



Study of tin-sulphur-carbon nanocomposites based on electrically exploded tin as anode for sodium battery



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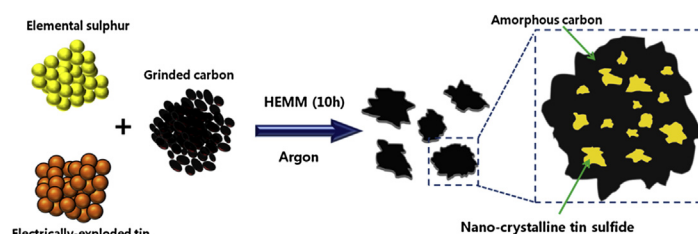
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HIGHLIGHTS

- Synthesis of Tin-Carbon nano-particles (Sn@C) through electrical wire explosion.
- Sn@C-sulphur-carbon nanocomposites synthesized through high energy mechanical milling.
- Response of electrode materials in fluoroethylene carbonate added electrolyte.
- Excellent electrochemical performance of the electrode materials.

GRAPHICAL ABSTRACT



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ABSTRACT

An electrochemical study of tin-sulphur-carbon nano-composites, based on electrically exploded tin-carbon nanoparticles as anode for sodium-ion battery (NIB), is carried out in electrolytes with and without fluoroethylene carbonate (FEC). The composites are synthesized through high energy mechanical milling (HEMM) of electrical exploded tin, sulphur nanoparticles and grinded carbon. The final product consists of tin sulfide nanoparticles embedded in amorphous carbon matrix. The results demonstrate an excellent response for the electrode materials in terms of initial discharge capacity ($>425 \text{ mAhg}^{-1}$) and cyclic performance (415 mAhg^{-1} after 50 cycles). Even more remarkably, at high current densities of 400, 600, and 800 mA g^{-1} , electrodes still offer specific capacities of about 375, 355, and 315 mAhg^{-1} , respectively, suggesting good rate capability of the materials. Furthermore, it is observed that the material response is much better when electrolyte has FEC as an additive which helped in the formation of an optimized SEI layer. Such an improved electrochemical performance of the electrode materials highlights their suitability for the recently emerging Na-ion battery technology.

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1. Introduction

Fueled by the ever growing demands for electric energy, a considerable awareness has been developed to build up sustainable pathways for fulfillment of the current and future energy needs.

Over the years, Li-ion battery (LIB) has been considered as one of the most promising device to fulfil the energy demands due to their high gravimetric and volumetric energy densities, which is why, as of 2013 they stand at a market worth of more than 10 billion dollars [1–3]. However, due to some serious concerns over the availability and cost of Li the interest has been shifted towards exploration of batteries technologies beyond LIB [4]. Na due to its high abundance (2% in earth crust compared to 0.005% for Li), good theoretical capacities of 1160 mA h/g and 1130 mA h/L, similar physical and

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chemical properties to Li, and suitable redox potential (-2.71 V vs. SHE), holds promise to perform comparable to Li-ion battery [5–8]. Recent research in sodium-ion battery (NIB) is mainly focused on the cathode material; however, their limited capacity due to intercalation chemistry and high redox potential is a major problem in achieving higher capacity [8]. This issue can be addressed by designing and developing anode materials based on conversion or (de-)alloying reaction and low redox potentials [9–15]. Similar to Li, Na can make alloys with different metals such as Sn, Sb, Si, Ge, Pb and so on to obtain high capacities [16,17]. Especially Sn, having a theoretical capacity of 847 mAhg^{-1} ($\text{Na}_{15}\text{Sn}_4$), has a very favorable chemistry with Na. However, Sn usually suffers from huge volumetric strain due to the large ionic radius of Na^+ with respect to Li^+ during (de-) sodiation resulting in poor capacity retention. In this regard, various strategies such as use of innovative binders [18], nanostructuring and making composites with carbon and other metals [10–12,18–20] have been reported to limit the volume expansion and enhance the electrode performance. In line with such strategies, synthesis of nano-powder through electrical explosion of metal wires is an interesting technique due to its simplicity and lower cost [21–26]. Following the technique, metal nanoparticle powder with an average particle size of 20–100 nm can be synthesized at a high productivity rate (up to 200 g/h) and lower energy consumption ($\sim 25 \text{ kWh/kg}$) which make it highly suitable for commercial purposes. It has been reported that by exploding metal wire in a carbon containing liquid media, metal-carbon structures can be synthesized [25]. Such structures can potentially assist in controlling the volume expansion of tin during (de-) sodiation.

Herein, tin-carbon nanoparticles (Sn@C) were synthesized through electrical explosion of tin wire in ethanol media. The obtained nanopowders were further mechanically milled with elemental sulphur (S) and grinded carbon (C) to form tin-sulphur-carbon (Sn@C-S-C) nano-composites as NIB anode and their electrochemical study in terms of initial charge/discharge capacity, cyclic performance and rate capability was carried out in electrolytes with and without FEC.

