Enhanced electrochemical stability of carbon-coated antimony nanoparticles with sodium alginate binder for sodium-ion batteries

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A B S T R A C T

The poor cycling stability of antimony during a repeated sodium ion insertion and desertion process is the key issue, which leads to an unsatisfactory application as an anode material in a sodium-ion battery. Addressed at this, we report a facile two-step method to coat antimony nanoparticles with an ultrathin carbon layer of few nanometers (denoted Sb@C NPs) for sodium-ion battery anode application. This carbon layer could buffer the volume change of antimony in the charge-discharge process and improve the battery cycle performance. Meanwhile, this carbon coating could also enhance the interfacial stability by firmly connecting the sodium alginate binders through its oxygen-rich surface. Benefitted from these advantages, an improved initial discharge capacity (788.5 mAh g⁻¹) and cycling stability capacity (553 mAh g⁻¹ after 50 times cycle) have been obtained in a battery using Sb@C NPs as anode materials at 50 mA g⁻¹.

1. Introduction

Sodium-ion batteries (SIBs) have attracted a rapidly increasing amount of interests recently, which has been put forward as a promising candidate to replace the currently state-of-the-art lithium-ion batteries (LIBs) as the next-generation energy storage system for the various renewable energy resources. Compared with LIBs, the energy storage mechanism of a SIB depends on the intercalation/deintercalation of Na ions in the electrode materials, which is similar to that of LIBs. However, the much larger size of Na ions (0.102 nm compared to 0.076 nm of Li ions) will not only lead to higher impedance of the intercalation/deintercalation process but also result in much larger volume change of antimony in the charge-discharge process and improve the battery cycle performance. Meanwhile, this carbon coating could also enhance the interfacial stability by firmly connecting the sodium alginate binders through its oxygen-rich surface. Benefitted from these advantages, an improved initial discharge capacity (788.5 mAh g⁻¹) and cycling stability capacity (553 mAh g⁻¹ after 50 times cycle) have been obtained in a battery using Sb@C NPs as anode materials at 50 mA g⁻¹.
has been adopted to improve the cycle performance of antimony-based anode materials. Different kinds of carbon/antimony structures have been prepared and explored as SIB anode materials, such as antimony/nitrogen-doping porous carbon [30,31] and antimony/graphene [32,33]. However, in these materials, the content of carbon-based buffer materials is high, sometimes even over 50 wt%. Consequently, the Na ion storage capacity of these carbon-based buffer materials is often much lower than that expected on antimony-based materials. In addition, the reported preparation process of such carbon-based buffer matrix is often quite complex with multiple steps. Hence, to facilely prepare a thinner carbon-based buffer layer on the antimony-based materials not only will be useful to improve their capacity but also will be positive to reduce cost.

With such a purpose, antimony nanoparticles with nanometer-thick carbon coating layer (Sb@C NPs) was prepared through a facile two-step method of liquid-phase reduction from SbCl₃ and following hydrothermal carbon-coating using glucose as carbon precursor. The carbon coating layer is beneficial to the interface binding between the sodium alginate binder and the active materials, which has enhanced the electrode’s cycle performance. The carbon content is only 1.5 wt%, which is much smaller than the values of previous works and thus does not significantly compromise the capacity of the materials. Sodium alginate has been utilized as the binder, which effectively improved the battery performance of the Sb@C NPs to achieve a higher capacity and better stability of 533 mA h g⁻¹ at a current of 50 mA g⁻¹.

2. Experimental section

The preparation of Sb NPs was conducted in a three-neck flask heated in an oil bath. In a typical synthesis, 45 mL of Diethylene glycol was added in the flask, then 0.7 g of Polyvinylpyrrolidone (PVP) (MW = 40,000) was added and dissolved under mechanical stirring. The solution was heated up to 180 °C, after which, 10 mmol of SbCl₃ was added. A freshly prepared solution of NaBH₄ (0.872 g in 8 mL of diethylene glycol) was then injected into the solution with stirring at 0.5 mL min⁻¹ by a syringe pump.

The carbon coating process was carried out through a hydrothermal carbon-coating process. 0.4 g Sb NPs was dispersed in 40 mL aqueous solution containing 0.0125 M glucose, under sonication. Then the solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave, sealed, maintained at 180 °C for 12 h, and cooled down naturally. The resulted brown solution was centrifuged and the brown solid product was collected, washed with distilled water and ethanol, and then freeze dried for 72 h. Finally, the dry brown product was put in a tube furnace and kept at 500 °C for 3 h in a 200 scm argon flow to carbonize the carbon coating.

