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Confinement of nanosized tin(IV) oxide particles on rGO sheets and its application to sodium-ion full cells as a high capacity anode material

Chang-Heum Jo, Jae-Hyeon Jo, Seung-Taek Myung*

Department of Nanotechnology and Advanced Materials Engineering & Sejong Battery Institute, Sejong University, Seoul, 05006, South Korea

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ABSTRACT

In this study, we report the synthesis and electrochemical reactions of nanosized SnO_2/reduced graphene oxide (rGO), as well as its cell performance that implement full cells coupled with carbon-coated $NaCrO_2$ cathodes. We synthesize nanosized SnO_2/rGO composites to mitigate main drawback that conversion and alloy reaction materials suffer from self-pulverization on discharge (reduction). Hydrothermally produced SnO_2 nanoparticles are simultaneously attached onto rGO sheets via a self-assembly process, in which rGO sheets provide sufficient electron conduction paths (~10^{-3} S cm^{-1}) during electrochemical reactions. As anticipated, this technique results in satisfactory cell performance with help from the effect mentioned above. For the first time, we apply the SnO_2/rGO composite materials to a full cell, adopting a carbon-coated $NaCrO_2$ (110 mAh (g-$NaCrO_2$)$^{-1}$ cathode. The full cell demonstrates an excellent capacity retention, approximately 84% of the initial capacity (88 mAh (g-$NaCrO_2$)$^{-1}$) for 300 cycles, and is active even at a rate of 10C (1.05 A g^{-1}), delivering 87 mAh (g-$NaCrO_2$)$^{-1}$. This result demonstrates the feasibility of using carbon-coated $NaCrO_2$//SnO_2/rGO sodium-ion cells for energy storage.

1. Introduction

Lithium-ion batteries (LIBs) have been used in a wide variety of applications, including mobile to energy conversion and storage systems, due to their high energy density and excellent cycling stability [1–3]. This increasing demand of LIBs will potentially lead to a scarcity of lithium resources in the near future. To address this concern, it is necessary to explore cost-effective battery systems as promising alternatives to LIBs; based on the chemistry, availability, and cost, sodium-ion batteries (SIBs) are considered as the most plausible alternative. More importantly, sodium is one of the most abundant resources on earth, attracting considerable attention in recent years, particularly for large-scale energy storage applications.

Graphite is one the most well-known anode materials used in LIBs. However, it can only accommodate for a few sodium ions; this is due to the large ionic radius of Na^+ ions and the low intercalation potential of ~0.1 V vs. Li/Li^+, corresponding to −0.2 V vs. Na/Na^+ where Na metal plating occurs at the potential. By contrast, hard carbon allows Na^+ insertion with the lowest operation voltage and a reasonable capacity of approximately 300 mAh g^{-1} at very low currents. Apart from the electrode performance, the low operation voltage of hard carbon increases energy density of SIBs. In addition, Na^+ insertion-type materials such as TiO_2, TiO_2(B), $Li_4Ti_5O_{12}$, P2-$Na_{0.66}Li_{0.22}Ti_{0.78}O_2$, $Na_2Ti_3O_7$ and $Na_2C_8H_4O_4$ are based on $Ti^{4+/3+}$ redox, demonstrating a reasonable cycling stability even though their capacities are lower than that of hard carbon [4–10]. Large capacities can be obtained through formation of alloy between metal and sodium. Because Si does not readily react with Na above 0 V vs. Na/Na^+, investigation towards alloy reactions with Na have mainly focused on Sn, P and Sb [11–13]. Similar to Li systems, however, formation of alloy usually causes significant volume expansion during the sodiation process. This indicates that degradation phenomena are serious concern in sodium systems.

