



Bismuth nano-spheres encapsulated in porous carbon network for robust and fast sodium storage

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HIGHLIGHTS

- The Bi-NS@C composite has been synthesized via a molten salt method.
- Bi nanoparticles are well-dispersed and incorporated into the carbon matrix.
- The composite boosts the electric conductivity and mass transport of Na⁺.
- The composite delivers excellent cycle performance for sodium ion battery.

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ABSTRACT

Sodium ion batteries (SIBs) have been considered as a promising cost-effective alternative for grid energy storage for renewable energy sources such as wind- and solar power. In this work, a bismuth nano-spheres and porous carbon composite (Bi-NS@C) is developed via an oleate-oriented dual-phase interfacial reaction and a molten salt calcination process. Materials characterizations suggest that the Bi-NS with a size of 20–30 nm are uniformly distributed in the sponge-like porous carbon network. Such a structure could enable a conductive network, prevent particle aggregation, shorten the ions transportation pathways, accommodate volume change and prevent the collapse of the electrode. As a result, this anode delivers a reversible discharge capacity of 106 mAh g⁻¹ after even 1000 cycles at 0.2 A g⁻¹. Even at 2 A g⁻¹, the specific capacity of the electrode can still retain at ~110 mAh g⁻¹. The remarkable electrochemical performance of the Bi-NS@C composite suggests that the as-prepared nanocomposite can simultaneously enhance the Na⁺ ion conductivity and electronic conductivity in the charge/discharge processes, which offer guidance in anode materials design and synthesis in SIBs.

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1. Introduction

In face of increasing demands for green and renewable energy, it is urgently desirable to develop efficient energy storage systems with high energy density, long cycle and shelf life, inexpensiveness and environmental friendliness [1–5]. Lithium ion batteries (LIBs) have dominated the current rechargeable battery market worldwide due to their outstanding energy capability and power density. However, lithium (Li) metal is expensive because of the scarce lithium sources and the safety issues. Unlike Li, sodium (Na) is one of the most abundant elements on the earth. Sodium exhibits

similar chemical properties as Li, which suggests that sodium ion batteries (SIBs) can be fabricated using similar battery chemistry as LIBs [6–9]. However, as sodium ion is 55% larger than lithium ion in term of size, it is difficult to find an anode material that could facilitate the insertion/extraction of metal ions in SIBs [10–12]. As an example, the most common anode materials graphite could not be used for SIBs directly. Besides, recent works revealed that there are more differences for the ions storage mechanisms between LIBs and SIBs [10,13–15].

For SIBs, several different materials have been attempted to use as anode materials, such as carbon composites [11,16,17], metal oxides [12,18–21], metal sulphides [22,23] and other materials. Among the alternative anode materials, metals of group IV (Si, Ge, Sn) [24–26], group V (Sb, Bi) and their corresponding alloys [13,14,27–29] have attracted much attention because of their

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ability to react reversibly with large amounts of Na per formula unit. Bismuth is one of them with high gravimetric and volumetric capacities for SIBs. By now, there are few works reported for the utilization of Bi as anode materials for SIBs, Su et al. [13] explored the possibility and the mechanism for sodium storage; Lai et al. [29] proposed Bi@carbon composite could enhance LIB battery performances. Sottmann et al. [14] claimed that the sodium storage mechanisms in bismuth are depending on the sizes of the Bi crystallites. In all, these works suggest that Bi would be a promising anode material for SIBs.

Nevertheless, the Bi-based anode materials are still suffering from severe cycling decay during long cycling ranges, which is mainly caused by the volume change during charge/discharge processes and their poor electronic and ionic conductivity [13,14,30]. Decorations or modifications of Bi for improving its electrochemical performances are highly needed. In the course of designing novel composites for SIBs, special considerations need to be given to *i*) electronic conductivity, *ii*) ionic mass transportation pathways and *iii*) stability of the electrode. Normally, nano particles can provide more active sites and enhance the battery rate capability, but severe aggregation due to their high surface energy, poor conductivity from the dissociation and probable volume change pulverisation of the electrode would be a huge barrier. Creating continuously conductive porous frameworks with uniformly distributions of Bi nano particles may meet all these requirements. Thus, we report a bismuth nano-spheres@carbon (Bi-NS@C) composite as anode material which was fabricated via a simple molten salt and subsequently carbonization strategy to increase the electrochemical performances.

Herein, the synthesized Bi-NS@C composite, in which use Na_2SO_4 as a reaction medium, which is inexpensive and easy to process. The molten salts phase under high temperature can be used to prevent the grain aggregation and control the particle size and evenly distributed the nanoparticles with high purity and good crystal morphology. The carbonization process would also be influenced by the molten salts since carbon frameworks with connecting hierarchical pores would be remained after Na_2SO_4 was washed away. Lastly, the porous structure can facilitate the rapid mass transport of sodium ions while the carbonaceous frameworks can facilitate the electron conductivity and current collection. The as-prepared Bi-NS were well-distributed and embedded in 3D porous conductive frameworks of carbon from the metal-oleate complex precursors, as schematically illustrated in Scheme 1.