The morphology and structure of Sb@C NPs was characterized by a scanning electron microscopy (SEM, TDCLS-8010, Hitachi Japan), transmission electron microscopy (TEM, Tecnai G2 F20, FEI, Holland), X-ray diffraction (XRD, D8 Advance, Bruker, German), Raman spectroscopy (Horiba Jobin Yvon, LabRAM HR800, 17 mW, 514 nm, He-Ne laser), and X-ray photoelectronic spectroscopy (XPS, Perkin-Elmer, PHI-1600), respectively. The carbon content of the products was evaluated by thermal gravimetric analysis and differential scanning calorimeter (TGA and DSC, TGA/DSC1/1100, METTLER, Germany) in an air flow (15 sccm) at a heating rate of 10 °C min⁻¹ using 15 mg samples.

The as-prepared Sb@C NPs were used as anode electrode materials and assembled into SIBs for electrochemical measurements. Specifically, the Sb@C NPs were mixed with acetylene black powders (conducting additives) and sodium alginate (binders) at a mass ratio of 85:10:5 for these three components. The mixture was then dipped in N-methyl-2-pyrrolidone and water, then mechanically grinded to form a
slurry. The slurry was pasted on a piece of Cu foil, dried for 24 h at 80 °C in vacuum, and cut into 10 mm-diameter circular disk electrodes. The loading of corresponding active material (mg cm⁻²) on the disc working electrodes is 0.6–0.8 mg cm⁻². The comparing experiments using normal binder of polyvinylidene difluoride (PVDF) for SIB electrode was also conducted.

The electrode was assembled into a battery in a glove box filled in argon. Na foil as counter and reference electrodes, 1 mol/L NaClO₄ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (3:7 by volume) adding with 10% fluoropolyethylene carbonate (FEC) as electrolytes, and Whatman GF/C borosilicate glass fiber film as separators. Galvanostatic charge-discharge cycle tests were performed on a battery testing system (LAND 2001A, Wuhan Jinnuo, China) at a current density of 100 mA h g⁻¹ and a potential range of 0.01–3.0 V vs. Na⁺/Na⁻.

The cyclic voltammetry (CV) and electrochemical Impedance Spectroscopy (EIS) test for SIB was conducted on an electrochemical workstation (VersaSTAT4, Princeton Instruments, American).

3. Results and discussion

The morphology of samples of Sb@C NPs was investigated by SEM (Fig. 1a). The majority of the Sb@C NPs were evenly dispersed without significant aggregation, and a small number of particles (ca. 10% NPs) can be found attached with the neighbouring ones to form lumps (Fig. 1b). Besides, it has also been found that the appearance of Sb@C NPs was irregular and the size distribution was wide, 20–80 nm. The crystal structures of the material were studied by XRD, which confirmed the main crystal phase of the as-prepared Sb@C NPs product was elemental antimony and the other scattering peaks in the XRD pattern could be indexed to hexagonal antimony (JCPDS No. 01-1010) (Fig. 1c). On the XRD pattern, there are also some small peaks at 27.5°, 32.1°, 45.7°, 54.5°, 57.1° and 73.6°, which do not correspond to the typical diffraction characteristics of antimony. Taking into account the possible oxidation in the process of hydrothermal carbon coating and thermal carbonization, the small peaks could be speculated to be possibly related with SbOX.

Raman analysis was further conducted to identify the composition of Sb@C NPs. Raman spectrum showed the characteristic E₆ band at 113 cm⁻¹ and A₁g band at 151.5 cm⁻¹ of antimony [34,35] and the D band at 1350 cm⁻¹ and G band at 1560 cm⁻¹ from the carbon coating (Fig. 1d) [36]. These characteristic Raman bands of the Sb@C NPs indicated that the product contained antimony and carbon, which agrees with our expectations and is in line with XRD analysis. It is interesting to find that although the existence of carbon could be confirmed by the Raman results, however, no obvious diffraction was not detected in the XRD test. This might be attributed to two factors, including the very small thickness of this carbon coating and its amorphous nature that only yielded too weak signal to be resolved in the XRD test. Moreover, in the Raman spectrum, a small peak at ca. 250 cm⁻¹ can be found (Fig. 1d inset), which is characteristic of the Sb-O bonds [37], further proving the existence of antimony oxides in the products and agreeing with the XRD results.

