One-step synthesis of Ni₃Sn₂@reduced graphene oxide composite with enhanced electrochemical lithium storage properties

Zheng Yi,^{†a, b} Xin Tian,^{†a, b} Qigang Han,^{a, b*} Yong Cheng,^b Jianshe Lian,^a Yaoming Wu,^b Limin Wang^{b**}

^a College of Materials Science and Engineering, Jilin University, Changchun 130025, China

^b State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, CAS, Changchun 130022, China

[†] Zheng Yi and Xin Tian contributed equally to this work.

*Corresponding author.

E-mail address: hanqg@jlu.edu.cn (Q. Han). Tel. / fax: +86 431 85094340.

**Corresponding author.

E-mail address: lmwang@ciac.ac.cn (L. Wang). Tel.: +86 431 85262447; fax: +86 431 85262836.

Abstract: A facile one-step solvothermal method has been put forward to construct Ni₃Sn₂@reduced graphene oxide (Ni₃Sn₂@rGO) composite. The Ni₃Sn₂ alloys in the composite with regular quasi-spherical morphology and an average size of 216 nm are homogeneously encapsulated into rGO sheets. As a promising anode material for lithium-ion batteries (LIBs), the as-prepared Ni₃Sn₂@rGO composite exhibits a high initial discharge capacity of 1315 mAh g⁻¹ and reversible capacity of 554 mAh g⁻¹ after 200 cycles at a current density of 100 mA g⁻¹. Even at a high current density of 800 mA g⁻¹, a substantial discharge capacity of 422 mAh g⁻¹ is delivered. The excellent cycling stability and remarkable rate capability of the designed Ni₃Sn₂@rGO composite can be attributed to the synergistic effects between Ni₃Sn₂ alloy and rGO matrix, and the rational cooperative advantage of the ball-like alloy morphology and the buffering effects of the inert nickel matrix as well as the flexible rGO matrix.

Keywords: Ni₃Sn₂; Reduced graphene oxide; Lithium-ion batteries; Anode material

1. Introduction

Lithium-ion batteries (LIBs) have become one of the promising available rechargeable energy store devices for the rapid development of portable electronics and electric vehicles [1, 2]. As an excellent anode material for LIBs, graphite has commendable performance such as low average voltage, good rate capability and low volume expansion during lithiation [3]. However, it cannot satisfy the demand

of high specific capacity on account of its modest theoretical specific capacity of 372 mAh g⁻¹. Therefore, researchers never discontinuously do a task to seek for new alternative anode materials involved in the development or combination of all of the merits in which the graphite has. Tin is considered as a alternative anode material with great promise because of its high theoretical specific capacity of 993 mAh g⁻¹ derived from the formation of a Li₂₂Sn₅ phase [4]. Nevertheless, the practical application of tin anode material is seriously hampered by its gigantic volume change (up to 360%) and dramatic mechanical stress generated upon lithiation-delithiation process, thereby leading to rapid capacity fading [5-7].

Therefore, many research efforts are need to devote to overcome above problems. Thereinto, the inert matrix M, which can react with tin to form stable alloy structure while cannot react with lithium upon lithiation-delithiation process, is introduced to the tin anode system to form M-Sn alloys. Because of the buffering effect of inert M matrix, the M-Sn alloy exhibits enhanced electrochemical cycling performance compared with pure tin anode. These inert matrixes such as copper [8-10], cobalt [11, 12], nickel [13, 14] and iron [15, 16], *etc.* have been explored to fabricate Cu-Sn, Co-Sn, Ni-Sn and Fe-Sn alloys as anode materials for LIBs. However, the enhancement of only utilizing inert M matrix to buffer volume change is insufficient [17]. To further enhance the cycling stability of M-Sn anode, carbon materials are widely introduced to prepare M-Sn-carbon composite [18-24]. For instance, Ruguang Ma *et al.*[22] and Ping Wu *et al.*[23] have prepared Sn-Ni@C composites using glucose hydrothermal carbonization method. By using electron beam evaporation and ultrasonic-pulse electrodeposition, the Sn-C-Ni composites thin films have been fabricated by Min Zhu [20] and Mehmet Uysal [24], respectively. All the Ni-Sn-C composites mentioned above have enhanced electrochemical lithium storage performances compared with the corresponding bare Ni-Sn alloy anodes.

Although there is a considerable success in synthesis of the Ni-Sn-C composites for LIBs, the composite with Ni-Sn alloys *in situ* embedded in carbon are difficultly designed with defined morphology. Solvothermal method is considered as a promising way to solve this challenge [13], but has never been explored in this field. In this work, we report the successful synthesis of a new type of Ni-Sn-C composite. In the composite, the two-dimensional (2D) reduced graphene oxide (rGO) is used as carbon source and buffering matrix, and the morphology of the *in situ* embedded Ni-Sn alloys is

controlled by one-step solvothermal method. Because of cooperative impact of well morphology of the embedded Ni-Sn alloys, buffering effects of flexible/conductive rGO matrix and inert nickel matrix as well as the nanospace existence in the composite, the $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite anode exhibits enhanced lithium storage performance such as reduced electrochemical impedance, excellent cycling stability and inspiring rate capability.

