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Synthesis and sodium storage performance of Sb porous nanostructure

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Abstract

Porous Sb nanostructure has been prepared via a magnesiothermic reduction reaction and a succedent HCl solution etching process. The Sb product is made up of connected uniform porous particles. The pores have an average pore size of ~80 nm. Sodium storage performance of porous Sb product has been investigated. An initial reversible capacity of 570.3 mAh/g was obtained at 50 mA/g. At the 50th cycle, a reversible capacity of 538.7 mAh/g was retained, corresponding to a high retention rate of 94.5%.

Keywords: Chemical Synthesis; Sb; Nanostructured Materials; Electrode materials

1. Introduction

It is possible for sodium ion batteries (SIBs) to replace lithium-ion batteries (LIBs) in the near future because there are rich sodium resources in the earth and sodium is environmentally friendly [1-5]. Therefore, researchers have paid close attention on SIBs recently. A most critical problem limiting the current SIBs technology lies in its development of anodes. Metal materials have been investigated the possibility as anodes for SIBs and some of them have been found to show potential for practical application[6]. Sb is highly conspicuous mainly due to its appropriate operating voltage among all metal alloy anodes for SIBs [7-10]. The theoretical capacity of metal Sb is 660 mAh/g based on reaction Sb + 3Na↔2Na₃Sb. Small electrode polarization (0.2 V) of Sb make the cycling caused self-heating decreased. Furthermore, the puckered-layer structure of Sb offers large space for sodium-ions to diffuse fast and interior stress induced by charging/discharging can be freed easily. As a result, the kinetics, cycle stability and other properties of Sb anode have the potential to be improved dramatically. However, Sb anode has a huge volume change (~ 290%) in SIBs during sodiation/desodiation process, which result into pulverization of Sb anode material [11, 12]. Thus, the delamination of active substances Sb occurs and electrical contact is weakened. Besides, huge volume changes would also give rise to the breaking of solid electrolyte interphase (SEI) layer, which in return causes the continuous consumption of electrolyte to reform SEI in each cycle. Consequently, fast capacity decaying and poor cycling performance come into being.

One of the effective approaches to alleviate volume expansion of Sb anode is to

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fabricate Sb with porous structures as the tremendous inner space of porous structure can buffer the large volume change of the materials. In addition, porous structures can also provide huge specific surface area, which facilities the permeation of the electrolyte and decrease the local current density of the electrode, thus beneficial for the high rate capability [13-16].

Herein, we successfully prepared Sb product with an interconnected porous structure via a magnesiothermic reduction reaction and a succedent HCl solution etching process. A mean size of pores of ~80 nm exists in the interior of Sb particles. Sodium storage performance of Sb nanostructure has been investigated. The porous Sb reveals excellent electrochemical behavior.

2. Experimental section

Synthesis

0.6 g Sb₂O₃, 0.58 g NaCl, 0.75 g KCl and 0.6g Mg powder were ground intensively for 10 minutes. The fully mixed precursors were transferred into a corundum boat, which was then covered with another corundum boat. The above mixture in the closed corundum boat was pushed carefully to the center of a tube furnace and heated at 680 °C for 180 minutes. During heating process, the tube was passed through an mixed gases of Ar (95 vol %)/H₂ (5 vol %) with a flowing velocity of 100 sccm. After finishing the heating and the furnace becoming cooled, the corundum boat was taken out. The powder in the corundum boat was immersed in 1M HCl solution for several hours to remove NaCl, KCl and MgO. NaCl and KCl dissolved in water. MgO reacted with HCl based on MgO + 2HCl = MgCl₂ + H₂O and became dissolved. The precipitated substance was separated via centrifugation, rinsed by using ethanol and deionized H_2O , and dried under vacuum at 50 °C. Finally, dry Sb powder was produced.

Material Characterization

X-ray diffraction patterns were conducted on Rigakau RU-300 with CuK α radiation. Scanning electron microscopy (FESEM QF400) was used to observe the Sb sample's morphology. The SEM microscope had an attachment of an energy dispersive X-ray (EDX) spectrometer. Detailed microstructure investigation was conducted with transmission electron microscopy (TEM Tecnai 20ST). Brunauer–Emmett–Teller (BET) surface area measurements were carried out using N₂ in a Micrometrics ASAP 2420 instrument.

