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A comparative study of enhanced electrochemical stability of tin–nickel alloy anode for high-performance lithium ion battery

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ABSTRACT

Sn and Sn–Ni alloy nanoparticles are synthesized readily by co-precipitation method for their applications in Li-ion batteries. It is found that nickel not only affects the phase structure and morphology of the alloy, but also impacts Li–Sn alloying and dealloying behaviors. In Li-ion batteries, the alloy electrodes deliver stronger cycling stability than the pure Sn anode. In tests the former exhibits a final capacity of 228.5 mA h g^{-1} over 50 cycles, while the latter displays 14.3 mA h g^{-1}. Smaller current for battery cycles increases capacities of the alloys beyond 408.4 mA h g^{-1}. The mechanism of enhanced stability of Sn–Ni alloys is examined. Redox reaction characteristics and Li-ion transfer kinetics at these anodes after different cycles are investigated by cyclic voltammetry and electrochemical impedance spectroscopy, which are considered to associate with buffering effects of nickel and structural integrity of electrodes. Li–Sn alloying and dealloying reactions cause volume changes and induce stress that releases in the formation of tiny cracks within the particles. The cracks accelerate side reactions and decelerate charge transport, detrimental to the electrode stability. Nickel cushions the volume variations and reduces the stress and cracks at Sn–Ni alloy anodes to allow them to maintain better electrode integrity and smaller charge resistance, thus yielding their improved Li-ion intercalation stability during long-term cycling.

1. Introduction

Currently, soaring development in electronic devices and electric vehicles urgently demands mobile power sources with high energy capacity, large power density, good safety and durability in quite restricted volume and weight. Rechargeable lithium-ion batteries (LIBs) have become an excellent candidate due to their good energy storage density, light weight, low self discharge and long lifespan without memory effects [1,2]. Graphite is the most commonly-used anode material in currently commercial LIBs, with a theoretical capacity of 372 mA h g^{-1}. However, the capacity of carbon materials is still too low to meet the demands of LIBs with large energy and power density [3], so a group of novel anode materials have been developed to replace it, such as Si [4], Sn [5], Al [6], alloys [7], metal oxides [8–10] and $Li_4Ti_5O_{12}$ [11,12]. Among them, Sn is one of the most prospective anode materials in LIBs as a result of its large theoretical capacity (993 mA h g^{-1} [13]), high conductivity and non-toxicity. However, Sn particles are easily cracked and pulverized by its huge volume change (~300%) during Li–Sn alloying and dealloying activities. It causes a loss of contact between the active material and current collector, resulting in the poor electrochemical stability of Sn anodes. To alleviate this problem, a series of tin-based intermetallic compounds have been proposed, such as Co–Sn, Cu–Sn, Fe–Sn, Sn–Ni and Sb–Sn [14,15]. Nickel, a Li-inactive element, serves as a buffer matrix of Sn in Sn–Ni alloys, which can restrict the volume change of Sn and maintain the structural integrity of alloy electrodes to yield greatly enhanced cycling performance at a loss of certain specific capacities with respect to the theoretical capacity of pure tin. Optimization of the Sn–Ni alloys is indispensable to improve their cycle stability and specific capacities because they are not totally satisfactory yet with prolonged cycling. Some methods have been described in previous literature, including composition adjustment [16], doping or coating [17–19], and composites with carbonaceous materials [20,21]. On the other hand, a detailed study on effects of nickel content on the electrochemical reaction and stability of Sn–Ni alloy anodes in long-term battery cycling has been rarely seen hitherto. As a result, this study is initiated to discuss the characteristics of electrode reactions, structural integrity and charge transfer at Sn and Sn–Ni alloy electrodes post various cycles by means of cyclic voltammetry (CV) and impedance spectroscopy techniques. The characteristics of CV peaks reflect Li–Sn alloying and dealloying behaviors that cause volume change, stress relaxation and particle cracking at electrodes, and the impedance analyses unveil the electronic and ionic transfer processes that

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are affected by the mechanical integrity of these electrodes during cycling. Evolutions of the integrity and conductivity of tin-based electrodes further determine their cycling stability. Therefore, the correlation between electrode reactions, charge transfer resistance and capacity retention may serve as a useful indicator to optimize the design of Sn-based intermetallic anode materials for high-performance LIBs.