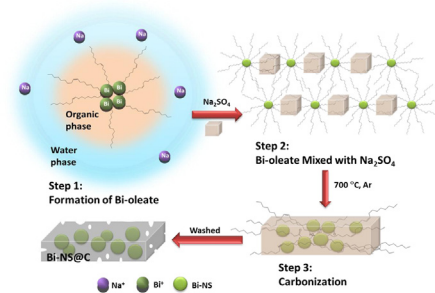
The functions of oleate can be classified into 3 folds: firstly, oleate is able to reaction with $\text{Bi}(\text{NO}_3)_3$ to form Bi-oleate complex, that can be distribute evenly in the Na_2SO_4 solute under grinding conditions. Secondly, at high temperature, the oleate could reduce Bi^{3+} into metal Bi nano-spheres and thirdly, the oleate is converted into porous carbon networks in the presence of molten Na_2SO_4 salt.

It is envisaged that the porous and conductive carbon 3D structures would significantly boost the electric conductivity and ions transportation; moreover, since the volume change of Bi during the charge/discharge processes could be restricted by the carbon frameworks, pulverization of the electrodes could be effectively prevented. Thus, the Bi-NS@C composite electrodes could be expected for delivering remarkable electrochemical performances including high specific capacity, rate capability and most importantly, long cycling stability.

2. Experimental

2.1. Synthesis of Bi-NS@C composite

The synthesis process is based on our previous work for the preparation of ultra-small metal or metal oxide nanoparticles



Scheme 1. The synthesis process of the Bi-NS@C composite.

encapsulated with thin carbon layers [31,32]. In detail, 0.01 M $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 0.06 M Na-oleate were first dissolved in 120 mL water: ethanol: hexane (*v/v* 1:2:3) mixture solution and stirred at 70 °C for 30 min until a clear and homogeneous solution formed. Then 0.03 M KOH was added and the resulting mixture was refluxed at 70 °C for 4 h. The obtained suspension was cooled down to room temperature and two layered liquids were clearly seen. The oil layer on top was milky white organic phase and bottom layer was transparent water phase. The top layer solution was subsequently separated, volatilized and dried at 80 °C for 24 h and 110 °C for 14 h. The as-obtained product is white yellow bismuth oleate complex.

Bi-NS@C composite was synthesized by the molten salt method with the follow process. Briefly, the bismuth oleate precursor (3.5 g) was grinded thoroughly with Na_2SO_4 (50 g), and then heated at 700 °C for 3 h under Ar atmosphere. After cooling down, the resultant powder was further washed with water and ethanol in turns for several times to completely remove Na_2SO_4 and dried in a vacuum oven at 80 °C. Subsequently, a black colour powder, i.e. Bi-NS@C composite is obtained.

2.2. Material characterizations

The microstructure and morphology of materials were examined by scanning electron microscope (SEM, JSM-7001F) and transmission electron microscopy (TEM) (FEI Model Tecnai G20). The multipoint Brunauer-Emmett-Teller (BET) surface area was estimated using adsorption data obtained from a surface area analyser (Micromeritics Tristar 3020). X-ray diffraction (XRD) was characterized (Model LabX-6000, Shimadzu, Japan) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 40 mA over the 2θ range of 20–80°. The carbon content of the as-prepared material was obtained by using a TG-DSC analyser (Perkin Elmer) in air from room temperature to 800 °C at a heating rate of 5 °C min^{-1} . For X-ray photoelectron spectroscopy (XPS, Kratos Axis ULTRA incorporating a 165 mm hemispherical electron energy analyzer) test, all binding energies were referenced to the C 1s peak (284.8 eV).

2.3. Cell assembly and tests

The electrodes were prepared by mixing 80 wt% Bi-NS@C composite, 10 wt% carbon black and 10 wt% PVDF binder in NMP and pasted on copper foil. The electrodes were rolled and cut into 1 × 1 cm and the mass of the active material on copper foil was about 1–2 mg cm^{-1} .

The SIBs were assembled in a standard 2032-type coin cell in argon-filled glove box ($\text{H}_2\text{O} < 0.1 \text{ ppm}$ and $\text{O}_2 < 0.1 \text{ ppm}$) with a sodium foil as anode. Electrodes are separated by a porous glass fibre membrane. The electrolyte is 1 M NaClO_4 in EC and propylene carbonate (PC) (*v/v* 1:1).

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