Electrochemical measurements

The electrode slurry was made by mixing the powders of 80 wt% Sb porous powder, 10 wt% multi-walled carbon nanotubes, and 10 wt % carboxyl methyl cellulose sodium salt (NaCMC). A Cu foil with the as-prepared slurry cast on its surface was dried under vacuum at 60 °C for 12 hours. Disk electrodes were fabricated by pressing and punching the Cu foil. Every electrode was loaded with about 1.0 mg Sb active material. The electrochemical performances of Sb anodes were tested by fabricating 2032 coin-type cells. Metal sodium was selected to be the counter electrode. Electrolyte was 1M NaClO₄ solution in propylene carbonate with 5wt% fluoroethylene carbonate. A GD-120 glass fiber filter was used as separator. Galvanostatic charge-discharge was performed on a battery testing system (LAND CT2001A). Cyclic voltammetry (CV) was acquired on an electrochemical workstation (CHI6009D).

3. Results and discussion



Fig. 1 is a typical XRD illustration of porous Sb product. XRD result is well congruent with the hexagonal phase metallic Sb. Sb lattice constants have been calculated based on the XRD data. They are a = b = 4.308 and c = 11.322 Å, being coincide with the data from JCPDS card, No. 85-1323. No peaks from NaCl, KCl or MgO appear, revealing that impurities are removed completely and phase-pure Sb product has been obtained.



Fig. 2. (a) SEM, (b) EDX, (c) TEM, SAED (insert of Fig. 2c) and (d) HRTEM images of Sb product

SEM and TEM have been conducted to study the porous Sb sample. The SEM image in Fig. 2a displays that the Sb product sample is actually a network structure composed of coherent uniform porous particles. A TEM image in Fig.2b confirms the SEM result. Average pore size is about ~80 nm. Wall thicknesses between those pores vary from 30 nm to 100 nm.

The elemental composition of porous Sb sample has been investigated with EDX

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technique. Only Sb elemental signal can be found in the EDX pattern, as shown in Fig. 2b, confirming the pure single phase of the Sb product. A typical SAED pattern recorded from the Sb sample is shown in the inset of Fig. 2c. The diffraction rings disclose polycrystalline feature of Sb nanoparticles. High resolution TEM result shown in Fig. 3d exhibits clear parallel fringes with a space of 0.31 nm, originating from the (012) planes in hexagonal structured Sb.

Such a porous network nanostructure is beneficial to the Na storage performance of Sb electrode. Firstly, the porous nanoparticles can provide a large surface area. The BET specific surface area of the sample has been measured to be $17.5 \text{ m}^2/\text{g}$. Second, good permeability of electrolyte and short sodium ions diffusion length are enabled by nano-sized effects. Lastly, pores in Sb particles can effectively counteract the negative effects of volume change during charge/discharge cycling. As a result, the reaction kinetics, specific capacity and rate capacity can be improved obviously [10, 17, 18].

In our present reaction approach, metal Mg powder acted as a reductant and excess Mg was used to ensure the complete reduction of Sb_2O_3 to Sb. The reaction can be described as follows, Mg + $Sb_2O_3 \rightarrow Sb + MgO$. During the reaction, a liquated environment appeared when 680 °C reached due to heating because 680 °C is above fusing point of each precursor (Mg: 650°C, Sb₂O₃: 656°C, blending of KCl and NaCl: ~657 °C). Long time magnesiothermic reduction reaction produced Sb and MgO. The liquated molten state resulted into a homogeneous distribution of each components, which is important for the formation of uniform porous structure. After the removing of NaCl, KCl and MgO with HCl solution's etching, the final product of

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Sb was remained with an interconnected three dimensional porous structure.

