Observing sodiation process and achieving high efficiency of yolk-shell antimony@carbon rods

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ABSTRACT As a promising anode material candidate for sodium-ion batteries, antimony (Sb) has attracted enormous research interest due to its high specific capacity and low sodiation voltage. However, its dramatic volume expansion upon sodiation adversely affects its cycle stability. We have developed an oxidation-coating-reduction strategy for fabricating yolk-shell Sb@C rods from commercially available Sb powder. In particular, the thermal reduction of vaporized Sb₂O₃ generates densely distributed Sb single atoms and clusters on the carbon shell. The sodiation process of the Sb@C sample was recorded through *in situ* transmission electron microscopy. Irregular expansion of Sb particles was observed, and it was also revealed that the carbon shell could deform with the expanded Sb particles. Beyond the intuitively understood advantage that internal voids can provide space for expansion of internal active materials, the deformability of carbon shells can add further ability to withstand the volume expansion. The two structural merits of the yolk-shell construction enable the Sb@C material to deliver an enhanced cycle performance. Its reversible capacity exceeds 620 mA h g⁻¹ at 0.1 C, with an initial coulombic efficiency of up to 84.9%, and about 95% of the capacity in the charging voltage profile is delivered below 1.0 V vs. Na⁺/Na. These performance metrics are very promising for potential practical applications.

Keywords: sodium-ion batteries, antimony, *in situ* TEM, yolk-shell, anode materials

INTRODUCTION

The ever-increasing growth of electricity generation from renewables has led to a tremendous demand for energy storage systems. Batteries with high cost and energy efficiency are a good fit for such applications. Sodium-ion batteries (SIBs), which have been developed as low-cost alternatives to the lithium-ion batteries (LIBs) that dominate the current market, are highly promising [1]. The commercialization of SIBs has been under discussion for years but has not yet been realized [2–4]. It is partially because the performance of electrode materials, both cathodes and anodes, has not been fully optimized to be satisfactory for practical applications. Remarkably, the lack of top-quality anode materials comparable to graphite in LIBs remains a major concern [5,6].

The ideal anode should have a low sodiation voltage, large capacity, high cost-effectiveness, and easy processability. A wide variety of anode materials have been identified. However, those with a (de-)sodiation voltage below 1.0 V vs. Na⁺/Na are mainly limited to the following types: sodium-metal anodes, hard carbon, phosphorous, and alloy-type anodes such as tin and antimony. All are considered promising candidates, with their own strengths and weaknesses. Metallic sodium is thermodynamically the ultimate choice for anodes, but the growth of dendrites during sodium plating can reduce capacity and cause safety issues. Phosphorous is very attractive due to its abundant resources and theoretical capacity of over 2000 mA h g⁻¹. However, it suffers from low electrical conductivity, significant swelling upon sodiation, poor processability, and the most annoying points, producing highly flammable white phosphorous [7]. Hard carbon is the choice of anodes in prototypes of various SIBs for cost and performance analysis [8,9]. Its sodiation plateau, close to 0 V vs. Na⁺/Na, improves energy density, making hard carbon sensitive to premature discharging or unwanted sodium plating, especially at high current rates. In contrast, antimony (Sb) with a sodiation voltage of about 0.6 V vs. Na⁺/Na has a much larger margin to compensate for polarization. In combination with its capacity of over 600 mA h g⁻¹, Sb is likely to be eventually used for future practical applications.

The primal drawback of the Sb anode is dramatic volume expansion up to 390% after complete sodiation [10]. Repeated volume expansion and shrinkage can pulverize and disconnect active materials in the electrode, destroying solid electrolyte interphases (SEI). The most common strategy to address this problem is structural engineering [11]. One typical case is to encapsulate Sb particles within carbon fibers *via* electrospinning [12]. The as-prepared Sb/C nanowires exhibit superior cycle stability, but the Sb content is only 54 wt%. As Sb is less active than many transition metals, a templating method based on galvanostatic replacement reactions has been developed, which is unique for synthesizing anode materials [13,14]. For example, Sb nanotubes are produced from the replacement reactions between antimony chloride and copper nanowires [13,15]. It has also been reported that Sb-based binary or tertiary alloy compounds, for example, bismuth-antimony alloy, can enhance anodic performance. Their fabrication is usually coupled with intentional structural engineering [16,17]. Incorporating Sb into the carbon matrix is another effective method to immobilize Sb

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components during battery operation [18]. For instance, Sb nanoparticles confined in chemically doped hollow carbon spheres can withstand 10,000 cycles at 20 A g⁻¹ with a capacity of 331 mA h g⁻¹ [19]. The reported performance metrics are highly impressive. However, it should be noted that the synthetic process is complex, the Sb content is low, areal capacity is small, and the initial coulombic efficiency (ICE) is not yet sufficient.

