



Hydrogel-Derived Nanoporous Sn–In–Ni Ternary Alloy Network for High-Performance Lithium-Storage



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ARTICLE INFO

Article history:

Received 26 February 2016
Received in revised form 23 May 2016
Accepted 27 May 2016
Available online 28 May 2016

Keywords:

Lithium-ion batteries
Anodes
Sn–In–Ni ternary alloy
nanoporous network
Hydrogels

ABSTRACT

Nanoporous multinary alloy networks containing multiple functional components, i. e. active Li-alloying main-group metals and inactive transition-metals, possess unique structural and compositional features toward lithium storage, and are thus anticipated to manifest desirable anodic performance in advanced lithium-ion batteries (LIBs). Herein, a general and scalable one-pot hydrogel-derived route has been developed for the construction of nanoporous multinary alloy networks via facile coordination-reduction processes using novel cyano-bridged coordination polymer hydrogels (cyanogels) as precursors. The formation of nanoporous Sn–In–Ni ternary alloy network has been illustrated as an example by using a Sn(IV)–In(III)–Ni(II)–Co(III) quaternary metallic cyanogel as a precursor. Meanwhile, nanoporous Sn–Ni binary alloy and metallic In networks have also been synthesized through coordination-reduction routes using Sn(IV)–Ni(II) and In(III)–Co(III) cyanogels as precursors, respectively. Moreover, the anodic performance of the nanoporous Sn–In–Ni ternary alloy network has been examined as a proof-of-concept demonstration of its structural and compositional superiorities toward lithium storage. Compared with separate Sn–Ni and In networks, the Sn–In–Ni ternary alloy network manifests markedly enhanced lithium-storage performance in terms of reversible capacities, cycling stability, and so forth, making it an ideal anodic candidate for advanced LIBs with long cycle life and high energy/power densities. Moreover, the proposed hydrogel-derived coordination-reduction strategy would open up new opportunities for constructing nanoporous multinary alloy networks as advanced anodes for LIBs.

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1. Introduction

As an important category of anodic materials in lithium-ion batteries (LIBs), Li-alloying main-group metals including Group II (Mg, Ca), Group III (Al, Ga, In), Group IV (Ge, Sn, Pb), and Group V (Sb, Bi) metals possess alloying-type Li-storage mechanism and manifest large specific capacity and high safety [1–6]. Thus, these Li-alloying metals have been considered to be ideal anodic candidates to replace commercial graphite-based anodes with limited capacity and poor safety [1–6]. However, these Li-alloying reactions are generally accompanied by huge volume variations during lithium insertion/extraction, which induces electrode pulverization and fast capacity fading and has become the primary obstacle for their practical application in advanced LIBs.

Recently, extensive research work has been focused on the rationally structural and compositional design of these metallic anodes to accommodate their volume variations and improve their cyclic stability [7–27]. On one hand, various nanostructures especially nanoporous structures have been adopted to improve their anodic performances to a large extent owing to their high surface area and large pore volume [7–14]. Among them, three-dimensional (3D) nanoporous networks possess the structural characteristics of both nano-sized building units and micro-sized assemblies, and are able to manifest enhanced strain-accommodation capability and structural stability [12–14]. For example, Ge nanoporous networks have been rationally designed to realize long-term cycling stability by virtue of their unique structural features [12–14]. On the other hand, alloy systems containing two or more active components have proven their superiorities compared with single-component metallic anodes toward lithium storage. The stepwise Li-storage processes of active components at different potentials can accommodate the volume variations of alloy systems, and the as-designed Sn–Ge [15,16], Sn–Sb [17], and Bi–Sb [18] binary alloy anodes display improved capacity retention

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and higher reversible capacities in comparison with single Sn, Ge, Sb, and Bi counterparts. Moreover, the incorporation of inactive transition metals ($M = \text{Fe, Co, Ni, Cu, etc}$) can further buffer the volume variations of active main-group metals during lithium insertion/extraction, and the as-constructed multinary alloy systems are expected to demonstrate further-enhanced structural and cyclic stability. Therefore, 3D nanoporous networks of multinary alloy systems containing multiple functional components, i. e. active Li-alloying main-group metals and inactive transition-metals, possess unique structural and compositional features toward lithium storage, and are thus anticipated to manifest desirable anodic performance in advanced LIBs.

Up to now, multinary alloy systems have been constructed through various synthetic routes including ball milling [19], magnetron sputtering [20], and wet chemical reduction [21–27] processes. Among them, the solution-based chemical/electrochemical reduction routes have been considered to be general and straightforward approaches. For example, various multinary alloy systems, such as Sn–Fe–Co [21,22], Sn–Sb–Cu [23], Sn–Sb–Co [24–26], Sn–Sb–P–Fe [27], and so forth, have been synthesized *via* sodium borohydride reduction [21–24] and electrodeposition [25–27] processes, and manifest enhanced Li-storage performance by virtue of their unique compositional characteristics. However, different kinds of metals prefer to nucleate and grow separately in conventionally wet-chemical synthetic routes owing to their distinct standard reduction potentials, and it still remains a significant challenge to the construction of multinary alloys with uniform distribution of each component [21–27]. Additionally, although the wet-chemical routes are applicable for the synthesis of 0D hollow and solid alloy nanospheres [21–23] and 2D alloy films on metal foil substrates [25–27], they are very difficult to construct 3D nanoporous alloy networks. Therefore, it is highly desirable to develop facile, general, and scalable routes to nanoporous multinary alloy networks for their practical utilization.