2. Experimental

2.1 Synthesis of $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite

All reagents were purchased from Aladdin Reagent Co., Ltd. (China). Graphene oxide (GO) was prepared by a modified Hummer's method [25]. To fabricate the $\text{Ni}_3\text{Sn}_2@\text{rGO}$, 32 mg of GO was well-dispersed in 25 mL ethylene glycol (EG) solvent, and then $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ with the appropriate mole ratio were added into the solution after ultrasonication for 1 h. After magnetic stirring for another 1 h, the sodium hydroxide solution was added into the above solution drop by drop under continuous magnetic stirring. Subsequently, the mixing was transferred to a 50 mL Teflon-lined autoclave and tightly sealed, then maintained at 190 °C for 8 h and cooled naturally to room temperature. The as-prepared products were collected by centrifugation, washed thoroughly by deionized water three times and absolute ethyl alcohol two times, and finally dried in a vacuum oven at 60 °C overnight. For comparison, the neat reduced graphene oxide (rGO) and Ni_3Sn_2 alloy were prepared by this similar process, only without presence of metal chloride and GO, respectively.

Materials Characterization

The phase purity of the as-prepared products was determined by X-ray diffractometer (XRD, Bruker Corporation, Germany) with copper target at a scan rate of 4 ° min⁻¹. Raman spectra were obtained on a JYLABRAM-HR Confocal Laser Micro-Raman spectrometer at room temperature. The morphology, energy-dispersive X-ray spectroscopy (EDS) element mapping and spectra of the Ni_3Sn_2 alloy were characterized by scanning electron microscope (SEM, HITACHI S-4800, Japan) at an acceleration voltage of 10 kV. Transmission electron microscopy (TEM) and EDS element mapping and spectra of the $\text{Ni}_3\text{Sn}_2@\text{rGO}$ were performed on a FEI Tecnai G2 S-Twin instrument with a field emission gun

operating at 200 kV. Thermogravimetric analysis (TGA) was performed in air from room temperature to 900 °C with a heating rate of 10 °C min⁻¹ by using an STA 449 Jupiter (NETZSCH) thermogravimetry analyzer.

Electrochemical Characterization

The working electrode was prepared by coating N-methyl-2-pyrrolidone (NMP) slurry containing active material (Ni₃Sn₂ alloy and Ni₃Sn₂@rGO composite), acetylene black (as the conductive agent), and polyvinylidene fluoride (PVDF, as the binder agent) with a weight ratio of 70:15:15 onto a copper foil and drying in a vacuum oven at 60 °C for 12 h. Then, the cells were assembled by using CR 2025 coin-type cell configuration with pure lithium as the counter electrode, a Celgard 2400 membrane as the separator, and 1 M LiPF₆ dissolved in ethylene carbonate and diethylene carbonate (1:1 in volume) as the electrolyte. Note that this process was carried out in a glove box filled with highly pure argon gas. The charge-discharge performance was tested between 0.01 V and 2.0 V using a programmable battery testing system (LAND CT2001A) at room temperature. The cyclic voltammogram (CV) measurements were conducted on a Bio-Logic VMP3 Electrochemical Workstation at a scan rate of 0.2 mV s⁻¹ in a potential range of 0-2 V vs. Li⁺/Li. Electrochemical impedance spectroscopy (EIS) measurements were also performed on a BioLogic VMP3 Electrochemical Workstation over frequency ranges from 700 kHz to 100 mHz in automatic sweep mode.

3. Results and Discussion

The strategy to synthesize the Ni₃Sn₂@rGO composite is schematically depicted in Fig. 1. The GO is firstly dispersed in ethylene glycol solution. Subsequently, NiCl₂·6H₂O and SnCl₂·2H₂O are added into homogeneous GO ethylene glycol solution under stirring treatment. Because of many oxygenic functional groups, the GO is to serve as locating centers of the nickel and tin ions and then as the nucleation centers for Ni₃Sn₂ alloy. After adding the sodium hydroxide solution, the mixing solution is treated by the solvothermal method. As a result, the Ni²⁺ and Sn²⁺ are both reverted to atoms and form alloys under the reducing action of ethylene glycol. At the same time, the GO is also reduced to rGO and then act as the substrate to load the Ni₃Sn₂ submicro spheres. Our design is to obtain submicro spheres with defined morphology homogeneously encapsulated in rGO sheets, in which rGO as a

promising matrix can enhance mechanical properties to buffer volume change of the tin in Ni_3Sn_2 submicro spheres, and the inert nickel matrix can also release the volume expansion of Sn due to the stable alloy structure. Furthermore, the nanospace existence between the rGO and Ni_3Sn_2 submicro spheres provides additional free volume to accommodate the volume change. By combining the uniform alloy morphology and buffer effects of the flexible rGO matrix, inert nickel matrix and the nanospace matrix in the composite anode, we attempt to establish a multiple protection system, and try to improve the electrochemical cycling performance of the $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite anode for LIBs.