It is well known that elaborate Sb/C structures help extend cycle life, but it is difficult to fabricate such structures with cheap materials and simple methods. From a practical point of view, it is important to reduce the carbon weight fraction and irreversible capacity in the initial cycle of Sb/C composites. This needs to be emphasized but is often ignored. In this research, we developed a simple method to process commercially available Sb powders into yolk-shell Sb@C rods. More precisely, Sb particles are encapsulated in carbon tubes decorated with Sb single atoms and clusters. Based on *in situ* transmission electron microscopy (TEM), Sb particles are trapped inside the carbon tube during the sodiation process to ensure good cycle stability. The resulting sample has a high Sb content of over 90%, providing good cycle and rate performance (632 mA h g⁻¹ at 0.1 C and 560 mA h g⁻¹ at 1 C). The ICE can reach 84.9%, which outperforms most values in the literature.

EXPERIMENTAL SECTION

Synthesis of Sb₂O₃ rods

Sb₂O₃ rods were obtained from the oxidation of commercially available Sb powder in ethylenediamine (EDA) and polyvinylpyrrolidone (PVP) aqueous solutions. Four gram of PVP (*M_w* = 24,000) and 70 mL of EDA were dissolved in 700 mL of deionized water. Then, 4 g of Sb powder (1200 Mesh) was added under magnetic stirring until the suspension turned from black to milky white, and no black particles were observed on the bottom. Sediments (Sb₂O₃ rods) were collected *via* centrifugation and washed with pure water.

Synthesis of yolk-shell Sb@C rods

Ultrasonication and magnetic stirring were used to disperse 1 g of Sb₂O₃ rods and 0.1 g of pyrrole in 300 mL of deionized water. Then, 10 mL of ammonium persulfate solution (0.5 mol L⁻¹) was added, and the suspension turned slowly from white into black due to the polymerization of pyrrole. Sb₂O₃ was reduced to Sb by recovering the obtained black precipitate and annealing it in an H₂/Ar mixed gas at 450°C for 4 h.

Characterization

The morphology of the samples was identified using scanning electron microscopy (SEM, Tescam Mira 3) and TEM (Talos F200X G2). High-resolution images showing single Sb atoms were collected by a double aberration-corrected scanning TEM (Titan Themis G2). The diffraction pattern was recorded using an X-ray diffractometer (XRD, Bruker D8 Advance). Antimony content was determined using an inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700) machine.

Electrochemical measurements

The samples were mixed with conductive additive (acetylene black) and aqueous binder (sodium carboxymethyl cellulose, NaCMC) solutions to form a viscous slurry. The weight ratio of the samples, acetylene black, and NaCMC was controlled at

80:10:10. The slurry was coated on copper foil and dried to fabricate electrode films, which were punched into disks with a diameter of 14 mm. The mass loading of the active materials on a single electrode disk was 1.8–2.5 mg. After being completely dried, these disks were assembled into 2032-type coin cells using sodium metal foil as the counter electrode and glass fiber as the separator. The electrolyte was 1 mol L⁻¹ NaClO₄ in ethylene carbonate (EC) and diethyl carbonate (PC) (volume ratio of EC: PC = 50:50) containing 5% fluoroethylene carbonate (FEC). Galvanostatic charge and discharge tests were performed on a Neware battery testing system. Cyclic voltammograms (CV) and electrochemical impedance spectroscopy (EIS) were recorded on an electrochemical workstation (Solartron 1470E MultiStat).

In situ TEM test

The yolk-shell Sb@C sample was attached to a gold grid and sodium metal with surface oxide layers on a tungsten tip. Both were mounted onto a scanning tunneling microscopy holder (Pico Femto FE-F20) and transferred into an environmental TEM (FEI G2). During the sodiation process, the Sb@C rod maintained contact with sodium, and a negative bias of -2 V was applied.

