Achieving highly stable Sn-based anode by a stiff encapsulation heterostructure

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ABSTRACT Rationally designed heterostructures provide attractive prospects for energy storage electrodes by combining different active materials with distinct electrochemical properties. Herein, through a phase separation strategy, a heterostructure of SnO₂ encapsulated by amorphous Nb₂O₅ is spontaneously synthesized. Insertion-type anode Nb₂O₅ outer shell, playing as reaction containers and fast ionic pathways, physically inhibits the Sn atoms' migration and enhances the reaction kinetics. Moreover, strong chemical interactions are found at the SnO₂/Nb₂O₅ interfaces, which ensure the solid encapsulation of the SnO₂ cores even after 500 cycles. When used for lithium-ion batteries, this heterostructured anode exhibits high cycling stability with a capacity of 626 mA h g⁻¹ after 1000 cycles at 2 A g⁻¹ (85% capacity retention) and good rate performance with the capacity of 340 mA h g⁻¹ at 8 A g⁻¹.

Keywords: heterostructure, encapsulation, SnO₂/Nb₂O₅ interface, chemical interaction, atom migration

INTRODUCTION

From high-speed rail to electric vehicles, humans are trying to electrify everything to achieve a cleaner world. In this course, electrochemical energy storage materials play a vital role. Although many electrode materials have been proposed for high-performance, next-generation lithium-ion batteries (LIBs), they all suffer from inherent problems. Alloying or conversion-type anodes (SnO₂, Si, Fe₂O₃, etc.) possess high specific capacities but suffer from repeated volume changes and uncontrolled atom migration, resulting in particle coarsening and poor cycling stability [1,2]. Insertion-type anodes (TiO₂, Nb₂O₅, etc.), benefiting from their high structure stability, exhibit great cycling stability, but their energy densities are limited due to the lack of redox couples [3–5]. It is hard to find a suitable electrode material with both high specific capacity and high cycling stability due to the fixed reaction mechanism of one single material.

In recent years, the concept of heterostructured electrode material [6] was proposed and prosperously developed, which provides a solution to achieve both high specific capacity and long-term cycling stability at the same time. SnO₂ as a promising high-specific-capacity anode has been designed into varieties of heterostructures, such as gradient Sn/SnO₂ microspheres [7,8],

TiO₂/SnO₂ core-branch arrays [9], SnO₂@SnS₂ quantum dots [10], and carbon-coated SnO₂ [11–13]. However, these heterostructures commonly need complicated, multi-step synthesis procedures and can only temporarily alleviate the problem of Sn atom migration in SnO₂-based electrodes. After long-term cycling, the coarsening problem will eventually occur in these heterostructures. Although heterostructures with carbon coating are fairly effective in preventing atom migration, carbon materials usually suffer from structure distortion and exfoliation in common electrolytes, resulting in unstable solid electrolyte interphase (SEI) and undermined cycling stability [14–16]. SEI is more stable on the surface of insertion type anodes, like TiO₂ and Nb₂O₅ [17–20] due to their inert nature to the electrolyte and the “zero strain” character during cycling. Moreover, their high ionic conductivity for lithium ions [21–23] makes them the most desirable materials for stabilizing the high-capacity conversion- or alloying-type anodes.

In our previous work [24], a Sn-Ti-O solid solution was synthesized to combine the advantages of TiO₂ and SnO₂. However, both identical crystal structures and similar atom sizes are necessary to obtain such a solid solution, which are very strict for material screening. On the other hand, 20% TiO₂ cannot fully restrict the Sn atoms' diffusion due to its random distribution. Ideally, the most desirable configuration is SnO₂ encapsulated by an insertion-type anode that acts as cages to eliminate the Sn migration completely. Nb₂O₅ is a promising candidate for this purpose: on the one hand, Nb₂O₅ and SnO₂ with different crystal structures can avoid the formation of solid solution, and the formation of the core-shell structure is feasible regarding their differences in crystalline temperatures (the low-crystallization-temperature oxide (SnO₂) can repel the non-crystalline oxide (Nb₂O₅) out of the crystal core at low temperatures). On the other hand, SnO₂ and Nb₂O₅ have similar octahedron building blocks and similar ways of connection. Therefore, a smooth and robust *in-situ* connection may exist between the Nb₂O₅ and SnO₂ to achieve a perfect encapsulation of the SnO₂ core.