In this work, both Sn and Sn–Ni alloy nanoparticles were prepared by a chemically reductive co-precipitation route. Effects of the nickel on the phase composition of the Sn–Ni alloys were examined by X-ray diffraction. Anodes consisting of these metal particles were charged and discharged for tens of cycles, and electrochemical behaviors of the materials were characterized at multiple cycling stages by cyclic voltammetry and electrochemical impedance spectroscopy. It was discovered that nickel is able to improve the capacity stability of tin anodes, which was analyzed in combination of electrode reactions, mechanical integrity and electrochemical impedance.

2. Experimental

0.45 g sodium citrate, 5.35 mg $NiCl_2{\cdot}2H_2O$ and a different amount of $SnCl_2{\cdot}2H_2O$ were mixed together and dissolved into 45 ml distilled water. After stirred for 15 min, this solution was added dropwise to 50 ml $NaBH_4$ (2 M) aqueous solution under vigorously stirring. The superfluous $NaBH_4$ was used to ensure a complete reduction of the metal ions. After 2 h redox reaction, the black product was collected by centrifugation on a Thermo IEC centrifuge at a speed of 10,000 rpm, washed with deionized water and ethanol thoroughly. Later, the product was dried at 100 °C for 12 h under vacuum. For comparison, neat Sn nanoparticles were prepared by the similar process without Ni source. Three samples were obtained and designated as SN-A, SN-B, SN-C according to nickel content; namely, SN-A for the bare Sn particles (or electrodes), SN-B for Sn–Ni alloy particles and SN-C for alloy particles containing more nickel.

A Hitachi S-4800 scanning electron microscope (SEM) and a Hitachi H9000NAR transmission electron microscope (TEM) were used to observe the Sn and Sn–Ni particles. Their crystallographic structure was determined by X-ray diffraction (XRD) using a Scintag XDS 2000 X-Ray diffractometer with Cu Kα radiation at a scan rate of 2° min^{-1}. Chemical composition of these particles was characterized by an energy dispersive X-ray spectroscopy (EDX) with an XFlash detector (Bruker AXS).

Cu foils (12 μm thick) were cleaned with acetone and dried in air. A slurry was made from a mixture of as-prepared powder, Super-P carbon black (Alfa Aesar, 99.5%), and carboxymethyl cellulose in a weight ratio of 80:10:10. The slurry was then spread on the copper foil using a blade casting method, followed by drying in air at room temperature and in vacuum at 100 °C for 12 h, to produce composite electrodes. Later, they were pressed by a Carver Lab Press with a pressure of 8 MPa for 10 s and then cut into disks with a diameter of 3/8 inch. Masses of the electrode material are ca. 1 mg. CR2032 coin cells were then assembled to investigate electrochemical behaviors of the samples acting as the working electrode. A lithium disc served as the counter and reference electrode in cells, which was separated from the working electrode by a porous Celgard-2320 separator composed of 20-μm-thick polypropylene (PP)/polyethylene/PP trilayer film. Organic electrolytes were 1 M lithium hexafluorophosphate ($LiPF_6$) dissolved in a mixed solvent of ethylene carbonate and diethylene carbonate with 1:1 volume ratio (Novolyte Technologies, Inc.). All the coin cells were assembled in an Ar-filled glove box with oxygen and moisture levels lower than 1 ppm. Cyclic voltammetric measurements were performed on a VersaSTAT 3F potentiostat/galvanostat with a frequency response analyzer (Princeton Applied Research, USA) at a scan rate of 0.1 mV s^{-1} between 0.05 and 2.0 V. The galvanostatic charge–discharge cycling was carried out on LANHE automatic battery testers at a small current (100 mA g^{-1}) for the first two cycles and a large current up to 500 mA g^{-1} for rest cycles. AC impedance measurements were also conducted on these cells at a potential of ~0.55 V from 100 kHz to 0.1 Hz with a perturbation of 5 mV applied.

3. Results and discussion

Fig. 1 presents the SEM images of as-prepared Sn and Sn–Ni alloy nanoparticles. After drying in vacuum, bare Sn particles are heavily agglomerated, which forms large particles in hundreds of nanometers size (Fig. 1a). On the other hand, the Sn–Ni alloy nanoparticles have a different morphology from the pure Sn (Fig. 1b). Considerable tiny particles with a size of about 30 nm are agglomerated to some extent, yielding particles smaller than those in SN-A. SN-C is also consisting of numerous nanoparticles showing the same appearance as those in SN-B. In order to see details of the as-prepared alloy nanoparticles, SN-B is further characterized by TEM technique. It can be observed clearly from Fig. 1c that the alloy nanoparticles are agglomerated, with a wide particle size ranging from 10 to 30 nm. Fig. 1d gives a high-resolution TEM image taken from a SN-B crystallite where an interplanar distance of 0.251 nm is believed to accord with (002) plane of Ni_3Sn_4 crystals.