RESULTS AND DISCUSSION

The easiest way to modify Sb for anode applications is downsizing and carbon coating. It is not allowed to create a hollow interior with these techniques. Unlike this intuitive method, we proposed an oxidation-reduction strategy that oxidizes Sb to Sb₂O₃ and then reduces Sb₂O₃ to Sb. This reduces the size of Sb and can create void space due to the volume difference between Sb₂O₃ and Sb of equivalent Sb weight. The processing of commercial Sb powders into our target sample is schematically shown in Fig. 1. Using stepwise oxidation and polypyrrole (PPy) coating treatment, Sb powders are converted to core-shell Sb₂O₃@PPy rods and subjected to thermal annealing in a reducing atmosphere. During the annealing process, the outer PPy shell is carbonized without noticeable structure changes, and the inner Sb₂O₃ rods are reduced to Sb particles trapped in the carbon shell. Thus, yolk-shell Sb@C rods are obtained by such an oxidizing-coating-reducing strategy. It should be noted that Sb₂O₃ vaporization is possible even at high temperatures, and the reduction of Sb₂O₃ vapor can produce Sb inside or outside the carbon shell.

Commercially available Sb powders used in this research are irregular particles at the scale of tens of micrometers (Fig. S1). They were gradually oxidized to Sb₂O₃ when dispersed in an aqueous EDA solution containing a certain amount of PVP. This was reflected in the color change of the resulting suspension from black into milky white. EDA was used to catalyze the reactions between Sb powders and oxygen in the solution, and PVP plays the role of structure-directing reagent [20]. After complete oxidation, the collected white precipitate was rods with lengths ranging from below 1 μm to over 10 μm, as shown in Fig. 2a. According to the XRD pattern, the precipitate was confirmed to be pure Sb₂O₃ (Fig. S2). The suspension of Sb₂O₃ rods in water is white, and it slowly turns black after adding pyrrole and an oxidizing reagent (ammonium persulfate). The black precipitate obtained was also rod-shaped (Fig. 2b) and uniformly coated with a thin layer of PPy (Fig. S3). After thermal annealing in a mixed Ar/H₂ atmosphere, the recorded XRD pattern was perfectly matched with a Sb phase (PDF#85-1324),

Figure 1 Schematic illustration of the oxidizing-coating-reducing strategy of processing Sb powders into yolk-shell Sb@C rods.

Figure 2 SEM images of (a) Sb_2O_3 , (b) $\text{Sb}_2\text{O}_3@\text{PPy}$, and (c) yolk-shell $\text{Sb}@\text{C}$ rods; (d) TEM image and (e) high-angle annular dark field (HAADF) image and the corresponding energy dispersive X-ray spectroscopy (EDS) mapping results at a selected area of yolk-shell $\text{Sb}@\text{C}$ rods; (f) high-resolution HAADF image of the carbon shell showing Sb single atoms (yellow circles) and clusters (red circle).

indicating a complete conversion from Sb_2O_3 to Sb. As shown in Fig. 2c, the annealed sample is composed of fine Sb particles inside a carbon shell derived from the PPy coating layers. The Sb content of the $\text{Sb}@\text{C}$ composite was 91% based on ICP-MS measurement.

The molar volumes of Sb and $\text{SbO}_{3/2}$ were calculated to be 17.5 and 25.3 $\text{cm}^3 \text{mol}^{-1}$, respectively. Thus, Sb particles theoretically take up 69% (namely 17.5/25.3) of the inner space of the carbon shell. Nevertheless, the total volume occupied by Sb particles is obviously less than 69%, and some rods are even empty, as shown in Fig. 2d. This is because the sublimation of Sb_2O_3 occurs at the annealing temperature, allowing the outward diffusion of Sb_2O_3 . The elemental mapping of selected regions with no visible particles revealed that Sb is also present (Fig. 2e). Many single atoms of Sb and some Sb clusters are observed in

the high-resolution images taken by the double aberration-corrected scanning transmission electron microscope (Fig. 2f). These are probably produced from the reduction of vaporized Sb_2O_3 .

Producing the yolk-shell $\text{Sb}@\text{C}$ has at least two benefits. Voids inside the carbon shell can accommodate the specific volume expansion of Sb during sodiation, and carbon shells can support the structure by trapping sodiation products inside. To demonstrate the two benefits, *in situ* TEM experiments allowed real-time observation of the sodiation process. Specifically, we built a nanobattery with the configuration shown in Fig. 3a. Therefore, the sodiation process can be initiated by applying a voltage bias using a potentiostat, and the TEM imaging can be performed throughout the process.

The expansion process of Sb particles inside the carbon shell

Figure 3 (a) The schematic of the cell setup for *in situ* TEM tests; (b–i) TEM images of a yolk-shell Sb@C rod at different sodiation times; electronic diffraction patterns of a yolk-shell Sb@C rod at the (j) initial and (k) final states.