Herein, through a simple one-pot process, we synthesized an enclosed, core-shell heterostructure SnO₂@Nb₂O₅. Insertion-type oxide Nb₂O₅ on the outside acts as the reaction containers, confining the volume changes and atomic migration of the high-specific-capacity SnO₂ anode. Due to the high oxygen affinity of

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niobium atoms, strong chemical interactions were found at the $\text{SnO}_2/\text{Nb}_2\text{O}_5$ interfaces, realizing the well-encapsulated configuration of SnO_2 even after 500 cycles. Moreover, 85% capacity was retained (relative to the result of the sixth cycle) after 1000 cycles, verifying the high structure stiffness of the core-shell heterostructure.

EXPERIMENTAL SECTION

Synthesis of pure SnO_2 and amorphous Nb_2O_5 -coated samples

Precursors of the $\text{SnO}_2@/\text{Nb}_2\text{O}_5$ samples were prepared by a sol-gel method. Here, we choose the $\text{SnO}_2@/\text{Nb}_2\text{O}_5$ 8-2 sample as an example. In a typical synthesis procedure, 8 mmol of tin oxalate and 2 mmol of ammonium niobate oxalate hydrate were dispersed in 10 mL of deionized water, and then 25 mL of hydrogen peroxide solution (30 wt%) was added to the above suspension. After stirring for 20 min, the suspension became a clear solution composed of peroxo-tin and peroxo-niobium. Ammonium hydroxide was added into the obtained clear solution to consume the excess H_2O_2 and change the pH to around 7 in an ice bath. Then, 30 mmol of citric acid was added to the above solution as a chelating agent to stabilize the metal cations. Finally, after stirring for 30 min, the solution was dried under 150°C for 24 h to obtain a fluffy precursor. The $\text{SnO}_2@/\text{Nb}_2\text{O}_5$ 8-2 sample was obtained by grounding and calcinating the fluffy precursor at 500°C for 1 h in a furnace with a heating rate of 3°C min^{-1} . Similarly, the $\text{SnO}_2@/\text{Nb}_2\text{O}_5$ 9-1 sample and the pure SnO_2 sample were synthesized by reducing or eliminating the addition of ammonium niobate oxalate hydrate.

Sample characterization

X-ray diffraction (XRD) patterns were collected from the Bruker D8 Advance diffractometer using $\text{Cu K}\alpha$ radiation. Brunauer-Emmett-Teller (BET) surface areas of the samples were measured on the Micrometrics ASAP 2020 at 77 K using nitrogen. Raman spectra were carried out on a LabRAM HR Evolution Raman microscope with an excitation wavelength of 633 nm. Electron paramagnetic resonance (EPR) spectra were obtained from a Bruker EMX-8 spectrometer at 300 K. X-ray photoelectron spectroscopy (XPS) results were collected on the Thermo Scientific ESCALAB 250Xi with $\text{Mg K}\alpha$ radiation. A TESCAN S9000 field emission scanning electron microscope was used to obtain the scanning electron microscopy (SEM) images and the energy dispersive spectroscopy (EDS) information of the obtained samples. Transmission electron microscopy (TEM) images, high-resolution TEM (HRTEM) images, and scanning TEM (STEM) images were all recorded on a JEOL-JEM 2100F.

