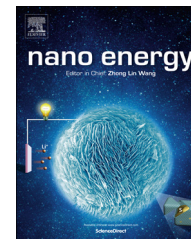




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RAPID COMMUNICATION

Control over large-volume changes of lithium battery anodes *via* active-inactive metal alloy embedded in porous carbon



Nasir Mahmood^a, Jinghan Zhu^a, Sarish Rehman^a, Quan Li^b,
Yanglong Hou^a

^aDepartment of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China

^bDepartment of Physics, The Chinese University of Hong Kong, Shatin, New Territory, Hong Kong, China

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Abstract

Large volume changes and limited access to redox sites of high capacity anode materials are great challenges. Although, various strategies were adopted but still results are far from required values for their practical usage. Here, we have designed a unique structure to prevent surface reaction and structural disintegration meanwhile intrinsic conductivity is improved to involve all redox sites in conversion reaction. CoSn_x@C-PAn hybrid was synthesized through aqueous chemical route, Co doping in tin make accessible all redox sites by faster conduction of electrons while its hard nature relaxes internal stress, carbon shell prevents surface reaction and brings well control on solid electrolyte interface (SEI) film by maintaining barrier between electrode surface and electrolyte and nitrogen doped porous carbon provides faster diffusion of Li⁺ deep in electrode make possible high mass loadings and conduction highway for electrons. Furthermore, porous carbon also provides room to compensate volume expansion and keeps electrode structure stable. Because of its unique structure hybrid shows excellent reversible capacity of 2044 mAh/g (retention 100%) with mass loading of 3.8 mg/cm² along with long cyclic life up to 1000 cycles and bears high rate capability (20 A/g). We believe that present study makes possible the use of high capacity materials in applications.

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Introduction

Presently, lithium ion batteries (LIBs) have got tremendous attention due to their high energy densities and have been considered as promising power source for future electric

E-mail address: houl@pku.edu.cn (Y. Hou).

vehicles (EV) [1-4]. Therefore, in order to achieve the practical applications of LIBs in EVs, there are numerous efforts on seeking for high performance anode materials that possess high capacity and excellent stability with long cyclic life [5-7]. Metallic tin (Sn) is considered as a potential substitute for conventional graphite anode (372 mAh/g) due to its high theoretical capacity (992 mAh/g) and thermal stability [8,9]. However, structural disintegration, larger diffusion barrier, limited access to redox sites and loss of electrical contact have long been identified as primary reasons for capacity loss and poor cyclic life of Sn-based anodes [10,11]. Although nanochemistry plays a critical role to accommodate volume strains by developing nanosized structures of Sn, their use is still limited by unstable solid electrolyte interface (SEI) layer on the surface and poor internal conductivity [8,10,12]. As the organic electrolytes decompose at the working potential of <0.5 V vs. Li^+/Li and forms a thin SEI layer [13,14]. But the expansion and contraction of Sn during alloying and de-alloying causes deformation and breakage of the SEI layer, respectively [11,15,16]. As a result, formation of new SEI on freshly exposed Sn surface eventually block Li^+ transport via accumulation within SEI and causes poor Coulombic efficiency (CE) of cell [10,17]. As a consequence, the capacity decays as SEI thickness increases while most of Sn active material remains electrically connected [12]. However, nanosized designing has improved the cyclic life with enhanced performance but simple reduction of crystallite size to nanoscale has introduced new fundamental challenges [18,19]. Large surface area exposed to electrolyte and higher surface energy that increase side reactions, results in lower CE and causes thermal runaway which leads to internal short circuit due to melting of separator [20-23]. Furthermore, low tap density increases thickness of electrode at high mass loading and leads to low volumetric capacity by increasing Li^+ transfer pathway [14]. Generally, poor electrical properties are observed due to higher inter-particle resistance which is further dominated by volume changes during charging-discharging, affecting cyclic life of electrode drastically [10]. A lot of efforts have been devoted by developing electrolyte blockage layers, creating void space via void engineering and making their composites with elastically strong graphene and inactive hard metals to sustain the structure and improve the cyclic life of Sn-based electrodes [21,24-29]. However, to the best of our knowledge, stability concerns for long cyclic life and high performance with good CE and capacity retention (CR_t) at higher mass loadings (>3 mg/cm²) has not been reported yet for Sn-based materials. To achieve this, a careful design of electrode materials, is highly required, that maintains faster and deep transfer of Li^+ , provides better pathway for electron and ions movement, prevents surface reactions with electrolyte and keeps the structural integrity of electrode [30]. Furthermore, Han et al. also investigated theoretically that fused graphitic C_6 can deliver >2000 mAh/g via accumulation of Li^+ through reversible reaction Li_6/C_6 [31]. Thus, utilizing the above design with conductive network containing fused C_6 backbone can bring higher capacity.

