



Embedding tin nanoparticles in micron-sized disordered carbon for lithium- and sodium-ion anodes



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ABSTRACT

Herein, a new and facile synthesis of a tin-carbon nanocomposite and its electrochemical characterization is presented. Tin nanoparticles were embedded in micron-sized carbonaceous particles, thus successfully preventing the aggregation of tin nanoparticles and buffering the occurring volume strain, which accompanies the reversible (de-)alloying process. Such active material presents specific capacities of around 440 and 390 mAh g⁻¹ for applied specific currents of 0.1 and 0.2 A g⁻¹, respectively, as lithium-ion anode using environmentally friendly and cost-efficient carboxymethyl cellulose as binder. Even more remarkably, at very high specific currents of 2, 5, and 10 A g⁻¹, electrodes based on this composite still offer specific capacities of about 280, 240, and 187 mAh g⁻¹, respectively. In addition, this tin-carbon nanocomposite appears highly promising as anode material for sodium-ion batteries, showing very stable cycling performance in a suitable potential range, and specific capacities of more than 180, 150, 130, and 90 mAh g⁻¹ for an applied specific current of 12.2, 122, 244, and 610 mA g⁻¹, respectively, thus highlighting the high versatility of this composite active material for both Li-ion and Na-ion battery technologies.

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1. Introduction

The tremendous success of lithium-ion batteries as power source for portable electronic devices since their first commercialization in 1991 [1], marking a breakthrough in battery technology, has rendered them as the most promising energy storage devices for hybrid and, most likely, fully electric vehicles [2–5]. However, further improvement in terms of energy and power density is still needed in order to meet the demands of modern society's transportation requirements [5]. For this purpose, with respect to the anode side, Sony recently launched an amorphous composite comprising tin, cobalt, and carbon to replace graphite, the state-of-the-art anode material [6–9]. While cobalt and carbon ensure that the material remains amorphous upon continuous (de-)lithiation [10], tin serves as the main active material, being able to reversibly (de-)alloy with lithium and offering a theoretical specific capacity of more than 990 mAh g⁻¹ [11–14]. In fact, this approach appears to be successful to buffer the occurring volume strain accompanying the (de-)alloying process upon cycling, leading to a pulverization of the electrode active material, finally resulting in a loss of electrical contact and accordingly in a rapid capacity fading [14–17]. Moreover, the aggregation of tin

particles upon continuous (de-)lithiation, observed for tin oxide-based electrodes [18–20] appears to be suppressed. Nevertheless, cobalt is not only toxic but also rather expensive. Therefore, other approaches were pursued, generally related to the integration of metallic tin in carbonaceous matrices. Initial attempts, for instance, reported the encapsulation of tin nanoparticles in hollow carbon spheres [21,22], tin-carbon core-shell particles [23], carbon coated hollow tin nanoparticles [24], tin-filled carbon nanotubes [25], nanofibers [26], nanorods [27], nanocables [28], or nanowires [29], as well as sponge-like [30], chestnut-like [31] or rambutan-like particle morphologies [32], and very recently tin nanoparticles encapsulated in nano- and/or submicron-sized carbon particles [33]. Although such materials certainly presented great improvements relatively to pure tin-based lithium-ion anodes, the most promising results with respect to a possible commercial application have been reported for the homogenous dispersion of fine tin nanoparticles incorporated in micron-sized carbon particles [34–38]. Such materials showed stable specific capacities exceeding 450 mAh g⁻¹ for more than 100 cycles [35,36], excellent rate performance (≈ 200 mAh g⁻¹ at 5C) [35], good compatibility with high voltage cathode materials as, for instance Li[Ni_{0.5}Mn_{1.5}]O₄ [35,37] or Li[Ni_{0.45}Co_{0.1}Mn_{1.45}]O₄ [38], and high thermal stability under ambient atmosphere [36]. Moreover, the introduction of nanoparticulate tin in micron-sized carbon particles provides substantial advantages in terms of safety, ease of handling and processing, as well as relatively high tap densities for increased volumetric energy densities of the final lithium-ion cells based on such anodes.

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Besides, such tin-carbon composites have also shown promising electrochemical performance when applied as sodium-ion anode material, providing specific capacities in the range of 130 [39] to 180 mAh g⁻¹ [40] and a substantially higher tap density compared to hard carbons [39,40], so far the anode material of choice for lab-scale sodium-ion batteries [41,42]. In fact, the obtaining of suitable anode materials for sodium-ion batteries represents certainly the greatest challenge for their commercialization [43–45] and alloying materials would be desirable rather than carbonaceous anodes with respect to the volumetric energy density, which is one of the most important characteristics for energy storage devices [46].

Herein, we report an alternative, extremely simple, cost-efficient, and environmentally friendly one-pot synthesis approach using only tin (IV) acetate and sucrose as precursors for embedding tin nanoparticles in micron-sized carbon particles, thus combining the great advantages of nanoparticulate tin with the high tapping density of micron-sized active material particles. Such morphology not only allows increased volumetric energy densities at the electrode level but moreover a safer handling upon sample processing and electrode preparation. Electrodes prepared based on this Sn-C nanocomposite provide very stable cycling performance and excellent high rate capability for lithium- as well as for sodium-ion anode applications. Moreover, to the best of our knowledge this is the first report on Sn-C composite-based electrodes utilizing sodium carboxymethyl cellulose as binder, enabling a fully water-based processing starting from the materials synthesis up to the electrode preparation.

