Sodium storage mechanisms of bismuth in sodium ion batteries: An operando X-ray diffraction study

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HIGHLIGHTS

- Na storage mechanisms of Bi with different shapes/sizes were probed by operando XRD.
- Three Bi anodes follow the same alloying/dealloying mechanisms (Bi ↔ NaBi ↔ Na$_3$Bi).
- Both Na$_3$Bi and NaBi are metastable and will easily decompose in ambient atmosphere.
- The inaccuracy of intercalation/deintercalation mechanism of Bi was rationalized.

GRAPHICAL ABSTRACT
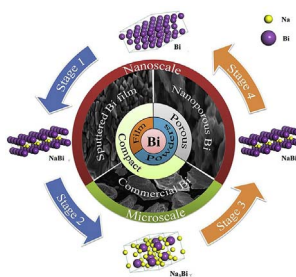
ABSTRACT

Understanding the sodium (Na) chemistry is crucial for development of high-performance sodium ion batteries (SIBs). Nanostructured bismuth (Bi) has shown great potentials as an anode in SIBs, however, the Na storage mechanisms of Bi are still unclear. Herein, the operando X-ray diffraction (XRD) technique was utilized to probe the Na storage mechanisms of three Bi anodes (sputtered Bi film, nanoporous Bi and commercial Bi). Despite different morphologies and sizes, all the Bi anodes follow the same two-step reversible alloying/dealloying mechanisms (Bi ↔ NaBi ↔ Na$_3$Bi) during the discharge/charge processes, associated with two voltage plateaus. As for the intercalation/deintercalation mechanism proposed for nanostructured Bi anodes in SIBs, we rationalize the reason why only the Bi phase is detected in the discharged/charged samples under ex-situ XRD conditions through addressing the stability issue of the Na-Bi system (NaBi and Na$_3$Bi).

1. Introduction

Considering the increasingly severe problems of climate change and the forthcoming exhaustion of fossil fuel resources, renewable energies, such as hydraulic, tidal and solar power, have achieved tremendous development in recent years. Thus grid-scale energy storage systems (ESSs), which are the decisive factor for smoothly integrating

sustainable energies into the power grid, have attracted widespread attention [1,2]. Under such circumstances there is thereby an urgent demand but it is still a great challenge to find a non-pollution operation, ease maintenance, high efficiency, long life span, and preferable safety technology among a variety of candidates proposed for grid-scale ESSs [3–5]. Lithium-ion batteries (LIBs), owing to high gravimetric/volumetric energy densities and long cycle life, are regarded as the most

ideal candidate for ESSs [6–8]. Nevertheless, lithium metal which is geologically constrained and has excessively high cost, has become the bottleneck faced with the ever-growing demand of ESSs [3,8–12]. On the contrary, room-temperature sodium-ion batteries (SIBs) largely associated with several features of sodium, such as abundance, low cost and electropositive nature closely related to that of the well-studied LIBs are expected to be a promising substitute for LIBs to satisfy the evolution of grid-scale ESSs where gravimetric energy densities are not indispensable [3,4,8–18]. Consequently, considerable efforts have been devoted to electrode materials of SIBs, but the progress is slow due to the lack of high-performance materials for both the anode and cathode [17]. On the cathode side, for instance, $Na_{0.95}Li_{0.15}(Mn_{0.55}Co_{0.10}Ni_{0.15})O_2$ [19], Na $[Ni_{0.60}Co_{0.05}Mn_{0.35}]O_2$ [20], $Na_{0.44}MnO_2$ [21], $NaFePO_4$ [22], $Na_3(VO_{0.8})_2(PO_4)_2F_{1.4}$ [23], $Na_4Fe(CN)_6$ [24], PTCDA-P [25], BPOE [26] etc., have received extensive attention, where the design line of the cathode in LIBs can be applied analogously in that of SIBs [15,16]. However, it remains challenging to develop high-performance anode materials for SIBs because of issues associated with low gravimetric/volumetric capacities, large volume expansion/shrinkage and low electronic conductivity [9,14]. Additionally, understanding the relationship between electrochemical performance and microstructures of electrode materials is of great importance for exploring the appropriate anode in SIBs [27–31]. Notably, operando (in situ) spectroscopic techniques like X-ray diffraction (XRD) have exerted a great influence on understanding the mechanisms of electrode reactions and optimizing the electrochemical performance of electrode materials [15,27,28,32–40].

Recently, metals (Sn, Pb, Sb, Bi) or metalloids (Si, P, Ge, As), which can form Na–Me intermetallic compounds in cell reactions, have shown great potentials to be applied in SIBs as an anode on the basis of the high theoretical capacity of 300–2000 mAh g^{-1} and low sodium storage potential (less than 1.0 V (vs. Na$^+$/Na)) [3,8,9,11,41]. Bi, with a large interlayer spacing along the c-axis for storing Na ions, has been regarded as a promising anode for SIBs [42,43]. Despite the lower gravimetric capacity in comparison with Sn and Sb, Bi has an ultrahigh volumetric capacity of approximately 3800 mAh cm^{-3} [15]. More importantly, its 250% volumetric expansion caused by alloying is obviously lower than that of Sn (423%), P (440%) and Sb (390%) [8,15]. As a result, much attention has been paid to nanostructured Bi-based anode materials for SIBs, such as 1D Bi@C nanofibers [44], sphere-like Bi@C [43] and Bi-NS@C [45]. However, limited information is available on the Na storage mechanisms of Bi in SIBs. Based upon ex-situ XRD, an intercalation/deintercalation mechanism was proposed for Bi-Na reactions during the charge/discharge processes [42,46]. Hence, monitoring the transformation of Bi in real time during the sodiation/desodiation processes is urgent and crucial for profoundly understanding the Na chemistry of Bi in SIBs.

