



Three-dimensional carbon foam supported tin oxide nanocrystallites with tunable size range: Sulfonate anchoring synthesis and high rate lithium storage properties



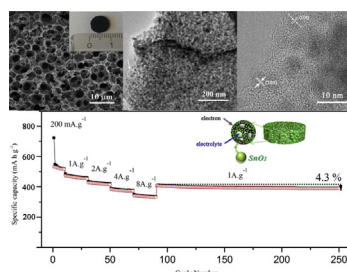
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HIGHLIGHTS

- A free-standing composite which employs porous carbon as the current collector.
- Tunable size range of SnO₂ nanocrystals via the control of annealing process.
- Excellent cyclability (250 cycles) and rate durability (8 A g⁻¹) are shown.

GRAPHICAL ABSTRACT



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ABSTRACT

The development of a free-standing electrode with high rate capability requires the realization of facile electrolyte percolation, fast charge transfer at the electrode-electrolyte interface as well as the intimate electrical wiring to the current collector. Employing a sulfonated high internal phase emulsion polymer (polyHIPE) as the carbon precursor, we developed a free-standing composite of carbon foam encapsulated SnO₂ nanocrystallites, which simultaneously satisfies the aforementioned requirements. When directly evaluated in the pouch cell without using the binder, carbon additive or metallic current collector, the best performing composite exhibits a good rate performance up to 8 A g⁻¹ and very stable cyclability for 250 cycles. This cycling performance was attributed to the synergistic coupling of hierarchical macro/mesoporous carbon foam and SnO₂ nanocrystals with optimized size range. Postmortem characterizations unveiled the significant influence of subtle size variation of oxides on the electrochemical performance.

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1. Introduction

Lithium-ion batteries (LIB) have become the most popular rechargeable energy storage system in consumer electronics during past two decades. The pressing need for vehicle electrification and applications in power grids, however necessitates innovating LIB

that far exceed the current technology [1,2].

Rational design of the electrode architecture is believed to be a promising strategy to address technological issues for enabling the high rate performance for LIB [3,4]. Extensive research efforts have been devoted to optimizing the electrochemical performance of alternative anode materials, i.e., to fabricate hierarchical structures with controllable morphology, composition, and internal microstructure with enhanced cyclability and rate behavior [5–8]. For conventional slurry-cast electrode configurations, the good

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electrochemical performance also hinges on uniform mixing of the electroactive materials with the binder and the carbon additive so that all reactant particles are mechanically and electrically wired to the metallic current collector, meanwhile a facile electrolyte diffusion pathway should be maintained [9]. Failure to achieve this ideal homogeneity of components and a firm attachment to the current collector would result in the performance deterioration. On the other hand, both the binder and the current collector are considered to be inactive mass and volume in the battery, hence the development of binder-free electrodes or lighter current collectors could increase the gravimetric energy densities of the anode part [10–14].

SnO₂ has long been regarded as an appealing anode candidate for LIBs owing to its natural abundance, low toxicity as well as much higher theoretical capacity (782 mA h g⁻¹) as compared to that of the commercial graphite anode (372 mA h g⁻¹). Unfortunately, the actual deployment of its bulk counterparts is restricted by some intrinsic drawbacks: 1) huge volume variation upon alloying and de-alloying processes (~300%) leads to pulverization of the electrode materials and loss of electrical contact with binders and current collectors [8,15,16]. 2) poor electrical conductivity at room temperature further restricts the electrode kinetics at high rates and compromises the cyclability. Various nanoengineering strategies for developing SnO₂ nanostructures and their composites have been explored to improve the electrode kinetics and accommodate the strain during lithiation and delithiation processes [7,17–20]. Recently the direct growth of low-dimensional Sn-based species on conductive substrates such as 3D Ni/Ti foams, copper pillar arrays or 3d graphene scaffold has been realized through template-assisted methods or hydrothermal/solvothermal processes [21–25]. The sufficient porosity of these electrode designs buffers the volume fluctuations upon the repeated Li–Sn alloying/dealloying processes. However, the tedious synthetic procedures, expensive and limited choice of the templates and precursors, and incompatibility issues among the components in the composite still hinder the scalable, cost-effective production of the electrode [22–24,26]. Additionally, realization of the free standing electrode with high rate performance requires the comprehensive consideration of all kinetic aspects, e.g. electrolyte percolation, electron/Li⁺ transfer at the interface, Li⁺ solid-state diffusion rate as well as the good electrical contact with the current collector [25,27]. So far, however, a sustainable high-rate behavior for Sn-based free-standing electrodes has rarely been achieved.

