MoS₂/C nanosheets Encapsulated Sn@SnO_x nanoparticles as high-performance Lithium-ion battery anode material

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ABSTRACT

A facile and scalable in situ synthesis strategy is developed to fabricate MoS₂/C nanosheets encapsulated in Sn@SnO_x nanoparticles as a high-performance lithium ion battery anode material. With assistance of NaCl particles, MoS₂/C nanosheets can be in situ synthesized with Sn@SnO_x nanoparticles encapsulated. In the constructed architecture, the MoS₂/C nanosheets can not only avoid the direct exposure of Sn@SnO_x to the electrolyte and preserve the structural and interfacial stabilization of Sn@SnO_x nanoparticles, but also accommodate the mechanical stress induced by the volume change of Sn@SnO_x nanoparticles during the charge/discharge process. As a result, tested as an anode material, the Sn@SnO_x@MoS₂@C composite exhibits super-high rate capability (950 mAh g⁻¹ at 0.2 A g⁻¹, 815 mAh g⁻¹ at 0.5 A g⁻¹, 715 mAh g⁻¹ at 1.0 A g⁻¹, 625 mAh g⁻¹ at 2.0 A g⁻¹ and 500 mAh g⁻¹ at 5.0 A g⁻¹) and

extremely excellent cycling performance at high rate (a high capacity of 530 mAh g⁻¹ is achieved after 800 cycles at current density of 2.0 A g⁻¹). The outstanding electrochemical performance of the composite indicates high potential as anode material for high-performance lithium ion battery.

Key words: Tin; Molybdenum disulfide; Ball milling; Anode; Lithium ion batteries;

1. Introduction

In the past decade, there is an increasing demand for advanced power sources with a high energy/power density [1]. However, the current commercial anode material, graphite, is far from meeting the requirements because of its low theoretical capacity (372 mAh g⁻¹) and poor rate capability [2]. Therefore, metallic tin (Sn) as anode material for lithium ion batteries (LIBs) has attracted enormous attention due to its high theoretical (993.4 mAh g⁻¹), abundance and environmentally-friendliness [3,4]. However, the practical application is limited due to the huge volume change during the lithiation/delithiation process resulting in poor cycle life and rate capability [5,6].

To overcome these obstacles, substantial efforts have been made to improve the structural stability and integrity of Sn anodes. Forming Sn-based alloy is an effective approach, such as porous Ni-Sn intermetallic microcages [7], Ge-Sn alloy [8,9], Sn-Ni alloy film [10,11], and so on. The result indicates that these inert metals can obviously improve the electrochemical performance due to it can not only buff the volume change of Sn but also maintain the stability of the structure during the charge/discharge process. On the other hand, carbon has drawn special attention and is preferable to replace other types of materials. Therefore, Sn/C composite was

investigated extensively and various structure materials have been developed. Such as Sn@C [12-14], Sn embedded in carbon [15-17], Sn/graphene composite [18-20] and Sn/CNT composite [21-23]. These carbons can not only provide spaces to buffer the mechanical stress induced by the volume change of the Sn during the charge and discharge process, further enhancing the electrical conductivity and significantly improved electrochemical performance.

Recently, molybdenum disulfide (MoS_2), a representative layered two-dimensional material, has received considerable attention as anode material for LIBs due to its high capacity [24-26]. However, low electrical conductivity and volume change during the cycling result in poor cycling and rate performance thus limiting their application. To address these issues, various MoS_2 directly decorated carbon composites have been developed to improve the electrochemical performance [27-29]. On the other hand, the layered structure of MoS_2 is beneficial for reversible Li^+ intercalation/extraction while serving as a substrate and preventing the agglomeration of active nanoparticles. Therefore, many hybrids systems based on MoS_2 nanostructure, such as Sn/ MoS_2 /C [30,31], SnO_2 / MoS_2 [32], Fe_3O_4 / MoS_2 [33] and TiO_2 @ MoS_2 [34-36] have been developed to exhibit improved electrochemical performance as anode material for LIBs.