Herein, operando XRD technique was utilized to real-timely investigate the Na storage mechanisms of Bi anodes with different morphologies and sizes (sputtered Bi film, nanoporous Bi and commercial Bi). Irrespective of their morphologies and sizes, the results demonstrate that the sodiation of three Bi anodes involves a two-step alloying process associated with two voltage plateaus, corresponding to the consecutive formation of NaBi and Na_3Bi respectively. The subsequent desodiation is correlated with a reversible dealloying process with the transformation of $Na_3Bi \rightarrow NaBi \rightarrow Bi$. Furthermore, we also verify the instability of Na-Bi intermetallic phases (Na_3Bi and NaBi), which could rationalize the inaccurate intercalation/deintercalation mechanism reported for nanostructured Bi anodes based upon ex-situ XRD.

2. Experimental section

2.1. Materials preparation

2.1.1. Fabrication of the sputtered Bi film electrode

As shown in Fig. S1a, the sputtered Bi film was directly deposited on stainless steel mesh (SS-mesh, stainless steel 304, thickness: 0.1 mm) by a radio frequency (RF) magnetron sputtering apparatus (SKY Technology Development Co., Ltd, China) using the high-purity Bi target (99.999 wt.%, Purui Material Instrument Co., Ltd, China). In a typical procedure, the SS-mesh used as a substrate was ultrasonically cleaned in acetone for 20 min, then rinsed with deionized water for several times to remove the residual acetone, and subsequently dried at 80 °C for 1 h in vacuum. The sputtering was operated at room temperature for 70 min, with the power of 100 W and Ar pressure of 1 Pa at a flow rate of 30 standard cubic centimeter per minute (sccm). Moreover, the sample holder was rotated at 5 revolutions per minute to guarantee the homogeneous coating on the substrate surface. Thus, the sputtered Bi film was obtained with the mass loading of around 0.79 mg cm^{-2}. Afterwards, the Bi film/SS-mesh was punched into a wafer with a diameter of 1.2 cm and used as the sputtered Bi film electrode.

2.1.2. Fabrication of nanoporous Bi

The nanoporous Bi was synthesized by chemical dealloying, as presented in Fig. S2. A binary $Mg_{92}Bi_8$ (nominal composition, at.%) was selected as the precursor for dealloying. The $Mg_{92}Bi_8$ ingot was prepared by melting pure Mg (99.99 wt.%) and pure Bi (99.99 wt.%) in a graphite crucible using an electric resistance furnace under the protection of covering flux. The $Mg_{92}Bi_8$ ingot was rapidly solidified into foils, which were typically 30–60 μm in thickness, 3–5 mm in width and several centimeters in length. Afterwards, the dealloying of $Mg_{92}Bi_8$ foils was performed in a 2 wt.% tartaric acid solution at room temperature until no obvious bubbles emerged. Then the as-dealloyed samples were rinsed, dried and slightly ground to obtain the nanoporous Bi powders.

In addition, the commercial Bi powders (200 meshes, Fig. S1b) were purchased from the Jiaming Platinum Nonferrous Metals Co. Ltd, China.

2.2. Microstructural characterization and electrochemical measurements

The phase constitution of the sputtered Bi film, nanoporous Bi and commercial Bi was identified using an XD-3 diffractometer (Beijing Purkinje General Instrument Co., Ltd, China) with Cu Kα radiation. Scanning electron microscope (SEM, ZEISS, SIGMA 300) was applied to characterize the microstructure of three pristine Bi samples and discharged/charged products of the commercial Bi powders. An energy dispersive X-ray (EDX) analyzer was used to determine the composition of nanoporous Bi. Raman spectra were obtained and detected utilizing a LabRAM HR Evolution Raman system (HORIBA Scientific, λ = 532 nm).

The nanoporous Bi electrode was prepared by a scraping-coating method. The slurry was prepared by mixing the nanoporous Bi powders, conductive acetylene black (Super P) and carboxymethyl cellulose (CMC) binder with a weight ratio of 60:25:15 in deionized water. The mixture was stirred for around 12 h to form a homogenous slurry. Then the slurry was coated onto the SS-mesh, further dried at 80 °C for 12 h in vacuum and then punched into disks (1.2 cm in diameter) with the mass loading of about 0.5 mg. As to the commercial Bi electrode, a similar procedure was adopted except the use of commercial Bi as the active material. The as-prepared electrodes (the sputtered Bi film, nanoporous Bi or commercial Bi) were used as the working electrodes. Na foil (99.99 wt.%, Sigma-Aldrich) was utilized as both the counter and reference electrodes, and glass fiber (GF/D, Whatman) was used as a separator. The electrolyte was 1 M $NaClO_4$ in propylene carbonate (PC) with 5 wt.% addition of fluoroethylene carbonate (FEC). A CR2016 coin