The representative SEM images of bare Ni_3Sn_2 alloy are shown in Fig. 2a and b, which indicate that the Ni_3Sn_2 alloy exhibits consistent ball-like shape and high monodispersivity. It is well-known that the ball-like shape is a well existence form with the lowest energy. Furthermore, it is highly symmetrical and isotropous. To give further insight into the morphology and structure of the as-synthesized bare Ni_3Sn_2 alloy, TEM analysis has been carried out. Fig. 2c reveals that the Ni_3Sn_2 submicro spheres are solid-sphere shape with approximately homogeneous diameter range. To quantificationally reveal their diameter ranges, histogram of diameter distribution for a representative set of derived Ni_3Sn_2 submicro spheres samples is depicted in Fig. 2d, which displays the diameters of submicro spheres are varied from 120 nm to 270 nm, and with the mean diameter of approximately 216 nm. The histogram of diameter distribution also presents that the diameter ranges of submicro spheres are mainly centered between 180 nm and 250 nm with an occupying proportion of about 82.5%. Because of their isotropous identical ball-like shapes and uniform size, the *in situ* formed 0D electroactive Ni_3Sn_2 submicro spheres can accommodate structural stress and prevent the aggregation of Sn during lithium ion insertion and exsertion.[26] Note that the particle size of Ni_3Sn_2 can be controlled by the one-step solvothermal method. As shown in Fig. S1 (Supplementary Materials), the Ni_3Sn_2 submicro spheres obtained in the different contents of Ni^{2+} at 0.5, 1, 2 and 4 mmol within different sizes of ~ 140 nm, ~ 220 nm, ~ 400 nm and ~ 500 nm, respectively. In order to determine the distribution of Ni and Sn in the Ni-Sn alloy anode, elemental mapping of the Ni_3Sn_2 alloy is performed. Fig. S2b and 2c (Supplementary Materials) display the energy-filtered SEM mapping for Ni and Sn, respectively. Both the energy-filtered SEM maps of the Sn and Ni match well with the SEM image (Fig. S2a, Supplementary Materials), indicating that the Sn and Ni are uniformly distributed throughout the alloy. In the meantime, the EDS spectrum of the Ni_3Sn_2 alloy is shown in Fig. S2d. There are strong characteristic peaks of Sn and Ni pointing to

the Ni_3Sn_2 alloy. In addition, the results show that the tin content in the binary Ni-Sn alloy is 57.4 wt. %, in consistent with the original designed value of Ni_3Sn_2 alloy.

The SEM (Fig. 3a and b) and TEM images (Fig. 3c and d) of the $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite are given to confirm its morphology. It can be seen that Ni_3Sn_2 submicro spheres are uniformly dispersed into the rGO sheets, indicating the successful formation of a $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite alliance. Because of the electrostatic interaction between oxygenic functional groups of GO and Ni^{2+} , Sn^{2+} , the Ni_3Sn_2 alloy can *in situ* form and embed in the rGO matrix (the SEM image of bare rGO is presented in Fig. S3b, Supplementary Materials). Furthermore, the contraction of GO layers in the redox process makes the $\text{Ni}_3\text{Sn}_2@\text{rGO}$ close-knit alliance. In addition, there are much nanospace existing between the Ni_3Sn_2 submicro spheres and rGO, which can strengthen its ability to buffer the volume change during lithiation-delithiation process. Elemental mapping is carried out to analyze the distribution of the nickel and tin in the composite. As shown in Fig. 3f and 3g, both the nickel and tin are uniform dispersed and coexisted over the whole Ni_3Sn_2 submicro spheres. To determine the atomic ratio of nickel and tin in the $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite, EDS (Fig. S4, Supplementary Materials) is obtained. Strong signals of C, Sn and Ni elements are present, suggesting the successful synthesis process. In addition, by calculating from the EDS result, the atomic ratio of nickel and tin is 3.05:2, agreeing well with the expected stoichiometric ratio of the Ni_3Sn_2 phase.

