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The different Li/Na ion storage mechanisms of nano Sb_2O_3 anchored on graphene

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HIGHLIGHTS

- The Sb_2O_3/rGO shows superior electrochemical properties in NIBs than in LIBs.
- During the first discharge, Sb_2O_3 are converted into Li_3Sb and Li_2O in LIBs.
- During the initial discharge, Sb_2O_3 are converted into Na_x-O_y-Sb and Na_2O in NIBs.
- The Na-ion can be transported to the inner part of Sb_2O_3, where the Li-ion cannot.
- The Na_2O display better chemical stability than Li_2O during cycles.

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ABSTRACT

The antimony oxide/reduced graphene oxide (Sb_2O_3/rGO) nanocomposites are used as anode of Li-ion and Na-ion batteries (LIBs and NIBs). However, it is unclear about Li-ion and Na-ion storage mechanism in Sb_2O_3/rGO nanocomposites. Herein, the conversion-alloying mechanisms of Sb_2O_3/rGO anodes for Na-ion and Li-ion storage are comparatively studied with a combined *in-situ* XRD and quasi *in-situ* XPS method. The distinct behaviours are monitored during (de)lithiation and (de)sodiation with respect to crystal structure and chemical composition evolution. It is evidenced that the Na-ion can be easily transported to the inner part of the Sb_2O_3, where the Li-ion almost cannot reach, leading to a fully transformation during sodiation. In addition, the conversion reaction product of amorphous Na_2O display their better chemical stability than amorphous Li_2O during electrochemical cycles, which contribute to a stable and long cycling life of NIBs. This work gain insight into the high-capacity anodes with conversation-alloying mechanism for NIBs.

1. Introduction

Li-ion batteries (LIBs) have been widely used in portable electronic devices and hybrid electric vehicles in the past couple of decades. However, considering the high cost and limited reserves of lithium, it is difficult for LIBs to continuously meet the demands of large-scale energy storage systems and applications [1–3]. Owing to the high natural abundance of sodium on earth crust and their similar insertion chemistry with LIBs, Na-ion batteries (NIBs) are now attracting worldwide attentions as alternative power sources [4]. To date, many efforts have been devoted to exploring high-performance anode materials for NIBs. A shortcut is to investigate the well-understood and widely used anodes of LIBs and verifying whether it is suitable on NIBs. For example, insertion compounds such as hard carbonaceous materials have been reported as anodes of NIBs. However, the low capacity of reversibly inserting and extracting Na-ions (about 200 mAh g^{-1}) was insufficient to the requirement of real application [5–7]. Moreover, materials based on the alloying mechanism, such as Si, Sn, Ge, etc., are being pursued as alternative anodes for NIBs as well [8,9]. Similar to LIBs, this type of material also delivers a large charge storage capacity in NIBs. For example, Sn possess a theoretical capacity of 993 mAh g^{-1} for lithium [10], which could deliver initial capacity of 864 mAh g^{-1} in NIBs,

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which make it attractive to the researchers. Even so, the use of alloy-type materials as electrodes are still impracticable at this stage since their low Na-ion reaction kinetics and severe volume change upon ion insertion and extraction [9]. Recently, materials combining conversion and alloying reactions, such as Sb_2O_3, Sb_2S_3 and SnO_2, were investigated as anodes for NIBs [11–14]. This type of material often undergoes a conversion reaction with Li/Na at the first step and then transforming to an amorphous structure containing nanosized alloys, in which could accommodate much more Li/Na atom, which highlights its application potential.

It is important to note that the electrochemical reaction process of a material in NIBs cannot related to its behavior in LIBs by trivially analogy. In fact, it may show great differences on ion storage and electrochemical performance [15–19]. Firstly, Na-ion is about 1.4 times larger in radius than Li-ion [4], leading to a higher volume expansion upon cycling. In the same time, the large ionic size limits fast kinetics by increasing the diffusion barrier. Secondly, the chemical activity of metal lithium and Sodium is quite different. Sodium has a lower electronegativity and giving up electrons more easily. Thus, the degrees of stability of electrode/electrolyte interface and electrochemical reaction products in NIBs may also different from LIBs. Actually, Darwiche et al. have revealed that the alloying-type Sb electrodes have different ions storage mechanisms [18]. The electrochemical alloying process of Sodium and Sb experienced instable intermediate phases during cycling, which is different from the reaction of lithium and Sb. Allan *et al*, in a further step, tracked the Na-Sb phase transformations during cycling by employing operando pair distribution function analysis and solid-state NMR spectroscopy [19]. The detailed reaction paths during the initial and subsequent cycles have been clearly discovered, which was proved much complicated than the lithium case. Considering that, it is essential to comparatively analyze the differences between LIBs and NIBs, and thus to fabricate electrode materials with a rational structure design, high specific capacity, as well as long cycle life.

As a conversion-alloying type anode, Sb_2O_3 have been investigated as a promising candidate material for both LIBs and NIBs. Xue *et al* found nanostructured thin film of Sb_2O_3 possesses a reversible capacity of 794 mAh g^{-1} in LIBs, corresponding to 8.6 Li per Sb_2O_3 [14]. Similarly, excellent success has been achieved for NIBs with pure Sb_2O_3 electrodes [13]. In the report by Hu *et al*, Sb_2O_3 have shown its great high capacity, high-rate, and durable anode for NIBs [13]. However, most of the previous studies put emphasis on the synthesis and structure design of Sb_2O_3 in LIBs or NIBs respectively, rather than focusing on the ion storage mechanisms of Sb_2O_3. Although part of the alloying process has been clarified using Sb metal anode, the conversion-alloying process is still unclear for Sb_2O_3 anode in LIBs and NIBs.