Hydrogels usually possess highly porous structure, large surface area, short charge-transport pathways, tunable chemical/physical properties, and so forth, and thus hydrogels and their derivatives could serve as promising functional materials in energy storage and conversion devices [28–30]. As a novel category of hydrogels, cyano-bridged coordination polymer gels (abbreviated as cyanogels) are pioneered by Bocarsly et al. in 1993 [31], and are generally formed *via* ligand-substitution reactions in aqueous solutions of noble-metal chlorides (K_2PdCl_4 [31–33], Na_2PdCl_4 [34], K_2PtCl_4 [34,35], etc) and transition-metal cyanometalates including $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{K}_4\text{Fe}(\text{CN})_6$, $\text{K}_3\text{Co}(\text{CN})_6$, $\text{K}_2\text{Ni}(\text{CN})_4$, and so forth. The nitrogen end from cyano ligand replaces chloride ligand and builds bridges between noble-metal and transition-metal centers, and the whole aqueous solutions experience sol-gel transitions to form stable hydrogels [31–35]. Recently, the cyanogel systems have been extended to main-group metal and transition-metal heterometallic hydrogels such as $\text{SnCl}_4\text{--K}_2\text{Ni}(\text{CN})_4$ [36,37], $\text{SnCl}_4\text{--K}_4\text{Fe}(\text{CN})_6$ [38], and $\text{InCl}_3\text{--K}_3\text{Co}(\text{CN})_6$ [39] cyanogels by our group. The cyanogel-derived hybrid oxides including $\text{SnO}_2\text{--NiO}$ [36], $\text{SnO}_2\text{--Fe}_2\text{O}_3$ [38], and $\text{In}_2\text{O}_3\text{--Co}_3\text{O}_4$ [39] exhibit enhanced anodic performance in LIBs owing to their nanoporous structure and homogeneous distribution of each oxide components.

Besides nanoporous hybrid oxides, the unique synthetic, structural, and compositional features of cyanogels also make them ideal precursors for nanoporous alloy networks, which can be specified as follows: (1) cyanogels can be simply and scalably obtained by mixing aqueous solutions of metal chlorides and cyanometalates at room temperature [38,39], facilitating the mass production of alloy products; (2) cyanogels possess flexible nanoporous structure, and metal species concentrate on their backbones rather than disperse uniformly in solutions [31–39];

Upon reduction, the metal nucleations connect each other one-by-one along cyanogel scaffold directions, resulting in nanoporous alloy networks [35,37]; (3) cyanogels are heterometallic coordination polymer hydrogels and can incorporate both main-group metals and transition metals bridged by cyano group ($M\text{--C}\equiv\text{N--M}'$) on their scaffold, and the homogenous distribution of heterometallic species at atomic scale favors the construction of multinary alloys with uniform distribution of each metallic component [35–39].

As inspired by this, we develop a general and scalable one-pot cyanogel-derived coordination-reduction route for the construction of nanoporous multinary alloy networks containing multiple functional components, i. e. active Li-alloying main-group metals and inactive transition-metals. The formation of nanoporous Sn–In–Ni ternary alloy network has been illustrated as an example by using a Sn(IV)–In(III)–Ni(II)–Co(III) quaternary metallic cyanogel as a precursor. For comparison, nanoporous Sn–Ni binary alloy and metallic In networks have also been synthesized through similar coordination-reduction routes using Sn(IV)–Ni(II) and In(III)–Co(III) cyanogels as precursors, respectively. Moreover, the anodic performance of the nanoporous Sn–In–Ni ternary alloy network has been examined as a proof-of-concept demonstration of its structural and compositional superiorities toward lithium storage. The Sn–In–Ni ternary alloy network manifests markedly enhanced lithium-storage performance in terms of reversible capacities, cycling stability, and so forth in comparison with separate Sn–Ni and In networks.

2. Experimental Section

2.1. Synthesis of the Nanoporous Sn–In–Ni Ternary Alloy

Network. The Sn(IV)–In(III)–Ni(II)–Co(III) cyanogels were obtained by simply mixing freshly-made 0.8 M SnCl_4 , 0.8 M InCl_3 , 0.8 M $\text{K}_2\text{Ni}(\text{CN})_4$ and 0.8 M $\text{K}_3\text{Co}(\text{CN})_6$ aqueous solutions with different volume ratios of 2:2:1:1, 1:2:2:1, 1:2:1:1, 2:1:1:1, 1:1:1:1, 1:1:2:1, 1:1:1:2, 2:1:1:2, and 1:1:2:2 at 20 °C. Subsequently, the final nanoporous Sn–In–Ni ternary alloy network was synthesized through a facile aqueous sodium borohydride reduction process at 20 °C by using the Sn(IV)–In(III)–Ni(II)–Co(III) 1:1:1:1 cyanogel as a precursor.

2.1. Characterization

The morphology, composition, and structure of the products were characterized by X-ray powder diffraction (XRD, Rigaku D/max 2500/PC), scanning electron microscopy (SEM, JEOL JSM 5610LV), and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010F, 200 kV) coupled with an energy-dispersive X-ray spectrometer (EDS, Thermo Fisher Scientific). The Fourier transform infrared (FTIR) spectra were recorded on a Bruker Tensor 27 spectrometer. Nitrogen adsorption and desorption measurement was performed at 77 K using a Micromeritics ASAP 2050 analyzer, and the surface area, pore volume, and pore diameter of the product were calculated using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo VG Scientific ESCALAB 250 spectrometer.

2.2. Electrochemical measurements

Electrochemical tests were carried out by 2025-type coin cells (can size: 20 mm in diameter and 2.5 mm in thickness), and the cells were assembled in an Ar-filled glove box (Innovative Technology, IL-2GB). The electrodes were made as follows: 70 wt % active material (e.g., nanoporous Sn–In–Ni ternary alloy network), 15 wt % conductive material (Super P carbon black), and 15 wt % binder (polyvinylidene fluoride, PVDF) were mixed in

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