Fig. 4a is the XRD results of the as-prepared products. It can be seen that all diffraction peaks of bare Ni_3Sn_2 and $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite agree well with the characteristic peaks of the Ni_3Sn_2 alloy (P63/mmc, JCPDS 06-0414), indicating the pure phase of the bare Ni_3Sn_2 submicro sphere and the embedded Ni_3Sn_2 submicro sphere in the $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite. Furthermore, a broad peak corresponding to the typical (002) crystal plane of rGO (Fig. S3a, Supplementary Materials) locates at diffraction angles of 20° - 26° , which is also observable in the $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite. The peaks of Ni_3Sn_2 alloy and rGO coexist in the XRD, suggesting the coexistence of the Ni_3Sn_2 submicro spheres and rGO nanosheets in the $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite. To further understand the structural properties, Raman spectra of bare Ni_3Sn_2 and $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite are measured. As shown in Fig. 4b, the $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite gives two characteristic peaks at 1355 and 1585 cm^{-1} , which are designated as the disorder (D) and graphitic (G) bands of carbon, respectively. The value of I_D/I_G for $\text{Ni}_3\text{Sn}_2@\text{rGO}$

composite is 1.087, indicating a higher extent of disorder in rGO, which may be due to the insertion of Ni_3Sn_2 spheres between rGO sheets, resulting in a more disordered structure and more defects in the reduction process. Furthermore, it can be also an evidence to confirm that the graphene nanosheets are successfully fabricated via the solvothermal reduction process.

To determine the actual content of rGO in the composite, thermogravimetry analysis (TGA, Fig. S5 in Supplementary Materials) has been conducted. The weight percentage of rGO in the composite is calculated based on the equation below assuming the final residues converted into SnO_2 and NiO [22];

$$\text{rGO}(\text{wt.}\%) = 1 - (\text{wt \% of composite at } 900^\circ\text{C}) / (\text{wt \% of } \text{Ni}_3\text{Sn}_2 \text{ sample at } 900^\circ\text{C})$$

Therefore, on the basis of the TG curves and the weight of final residues, the approximate proportion of rGO in the composite is evaluated to be 11.1 wt. %.

In view of the mixed composite and structure, the obtained samples are expected to dramatically benefit energy-related applications, such as LIBs, supercapacitors and magnetic materials. Herein, the Ni_3Sn_2 prepared with a Ni^{2+} content of 1 mmol and the composite with the rGO content of 11.1 wt. % have been taken as examples to evaluate their electrochemical performances as anode materials for LIBs by cyclic voltammetry (CV) and charge-discharge cycling tests using two-electrode CR 2025 coin-type cells.

Fig. 5a and b present the first four CV curves of the bare Ni_3Sn_2 alloy and the $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite at a scan rate of 0.2 mV s^{-1} , respectively. In the first cathodic sweep, peaks appear at 1.39 V for Ni_3Sn_2 and 1.59 V for $\text{Ni}_3\text{Sn}_2@\text{rGO}$ are contributed to the formation of a thin film resulting from a catalytic decomposition of electrolyte [27]. It is irreversible and disappears in the following cycles. The cathodic peaks appeared at approximately 0.6 V are related to the lithium insertion into Ni_3Sn_2 . Also, the anodic peaks observed at 1.04 V are connected with the de-insertion of lithium ion from Ni_3Sn_2 [19]. Another cathodic peak around 0.01 V is related to the formation of $\text{Li}_{4.4}\text{Sn}$ phase [26]. One anodic peak positioned at 0.45 V is corresponded to the de-alloying process. It is interesting to note that the intensity of peaks located at 0.63V increases along with cycles, but the intensity of peaks located at 1.04 V decreased. This result indicates that the de-lithiation process might have a dynamic change between two chemical states [28]. The dynamic changes reflect that the electrochemical process of the

Ni₃Sn₂ is expected to evolve a first irreversible activation step (1) and a reversible electrochemical process subsequently (2) [13, 29].

In addition, there are a new cathodic peak at 0.89 V and anodic peak at 1.25 V (Fig. 5b), which correspond to the lithium insertion into and extraction from rGO, respectively [7]. Moreover, the capacitive contribution from the carbon component leads to significant cathodic and anodic current densities over a wide potential window [30]. The CV results are well consistent with the data reported in the literatures [13, 22]. Notely, it can be observed in Fig. 5a that the CV behavior presents a slight decrease from second cycle to later cycles, indicating that the specific capacity of bare Ni₃Sn₂ continuous declines during cycles; By contrast, the nearly overlapped 2nd to 4th CV curves of the Ni₃Sn₂@rGO composite reveals its good cycle life.