In this study, Sb_2O_3/reduced graphene oxide (rGO) nanocomposites were synthesized and utilized as anode materials for both LIBs and NIBs. Interestingly, the Sb_2O_3/rGO used as anodes in NIBs shows a more stable electrochemical property than that in LIBs. Through *in-situ* XRD, quasi *in-situ* XPS, SEM amd GITT, the different ion storage mechanisms in LIBs and NIBs were systematically and comparatively investigated. The difference in the conversion reaction process, particularly the stability of reaction products and chemical composition were clarified for the first time, which broaden the understanding of inner mechanism on this conversion-alloying type material.

2. Experimental

Graphite oxide was prepared from natural graphite by the modified Hummers' method, and the GO suspension was prepared by dispersing graphite oxide powder in deionized water with the tip ultrasonication. $SbCl_3$ (0.25 g) was then dissolved in 30 ml GO suspension (8.33 mg ml^{-1}) under ultrasonication, and the mixture was stirred for additional 0.5 h to prepare $SbCl_3$ solution. After that, ethylene glycol (EG, 30 ml) was added in the $SbCl_3$ solution to form a lacteous colloid suspension under constant stirring for 0.5 h. Then $NaBH_4$ (0.3 g) was added in the solution and the resultant mixture was transferred directly into a sealed Teflon-lined stainless autoclave and maintained at 180 °C for 10 h, then cooled to room temperature on standing. The products were harvested by centrifugation and washed with deionized water and ethanol for three times respectively to remove the redundant impurity from the as-produced samples. After drying under vacuum at 80 °C temperature, a fine black powder (Sb_2O_3/rGO) was obtained. The resultant composite was heated in a tube furnace under argon and hydrogen mix atmosphere at 600 °C for 5 h, yielding Sb/rGO. The pure Sb_2O_3 nanoparticles were prepared via the same conditions with deionized water instead of the GO dispersion.

The crystal structure of synthesized Sb_2O_3/rGO was characterized by powder X-ray diffraction (XRD, Rigaku D/Max-KA diffractometer with CuKα radiation). *In-situ* time-resolved XRD studies were performed on specially designed electrochemical cells under operando conditions (D8 Advance, Bruker, $\lambda = 1.5406$Å). Raman spectra were collected via a Raman spectroscope (HORIBA Labram HR 800) with a 532 nm semiconductor laser. The X-ray photoelectron spectroscopy (XPS) was conducted with a PHI 5000 VersaPrboe-II X-ray instrument using X-rays aluminum anode (monochromatic Kα X-rays at 1486.6 eV) as a source. During the etching process, the etching rate of Ar^+ beam was confirmed by the SiO_2 standard sample and it is 29 nm min^{-1}, the etching time was set to 8 min. The thermogravimetric analysis (TGA) was carried out on a STA449F3 TG-DSC instrument with the heating rate of 5 °C min^{-1} from 30 to 700 °C in air. An automated adsorption apparatus (Micromeritics ASAP 2020) was used to determine the nitrogen adsorption/desorption isotherms at 77 K. The pore-size distribution was calculated using non-local density functional theory (NLDFT) method. The surface morphology of the samples was investigated using a field emission scanning electron microscope (FE-SEM, HITACH S4800) at 10kv. The composite microstructure was also investigated on a high-resolution transmission electron microscopy (HRTEM, FEI TECNAIG2 F30) at 300 kV, and the energy-dispersive X-ray spectroscopy (EDX) system was used to analyze the elemental distribution. Quasi *in-situ* analyses of the electrode, the electrodes (dis)charge to corresponding voltage during the first cycle were retrieved by disassembling the coin cells and rinsed with DMC, and the rinsed sample were transferred from the glovebox to the XPS and FE-SEM chamber under vacuum using an air-tight transfer device, respectively. All the procedures were performed in the glovebox.

The slurry was prepared by mixing 80 wt% active materials, 10 wt% conductive carbon black and 10 wt% polyvinylidene fluoride binder in an adequate amount of N-methyl-2-pyrrolidone. The resultant slurry was pasted onto Cu foil and dried in a vacuum oven at 110 °C for 12 h. Coin cells (2032-type) were assembled in an Ar-filled glovebox ($O_2 < 0.5$ ppm, $H_2O < 0.5$ ppm). The lithium and sodium foils were used as counter electrodes, and Celgard 2400 and glass fiber (GF/A, Whatman) were employed as separators for LIBs and NIBs, respectively. The mass loading of active materials was about 1.4 mg cm^{-2}. As the electrolyte, $LiPF_6$ (1.0 M) in dimethyl ethylene carbonate (DEC): fluoroethylene carbonate (FEC) (1:1 by volume) was used for LIBs, and $NaClO_4$ (1.0 M) in propylene carbonate (PC) with 5% fluoroethylene carbonate (FEC) was used for NIBs. The cutoff voltage window is 0.005–2.50 V and 0.005–2.00 V for the LIBs and NIBs, respectively. Galvanostatic charge-discharge was carried out on a LAND CT2001A instrument. The cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) were tested using a VMP-3 multichannel electrochemical station (Bio-Logic-Science Instruments SA, France). EIS was carried out over a frequency range from 100 kHz to 10 mHz. During GITT measurements, cells were tested using a VMP-3 multichannel electrochemical station (Bio-Logic-Science Instruments SA, France) and the cell was charged or discharged at a constant current of 0.05 C rate for an intermittent time of 1 h, followed by open-circuit relaxation for 7 h after three cycles.