Electrochemical performance of porous Sb product as an active material for anode in SIBs has been studied systematically. CV investigation, as shown in Fig. 3, was conducted to evaluate the electrochemical sodium alloying/dealloying process in Sb electrodes from 0.01V to 2.00 V (scanning rate: 50 μ V/s). For the first cathodic scan (sodiation process), there is only one high reduction peak at ~0.36 V. This 0.36 V peak arises from the production of a SEI layer and Na_xSb alloy phase. Na_xSb was turned into Na₃Sb with repeatedly sodiation [9, 17]. Peaks of 0.69 V, 0.51 V and 0.36 V appeared in CV's second cathodic scan. The three peaks can be attributed to the sodiation of Sb step by step in which sodium ions insertion induced finally the formation of a hexagonal Na₃Sb phase [19, 20]. It is also found that 0.51 V peak and 0.36 V peak show different variation trend of intensity with increasing CV cycles, 0.51 V peak became stronger while 0.36 V peak weaker. This should result from the crystalline structure change of Sb from hexagonal texture to amorphous phase [21]. In the reversed desodiation scan, a high peak of 0.88 V appeared. This peak is related to the reaction in which Na₃Sb is turned into Sb [19, 22]. Subsequent CV cycles after the first one show very similar anodic and cathodic peaks, suggesting that Sb porous electrode materials have good reversibility in SIBs.

The general electrochemical reactions of the Sb electrode in SIBs can be proposed as follows based on literature's report [22]:

Discharge:

Sb + Na⁺ + e⁻ → NaSb (1) NaSb + 2Na⁺ + 2e⁻ → Na₃Sb (2) Charge:

 $Na_3Sb - 3Na + - 3e^- \rightarrow Sb(3)$



Fig. 3. Cyclic voltammogram of Sb electrode (scan rate:50 μ V/s)

Fig. 4 is charge/discharge voltage curves of Sb electrode at 50 mA/g from 0.01V to 2.00 V. A charge sloping plateau at 0.88 V and discharge sloping plateaus at 0.69, 0.51 and 0.36 V are originated from Na alloying/dealloying. These plateaus correspond well to the CV profiles. The initial cycle discharge and charge capacities are 702.4 mAh/g and 570.3 mAh/g, which lead to a high initial Coulombic efficiency of 81.4% among Sb electrode for SIBs [22-24]. The beginning capacity wastage and insufficient Coulombic efficiency should arise from the production of a SEI on the Sb electrode surface [22]. The Coulombic efficiency rises up immediately to 97.2% in 2nd cycle. From the second cycle onwards, it is obviously that the charge/discharge voltage curves almost coincide, disclosing a high stable cycling behavior.



Fig. 4. The Sb electrode charge/discharge voltage curves at 50mAh/g

Fig. 5 is the cycling performance of porous Sb. A reversible capacity of 570.3 mAh/g and a high initial Coulombic efficiency of 81.2% have been obtained. A charge capacity of 538.7 mAh/g with capacity retention of 94.5% was achieved at the 50th cycle, disclosing a satisfying reversibility. The average Coulombic efficiency from 2^{nd} to 50^{th} cycles is 98.1%.



Fig. 5. Cycle performance of porous Sb from 0.01V to 2.0V at 50 mA/g.

The porous Sb reveals excellent rate capability based on the cycle testing with stepwise increasing current densities from 100 to 1000 mA/g, as shown in Fig. 6. Reversible capacities of 568.0, 558.0, 512.6 and 456.2 mA/g were obtained respectively at 100, 200, 500 and 1000 mA/g. The Sb electrode could cycle reversibly at 1000 mA/g, suggesting sodium ions were able to have a quick movement in porous Sb nanostructrue. When current density was set again to be 100 mA/g, the capacity was recovered immediately to 542 mAh/g, almost the same with the original capacity at this current density previously. The good capacity reversibility may be due to the porous structure of Sb electrode whose integrity could be well maintained in a big variation range of current density, as shown in Fig. S1. The electrochemical performance of porous Sb in the present work is excellent based on the comparison with literatures for different Sb-based anodes in SIBs (Table S1, Supporting Information).



Fig. 6. Rate capability of Sb electrode cycled in 2.0-0.01 V

Conclusions

Sb product has been prepared based on a magnesiothermic reduction reaction. The removal of by-product MgO and excess NaCl, KCl during the post-etching process results in an interconnected porous structure. The porous Sb product displays excellent sodium storage performance. The porous Sb has a stable reversible capacity of 538.7 mAh/g at 50 mA/g after 50 cycles and a high rate performance of 456.2 mA/g at 1000 mA/g for sodium ion batteries. The synthetic procedure may provide a novel approach to realize porous metal anodes for sodium ion batteries.

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Highlights

- 1, Porous Sb has been prepared via a magnesiothermic reduction reaction.
- 2, A succedent HCl solution etching process produced the uniform pores.
- 3, The porous Sb reveals excellent sodium storage performance.

Journal Proposition

Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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