Fig. 5c and d show the initial two charge and discharge curves of the bare Ni₃Sn₂ alloy and the Ni₃Sn₂@rGO composite measured between 0.01 and 2.0 V at a current density of 100 mA g⁻¹, respectively. For the insertion with lithium, the value of voltage decreases along with the increase of specific discharge capacity. A wide flat plateau from about 0.4 V to 0.01 V is attributed to the reaction of Sn to alloyed Li_{4.4}Sn. During lithium exsertion process, the delithiation reaction from Li_{4.4}Sn to Sn is represented by one plateau around 0.5 V. The discharge voltage platforms shown in the voltage-capacity curves (Fig. 5c and d) are homologous with the corresponding cathodic peaks in Fig. 5a and b, separately. The first discharge capacities of 1754 and 1315 mAh g⁻¹ and charge capacities of 874 and 561 mAh g⁻¹ deliver by the bare Ni₃Sn₂ alloy and the Ni₃Sn₂@rGO composite, corresponding to irreversible capacity losses of 880 and 754 mAh g⁻¹, respectively. Note that all the capacity values are calculated based on the contents of Sn and rGO. As shown in Fig. S6a (Supplementary Materials), the tremendous irreversible capacity loss of bare Ni₃Sn₂ alloy is probably ascribed to the formation of solid electrolyte interphase (SEI) films on the surface of Ni₃Sn₂ submicro sphere. However, there are no obvious SEI films on the surface of Ni₃Sn₂ submicro sphere which coated with rGO (Fig. S6b, Supplementary Materials). So, compared with the bare Ni₃Sn₂ alloy, decreased irreversible capacity loss of Ni₃Sn₂@rGO composite can be attributed to the decreased formation of SEI layer on the electrode surface because the coated rGO can decrease the contact area between active materials and

the electrolyte, which are in accordance of the reported literature [31].

Fig. 5e depicts the charge-discharge capacities *versus* cycle number profiles of as-prepared products at a current density of 100 mA g^{-1} . It is evident that the bare Ni_3Sn_2 exhibits an enhanced lithium storage performance compared with the commercial pure Sn microparticle electrode, which occurs rapid capacity degradation just cycled 20 times and a capacity of only 66 mAh g^{-1} is left (Fig. S7, Supplementary Materials). This enhancement may ascribe to the identical shapes and uniform sizes of Ni_3Sn_2 alloy as well as the addition of inert nickel matrix. However, the specific capacity of bare Ni_3Sn_2 still displays a continuous decline and decreases from 951.4 mAh g^{-1} after first cycle to 181.7 mAh g^{-1} after 200 cycles. Therefore, much improvement is still need to its capacity retention. This barrier can be broken through by the $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite. Though the second discharge capacity decays to 673 mAh g^{-1} , the $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite anode shows a stable cycling performance after the first cycle. A high reversible discharge capacity of 554 mAh g^{-1} can be retained even after 200 cycles. For comparison, the electrochemical behavior of pure rGO as anode material for LIBs is exhibited in Fig. S8 (Supplementary Materials). It can be seen that the pure rGO has long cycling stability but low capacity, indicating that the specific capacity of $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite anode delivered mainly by the tin in Ni_3Sn_2 intermetallic instead of the rGO. In addition, the cycling performances of the Ni_3Sn_2 submicro spheres prepared with different contents of rGO 0 wt. %, 4.5 wt. %, 11.1 wt. % and 22.0 wt. % are comparatively illustrated in Fig. S9 (Supplementary Materials). With addition of a small number of rGO, the cycling stability of the composite enhances but not markedly. When the additive amount of rGO reaches 11.1 wt. %, the composite has the best comprehensive performances in terms of specific capacity and cycling stability. However, once the additive amount of rGO exceeds the best point, such as 22.0 wt. %, the specific capacity of the composite begins to decline, although possessing excellent cycling stability. Therefore, the additive amount of rGO should be controlled in a value of about 11.1 wt. %. All results demonstrate that the cycling life of $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite can be remarkably improved by using promising rGO matrix.

Along with the high specific capacity and excellent cycling stability, the high rate discharge ability of the $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite electrode is shown in the Fig. 5f. It can be seen that the $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite electrode shows a decent rate capability with average discharge capacities of 631.1, 525.8,

421.9 and 300.1 mAh g⁻¹ at current densities of 200, 400, 800 and 1600 mA g⁻¹, separately. Importantly, the discharge specific capacity resumes well to 561 mAh g⁻¹ and maintains at the value of 583 mAh g⁻¹ after 100 cycles when the current density is lowered to 100 mA g⁻¹. Therefore, in consideration of the excellent cycling and rare performances, the Ni₃Sn₂@rGO composite is deemed as a promising candidate anode material for future LIBs.

EIS measurements of bare Ni₃Sn₂ and the Ni₃Sn₂@rGO composite before and after 200 cycles have been conducted and well fitted on the corresponding equivalent circuit. The EIS measurements are carried out at the open circuit potential in the frequency range from 700 kHz to 100 mHz with perturbation amplitude of 5 mV. As displayed in Fig. 6a and b, the bulk resistance (R_s) of electrodes, electrolyte and separator is reflected by the high frequency intercept of the semicircle. During cycles, R_s equals to 1.98 and 5.49 Ω for bare Ni₃Sn₂ and Ni₃Sn₂@rGO composite, respectively. Before cycles, the depressed semicircles at high frequency are generally considered as charge transfer impedance (R_{ct}). It can be seen that the Ni₃Sn₂@rGO composite exhibits decreased charge transfer impedance (R_{ct} = 80.49 Ω), lower than that of bare Ni₃Sn₂ (R_{ct} = 190.3 Ω). This result indicates that the rGO matrix can provides a highly conductive network to boost the electronic conductivity, promote the electronic transport and enable much easier charge transfer on the electrode/electrolyte interface. After 200 cycles, the R_{ct} is replaced by the SEI layer impedance (R_f) as well as the R_{ct}. The R_f appears to be 149.2 Ω for bare Ni₃Sn₂ and 115.5 for Ni₃Sn₂@rGO composite, indicating the thick SEI layer formed during cycles. Notely, the decreased R_f for Ni₃Sn₂@rGO composite further confirms that the coated rGO can decrease formation of SEI film. In addition, the little variation of R_{ct} for bare Ni₃Sn₂ and Ni₃Sn₂@rGO composite before and after 200 cycles implies that the kinetic process is favored and structural stability is maintained.