(see Movie S1) was recorded, and eight selected frames are shown in Fig. 3b–i. Four particles marked in Fig. 3b indicate that they have undergone volume expansion in various ways. As sodium moved along the carbon shell, the sodiation of particles close to metal sodium began preferentially. Particle 1, which was close to metal sodium, became much larger than it was in the original state after 300 s. In such conditions, the other particles basically remained unchanged. It grew slowly and became more spherical along the sodiation process. It should be noted that the radius of the carbon shell increased with the expansion of Particle 1, but no cracks were observed. This means that the carbon shell is deformable rather than rigid, providing the yolk-shell Sb@C structure with the ability to accommodate volume expansion beyond the inner void space. Particle 2, which was much smaller, exploded during the sodiation (Fig. 3d) and did not change after 600 s, indicating that the sodiation was completed within 300 s. The sodiation process for Particle 3 with a similar size of Particle 2 was also finished within 300 s, but no branches occurred after sodiation. Particle 4 was an elongated rod whose expansion was mainly along the radial direction. Differences in structure evolutions suggest that the expansion of Sb particles is in random directions.

In the selected area electron diffraction (SAED) patterns at the initial and end states, circles corresponding to the plane spacing of Sb (PDF#85-1324) and Na₃Sb (PDF#74-1162) are drawn, respectively (Fig. 3j, k). As expected, the scattered bright spots are arranged on the circles. The identification of Na₃Sb after

sodiation is consistent with the literature, indicating that Sb is sodiated to Na₃Sb. Based on these results, the theoretical expansion after sodiation is calculated to be 390%, and if the structure evolution is conformal, the size change will be 157% (namely 390%^{1/3}). As these particles are irregular, it is impractical to quantify the volume expansion. However, it is still reasonable to conclude that the observed expansion is in good agreement with the theoretical value of the trend. This undoubtedly shows that Sb particles are trapped in the carbon shell throughout the sodiation process. Therefore, outstanding cycle stability can be expected.

Fig. 4a shows the CV of the yolk-shell Sb@C rods at 0.1 mV s⁻¹. Sodiation in the initial cycle is a direct conversion from Sb to Na₃Sb, as reflected in the only cathodic peak at 0.27 V vs. Na⁺/Na. However, three peaks are identified in the second cycle, corresponding to a multi-step sodiation process as previously reported [14]. Based on these results, the voltage profile at 0.1 C (1 C is defined as 0.6 A g⁻¹ for simplicity), shown in Fig. 4b, features one discharge plateau in the first cycle but three in the second. As the first plateau covers about one-third of the total capacity, an intermediate phase of NaSb is proposed. Based on the formation enthalpy data from the Materials Project (www.materialsproject.org), the theoretical average voltage values of Sb into Na₃Sb, Sb into NaSb, and NaSb into Na₃Sb are evaluated to be 0.58, 0.65, and 0.54 V vs. Na⁺/Na, respectively. In consideration of voltage polarization in real batteries, the data presented are in good agreement with theoretical results. The

Figure 4 Battery testing results of the yolk-shell Sb@C. (a) CV at 0.1 mV s^{-1} ; (b) voltage profile at 0.1 C ; (c) EIS at various states of charge; (d) rate performance and (e) the corresponding voltage profiles from 0.1 to 2 C ; (f) cycle performance at 0.33 C .

CV curve in the 3rd cycle overlaps with the CV curve in the 4th cycle. The voltage profiles are essentially identical after the initial cycle, indicating the high reversibility of the anode reactions.

In contrast, the commercially available Sb powders are highly unstable during the battery test, and the specific capacity decreases to below 50 mA h g^{-1} in only five cycles (Fig. S4). As shown in Fig. 4c, during stepwise sodiation, the EIS depends on the discharge/sodiation depth. From the changes in the semi-circle (Fig. S5), it is roughly speculated that the sodiation kinetics should be inversely proportional to the degree of sodiation [21].