More structural information was then revealed by TEM observations, which showed that the products were consisted of fine NPs (Fig. 2a). The fine structure of NPs was observed under high-resolution TEM, and the very thin amorphous carbon coating layer of a few nanometers can be found evenly covering the particles, as shown in the (Fig. 2b). The distribution of various elements on the particles was then probed by X-ray energy dispersive spectrum (EDS) elemental mapping (Fig. 2c and d). It showed that carbon and antimony were the main composition elements of NPs. It can be found that carbon and antimony were homogeneously distributed on the material, and the mapping shape overlapped very well with the outline of the analysed NPs, which again indicates the continuity of carbon coating on the nanoparticles. From the high-resolution TEM images (Fig. 2e), the crystal lattice could be observed in the middle area of NPs, with an inter-lattice distance of 0.21 nm, corresponding to the (110) direction of the Sb crystal. The core Sb NPs have fine crystal structure as the corresponding rule diffraction spots have been obtained (inset of Fig. 2e). The amorphous morphology of carbon layer, as observed under TEM, could thus be regarded the cause of carbon singles detected by Raman, but not from XRD. These observations all confirms that the fine structure of the NPs is antimony covered with a nano-thickness carbon layer, confirming Sb@C NP core-shell structure have been obtained.

TGA analysis of the Sb@C NP in an air flow displays an obvious weight gain of 11.4 wt%, when the material was heated to 950 °C in air (Fig. 3), which could be attributed to the oxidation of antimony. Assuming that antimony was oxidized to Sb₂O₄, the carbon content of Sb@C NPs was calculated to be 1.5 wt%, which is far lower than the carbon contents in the previously reported composites of antimony-porous carbon [30,31], antimony-carbon nanotubes [38], and antimony-carbon fibers [39]. The corresponding DSC curve showed three exothermic peaks at 280 °C, 430 °C, and 555 °C, all of which were in accordance with the increase of weight, that should be related to the different oxidation level of antimony. At 520 °C, there is another small exothermic peak and corresponding ratio of weight increase became smaller at this temperature point, which can be related to the amorphous carbon coating layer oxidation [40], further confirming the existing of the carbon layer in this material.

The chemistry of the materials was then analysed by XPS. The survey scan of the NPs showed the existence of carbon, oxygen, and antimony, and the corresponding atomic percentages were 22.90%, 55.92%, and 21.18% respectively (Fig. 4a). The high-resolution scan of Sb₄p and C₁s species were also conducted to further probe the chemical states of these elements. The analysis of Sb₄p revealed that the surface of NPs contained trivalent and tetravalent antimony species, which indicated that the surface antimony has been oxidized, in good agreement with the analysis by XRD and Raman (Fig. 4b). The C₁s spectrum can be deconvoluted into three peaks, corresponding to C-C, C-OH and COOH species, with relative atomic percentages of 31.35%, 41.40%, and 27.25%, respectively (Fig. 4c), indicating the abundant oxygen-containing functional groups on the surface of the carbon coating. This oxygen rich surface is beneficial to the interface binding between Sb@C NPs and sodium alginate binder [41]. A weak hydrogen-bond is possible to be formed between surface -OH groups of Sb@C NPs and -COOH groups of the alginate binder, which is highly desirable to achieve a higher cycling stability and capacity.

To utilize these surface functionalities, sodium alginate was chosen as the binder and the electrochemical performance of Sb@C NPs for SIB anode was been assessed in a coin-type half cell with a Na foil counter electrode and 1 M NaClO₄ in EC/DMC/FEC electrolyte [41]. Fig. 5a presents the initial and second charge-discharge profiles of the Sb@C NP materials at 50 mA g⁻¹ in the range of 0.01–3 V. In the initial discharge curve, there is a long plateau at around 0.5 V, which is in line with bulk antimony [42]. It could be contributed to the formation of solid electrolyte interphase (SEI) layer and Na₃Sb alloy. And on the initial charge curve, obvious plateaus at around 0.78 V and 0.92 V could be observed, which should be ascribed with two-step de-alloy reaction of Na-Sb. In the second discharge/charge curve, the main plateaus were almost identical with that of the initial, which indicate that the same alloy and de-alloy reaction still plays the main role of Na ion intercalation/deintercalation. According to the discharge/charge curves, the initial discharge specific capacity was 788.5 mAh g⁻¹, and the following second cycle discharge specific capacity decreased to 588.1 mAh g⁻¹, corresponding a first cycle coulombic efficiency of 74.6%.

To better understand the electrochemical process of Sb@C NPs during sodium insertion and desertion, CV test of the material with sodium alginate binder was then carried out at a scanning rate of 0.1 mV s⁻¹ in the voltage range of 0.01–3.0 V (Fig. 5b). The first negative scan showed three reduction peaks, one weak peak at 0.67 V and two strong peaks at 0.43 V and 0.01 V, respectively. The reduction peak
at 0.67 V could be assigned with SEI formation; the one at 0.43 V could be assigned with the alloying reaction of Sb with Na; and peak at 0.01 V could be resulted from the insertion of Na-ions into carbon [42–44].