Electrochemical measurement

The electrochemical performances were tested using coin cells. The active material (80 wt%) was mixed with super P (10 wt%) and carboxymethylcellulose sodium (CMC) binder (10 wt%) using water as the solvent and then coated on copper foils. The coin cells were assembled in an argon glovebox with moisture and oxygen contents below 0.5 ppm. Lithium foils were used as both the counter and reference electrode, with Celgard 2325 as separators. The electrolyte consisted of 1 mol L^{-1} LiPF_6 in ethylene carbonate and dimethyl carbonate (EC:DC, the volume ratio of 1:1) with 10 wt% 4-fluoro-1,3-dioxolan-2-one (FEC) and 1 wt% vinylene carbonate (VC). Cycling and rate performances were tested on the LAND-CT2001C test system. Other electrochemical characterization techniques, including electrochemical impedance spectroscopy (EIS), galvanostatic intermittent titration technique (GITT), and cyclic voltammetry (CV), were all measured on the electrochemical workstation (CHI760E).

RESULTS AND DISCUSSION

The synthesis route is illustrated in Scheme 1. Starting from the oxalate of tin and niobium, we used hydrogen peroxide as both the oxidant and capping agent to achieve the homogeneous mixing of Sn and Nb in their peroxide complex form [25–27]. Then a certain amount of citric acid was added as the complexing agent to stabilize the system further. After drying the sol into a fluffy foam, it was then calcined. During the calcination, a phase separation reaction [28–30] occurred: SnO_2 with much lower crystallization temperature first crystallized and pushed out the amorphous Nb_2O_5 due to their differences in crystal structures. After this reaction, a core-shell configuration with crystallized SnO_2 core and amorphous Nb_2O_5 shell was successfully synthesized (the samples were named $\text{SnO}_2@/\text{Nb}_2\text{O}_5$ 8-2, $\text{SnO}_2@/\text{Nb}_2\text{O}_5$ 9-1 and SnO_2 according to different niobium contents).

Many other groups also reported similar phase separation reactions in various systems. Generally, the driving forces for these phase separations can be classified into three categories: (1) mismatch of different crystal structures, like the $\text{SnS}@/\text{SnS}_2$ core-shelled structure reported by Sutter *et al.* [28]; (2) differences in the atom diffusion rate, like the case in the core-shelled $\text{Cu}_{11}\text{V}_6\text{O}_{26}@/\text{V}_2\text{O}_5$ reported by Pei *et al.* [29]; (3) surface energy or Gibbs free energy differences, which were widely reported in multi-metallic nanomaterials [30,31] and spinodal decomposition reactions. Recently, Susarla *et al.* [32] prepared a lateral heterostructure using the spinodal decomposition reaction.

SEM showed the morphologies of the samples with 0, 10, and 20 wt% niobium addition in Fig. 1a, c, and Fig. S1, respectively.

Scheme 1 Schematic illustration for the synthetic route of the $\text{SnO}_2@/\text{Nb}_2\text{O}_5$.

Figure 1 (a, c) SEM images and (b, d) TEM images of the pure SnO₂ and SnO₂@Nb₂O₅ 8-2 sample, respectively. (e) Box chart of the particle size distribution of the three obtained samples. (f, g) HRTEM images of the pure SnO₂ and SnO₂@Nb₂O₅ 8-2 sample. (h) SAED pattern of the SnO₂@Nb₂O₅ 8-2 sample. (i) STEM image of the SnO₂@Nb₂O₅ 8-2 sample and the corresponding element mapping of (j) Sn, (k) Nb and (l) O.

Particle sizes of the obtained samples decreased dramatically upon the addition of niobium. TEM images from Fig. 1b, d and Fig. S2a further confirmed the results obtained from the SEM measurements. Moreover, we counted the particle size distributions of the three samples from the TEM images and listed them in Fig. 1e. A strong relationship can be seen between the particle sizes and the niobium content: with the increment of niobium content, the samples' median particle sizes decrease from ~15 to ~6 nm with much-narrowed size distributions.