The EIS results can also be recorded to calculate the lithium-ion diffusion coefficient in electrode by using the following formula [32, 33].

$$D = \frac{RT}{n^2 F^2 A \sqrt{2} \cdot \sigma C_{Li}}$$

Here, the D is the diffusion coefficient of lithium-ion in electrode, the R is the gas constant (R = 8.314), the T is the indoor temperature (T = 298.15 K), the n is the number of transferred electrons, the F is Faraday constant (F = 96485.3 C mol⁻¹), the A is the reaction area of electrode (A = 1.13 cm²), the σ is

the coefficient of Warburg impedance obtained from the slope of straight line of Z_{Real} against $\omega^{1/2}$, and the C_{Li} is the lithium-ion concentration in the electrode. After calculating according to the above-mentioned formula, the lithium diffusion coefficients for the bare Ni_3Sn_2 and the $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite are $1.346 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ and $1.886 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$, respectively. In comparison, the $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite shows the higher lithium diffusion coefficient, which could be attributed to the addition of conductive rGO serving as an efficient diffusion channel for lithium-ion. Furthermore, the higher lithium diffusion coefficient also endows the $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite with high rate discharge ability (Fig. 5f).

Based on the above analysis, the splendid electrochemical performances of the $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite can be attributed to the synergistic effect of Ni_3Sn_2 alloys and rGO conductive matrix: (1) the *in situ* embedded Ni_3Sn_2 submicro spheres in the composite with identical shape and uniform size can accommodate structural stress and prevent the aggregation of Sn; (2) the inert nickel matrix in the Ni_3Sn_2 alloy could buffer the volume change produced by tin in the lithiation-delithiation process; (3) the rGO acts as a good buffering matrix and provides a highly conductive network, to further enhance the electrochemical performances; (4) much nanospace exists between the Ni_3Sn_2 submicro spheres and rGO during the reduction process of Go, which can also contribute to buffer the volume change in charge-discharge process. Because of the comprehensive impacts of the above mentioned factors, the $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite prepared by one-step solvothermal method exhibits enhanced electrochemical performances.

4. Conclusions

In summary, the $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite has been successfully synthesized by a one-step solvothermal method. In this composite, the Ni_3Sn_2 submicro spheres are *in situ* encapsulated in the rGO matrix with identical ball-like shapes and uniform sizes, accompanying with much nanospace existence between the Ni_3Sn_2 submicro spheres and rGO. Owing to the mechanical capacity to accommodate volume variations of Sn, the as-prepared $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite exhibits superior lithium storage performances in terms of cycling stability and rate discharge ability. The significant electrochemical performances are attributed to the synergistic effect of synergistic effects between Ni_3Sn_2 alloy and rGO matrix. Based on its excellent electrochemical performances, the $\text{Ni}_3\text{Sn}_2@\text{rGO}$ composite is

considered as one of promising candidate anode materials for future LIBs.

Acknowledgements

This work is financially supported by the National Science Foundation of China (Project No. 11204102, 20111061, 21373198 and 51475207), the station Foundation of Ministry of Education for New Teachers (Project No. 20120061120041), Open Project of State Key Laboratory of Superhard Materials (Project No. 201410), and the China Postdoctoral Science Foundation (Grant No. 2015m580253).