2. Experimental

2.1. Synthesis of SnO₂ nanoparticles and Sn-carbon composite

Tin (II) acetate (4 g, Sigma–Aldrich) and sucrose (20 g, Acros Organics) were dissolved in 150 ml of deionized water (Millipore) under magnetic stirring. 10 ml of acetic acid (BDH Prolabo) was added in order to improve the solubility of tin (II) acetate in water. Subsequently, the temperature of the solution was slowly increased up to 300 °C until a dry solid remained (SnO_x/C), which was then briefly ground using an agate mortar and transferred into a tubular furnace (R50/250/12, Nabertherm). For obtaining SnO₂ nanoparticles, the solid residue was simply calcined at 450 °C for 3 h under air (heating rate ≈ 3 °C min⁻¹) to remove the residual volatile decomposition products. For obtaining a Sn-carbon nanocomposite (Sn-C), the solid residue was annealed at 1000 °C for 3 h under argon (heating rate ≈ 3 °C min⁻¹) to fully carbonize the organic matter. The weight ratio of the remaining carbon was determined by means of elemental analysis (ElementarVario EL III).

2.2. Morphological, structural, and electrochemical characterization

The prepared samples were characterized by means of X-ray diffraction (XRD) analysis (BRUKER D8 Advance; Cu-K α radiation, λ = 0.154 nm) and scanning electron microscopy (SEM) carried out on a ZEISS Auriga[®] microscope equipped with an energy-dispersive X-ray spectrometer (Oxford Instruments, X-Max^N, 80 mm²). Electrodes based on the Sn-carbon nanocomposite were prepared by dissolving sodium carboxymethyl cellulose (CMC, WALOCEL[™] CRT 2000 PPA 12, Dow Wolff Cellulosics) in deionized water, leading to a 1.25 wt.% solution. Subsequently, the active material (Sn-C) and the conductive carbon (SuperC65[®], TIMCAL) were added, according to an overall electrode composition of 75:20:5 (Sn-C:SuperC65[®]:CMC). The resulting mixture was then dispersed by planetary ball-milling for 2 h using a Vario-Planetary Mill Pulverisette 4 (FRITSCH) set at 800 rpm and the thus obtained

slurry was casted on dendritic copper foil (Schlenk) utilizing a laboratory doctor blade (wet film thickness: 120 μ m). Disk electrodes (ϕ = 12 mm) were punched and dried at room temperature overnight and for 12 h at 120 °C under vacuum. The final electrodes comprised an average mass loading of 1.7–2.0 mg cm⁻². All electrochemical characterizations were performed using three-electrode Swagelok[™]-type cells with either lithium metal foils (Rockwood Lithium, battery grade) or sodium metal (99.8%, Acros Organics) as counter and reference electrodes. Cells were assembled in an MBraun glove box with an oxygen and water content of less than 0.5 ppm. When metallic lithium was used as counter and reference electrodes, a stack of polypropylene fleeces (Freudenberg FS2190) drenched with a 1 M solution of LiPF₆ in a 3:7 volume mixture of ethylene carbonate and diethyl carbonate served as separator. For the cells comprising metallic sodium the working, counter, and reference electrodes were separated by a sheet of Whatman glass fiber drenched with a 0.5 M solution of NaPF₆ in propylene carbonate, containing 2 vol.% of fluoroethylene carbonate (FEC) as electrolyte additive, since it was shown that the addition of a small amount of FEC significantly improves the cycling performance of sodium-ion active materials (including Sn-based electrodes) [42,47–49]. The given potential values refer accordingly either to the Li/Li⁺ or the Na/Na⁺ reference couple. Galvanostatic cycling was performed using a Maccor Battery Tester 4300. Cyclic voltammetry was carried out by means of a VMP3 potentiostat (BioLogic). All electrochemical studies were performed at 20 °C \pm 2 °C. Specific capacity and current values were calculated based on the composite weight, including tin and carbon.

3. Results and discussion

3.1. Structural and morphological characterization

SnO₂ nanoparticles and tin-carbon (Sn-C) nanocomposite are prepared following the same synthesis procedure based on tin (VI) acetate and sucrose as precursors, differing only in the subsequent thermal treatment. The utilization of the organic tin salt offers the great advantage that no washing step(s) are required in order to remove inorganic residues. In Fig. 1 a comparison of the XRD patterns of the two samples prior to any thermal treatment ('SnO_x/C', lower pattern, black) and after 3 h at 450 °C under air ('SnO₂', upper pattern, red) is presented. It is obvious that 'SnO_x/C' shows very poor crystallinity. Nevertheless, the observed reflections match rather well the JCPDS reference for cassiterite tin (IV) oxide (01-070-6153). This is even more obvious, when comparing it with the XRD pattern of the same sample after calcination at 450 °C for 3 h. The reflections for the latter are significantly sharper, indicating an increased crystallinity. No other reflections are observed, indicating phase-pure SnO₂. However, the reflections still remain rather broad, indicating a small crystallite size. This is confirmed by SEM analysis of the calcined sample (Fig. 2). The obtained SnO₂ powder has a particle size of around 15–30 nm. In fact, having a closer look at the SEM image with the highest magnification (Fig. 2d) reveals that these already rather small particles are composed of even smaller aggregated primary particles, having an average diameter of only a few nanometers.

However, although the utilization of nanoparticulate SnO₂ particles as active material for lithium-ion batteries has shown a great improvement relatively to micron-sized particles in terms of electrochemical performance [50,51], the initial irreversible formation of Li₂O [52], resulting in a large capacity loss within the first cycles hampers its practical use. Moreover, the inactive matrix of Li₂O, dispersing the nanoparticulate metallic tin [30,31], hampers but does not prevent the continuous aggregation of tin particles [16–18], which eventually results in the previously mentioned drawbacks of electrode pulverization and thus in an continuous capacity fading.

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