Tin(IV) oxide is of interest because of its large theoretical capacity of 711 mAh g^{-1} in Na cells, followed by the conversion reaction: $SnO_2 + 4Na + 4e^- \leftrightarrow Sn + 2Na_2O$ [14]. Although there is a large irreversible capacity during the first sodiation process, this can be overcome by the formation of nanosized composites such as nanosized particles, nanotubes, porous nanostructure [15–18]. However, large surface areas for the electrodes can result in reductive electrolytic decomposition of the interface between the electrode and electrolyte, which thickens the solid electrolytic interphase (SEI) layer [19]. Recent elaboration has been focused to

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* Corresponding author.
E-mail address: smyung@sejong.ac.kr (S.-T. Myung).

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attach active materials onto the inactive matrix, which is used as a mechanical buffer during volume expansion [20]. Those inactive matrixes were suggested, as follows: carbon nanotubes, amorphous carbon, mesoporous carbon, and graphene [21]. Electrode materials can improve their electric conductivities and minimize the byproduct formation by mitigating volume expansion. Furthermore, electron conduction is facilitated by the presence of carbon within the electrode [22–33].

Due to the higher theoretical capacity of SnO_2 (711 mAh g^{-1}) relative to that of SnO (398 mAh g^{-1}) based on conversion reactions, we synthesized nanosized SnO_2 via in-situ decomposition of SnC_2O_4 during a hydrothermal reaction. In addition, the as-synthesized nanosized SnO_2 was attached onto rGO sheets via a self-assembly layer-by-layer process in poly (diallyldimethyl ammonium chloride) solution at 25 °C, utilizing electrostatic adsorption to produce the SnO_2/rGO composite. The composite electrode demonstrated remarkable electrode performance, including high capacity, retention, and rate capability. We also studied the reaction process to better understand the suggested conversion reaction in Na cells. Furthermore, we report the conversion of a SnO_2/rGO composite anode via pairing with a $NaCrO_2$ cathode in full cells for sodium storage. This report demonstrates that SnO_2/rGO composite is suitable for use in SIBs for energy storage applications.

2. Experimental

2.1. Synthesis of SnO_2

$SnCl_2 \cdot 2H_2O$ (Kanto), $Na_2C_2O_4$ (Kanto), and ethylene glycol (Kanto) were dissolved in distilled water and the mixed solution was stirred at room temperature for 6 h. The solution was then poured into a Teflon-lined stainless steel autoclave. The autoclave was hermitically sealed and heated in the temperature range of 130–200 °C for 12 h under autogenous pressure. After the reaction, the autoclave was cooled to room temperature. Finally, the products were washed with deionized water and ethanol and then dried at 80 °C for 24 h in a vacuum oven.

2.2. Synthesis of SnO_2/rGO composite via a self-assembly layer-by-layer (SA-LBL) process

The as-synthesized SnO_2 powder was sonicated to disperse SnO_2 nanoparticles in distilled water for 10 min, and poly (diallyldimethylammonium chloride) (PDDA, Aldrich) was consequently poured into the suspension. The PDDA-added suspension was vigorously stirred for 30 min. Then, the suspension was mixed with rGO (IDT International) and stirred for 1 h, which the starting ratio of active material versus rGO was 9:1 in weight. The product was isolated and the residual PDDA was removed through centrifugation at 10,000 rpm for 30 min, followed by two consecutive cycles of washing/centrifugation with distilled water. Finally, the products were dispersed in water to produce colloidal SnO_2/PDDA/rGO suspension, and then the suspension was dried in a vacuum at 80 °C overnight.

2.3. Physical properties

The crystalline phases of the products were characterized using powder X-ray diffraction (XRD, Rint-2000, Rigaku) analysis using Cu-Kα radiation. The XRD data were obtained with a step size of 0.03° and a count time of 1s. The products were analyzed using high resolution dispersive Raman microscopy (Renishaw inVia Raman microscopy). The particle morphologies of the produced powders were observed using scanning electron microscopy (SEM, JXA-8100, JEOL) and transmission electron microscopy (TEM, H-800, Hitachi). The DC electric conductivity was measured using a direct volt–ampere method (CMT-SR1000, AIT) in which disc samples were contacted by a four-point probe. An elemental analyzer (EA110, CE Instrument, Italy) was employed to determine the amount of carbon in the final products.