We can get a closer look at the synthesized samples by HRTEM. Pure SnO₂ with high crystallinity and sharp edges can be identified in Fig. 1f. In contrast, samples with 10 wt% (Fig. S2b) or 20 wt% (Fig. 1g) niobium element addition showed distinct core-shell configuration. The crystalline core has an inter-planar spacing of 0.34 nm, corresponding to the (110) plane of SnO₂. The shell is composed of amorphous Nb₂O₅ since Nb₂O₅ cannot crystallize under such a low temperature [33]. As shown in Fig. 1h, the selected area electron diffraction (SAED) pattern of the SnO₂@Nb₂O₅ 8-2 sample showed no other diffraction rings except for SnO₂, further excluding the existence of crystalline Nb₂O₅. EDS mapping was further carried out to show the element distributions to verify the core-shell configuration. The STEM image in Fig. 1i presents a particle with an elliptical outline. As shown in Fig. 1j, k, the element mapping image of niobium in this area has a similar elliptical figure, while the distribution of Sn appears in a more confined circle-like area, strongly supporting the formation of the core-shell configuration.

Crystal structures of the obtained materials with different niobium contents were characterized by XRD measurement. As

shown in Fig. 2a, all diffraction peaks can be indexed to the tetragonal SnO₂ (JCPDS no. 41-1445). No peak splitting or position shift can be identified in the XRD patterns, suggesting that niobium is not doped into SnO₂, and no secondary crystalline phase exists (standard XRD pattern of Nb₂O₅ is also given in Fig. 2a). Meanwhile, the entire width of the half maximum of the diffraction peaks for different samples becomes larger with the increment of niobium content, indicating the downsizing of particle sizes. On the other hand, adsorption-desorption isotherms (Fig. 2b) show that SnO₂@Nb₂O₅ 8-2 and SnO₂@Nb₂O₅ 9-1 have comparable surface areas of 72.4 and 74.2 m² g⁻¹, respectively, 1.6 times as large as that of the pure SnO₂ (45.0 m² g⁻¹). The increased surface areas of the SnO₂@Nb₂O₅ samples are the result of their smaller particle sizes. Corresponding pore size distributions are also given as an inset in Fig. 2b. SnO₂@Nb₂O₅ 8-2 shows narrower size distribution and smaller pore sizes when compared with pure SnO₂. It is also worth mentioning that without incorporating carbon, satisfying tap densities of 1.09 and 1.15 g cm⁻³ are achieved for SnO₂@Nb₂O₅ 9-1 and SnO₂@Nb₂O₅ 8-2, respectively (the tap density of pure SnO₂ nanoparticles is about 1.00 g cm⁻³).

Detailed structure variations of the obtained samples were characterized by Raman spectra. There are four characteristic Raman modes for SnO₂: E_u, E_g, A_{1g} and B_{2g} [34,35]. Compared with pure SnO₂, the A_{1g} mode of the amorphous Nb₂O₅-coated sample downshifts significantly from ~638 to ~617 cm⁻¹ (Fig. 2c). This is closely correlated to the existence of the bridging oxygen vacancies. The presence of Nb₂O₅ can cause strong competition of oxygen atoms between Sn and Nb at the SnO₂/Nb₂O₅ interfaces, leading to the appearance of bridging oxygen

Figure 2 (a) XRD patterns, (b) N₂ adsorption-desorption isotherms and the corresponding pore size distributions, and (c) Raman spectra of the three obtained samples. (d) EPR spectra of the pure SnO₂, SnO₂@Nb₂O₅ 9-1 sample and SnO₂@Nb₂O₅ 8-2 sample. Comparison of (e) Sn 3d, (f) Nb 3d XPS spectra for the obtained samples.

vacancies on the surface of SnO₂ (Fig. 3a). EPR measurement is susceptible to unpaired electrons, which can reveal more details on the defective structure. EPR results of the obtained samples are given in Fig. 2d. Two resonance peaks in the EPR data at $g = 2.00$ and $g = 1.89$ were observed, corresponding to the single oxygen vacancy and oxygen vacancies group, respectively [36–38]. Compared with pure SnO₂, Nb₂O₅ coating significantly increases the concentration of oxygen vacancies. The Nb₂O₅ outer shell isolates the SnO₂ core from the air, increasing the concentration of single oxygen vacancy ($g = 2.00$). The peak representing the oxygen vacancies group ($g = 1.89$) was initially found at the interface of SnO/SnO₂ [36]. Similarly, in our case, we believe that this signal of oxygen vacancies group is probably caused by the competition between Nb and Sn on oxygen atoms at the core-shell interfaces, which is also presented as the bridging oxygen vacancy signal in the Raman spectrum.