Herein, we reported a novel and scalable strategy using three-dimensional (3D) self-assembly of NaCl particles as a template in situ fabricate Sn@ SnO_x nanoparticles encapsulated within MoS_2 anchored on carbon nanosheets (Sn@ SnO_x @ MoS_2 @C nanosheets) network as a superior LIBs anode. This novel strategy for preparing

Sn@SnO_x@MoS₂@C composite with large surface area involves self-assembly of water-soluble NaCl particles uniformly coated with an ultrathin film of Sn-C₆H₈O₇-NH₂CSNH₂-Na₂MoO₄ by ball milling process and subsequent calcination of this products in an Ar environment at 750 °C. In this constructed architecture, the MoS₂ with excellent mechanical property can suppress the aggregation of Sn nanoparticles and buffer the volume expansion, while the amorphous carbon not only avoid the direct exposure of Sn to the electrolyte but also enhance the electrical conductivity of the composite. As a consequence, this novel composite exhibits high rate performance (950 mAh g⁻¹ at 0.2 A g⁻¹, 815 mAh g⁻¹ at 0.5 A g⁻¹, 715 mAh g⁻¹ at 1A g⁻¹, 625 mAh g⁻¹ at 2A g⁻¹ and 500 mAh g⁻¹ at 5A g⁻¹) and extremely cycling stability even at high rates (a high capacity of 546 mAh g⁻¹ is achieved at 3 A g⁻¹ after 500 cycles), which is much higher than the theoretical capacity of the commercialized graphite anode. The outstanding electrochemical performance of the composite indicate high potential as anode material for high-performance lithium ion battery.

2. Experimental

2.1 Synthesis of Sn@SnO_x@MoS₂@C composite

Commercial micrometric tin (99.9%, 5-10 micron, yfnano) powders, Na₂MoO₄·2H₂O and NH₂CSNH₂ were used as starting materials without further purification. 0.5 g Sn powder, 3 g citric acid, 0.45 g Na₂MoO₄·2H₂O, 0.7 g NH₂CSNH₂, 10 g water and 25 g NaCl along with 30 g stainless-steel balls were put into a stainless-steel vial. The vial was sealed and with a rotation speed of 500 rpm for 20 h. Then the obtained hybrids were dried at oven and then heat-treated at 750 °C for

2 h under a flowing Ar atmosphere. The as-synthesized products were washed with deionized water several times to remove NaCl and dried at 80 °C in a vacuum oven. For comparison, Sn@SnO_x@C composite was also synthesized by ball milling and heat-treated without Na₂MoO₄·2H₂O and NH₂CSNH₂ at the same conditions.

2.2 Materials characterization

The as-prepared samples were characterized by using X-ray diffraction (XRD, Rigaku D/max 2500) with Cu K radiation. The microscopy feature of the samples were characterized by scanning electron microscopy (SEM, Philips, FEI Quanta 200 FEG) and transmission electron microscopy (TEM, JEOL-2100). Raman measurement of the composite was performed by laser Raman spectroscopy (Jobin Yvon, T6400). Thermogravimetric analysis (TGA) was carried out with a NETZSCH STA 409 PC apparatus at a heating rate of 5 °C min⁻¹ in air flow. X-ray photoelectron spectroscopy (XPS) experiments were carried out with an AXIS ULTRA DLD instrument, using aluminum K α X-ray radiation during the XPS analysis. The exact Mo : Sn molar ratio in the composite was also measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent 730).