2.4. Electrochemical properties

Electrochemical properties were measured with R2032 coin type cells. Electrodes were fabricated as a mixture of the as-synthesized SnO_2 powder (85 wt%), carbon black super P (10 wt %), and polyacrylic acid (5wt%) in *N*-methyl pyrrolidinon. For the SnO_2/rGO composite (for which the final amount of carbon residue based on rGO sheet was approximately 9.9 wt% as analyzed by an elemental analyzer), the electrode was a mixture of SnO_2/rGO (94.5 wt%), carbon black super P (0.5 wt%), and polyacrylic acid (5 wt%) in *N*-methyl pyrrolidinon, finally equalizing the amount of SnO_2 and carbon content for both the rGO-free and SnO_2/rGO composite electrodes. The obtained slurry was thus applied onto copper foil and then dried in an oven at 80 °C for 1 h in air. The electrode was further dried over night at 80 °C under a vacuum prior to use. The typical amount of loaded active material was approximately 5 mg cm^{-2}. Charge-discharge tests were performed using R2032 type coin cells as the half cells (Na metal anode). The fabricated cells were charged and discharged in a range of 0–3 V by applying different current densities at 25 °C. For the full cell test, $NaCrO_2$/C (recently used as a high rate cathode)[21] blended with KS-6 and Super-P (1:1 in weight) was used as the conducting materials, and polyvinylidene fluoride (85:7.5:7.5 in weight) was used as the cathode. SnO_2/rGO was employed as the anode after presodiation via the direct physical contact of SnO_2/rGO with Na metal for 30 min in electrolyte in order to minimize the first irreversible capacity, which the physically sodiated SnO_2/rGO electrode was optimized based on sodiation time in Fig. S1. Galvanostatic electrochemical charge and discharge tests were carried out in 0.5 M $NaPF_6$ in PC:FEC (98:2 v/v mixture) solution at room temperature. The presence of small amount of FEC in PC solutions was important for maintaining good electrode passivation [34].

3. Results and discussion

3.1. Synthesis from SnC_2O_4 to SnO_2/rGO composite

The synthetic process of the SnO_2/rGO composite is illustrated in Fig. 1a, and the resulting SEM image of the final product is shown in Fig. 1b that the SnO_2 particles were confined on the rGO sheets. As shown in Fig. 1c, highly crystalline SnC_2O_4 was produced via the hydrothermal reaction at 100 °C: $SnCl_2 \cdot 2H_2O + Na_2C_2O_4 \rightarrow SnC_2O_4 + 2NaCl + 2H_2O$. Here, the resultant was crystallized into the *C*2/*m* space group for which all the diffraction peaks are indexed to monoclinic tin oxalate (JCPDS Card No. 51-0614) without impurities. The crystal structure was maintained at 140 °C, but broadening of the (−112) peak at around 26–27° (2θ) was noticed when further heated to 170 °C. This broadening indicates the formation of a SnO_2 phase, which was confirmed at 200 °C, yielding phase-pure SnO_2 corresponding to the tetragonal rutile structure (JCPDS Card No.41-1445, space group $P4_2/mnm$, $a = b = 4.738(1)$ Å, $c = 3.187(1)$ Å). This indicates that the SnC_2O_4 product was decomposed under the hydrothermal condition; specifically, $SnC_2O_4 \rightarrow SnO_2 + 2CO$, finally yielding SnO_2.

To confine the hydrothermally produced SnO_2 particles onto planar rGO sheets, we employed an SA-LBL process, as illustrated in Fig. 1a. First, rGO sheets were poured into distilled water and then the solution was sonicated to disperse rGO sheets. Simultaneously, negatively charged SnO_2 was mixed with the positively charged