The XPS spectrum also recorded the solid chemical interaction at the SnO₂/Nb₂O₅ interface. In Fig. 2e, the presence of Nb₂O₅ downshifts the binding energy of Sn significantly. Meanwhile, no chemical state change of niobium can be observed, as shown in Fig. 2f. The strong Nb–O chemical bonding at the SnO₂/Nb₂O₅ interface induces the electron cloud redistribution and decreases the overlap of the O 2p orbital with the Sn 3d orbital, resulting in the electron-rich status of Sn and lowering its binding energy. The significant binding energy variations also indicate the formation of the Nb–O–Sn bond at the interfaces, which enhances the connection between the amorphous Nb₂O₅ and the SnO₂. Similar strong chemical interactions between Nb₂O₅ and other oxides or metals [39–43] are also identified in many catalyst systems. Recently, strong interactions between Nb₂O₅ and polysulfide are also found in lithium-sulfur batteries [44,45].

As shown in Fig. 3a, the Nb₂O₅-coated sample is schemed. Single oxygen vacancies are present in the bulk of SnO₂, and the oxygen vacancies groups are located at the Nb₂O₅/SnO₂ interfaces. As mentioned above, oxygen vacancies groups are present as the result of the strong interaction between Nb and the bridging oxygen atoms on the surface of SnO₂, which also helps the amorphous Nb₂O₅ shell anchor on the SnO₂ tightly. Ideally, this strong encapsulation may endow the electrode with better cycling and structure stability. Therefore, the electrodes after 500 cycles were characterized by TEM to identify the morphology evolution. As shown in Fig. 3c, g, the SnO₂@Nb₂O₅ 8-2 electrode could maintain the sub 10-nm scale nanoparticle morphology after the long-term cycling. XRD patterns of the cycled electrode showed no Sn diffractions, further suggesting its nano-sized nature (Fig. S3). At the same time, the SAED pattern exhibits ring-like diffractions with few diffraction dots, indicating the uniformity and small size nature of the obtained Sn. On the contrary, pure SnO₂ suffered from uncontrolled coarsening with sharp and discrete diffraction spots in the SAED pattern [24,46]. From HRTEM images, we can also identify the influential role of the Nb₂O₅ coating. Amorphous Nb₂O₅ can realize a full coverage of the SnO₂ cores preventing them from aggregation and coarsening even after the repeated cycles (Fig. 3d).

Ex-situ XPS measurements were further conducted to elucidate the reaction mechanism and the role of the Nb₂O₅ coating. The valence state of niobium changes reversibly between +5 and +4 within the operating potential range (Fig. 3e), confirming its insertion reaction mechanism. On the one hand, the amorphous Nb₂O₅ outer shell can act as the protective layer, preventing the degradation of electrolyte on the surface of SnO₂. On the other hand, it can also play as a selective conduction layer with high lithium-ion conductivity [22,23], but prevent the Sn atoms'

Figure 3 Structure schematic of the $\text{SnO}_2/\text{Nb}_2\text{O}_5$ interface on the $\text{SnO}_2/\text{Nb}_2\text{O}_5$ 8-2 sample (a) at the initial state and (b) after being discharged to 0.01 V. (c, d, g, h) Different magnification TEM images of the SnO_2 and the $\text{SnO}_2/\text{Nb}_2\text{O}_5$ 8-2 sample after 500 cycles. (e, f) Sn 3d and Nb 3d XPS spectra of the $\text{SnO}_2/\text{Nb}_2\text{O}_5$ 8-2 sample charged back to 3 V and discharged to 0.01 V for the 5th cycle respectively. (i) Schematic illustration of the electrochemical morphology evolution of the SnO_2 electrode with or without Nb_2O_5 coating. (j) Schematic showing the selective ion permeability of the Nb_2O_5 coating.

