Bi_2O_3) (2.10 V) which has been reported as the cathode material based on conversion reaction. Thus, theoretically, to render $BiPO_4$ as a positive electrode material has possessed the feasibility.

In the present study, we provide a new scientific insight in the field of lithium-ion batteries, where a new class of $BiPO_4$-based cathode material is reported for the first time. We explore whether the conversion reactions are also possible in such systems. Besides, the effects of phase transformation on electrochemical properties of $BiPO_4$ have been also examined in detail.

2. Experimental section

Hexagonal $BiPO_4$ (HBP) was directly prepared using a chemical liquid precipitation method at room temperature. In a typical synthesis, $Bi(NO_3)_3{\cdot}5H_2O$ was dissolved in 10 wt.% acetic acid solution under magnetic stirring, and equimolar $(NH_4)_2HPO_4$ was dissolved in isopyknic deionized water. Subsequently, $Bi(NO_3)_3$ solution was added dropwise to $(NH_4)_2HPO_4$ solution under vigorous stirring, then a white homogeneous precipitate was observed. The suspension solution was kept on stirring for 2 h. Finally, the product was filtered, sufficiently washed with deionized water and absolute ethyl alcohol, and then dried in an oven at 80 °C for 24 h to obtain HBP.

Low-temperature phase (LTMBP) and high temperature phase (HTMBP) were obtained by thermal treatments over HBP at high temperatures. The HBP was sintered at 600 °C and 900 °C for 6 h with a heating rate of 5 °C min^{-1} to obtain LTMBP and HTMBP [36,40], respectively. All samples were obtained after naturally cooling to room temperature.

The structural and crystallographic analyses of the samples were performed using powder X-ray diffraction (XRD) techniques (D/max-2550 Rigaku, Japan) using Cu Kα radiation (λ = 1.54178 Å) and a graphite monochromator at 40 kV, 20 mA. XRD data were collected at 4° min^{-1} in the 2θ range of 10–90°. The surface morphology of the samples was observed using the Hitachi S-3500N scanning electron microscope (SEM) and field emission scanning electron microscope (FE-SEM; LEO1525, Germany). The FT-IR measurements of the samples were carried out via a Fourier transform infrared (FT-IR) spectrometer (Perkin–Elmer Spectrum One). Selected area electron diffraction (SAED) and high resolution transmission electron microscopy (HRTEM) pictures were taken with JEOL JEM100SX electron microscope.

The electrochemical measurements of the samples were carried out using coin-type cells (CR2025) assembled in an argon-filled glove box (MIKROUNA 1220/750). The cathodes were made by mixing 80 wt.% active material, 6 wt.% acetylene black, 6 wt.% graphite and 8 wt.% polyvinylidene fluoride (PVDF) binder. The mass of electrode material per 1 cm^2 of electrode is 3–4 mg. In all cells, lithium was served as the counter and reference electrodes, Celgard 2400 was used as separator, and the electrolyte was a 1 M $LiPF_6$ solution in ethylene carbonate (EC):dimethyl carbonate (DMC) (1:1, v/v). Galvanostatic discharge–charge measurements were carried out in Neware battery test system (BTS-51, Shenzhen, China) at various current densities between 1.5 and 4.5 V (vs. Li^+/Li) at room temperature. The EIS experiments were conducted using a CHI 660a Electrochemical Analyzer (CH Instrument Inc., USA). The ac perturbation signal was ±5 mV, and the frequency range was from 10^5 to 10^{-2} Hz.

3. Results and discussion

3.1. Phase identification

To distinguish the crystal structure of three polymorphs of $BiPO_4$, the powder X-ray diffraction techniques were carried out

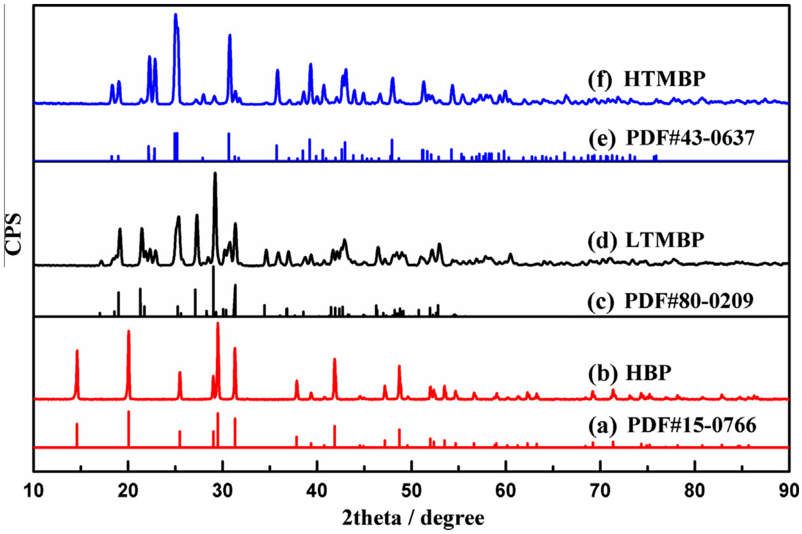

Fig. 1. XRD patterns of HBP, LTMBP, and HTMBP (b, d and f) and their corresponding standard patterns (a, c and e).