2. Experimental

The Sn@C was obtained by wire explosion of a Sn wire (1 mm in diameter, 60 mm in length, 99.9% in purity) in ethanol. After the explosion, the nano-particles were allowed overnight to sediment gravimetrically. Afterwards, the suspension was dried under vacuum for 2 h at 70°C to obtain Sn@C in nanopowder form. The Sn@C-S-C nanocomposite was prepared by HEMM of Sn@C, elemental S (Alfa-Aesar 99.5% purity, ~ 325 meshes) and grinded carbon (Super-P Black). HEMM was conducted under an argon atmosphere for 10 h. The Sn@C: S was 1: 1 by molar ratio, and the Sn@C-S: C was 8: 2 by weight ratio.

The morphology, phase, and crystal structure of the nanocomposite were determined via FE-SEM (Hitachi S4800), TEM (Philips TF30ST) and X-ray diffractometer (Philips X'pert-MPD) with a Panalytical X'celerator detector with graphite monochromized $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$).

To prepare the electrodes, 70 wt% Sn@C-S-;C composite, 20 wt% Super P-Black, and 10 wt% polyacrylic acid (PAA, 25 wt%) were mixed at 2000 RPM for 15 min to form a slurry, which was then coated onto a copper foil and cured at 100°C for 4 h under vacuum. The active material loading in the electrode was about 2.9 mg cm^{-2} . Coin half-cells were assembled in an argon filled glove box using punched Sn@C-S-;C electrodes, propylene membrane (Celgard 2325, Celgard, Inc., USA) as a separator and Na-metal (purity 99.9%) as the counter electrode. The electrolyte was 1 M NaPF_6 in ethylene carbonate/dimethyl carbonate (1:2, v/v) with and without 5% FEC.

The assembled cells had an open circuit voltage of approximately 2.5 V and were galvanostatically charged/discharged at current densities ranging from 100 mA g^{-1} to 800 mA g^{-1} across a potential range of 0.01–2 V using a multichannel battery tester (TOYO TOSCAT-3100U). dq/dv plots were obtained using WanAtech battery cycler (WBSC3000). The electrochemical impedance spectroscopy (EIS) were conducted via an electrochemical setup (model VMP3, Bio Logic, France) at different bias potentials in a frequency range of 10 kHz–100 MHz with an AC signal amplitude of 10 mV. ZFit software was used to analyze the impedance data.

3. Results and discussion

Fig. 1 shows the schematic representation of the synthesis process for Sn@C-S-C nanocomposites. The tin-carbon core-shell structures obtained through electrical wire explosion process were mechanically milled with elemental S and grinded C for 10 h in Argon atmosphere to obtain the nanocomposites. The final materials consisted of nano-crystallites of tin-sulfide embedded in amorphous carbon, as shown in the figure.

Fig. 2(a) shows the FE-SEM image of the as-prepared Sn@C through electrical explosion technique. From the image the particle size is ca. 60 nm. Also the TEM image (inset: Fig. 2(a)) revealed a core shell type structure with a few nanometers carbon layer coating the Sn nanoparticle. The schematic diagram and digital images of the experimental setup and obtained suspension of the materials are shown in Fig. S1. In a typical experiment, a Sn wire loaded at the electrodes and fully immersed in the ethanol was electrically exploded in a fully covered chamber. For the explosion, a capacitor connected to the electrodes with a coaxial cable through a gap switch, was charged up to 12 kV (3.7 kJ) and then fully discharged through the Sn wire and a discharge circuit. The discharge waveform (Fig. S2) showed an instantaneous current rise up to 60 kA at around 50 μs , after which the current drops instantaneously due to the explosion. Due to high voltage and current a huge energy was build-up resulting in vaporization and ionization of the wire. The plasma generated from the vaporized and ionized wire material is cooled down when interacted with ethanol, resulting in carbon coated Sn nanoparticles in the form of core-shell structure. The obtained Sn@C along with S and grinded C were subjected to HEMM to synthesize Sn@C-S-C nanocomposite as shown in Fig. 2(b) and (c). The FESEM image reveals the porous structure of the composite while the TEM image shows the product to be in the form of agglomerated alloy compounds of SnS well dispersed in an amorphous carbon matrix with nano-crystallite particle size in between a range of approximately 70–100 nm. Such a structure composing SnS alloys well dispersed in carbon matrix offer buffer to excessive volumetric expansion of Sn due to Na (de-) insertion. It is worth mentioning here that the source of carbon in the final structure is partially from the carbon coating due to wire blasting in ethanol and partially from grinded carbon. From the HRTEM image (Fig. 2(d)), two different lattice spacings of 2.3 \AA° and 3.42 \AA° are observed which correspond to the d-spacing of [311] and [201] planes of orthorhombic SnS (JCPDS No. 73-1859), respectively.

Fig. 3(a) shows the XRD patterns for the Sn@C and Sn@C-S-C nanocomposites. For Sn@C the diffraction peaks confirms presence of only Sn in the structure, corresponding to the tetragonal phase of Sn (JCPDS no. 86-2265). On the other hand, for the Sn@C-S-C samples all the peaks correspond to orthorhombic phase of SnS, without presence of either Sn or S impurities. This suggests a complete transformation of the materials to SnS after HEMM.

In Fig. 3(b–e), the TEM elemental mapping of the Sn@C-S-C provide insight into the presence and distribution of Sn, S and C atoms in the structure. The analysis verifies that Sn, S, and C are

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