outer diffusion, eliminating the coarsening problem of SnO_2 [47]. In the XPS spectrum of Sn, some Sn atoms can be still converted back to +4 valence at the charged state after 5 cycles, but the majority of the Sn atoms stay at 0 valence, corresponding to the capacity loss in the first dozens of cycles. Notably, the XPS results of Sn at the fully discharged state showed a small amount of element Sn remained except for the Li_xSn alloy [48] (Fig. 3f). This small portion of un-lithiated Sn may be related to the Sn atoms constituting the Nb–O–Sn bonds at the $\text{SnO}_2/\text{Nb}_2\text{O}_5$ interfaces, which cannot form alloy with lithium. From the above XPS results, after the repeated cycling, the alloying reaction of Sn and the insertion reaction of Nb_2O_5 contribute to the primary capacity of the electrode. Fig. 3i, j give the electrode evolution schematic graphs of the sample with Nb_2O_5 coating. The *in-situ* formed amorphous Nb_2O_5 , strongly connected to the surface of SnO_2 through the Nb–O–Sn bond, prevents the outer diffusion of Sn and eliminates the coarsening problem.

To evaluate the electrochemical performances of the pure SnO_2 , $\text{SnO}_2/\text{Nb}_2\text{O}_5$ 9-1 and $\text{SnO}_2/\text{Nb}_2\text{O}_5$ 8-2, half cells with metallic lithium as the counter and reference electrodes were assembled and tested. As shown in Fig. 4a, the first three CV cycles of the $\text{SnO}_2/\text{Nb}_2\text{O}_5$ 8-2 sample are presented. The reduction peak at 1 V in the initial discharge process may be related to the decomposition of electrolyte and the formation of SEI. Other peaks can well correspond to the conversion and alloy reaction of Sn: (1) and (1') $\text{Sn} \leftrightarrow \text{Li}_{4.4}\text{Sn}$; (2) and (2') $\text{SnO} \leftrightarrow \text{Sn}$ and (3) and (3') $\text{SnO}_2 \leftrightarrow \text{SnO}$ [46]. The performances of the three samples under stepwise charge-discharge current from 0.2 to 8 A g^{-1} are shown in Fig. 4b. The theoretical capacity of

SnO_2 is $782.4 \text{ mA h g}^{-1}$ (only accounting for the alloying reaction). Increasing the content of Nb_2O_5 will decrease the total capacity of the composite; therefore, the capacity of the $\text{SnO}_2/\text{Nb}_2\text{O}_5$ 9-1 sample is $724.3 \text{ mA h g}^{-1}$ and decreases to $666.2 \text{ mA h g}^{-1}$ for the $\text{SnO}_2/\text{Nb}_2\text{O}_5$ 8-2 sample. As shown in Fig. 4b, the capacity in the first dozens of cycles is slightly higher than the theoretical value, resulting from the partially reversible conversion reaction of SnO_2 . Pure SnO_2 showed the highest capacity in the initial cycle but decreased very quickly due to its poor stability. The capacity differences under small current densities (0.2 and 0.5 A g^{-1}) are relatively small for all the three samples. However, when the current density increased to 1 A g^{-1} , the capacity of pure SnO_2 dropped significantly to 42% of its initial capacity. When the current density further increased, the capacity retention of the $\text{SnO}_2/\text{Nb}_2\text{O}_5$ 9-1 sample was also significantly reduced. The $\text{SnO}_2/\text{Nb}_2\text{O}_5$ 8-2 sample exhibited satisfied capacity retention under the tested current densities with 591 mA h g^{-1} at 1 A g^{-1} , 544 mA h g^{-1} at 2 A g^{-1} , 515 mA h g^{-1} at 3 A g^{-1} , 487 mA h g^{-1} at 4 A g^{-1} , 413 mA h g^{-1} at 6 A g^{-1} , and 341 mA h g^{-1} at 8 A g^{-1} . After the charge-discharge process under high currents, the electrode could still exhibit a capacity of 618 mA h g^{-1} when the current changed back to 0.2 A g^{-1} .