Here, we present an architected design to overcome the aforementioned problems associated with Sn-based electrodes to bring high performance with longevity at low cost. An active-inactive metal alloy sealed in carbon shell and embedded in nitrogen-doped porous graphitic

carbon (N-PGC) matrix named as $\text{CoSn}_x\text{@C-PAN}$ is developed via *in-situ* polymerization and annealing processes. This nanostructure has multiple advantages: (1) doping of electrochemically inactive Co prevents structural changes and enhances internal conductivity of Sn to involve all redox sites in conversion reaction. (2) The nanosized particles can accommodate large volume strains, hard Co improves CR_t and electrochemical active Sn brings about high capacity. (3) The mixed phase provides large grain boundary densities for enhanced interfacial Li^+ storage, channels for faster Li^+ diffusion by reducing the diffusion path below 10 nm. (4) Carbon shell completely encapsulates nanoparticles (NPs) and thus prevents surface reactions by controlling direct contact with electrolyte and limit SEI on outer side with controlled thickness. (5) The carbon framework provides faster transport highways for electrons and Li^+ via pore walls and pores, respectively. (6) High surface area and well-defined pore size distribution improves the active surface area of the hybrid minimizing percentage of inactive material through deep transport of electrolyte and make possible high mass loadings. (7) The existence of large nitrogen contents and graphitic ring (make possible Li_6/C_6 conversion reaction) improve the overall conductivity and electrochemical activity of hybrid to bring high performance. With such a rational design, $\text{CoSn}_x\text{@C-PAN}$ hybrid shows excellent discharge capacity of 2044 mAh/g with extraordinary CE and CR_t of $\sim 100\%$ after 100 cycles at 0.2 A/g with mass loading of 3.8 mg/cm². Furthermore, hybrid was tested at current density of 10 A/g for 1000 cycles to explore the stability for long cyclic life and rate capability at higher charge-discharge rates (20 A/g), interestingly, hybrid shows excellent capacity (1256 mAh/g) with high CE and CR_t ($\sim 100\%$) after 1000th cycle at current density of 10 A/g. It is believed that the presented design will be very helpful to overcome the large-volume changes in electrode materials for energy storage devices with much improved capacity values.

Experimental section

The synthesis of Sn, Sn@C , PAN, N-PGC and characterization part are provided in supporting information.

Synthesis of Co_2SnO_4 nanoparticles

Initially, the stoichiometric amounts of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (176 mg), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (238 mg) and CTAB (400 mg) are mixed in 20 mL of water and stirred with heating unless temperature reaches to 85 °C. Subsequently, 20 ml of 4 M NaOH solution was added and the mixture was stirred for 60 min at 85 °C. After the completion of reaction, the product was collected by centrifugation and washed six times with water and ethanol, repeatedly. Finally, the solid product was dried at 70 °C for 6 h in a vacuum oven.

Synthesis of Co_2SnO_4 -PAN hybrid

Co_2SnO_4 -PAN hybrid was synthesized via *in-situ* polymerization of aniline monomers with Co_2SnO_4 NPs. Initially 50 mg of aniline monomers was stirred for 5 min in water and pH of the solution was turned acidic using HCl. Afterward, the

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