References

- [1] R. Van Noorden, A Better Battery, *Nature*, 507 (2014) 26-28.
- [2] J.S. Zhu, D.L. Wang, T.F. Liu, C.F. Guo, Preparation of Sn-Co-graphene composites with superior lithium storage capability, *Electrochimica Acta*, 125 (2014) 347-353.
- [3] M.N. Obrovac, V.L. Chevrier, Alloy Negative Electrodes for Li-Ion Batteries, *Chemical reviews*, 114 (2014) 11444-11502.
- [4] Y.H. Xu, Q. Liu, Y.J. Zhu, Y.H. Liu, A. Langrock, M.R. Zachariah, C.S. Wang, Uniform Nano-Sn/C Composite Anodes for Lithium Ion Batteries, *Nano letters*, 13 (2013) 470-474.
- [5] B. Scrosati, J. Hassoun, Y.K. Sun, Lithium-ion batteries. A look into the future, *Energ Environ Sci*, 4 (2011) 3287-3295.
- [6] Y. Zhao, X.F. Li, B. Yan, D.J. Li, S. Lawes, X.L. Sun, Significant impact of 2D graphene nanosheets on large volume change tin-based anodes in lithium-ion batteries: A review, *J Power Sources*, 274 (2015) 869-884.
- [7] Y.J. Zhang, L. Jiang, C.R. Wang, Preparation of a porous Sn@C nanocomposite as a high-performance anode material for lithium-ion batteries, *Nanoscale*, 7 (2015) 11940-11944.
- [8] K.D. Kepler, J.T. Vaughey, M.M. Thackeray, Copper-tin anodes for rechargeable lithium batteries: an example of the matrix effect in an intermetallic system, *Journal of Power Sources*, 81 (1999) 383-387.
- [9] R.Z. Hu, M.Q. Zeng, M. Zhu, Cyclic durable high-capacity Sn/Cu₆Sn₅ composite thin film anodes for lithium ion batteries prepared by electron-beam evaporation deposition, *Electrochimica Acta*, 54 (2009) 2843-2850.
- [10] D.B. Polat, J. Lu, A. Abouimrane, O. Keles, K. Amine, Nanocolumnar Structured Porous Cu-Sn Thin Film as Anode Material for Lithium-Ion Batteries, *Acs Appl Mater Inter*, 6 (2014) 10877-10885.
- [11] J.T. Li, J. Swiatowska, A. Seyeux, L. Huang, V. Maurice, S.G. Sun, P. Marcus, XPS and ToF-SIMS study of Sn-Co alloy thin films as anode for lithium ion battery, *Journal of Power Sources*, 195 (2010) 8251-8257.
- [12] G. Ferrara, C. Arbizzani, L. Damen, M. Guidotti, M. Lazzari, F.G. Vergottini, R. Inguanta, S. Piazza, C. Sunseri, M. Mastragostino, High-performing Sn-Co nanowire electrodes as anodes for lithium-ion batteries, *J Power Sources*, 211 (2012) 103-107.
- [13] J. Liu, Y.R. Wen, P.A. van Aken, J. Maier, Y. Yu, Facile Synthesis of Highly Porous Ni-Sn

Intermetallic Microcages with Excellent Electrochemical Performance for Lithium and Sodium Storage, *Nano letters*, 14 (2014) 6387-6392.

[14] M. Tian, W. Wang, Y.J. Wei, R.G. Yang, Stable high areal capacity lithium-ion battery anodes based on three-dimensional Ni-Sn nanowire networks, *Journal of Power Sources*, 211 (2012) 46-51.

[15] X.L. Wang, M. Feygenson, H.Y. Chen, C.H. Lin, W. Ku, J.M. Bai, M.C. Aronson, T.A. Tyson, W.Q. Han, Nanospheres of a New Intermetallic FeSn₅ Phase: Synthesis, Magnetic Properties and Anode Performance in Li-ion Batteries, *J Am Chem Soc*, 133 (2011) 11213-11219.

[16] M. Chamas, P.E. Lippens, J.C. Jumas, K. Boukema, R. Dedryvere, D. Gonbeau, J. Hassoun, S. Panero, B. Scrosati, Comparison between microparticles and nanostructured particles of FeSn₂ as anode materials for Li-ion batteries, *J Power Sources*, 196 (2011) 7011-7015.

[17] F.X. Xin, H.J. Tian, X.L. Wang, W. Xu, W.G. Zheng, W.Q. Han, Enhanced Electrochemical Performance of Fe_{0.74}Sn₅@Reduced Graphene Oxide Nanocomposite Anodes for Both Li-Ion and Na-Ion Batteries, *ACS applied materials & interfaces*, 7 (2015) 7912-7919.

[18] H. Guo, H.L. Zhao, X.D. Ha, Spherical Sn-Ni-C alloy anode material with submicro/micro complex particle structure for lithium secondary batteries, *Electrochem Commun*, 9 (2007) 2207-2211.

[19] H.R. Jung, W.J. Lee, Preparation and Characterization of Ni-Sn/Carbon Nanofibers Composite Anode for Lithium Ion Battery, *Journal of the Electrochemical Society*, 158 (2011) A644-A652.

[20] R.Z. Hu, H. Liu, M.Q. Zeng, H. Wang, M. Zhu, Core/shell and multi-scale structures enhance the anode performance of a Sn-C-Ni composite thin film in a lithium ion battery, *J Mater Chem*, 21 (2011) 4629-4635.

[21] X.Y. Fan, Y.X. Shi, J.J. Wang, J. Wang, L. Xu, L. Gou, D.L. Li, Electrochemical synthesis and lithium storage properties of three-dimensional porous Sn-Co alloy/CNT composite, *Ionics*, 19 (2013) 1551-1558.