Inspired by the integrated electrode design with weight saving on the current collector and auxiliary binder, we rationally developed a three-dimensional bicontinuous architecture consisting of a layer of SnO₂ nanocrystals (NC) with tunable size, sandwiched between interconnected macroporous Li⁺ pathway and electrical conductive carbon foam. Employing a sulfonated high internal phase emulsion polymer (polyHIPE) as the carbon precursor and nucleation sites for the oxide growth, the SnO₂ NCs were intimately coupled with the macro/mesoporous carbon network via a controlled thermal treatment. The integrated electrode design avoids the processing steps for incorporating the binder into electrode formulation [28]. The hierarchical porous carbon foam, additionally serving as the built-in current collector, eliminates the necessary use of a heavy metal foil or mesh. Galvanostatic tests show that this bicontinuous SnO₂/C composite delivers a long-term cyclability for 250 cycles and good rate durability up to 8 A g⁻¹. These encouraging results emphasize that multiple modification strategies (e.g., nanoscale and morphology engineering, integrated electrode design, hierarchical porosity control and etc.) could be comprehensively employed with a right balance to render the facile kinetics and excellent structural robustness for free-standing electrodes.

2. Experimental

2.1. Materials

All chemicals were used as received. Polyvinyl alcohol (PVA, MW = 115 000) were obtained from Lancaster and BDH Chemicals respectively. Tin(IV) chloride (SnCl₄, 98%), styrene (C₆H₅CHCH₂, 99%), divinylbenzene (DVB, 80%), Span[®]80, calcium chloride hexahydrate (CaCl₂·6H₂O, 99%), 1,2-dichloroethane (ClCH₂CH₂Cl, 99%), acetic anhydride ((CH₃CO)₂O, 99%), urea (H₂NCONH₂, 98%), metallic Li foil (99.9%) were purchased from Sigma–Aldrich. Potassium persulfate (K₂S₂O₈, 99%) was obtained from Merck KGaA. 4-vinylbenzyl chloride (VBC, 90%) was purchased from Fluka. Ultrapure water (Millipore) with resistivity higher than 18.2 MΩ cm was used as the solvent.

2.2. Synthesis of high internal phase emulsion polymer (polyHIPE)

The synthetic procedure of the polyHIPE was described in our previous work [29]. In brief, The oil phase (the stoichiometric amount of styrene, DVB, VBC and Span 80 at pre-determined ratio) was mixed with the aqueous phase (6 mL water solution of 0.165 g stabilizing salt CaCl₂·6H₂O and 0.0150 g initiator K₂S₂O₈) to form an emulsion under constant stirring. The addition of VBC reduces the surface tension by adsorbing at the water-in-oil emulsion interface, thus leading to overall emulsion stability and the decrease in void sizes. This emulsion phase was then transferred to a polytetrafluoroethylene (PTFE) mold and stored in an oven at 65 °C for 48 h. During this process, the monomers in the continuous oil phase started to polymerize while the aqueous phase progressively evaporated, leaving the interconnected macropores within the polymer. The dried polymer was sulfonated with concentrated sulfuric acid at 90 °C for 24 h.

2.3. Synthesis of bicontinuous carbon foam encapsulated Sn-based species composites

In a typical preparation, 300 mg PVA was dissolved in 40 ml deionized water under constant magnetic stirring. Calculated amounts of SnCl₄ (0.84 mL) were then added to complete the preparation of the precursor solutions. 4.5 g polyHIPE was then added and soaked in the precursor solution at room temperature for 2 h. The precursor-solution-impregnated polymer was then removed, rinsed with deionized water and dried in vacuum at 100 °C for 30 min. The rinsed polymer was heated in a muffle furnace from ambient temperature to 250 °C with ramping rate of 3 °C min⁻¹ and maintained for 30 min to remove the residue sulfate functional groups. Afterwards, the polymer was carbonised in alumina boats under a N₂ atmosphere in a tube furnace for 30 min (Heraeus Tube Furnace). The composite products annealed at 550 °C, 600 °C, 650 °C and 700 °C were designated as CF/SnO₂-1, CF/SnO₂-2, CF/SnO₂-3, CF/SnO₂-4, in order of increasing calcination temperature. If the PVA surfactant was not employed in the precursor solution while keeping all other preparation conditions identical as CF/SnO₂-2, the as-fabricated composite was designated as CF/SnO₂-W/O-PVA. When the precursor-solution-impregnated polymer as described above was directly calcinated under a N₂ atmosphere for 30 min in a tube furnace without the pre-treatment in the air at 250 °C, the as-fabricated composites were designated as CF/SnS-600, CF/SnS/Sn-650, CF/Sn-700, CF/Sn-750 when annealing temperature was adjust to 600 °C, 650 °C, 700 °C, 750 °C, respectively.

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