2.3 Electrochemical measurements

The electrochemical performance of all samples were tested using CR2025 coin-type cells. The working electrodes were firstly prepared by mixing 80 wt% active materials, 10 wt% carbon black (Super P), and 10 wt% Polyvinylidene Fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP) solution, followed by drying it before usage. The electrolyte was 1 M LiPF₆ in ethylene carbonate/dimethyl

carbonate/diethyl carbonate (1:1:1 vol%). The cell assembly was in an Air-filled glovebox. Galvanostatic charge/discharge cycles were tested by a LAND (BT2013A, Wuhan, China) battery measurement system at various current densities in the cut off voltage range of 3.00 V to 0.005 V versus Li/Li^+ at room temperature. Cyclic voltammograms (CVs) measurements were carried out on electrochemical workstation (IM6, Germany) over the potential range of 3.0 to 0 V at a scan rate of 0.1 mV s^{-1} . Electrochemical impedance spectroscopy measurements were performed using a IM6 electrochemical workstation by employing an ac voltage of 5 mV amplitude in the frequency range 10 mHz-100 kHz.

3. Results and discussion

Fig.1. Schematic illustration of the fabrication procedure of $\text{Sn@SnO}_x\text{@MoS}_2\text{/C}$ composite.

The overall synthetic procedure leading to $\text{Sn@SnO}_x\text{@MoS}_2\text{/C}$ composite is illustrated in Fig.1. During the synthesis process, the 3D self-assembly of water-soluble NaCl particles were used as the template for contributing a confining

structure to suppress the agglomeration of Sn nanoparticles and promote the growth of nanosheets during the carbonization process [14]. In the synthesis, the NaCl, citric acid, Na_2MoO_4 and NH_2CSNH_2 were firstly dissolved in distilled water to get a homogeneous suspended solid by ball milling process, which was subsequently dried in oven. Then the NaCl particles were uniformly coated with an ultrathin $\text{Sn-Na}_2\text{MoO}_4\text{-NH}_2\text{CSNH}_2$ complex film. Assisted by heating the complex at high temperature under Ar, in which the citric acid transformed into carbon, MoS_2 was synthesized by CVD and that anchored on carbon nanosheets [37]. After moving the NaCl with distilled water, the $\text{Sn@SnO}_x\text{@MoS}_2\text{@C}$ composite was obtained.

Fig. 2. (A) XRD pattern and (B) TGA profiles of $\text{Sn@SnO}_x\text{@MoS}_2\text{@C}$ composite. (C) The

survey XPS spectrum of Sn@SnO_x@MoS₂@C composite, (D, E and F) High-resolution spectra of Sn3d, Mo3d and S2p, respectively.

The chemical composition of the sample was characterized by using X-ray diffraction (XRD, Fig. 2A). It is clear from pattern that the peaks are at $2\theta = 30.64^\circ$, 32.02° , 43.87° , 44.9° , 55.33° , 62.54° , 63.78° , 64.58° , 72.41° , 73.2° and 79.47° , which can be assigned to β -Sn crystal structure (JCPDS No. 04-0673). The peaks at $2\theta = 14.38^\circ$, 33.51° , 39.54° , 58.33° , 60.14° and 72.79° corresponds to the diffraction of MoS₂ (JCPDS No. 37-1492). In addition, there are small amount of SnO₂ and SnO existing in the final product due to the oxidation of parts of Sn during the ball milling process. To gain insight into the chemical composition, thermo-gravimetric analysis (TGA) was performed on the Sn@SnO_x@MoS₂@C composite (Fig. 2B). The sample is annealed under air to oxidize Sn@SnO_x to SnO₂ and MoS₂ to MoO₃. Then the SnO₂/MoO₃ composite was digested into the solution and diluted appropriately before measuring for the presence of Mo and Sn elements (molar ratio: Mo : Sn = 1 : 2.64) by ICP-OES. Based on the TGA and ICP results, the mass fraction of Sn@SnO_x, MoS₂ and C can be calculated to be around 30.22%, 15.52% and 54.26%, respectively.