In the rate performance test (Fig. 4d), as the rate current increases from 0.1 to 0.5 C , the capacity decreases only from 632 to 601 mA h g^{-1} . Also, from the voltage profiles shown in Fig. 4e, the polarization during charging or discharging does not deteriorate significantly. As the current increases to 2 C , a capacity reduction becomes apparent. From our point of view, this is because dramatic changes in volume over a short period of time are out of control. Thus, fast discharging should be avoided. In the cycle test at 0.33 C , the capacity reduction in the first 40 cycles is negligible, and the capacity retention after 100 cycles is about 87%. The reversible capacity at 0.1 C exceeds 620 mA h g^{-1} , the ICE is as high as 84.9%, the average voltage of the entire charging process is calculated to be $0.81 \text{ V vs. Na}^+/\text{Na}$ (Fig. S6), and about 95% of the capacity is below $1.0 \text{ V vs. Na}^+/\text{Na}$.

These performance metrics are very promising for the development of SIB anode materials. As shown in Table S1, the introduction of a carbon matrix generally improves Sb utilization and cycle stability. High Sb content is very important to promise a specific capacity advantage over other candidate anode materials such as hard carbon. This study is one of the few cases with an Sb content of over 90% and a reversible capacity of over 600 mA h g^{-1} . Compared with the two pioneering studies on Sb anodes [12,22], it is necessary to improve the ICE, which is currently approaching the documented records. Such high effi-

ciency in the initial cycle indicates low consumption of Na in SEI generation and high reversibility of the alloying reaction between Na and Sb. It should also be pointed out that the cycle stability in high-rate or long-term tests needs to be further improved. The coulombic efficiency after the initial cycle (mainly in the range of 98.5 to 99.1) is decent in the literature but not sufficient for practical applications.

CONCLUSIONS

In summary, a simple method of processing commercially available Sb powders into yolk-shell Sb@C rods was developed. Sb powders were oxidized to Sb_2O_3 rods under the catalysis of EDA and processed into Sb@C rods after PPy coating and thermal reduction. The void space in such structures originates from the difference in molar volume between Sb and Sb_2O_3 . On the other hand, the sublimation of Sb_2O_3 at high annealing temperatures also contributes to some extent. It is worth mentioning that the reduction of vaporized Sb_2O_3 gives rise to the dense distribution of Sb single particles on the carbon shell. This is probably of interest to scientists working on single-atom catalysts.

We conducted *in situ* TEM by assembling the Sb@C sample and metal sodium into a nanobattery. Although the volume expansion of Sb particles is irregular, it is found that the particles are trapped inside the carbon shell during the entire sodiation process. Based on the real-time observations, two benefits of the yolk-shell structures become apparent: the internal void space can accommodate volume expansion, and the deformable carbon shell can be expanded to provide additional space. Electrochemical measurements demonstrate excellent reversibility between sodiation and de-sodiation. As a result, several exciting performance metrics have been reported, including an ICE of up to 84.9%, specific capacities over 620 mA h g^{-1} , and about 95% capacity below $1.0 \text{ V vs. Na}^+/\text{Na}$ at a low current rate. We believe that these results will encourage battery researchers to re-

examine the practicality of antimony anodes and inspire those who work with similar battery systems, such as potassium-ion batteries, in which Sb anodes are also applicable [23].

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Author contributions Gu M conceived the idea and led the project. Yang X designed, prepared and tested the samples. Zhu Y conducted the *in situ* TEM experiments and the analysis of relevant data. Wu D and Zhao H were involved in the electrochemical tests. Liu K and Li M helped to characterize the samples. Yang X wrote the paper under the supervision of Gu M. Chang Z helped to improve the manuscript. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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中空核壳型铈碳材料的钠化过程观测与高效率储钠

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摘要 铈因其高容量、低电压等优点成为备受关注的钠离子电池负极材料, 但钠化过程中巨大的体积膨胀使其难以实现稳定的循环. 本文提出了一个氧化-包覆-还原的策略, 将不适合直接用作负极的商业化铈粉加工成中空核壳型棒状铈碳复合材料. 氧化铈受热升华还原的过程中, 在碳层上形成了密集分布的铈单原子. 利用原位环境电镜, 将该材料构建成微观纳米电池, 实现了钠化过程的实时观测. 发现铈在钠化过程中发生不规则膨胀, 碳层可随铈膨胀产生相应变形. 碳层内部的原有空间以及碳层向外扩张的能力, 均有利于维持碳层对铈在钠化膨胀过程中的包覆效果. 在电池测试中, 该材料在0.1 C下的可逆比容量超过 620 mA h g^{-1} , 首圈的库伦效率高达84.9% (显著高于文献报道的水平), 以及在1 V vs. Na^+/Na 的电位以下可完成95%的充电容量. 该材料优异的电池性能说明中空核壳型结构设计可用于开发实用型铈基钠电负极材料.