[22] R.G. Ma, Z.G. Lu, S.L. Yang, L.J. Xi, C.D. Wang, H.E. Wang, C.Y. Chung, Facile synthesis and electrochemical characterization of Sn₄Ni₃/C nanocomposites as anode materials for lithium ion batteries, *J Solid State Chem*, 196 (2012) 536-542.

[23] J.P. Li, P. Wu, Y.W. Tang, X.L. Xu, Y.M. Zhou, Y. Chen, T.H. Lu, Three-dimensional mesoporous Sn-Ni@C network derived from cyanogel coordination polymers: towards high-performance anodes for lithium storage, *Crystengcomm*, 15 (2013) 10340-10345.

[24] M. Uysal, T. Cetinkaya, A. Alp, H. Akbulut, Active and inactive buffering effect on the electrochemical behavior of Sn-Ni/MWCNT composite anodes prepared by pulse electrodeposition for lithium-ion batteries, *J Alloy Compd*, 645 (2015) 235-242.

[25] W.S. Hummers, R.E. Offeman, Preparation of Graphitic Oxide, *J Am Chem Soc*, 80 (1958) 1339-1339.

[26] J.Z. Chen, L. Yang, S.H. Fang, Z.X. Zhang, S.I. Hirano, Facile fabrication of graphene/Cu₆Sn₅ nanocomposite as the high performance anode material for lithium ion batteries, *Electrochimica Acta*, 105 (2013) 629-634.

[27] D.S. Guan, J.Y. Li, X.F. Gao, C. Yuan, A comparative study of enhanced electrochemical stability of tin-nickel alloy anode for high-performance lithium ion battery, *J Alloy Compd*, 617 (2014) 464-471.

[28] H.Y. Qin, X.B. Zhao, N.P. Jiang, Z.P. Li, Solvothermal synthesis and ex situ XRD study of nano-Ni₃Sn₂ used as an anode material for lithium-ion batteries, *J Power Sources*, 171 (2007) 948-952.

[29] J. Hassoun, S. Panero, P. Simon, P.L. Taberna, B. Scrosati, High-rate, long-life Ni-Sn

nanostructured electrodes for lithium-ion batteries, *Adv Mater*, 19 (2007) 1632-1635.

[30] Z. Edfouf, C. Fariaut-Georges, F. Cuevas, M. Latroche, T. Hezeque, G. Caillon, C. Jordy, M.T. Sougrati, J.C. Jumas, Nanostructured Ni_3Sn_4 intermetallic compound: An efficient buffering material for Si-containing composite anodes in lithium ion batteries, *Electrochim Acta*, 89 (2013) 365-371.

[31] N. Liu, Z.D. Lu, J. Zhao, M.T. McDowell, H.W. Lee, W.T. Zhao, Y. Cui, A pomegranate-inspired nanoscale design for large-volume-change lithium battery anodes, *Nat Nanotechnol*, 9 (2014) 187-192.

[32] M. Uysal, T. Cetinkaya, M. Kartal, A. Alp, H. Akbulut, Production of Sn-Cu/MWCNT composite electrodes for Li-ion batteries by using electroless tin coating, *Thin Solid Films*, 572 (2014) 216-223.

[33] J. Wang, H.L. Zhao, X.T. Liu, J. Wang, C.M. Wang, Electrochemical properties of SnO_2 /carbon composite materials as anode material for lithium-ion batteries, *Electrochim Acta*, 56 (2011) 6441-6447.

Figure Captions

Fig. 1. Schematic illustration of the synthesis route for Ni_3Sn_2 @rGO composite.

Fig. 2. (a, b) SEM images; (c) TEM image and (d) histogram of diameter distribution of bare Ni_3Sn_2 submicro spheres.

Fig. 3. (a, b) SEM images, (c, d) TEM images of the Ni_3Sn_2 @rGO composite, (e) HAADF-STEM image and (f, g) element mappings of the as-synthesized Ni_3Sn_2 @rGO composite.

Fig. 4. (a) XRD patterns and (b) Raman spectra of (1) bare Ni_3Sn_2 and (2) Ni_3Sn_2 @rGO composite.

Fig. 5. CV curves of (a) Ni_3Sn_2 and (b) Ni_3Sn_2 @rGO; voltage-capacity curves of (c) Ni_3Sn_2 and (d) Ni_3Sn_2 @rGO; (e) cycling performances of Ni_3Sn_2 and Ni_3Sn_2 @rGO; and (f) rate capability of Ni_3Sn_2 @rGO composite.

Fig. 6. Nyquist plots of bare Ni_3Sn_2 alloy and Ni_3Sn_2 @rGO composite (a) before cycles, (b) after 200 galvanostatic cycles; (c) the corresponding equivalent circuit used for EIS measurements (c) before cycles, (d) after 200 galvanostatic cycles.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6