The chemical composition on the surface of Sn@SnO_x@MoS₂@C composite was further investigated by X-ray photoelectron spectroscopy (XPS). Fig. 2C shows the survey XPS spectrum of Sn@SnO_x@MoS₂@C composite, which suggest the presence of C, Sn, Mo, S and O element. Fig. 3D shows the typical high-resolution XPS spectra of Sn 3d, in which two peaks at 487.1 and 495 eV are observed, corresponding to the binding energies of Sn 3d_{5/2} and Sn 3d_{3/2}. The result indicates

that the Sn element detected in the form of Sn^{4+} state, which can be explain that Sn on the surface of the composites have been oxidized . In Fig. 2E, two peaks for the Mo 3d are observed at 232.5 and 229.3 eV, which are assigned to Mo 3d_{3/2} and Mo 3d_{5/2}, respectively, while S 2s is with a broadened low intensity peak can be observed in the same spectrum. Such Mo peaks corresponded to +4 oxidation state, confirming the successful synthesis of MoS₂. The peaks for S 2p (Fig. 2F) were resolved into two distinctive doublets, which were S 2p_{1/2} and S 2p_{3/2} peaks at 163.3 and 161.9 eV, respectively. All these indicate that we successfully prepared the Sn@SnO_x@MoS₂@C composite [20,32].

Fig. 3. SEM images of (A) pure Sn, and (B-D) Sn@SnO_x@MoS₂@C composite.

The morphologies of the Sn@SnO_x@MoS₂@C composite and commercial Sn powders were investigated by scanning electron microscopy (SEM). From SEM image of Fig. 3A, it can be discerned that the pure Sn particles possess a spherical shape with a diameter in the range of 5 μm -10 μm . SEM images of Fig.3B and 3C

show that the $\text{Sn@SnO}_x\text{@MoS}_2\text{@C}$ composite presents well-maintained nanosheets and we can clear see that some particles with a diameter of about 100 nm embedded in and encapsulated with $\text{MoS}_2\text{/C}$ nanosheets completely from SEM image of Fig. 3D. The energy dispersive spectrometer (EDS) mapping (Fig. 4) of the as prepared sample demonstrates that nanoparticles and MoS_2 are highly dispersed in the carbon matrix. Besides tin, carbon, molybdenum and sulfur, oxygen was also detected, consistent with the XRD result.

Fig. 4. SEM and EDS mapping images of $\text{Sn@SnO}_x\text{@MoS}_2\text{@C}$ composite.

Fig. 5. (A,B,C) TEM images and (D,E,F) HRTEM images of Sn@SnO_x@MoS₂@C composite.

The microstructure of the Sn@SnO_x@MoS₂@C composite was further studied by TEM and high-resolution TEM (HRTEM). As shown in Fig. 5A, many Sn nanoparticles with a diameter of around 100 nm anchored and encapsulated with nanosheets are observed, which is in agreement with the SEM observations above. Fig. 5 D, E and F show HRTEM images of the Sn@SnO_x@MoS₂@C composite. As are seen in Fig. 5 D and 5 E, it can be observed clearly that these nanoparticles have a core-shell structure, and the Sn@SnO_x nanoparticles are perfectly encapsulated by MoS₂/C nanosheets. The HRTEM images of Fig. 5 D, E and 5 F exhibit clear lattice fringe for a core-shell structure. The spacing of the adjacent lattice planes for the shell are 0.27 nm and 0.34 nm, corresponding to (100) planes of the pristine MoS₂ and (110) planes of SnO₂, respectively. The spacing of the lattice plane for the inner core is 0.29 nm, consistent with the (200) plane of Sn crystal, which are in good agreement with

above XRD results.

Fig. 6. (A) CV curves of the Sn@SnO_x@MoS₂@C composite at a voltage range of 0.005 to 3.0 V and scan rate of 0.1 mV/s. (B) Cycle performance of the Sn@SnO_x@MoS₂@C composite and Sn@SnO_x@C composite at current density of 0.5 A/g. (C) Rate cycle performance of the Sn@SnO_x@MoS₂@C composite and Sn@SnO_x@C composite at charge/discharge rate from 0.2 to 5.0 A/g. (D) Cycle performance of the Sn@SnO_x@MoS₂@C composite at current density of 2.0 A/g.