The improved rate performances are probably related to the improved surface condition of the electrode. As shown in Fig. 4e, the charge transfer resistance of the $\text{SnO}_2/\text{Nb}_2\text{O}_5$ 8-2 sample decreases from 50 to 25 Ω after the repeated cycling. In contrast, the charge transfer resistance of the pure SnO_2 increases from ~10 to 40 Ω . Compared with the pure SnO_2 nanoparticles, the high initial charge transfer resistance of the

Figure 4 (a) CV curves of the first three cycles for the $\text{SnO}_2@\text{Nb}_2\text{O}_5$ 8-2 sample. (b, d) Rate performances and cycling stability of the obtained three samples. (c) Galvanostatic charge/discharge curves of the $\text{SnO}_2@\text{Nb}_2\text{O}_5$ 8-2 sample at different cycles. (e) EIS curves of the SnO_2 and $\text{SnO}_2@\text{Nb}_2\text{O}_5$ 8-2 sample before and after 500 cycles. Corresponding equivalent circuit diagram is also shown as an inset, in which R_s represents the contact resistance, R_{ct} stands for the charge transfer resistance, and Z_w represents the ion diffusion resistance in the electrode materials.

Nb_2O_5 -coated samples may vary due to the poor electronic conductivity of Nb_2O_5 [49,50]. The corresponding equivalent circuit is given as an inset in Fig. 4e. Since Nb_2O_5 has high structure and chemical stability, Nb_2O_5 coating can decrease the side reactions on the electrode surface and guarantee a high ionic conductivity of Li^+ . Moreover, it can also prevent the agglomeration of Sn and restrict the diffusion of Li_2O , keeping a high electric conductivity of the electrode. Therefore, much-improved rate performances can be obtained in the heterostructured electrode.

As discussed above, the Nb_2O_5 shell can be firmly coated on the surface of SnO_2 due to the Nb–O–Sn bond. Therefore, the coarsening of SnO_2 may be successfully suppressed, and high cycling stability should be obtained. The cycling performances are shown in Fig. 4d. Under a high current density of 2 A g^{-1} , the $\text{SnO}_2@\text{Nb}_2\text{O}_5$ 8-2 sample can still deliver a capacity of 627.8 mA h g^{-1} after 1000 cycles, much superior to the pure SnO_2 and the $\text{SnO}_2@\text{Nb}_2\text{O}_5$ 9-1 samples. Galvanostatic charge/discharge curves of the $\text{SnO}_2@\text{Nb}_2\text{O}_5$ 8-2 sample in Fig. 4c clearly show that the capacity loss in the first dozens of cycles is mainly caused by the irreversible conversion reaction of Sn ($>1\text{ V}$). Nevertheless, no capacity loss can be identified from the 50th cycle to the 200th cycle, demonstrating the high cycling stability of the coated sample. We also tried the sodium ion storage capability of the coated sample, but the results were far from satisfactory (only showed a reversible capacity of 60 mA h g^{-1}). We believe that the inferior performances result from the poor electronic conductivity of the coated sample [51,52] and the sluggish Na^+ diffusivity in the amorphous Nb_2O_5 [53].

CV measurements under various scan rates were further carried out to discern the diffusion-controlled and pseudo capacitive contribution of the obtained samples to explore the

reason for the superior rate performances. As shown in Fig. 5a, the capacitive contributions of the obtained samples are demonstrated under various scan rates. The capacitive contributions of the three samples increase with the enhanced scan rate, and the samples with Nb_2O_5 coating have much higher capacitive contributions than the pure SnO_2 . $\text{SnO}_2@\text{Nb}_2\text{O}_5$ 8-2 sample possesses the highest proportion of capacitive contribution. Even at a low scan rate of 0.2 mV s^{-1} , the capacitive contribution still accounts for 49.4% of the total capacity (only 30.5% for pure SnO_2). The higher capacitive contribution of the Nb_2O_5 -coated sample is probably rooted in the decreased particle sizes since nanoparticles can shorten the ion diffusion distances, resulting in fast faradic reactions with capacitive-like behaviors. On the other hand, the decreased particle sizes and the amorphous Nb_2O_5 coating layer can create more active sites on the surface, resulting in higher capacitive percentage.