The alloying reaction of Sb with Na at 0.43 V contributed most of the capacity, which is in line with the battery discharge plateau. In the positive scan, there is only one oxidization peak at 0.86 V, agreeing with the plateau voltage on the charge profile (Fig. 5a) and corresponding to the Na-ions extraction process from Sb@C NPs [42–44].

The cycling performance of Sb@C NPs was subsequently evaluated on the battery using sodium alginate as the binder in comparison with the PVDF binder (Fig. 6). The initial discharge specific capacity is 788.5 mA h g⁻¹, after 50 cycle times, the Sb@C NP maintained a discharge specific capacity of around 553 mA h g⁻¹ as well as a high coulombic efficiency of 100%. In comparing, Sb@C NPs using PVDF binder was also tested to illustrate the effect of sodium alginate, which exhibit a lower initial discharge specific capacity of 666.5 mA h g⁻¹ and a much higher capacity decay rate to result in a final capacity as low as 435 mA h g⁻¹. In addition, the electrochemical performance of bare Sb NPs using sodium alginate binder has not been significantly improved.

Based on these results, it is reasonable to deduce that the enhanced performance of Sb@C NPs can be attributed to the effect of the carbon coating in strongly binding with the sodium alginate binders, which stably maintains the structural integrity of the Sb NPs during cycling.

In order to better understand the effect of the different binders of sodium alginate and PVDF, electrochemical impedance spectroscopy (EIS) measurements of Sb@C NPs electrode were carried out (Fig. 6b). For the two systems, their EIS showed similar characteristics with one depressed semicircle in the high-frequency range that could be attributed to the charge-transfer resistance between the electrode and electrolyte, and an inclined line in the low-frequency range that could be ascribed to the ion-transfer process in the electrolyte [45]. The radius of the semicircles of electrode with the sodium alginate binder is much smaller than the one with PVDF binder (ca. 200 Ω vs. ca. 350 Ω), which indicates that the charge-transfer resistance of the electrode using sodium alginate binder is lower than that of the electrode using PVDF as binder. This clearly indicates a smaller impedance in the sodium intercalation process in the system with the sodium alginate binder, due
to the more intimate binding between the oxygen-rich carbon coating surface and the sodium alginate binder [46].

To further verify the role of the sodium alginate binder, an equivalent circuit has been obtained from the EIS to simulate the electrochemical process during the charge/discharge of the material, as shown the inset of Fig. R2. The symbols of $R_s$, $R_{sf}$, CPE$_{sf}$, $R_{ct}$, CPE$_{ct}$ and $Z_w$ were the solution resistance, SEI film resistance, surface film capacitance, charge transfer resistance, double layer capacitance, and Warburg impedance. The calculated $R_{ct}$ values of the Sb@C NP electrode with sodium alginate and PVDF binders were 185.3 $\Omega$ and 720.1 $\Omega$, respectively. These results thus proved that sodium alginate can maintain the integrity of the anode, reduce the overall impedance of electrode, and result in an enhanced cycle performance.

In comparison, electrochemical tests were also conducted to...
evaluate the cycle performance of the bare Sb materials. The initial specific capacity (i.e. for Na\(^+\) alloy) was 612.9 mAh g\(^{-1}\), and this value decreased to 341.9 mAh g\(^{-1}\) after 50 cycles, which was obvious lower than that of the Sb@C NPs (553 mAh g\(^{-1}\)). We further observed the materials bare Sb NPs under SEM and TEM to better verify the difference between the cycle performances of the Sb@C NPs and the Sb NPs (Fig. 7). SEM and TEM observations shown that the bare Sb NPs were connected with each other and severely agglomerated, forming big clusters that were obviously different from the discrete Sb@C NPs. The large clusters consisting of bare Sb NPs could be an essential drawback considering they are incapable of buffering the large volume change accompanied with the Na alloying/dealloying process, which will deteriorate the cycle performance of the bare Na NP electrode.

4. Conclusion

In summary, Sb@C NPs with nanometer-thick carbon coating for sodium-ion battery anode have been prepared by a facile two-step method consisting of the liquid-phase reduction of SbCl\(_5\) and the following carbon coating by a hydrothermal treatment. This thin carbon coating plays a key role to improve the interface between active materials and binder, and improve the electrode stability during discharge/charge. The Sb@C NP electrode with sodium alginate binder coating plays a key role to improve the interface between active materials and binder, and cycling stability capacity (553 mAh g\(^{-1}\)) of the Sb@C NPs (553 mAh g\(^{-1}\)) scheme.

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Fig. 7. SEM image (a) and TEM images (b) of bare Sb NPs.