Fig. 6A shows the first three cyclic voltammetry (CV) curves of the Sn@SnO_x@MoS₂@C electrode from 0.005 to 3.0 V vs. Li⁺/Li at a scanning rate of 0.1 mV/s. In accordance with previous reports [12,32], it can be seen that the CV curves especially for the discharge branch in the first cycle is different from that of subsequent cycles. Similar to MoS₂ anode reported previously [38], two dominant

reduction peaks at 1.09 V and 0.5 V appear only in the first cycle, which are commonly ascribed to insertion of lithium ions into the interlayer space of MoS₂ to form Li_xMoS₂, and then reduce of Li_xMoS₂ to Li₂S and metallic Mo nanoparticles via a conversion reaction, respectively. After the first cycle, the cathodic peak at 0.30 V, correspond to lithium alloying with Sn. As for the oxidation peak around 2.3 V, which is due to the oxidation of Li₂S to S and lithium ions, and the distinct two oxidation peaks at 0.68 V and 1.29 V, correspond to lithium dealloying with Sn [39]. Note that after the first cycle the CV curves are well overlapped during the subsequent cycles, suggesting that stable SEI film forms and thereby results in excellent reversibility of the Sn@SnO_x@MoS₂@C electrode.

Fig. 6B shows the cycle performance of the Sn@SnO_x@MoS₂@C composite and Sn@SnO_x@C composite. The Sn@SnO_x@MoS₂@C composite exhibits stable cycle performance up to 100 cycles without the significant capacity fading, obtaining a high discharge capacity of 791 mAh g⁻¹ even after 100 cycles at current density of 0.5 A g⁻¹. In contrast, the Sn@SnO_x@C composite with a discharge capacity of 533 mAh g⁻¹ after 100 cycles at the same rate. Therefore, the Sn@SnO_x@MoS₂@C composite demonstrates higher reversible capacity and cycling stability, which is ascribed largely to the strong synergistic effect MoS₂/C nanosheets and encapsulated the Sn@SnO_x nanoparticles. During the charge/discharge process, the MoS₂/C nanosheets can avoid the direct exposure of Sn@SnO_x to the electrolyte and preserve the structural and interfacial stabilization of Sn@SnO_x nanoparticles, leading to excellent cycling stability. As for the MoS₂/C nanosheets with high mechanical

flexibility, they can not only restrain the agglomeration of Sn@SnO_x nanoparticles but also accommodate the mechanical stress induced by the volume change of Sn@SnO_x nanoparticles during the charge/discharge process, which is also very helpful for enhancing the cycling stability [14,32,40].

Moreover, we investigated the rate capabilities of Sn@SnO_x@C and Sn@SnO_x@MoS₂@C composite at various current densities. In general, the capacity retention of all samples decreased with the increased rate, while the Sn@SnO_x@MoS₂@C had a better rate performance than the Sn@SnO_x@C electrode, as shown in Fig. 6C. The cells are first tested at the same charge and discharge current densities of 0.2 A g⁻¹, and then at increased current densities from 0.5 A g⁻¹ to 5.0 A g⁻¹. Sn@SnO_x@MoS₂@C and Sn@SnO_x@C electrode delivers a high average capacity of 966 mAh g⁻¹ and 840 mAh g⁻¹ at 0.2 A g⁻¹, respectively. When the cycle rate was changed from 0.2 A g⁻¹ to 2.0 A g⁻¹, an average capacity of 625 mAh g⁻¹ and 480 mAh g⁻¹ were observed. However, when the current density increased to 5.0 A g⁻¹, Sn@SnO_x@MoS₂@C exhibits a high capacity of 500 mAh g⁻¹, which was higher than the capacity of Sn@SnO_x@C (360 mAh g⁻¹). Finally, when the cycle rate was reduced to 0.2 A g⁻¹ after 50 cycles at different current densities, the discharge capacity of Sn@SnO_x@MoS₂@C electrode returns to 935 mAh g⁻¹, corresponding to 96.8 % of the initial capacity obtained at 0.2 A g⁻¹. In contrast, the Sn@SnO_x@C electrode exhibited lower average capacity of 565 mAh/g, corresponding to only 67 % of the initial capacity obtained at 0.2 A g⁻¹, which is lower than the Sn@SnO_x@MoS₂@C composite.