An EDX analysis was also performed on these nanoparticles under SEM observation. In the EDX spectrum of SN-A (Fig. 2a), distinct peaks between 3.0 and 4.1 keV correspond to the tin element, with no Ni peak detected in this sample. The aluminum is from the holder used for placing the sample during EDX. In contrast, peaks at 0.85 KeV and 7.46 KeV in the SN-B spectrum are indexed to Ni element (Fig. 2b), together with a series of Sn peaks recorded, indicating the coexistence of Sn and Ni in the SN-B nanoparticles. A quantitative analysis of SN-B spectrum further reveals the Sn/Ni atomic ratio of ca. 32/23 in this sample. Both tin and nickel elements are also found in SN-C particles by EDX, but the atomic ratio of Sn/Ni drops to ca. 23/32. According to the two spectra, impurities, such as sodium and chlorides, are not observed in these particles. Hence, it is verified that Sn and Sn–Ni alloy nanoparticles have been successfully produced by the co-precipitation approach, and the content of tin is decreased from 100 at% in SN-A, to 58 at% in SN-B and finally to 42 at% in SN-C.

Fig. 3 illustrates XRD patterns of as-obtained bare Sn and Sn–Ni alloy nanoparticles. In the pattern of SN-A diffraction peaks (200), (101), (220), (211), (301), (112), (400) and (321) of tetragonal Sn phase (JCPDS no. 04-0673, space group I41/amd) are observed at the 2θ angles of 30.6°, 32°, 43.8°, 44.9°, 55.3°, 62.5°, 63.7° and 64.5°, which demonstrates good crystallization of as-prepared tin. The average size of Sn crystallites is estimated around 30 nm using Scherrer equation [22]. In contrast, XRD patterns of Sn–Ni alloys appear very differently. In the pattern of SN-B, intermetallic Ni_3Sn_4 phase is observed, with peaks viewed at 2θ angles of 30.4°, 31.7°, 35.8°, 43.5° and 44.6°, corresponding to the crystal plane (111), (310), (002), (-511) and (112) of its monoclinic structure (JCPDS no. 04-0845, space group I2/m), respectively. In addition to Ni_3Sn_4, diffraction peaks of a metastable alloy phase (M) are also present at 2θ angles of 28.5°, 40.7°, 42.4° and 46.5° in SN-B. The metastable phase is thought as formed by melting of nickel into tin crystals, which does not appear in the equilibrium phase diagram of Sn–Ni bimetal system [23,24]. As the ratio of Sn/Ni decreases, XRD patterns of Sn–Ni alloys vary accordingly. A remarkable discrepancy in the patterns of SN-B and SN-C is the absence of diffraction peaks of the metastable phase due to lack of tin crystals. Moreover, it is worth noting that there is no any diffraction peaks belonging to nickel, metal oxides or other Sn–Ni alloys phases as identified from these patterns.

In this study the lithiation and delithiation process of Sn and Sn–Ni alloy nanoparticles are compared to investigate the effects of nickel content on the electrochemical properties. Fig. 4a displays capacities of the three electrodes over 50 electrochemical cycles at 500 mA g^{-1} with two initial cycles at a small current of 100 mA g^{-1} in a potential range from 0.05 V to 2.0 V versus Li/Li^+. Obviously, a rapid capacity drop occurs in the first two cycles for all samples, mainly due to the decomposition of electrolytes and formation of SEI layers on the electrode surface, or the irreversible Li-ion insertion into the electrode materials (Li^+ trapping effects [24]). Their capacities decline again upon the current switched to 500 mA g^{-1} at the third cycle, but proceed differently in the following cycles. That is, SN-A anode continues its rapid capacity decay, while the capacity fading of SN-B and SN-C is greatly slowed down. In general, the two alloy electrodes deliver significantly higher capacities than the bare Sn anode during prolonged cycling. As shown in the figure, SN-B delivers the largest discharge capacity of 487 mA h g^{-1} and