GITT tests were also conducted to calculate the Li^+ diffusion coefficients:

$$D = \frac{4}{\pi\tau} \left(\frac{n_m V_m}{S} \right)^2 \left(\frac{\Delta E_s}{\Delta E_t} \right)^2, \quad (1)$$

where D is the Li^+ diffusion coefficient, τ is the duration of the current pulse, n_m is the mole quantity of the active material, V_m is the molar volume, and S is the surface area of the electrode. We measured the electrode thickness to complete the second term in the formula since the active material is not a single phase in our case. ΔE_s is the equilibrium potential change after the relaxation, and ΔE_t is the potential after the applied current pulse, as shown in Fig. S4. Li^+ diffusion coefficients of the $\text{SnO}_2@\text{Nb}_2\text{O}_5$ 8-2 sample and pure SnO_2 are listed in Fig. 5b (for clarity, $\text{SnO}_2@\text{Nb}_2\text{O}_5$ 9-1 sample is omitted, and the complete results are shown in Fig. S5). All the three samples have similar

Figure 5 (a) Capacitive contribution of the obtained three samples. (b) Comparison of the lithium ion diffusion coefficients calculated from the GITT measurement of the SnO₂@Nb₂O₅ 8-2 sample and pure SnO₂.

behaviors within the test potential range, yet the SnO₂@Nb₂O₅ 8-2 sample exhibits slightly higher diffusion coefficients coinciding with the best rate performances among all the three samples.

CONCLUSIONS

In conclusion, we successfully synthesized a novel heterostructured SnO₂/Nb₂O₅ composite through a simple one-pot process. Due to the differences in crystallization temperature, phase separation occurred during the calcination. With crystalline SnO₂ continuously pushing out the amorphous Nb₂O₅, the core-shelled SnO₂@Nb₂O₅ heterostructure was finally formed. Moreover, thanks to the strong oxygen affinity of niobium atoms, Nb–O–Sn bonds were formed at the SnO₂/Nb₂O₅ interface ensuring the firm wrapping of SnO₂ by the amorphous Nb₂O₅. Even after 500 cycles, the encapsulation of the amorphous Nb₂O₅ can still be identified with no coarsening or agglomeration of Sn. When used in LIBs, the composite achieved high cycling stability for 1000 cycles at 2 A g⁻¹ with a capacity of 626 mA h g⁻¹ (85% capacity retention). Under a high current density of 8 A g⁻¹, a capacity of 340 mA h g⁻¹ was obtained, demonstrating its good rate performances. Since the uncontrolled atom migration is also present in many other alloying- or conversion-type anodes, this *in-situ* encapsulation strategy may also effectively stabilize other high-energy-density anodes.

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

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牢固的封装异质结构实现锡基负极的长循环稳定性

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摘要 通过异质结构可以将不同电化学性质的电极材料人为地进行设计组合实现优势互补, 这一方法为储能材料的未来发展提供了广阔前景. 本文中, 我们通过一步自发相分离策略, 实现了 SnO_2 封装于无定形 Nb_2O_5 中的特殊异质结构. 嵌入型反应负极 Nb_2O_5 充当合金型负极 SnO_2 的反应容器和快速离子传输层, 空间上限制了 Sn 原子的迁移并增强了反应动力学. 此外, 我们在 $\text{SnO}_2/\text{Nb}_2\text{O}_5$ 界面处发现了强化学相互作用, 使得 Nb_2O_5 封装层即使在500次充放电循环后仍能牢固封装在 SnO_2 核的表面. 这种异质结构材料作为锂离子电池负极表现出高循环稳定性, 在 2 A g^{-1} 的大电流下循环1000次后容量为 626 mA h g^{-1} (容量保持率为85%), 同时在 8 A g^{-1} 的电流下容量仍可保持在 339.9 mA h g^{-1} , 展现出良好的倍率性能.