In order to further confirm the durability has been upon 800 cycles at high current density of 2.0 A g^{-1} and the evolution of the specific capacity is displayed in Fig. 6D. It can be seen that the reversible capacity is 530 mAh g^{-1} even after 800 cycles at 2.0 A g^{-1} , further demonstrating extraordinary superior cycling stability of this $\text{Sn@SnO}_x\text{@MoS}_2\text{@C}$ composite even at high charge/discharge rate. The extremely high specific capacity and superior capacity retention achieved at such a high rate are larger than most of previously reported works on Sn-based materials [19,20,31-45].

Electrochemical impedance spectroscopy (EIS) measurements were investigated to further identify the resistance of $\text{Sn@SnO}_x\text{@MoS}_2\text{@C}$ electrode. Fig. 7 displays the Nyquist plots of $\text{Sn@SnO}_x\text{@MoS}_2\text{@C}$ electrode before and after the 500th charge/discharge cycle. Each Nyquist plot composed of a semi-circle in the high frequency and a linear line in the low frequency [14]. It clearly seen that the ohmic resistance before cycling was considerably higher than after 500th cycle, which was mainly caused by the lack of electrolyte wetting in the electrode materials before cycling. After the process of activation and formation of the SEI film during the cycling, the ohmic resistance greatly decreases. The small value of ohmic resistance explains the excellent rate performance of $\text{Sn@SnO}_x\text{@MoS}_2\text{@C}$ electrode, implying that it has a rapid Li^+ diffusion and formation a stable SEI film [46,47].

Fig. 7. Nyquist plots of Sn@SnO_x@MoS₂@C electrode in the frequency range from 0.01 Hz to 10⁵ Hz before, and after 500 charge and discharge cycles; an enlarge view of EIS of electrode (inset).

The above results clearly confirm that the Sn@SnO_x@MoS₂@C composite has superior cycle and rate performance as anode material, which can be ascribed to following factors. First, the MoS₂/C nanosheets coating Sn@SnO_x nanoparticles that can not only avoid the direct exposure of Sn@SnO_x nanoparticles to the electrolyte but also preserve the structural and interfacial stabilization of Sn@SnO_x nanoparticles. Second, the MoS₂/C nanosheets can suppress the aggregation of Sn@SnO_x nanoparticles and accommodate the volume expansion during the charge/discharge process [14,48]. Third, the MoS₂/C nanosheets can offer a mass of active sites for hosting lithium ions and also can greatly shorten the diffusion distance of both electrons and lithium ions, which is favorable for enhancing the high-rate cycling stability and high capacity [37,38]. All these points are responsible for the superior high-rate cycling performance of the Sn@SnO_x@MoS₂@C composite.

4. Conclusion

In summary, a novel MoS₂/C nanosheets encapsulated Sn@SnO_x nanoparticles composite has been successfully fabricated by a facile and scalable in situ synthesis method with assistance of the surface of water-soluble NaCl particles. In this architecture, the MoS₂/C nanosheets can effectively avoid the direct exposure of Sn@SnO_x nanoparticles to the electrolyte and preserve the structural and interfacial stabilization of Sn@SnO_x nanoparticles. Meanwhile, the nanosheets can accommodate the mechanical stress induced by the volume change of Sn@SnO_x nanoparticles as well as inhibit the aggregation of Sn@SnO_x nanoparticles during the charge/discharge process. As a result, this novel composite exhibits high rate performance (950 mAh/g at 0.2 A g⁻¹, 815 mAh g⁻¹ at 0.5 A g⁻¹, 715 mAh g⁻¹ at 1.0 A g⁻¹, 625 mAh g⁻¹ at 2.0 A g⁻¹ and 500 mAh/g at 5.0 A g⁻¹) and extremely cycling stability even at high rates (a high capacity of 530 mAh g⁻¹ is achieved at 2.0 A g⁻¹ after 800 cycles).

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