Journal of Alloys and Compounds 772 (2019) 507–515

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Skein-shaped ZnO/N-doped carbon microstructures as a high performance anode material for lithium-ion batteries

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ARTICLE INFO

Article history:
Received 2 August 2018
Received in revised form
10 September 2018
Accepted 17 September 2018
Available online 18 September 2018

Keywords:
Li-ion batteries
Anode
Zinc oxide
Skein-shaped morphology
N-doped carbon coating layers

ABSTRACT

Zinc oxide (ZnO) has significant attentions as an alternative anode material for lithium-ion batteries because of its high theoretical capacity (987 mA h g^{-1}), lack of toxicity, abundance, and environmental friendliness. In particular, the theoretical capacity of ZnO is almost three times higher than that of the commercial graphite anode (about 372 mA h g^{-1}) as a result of its alloying and conversion reactions with lithium ions. However, severe capacity fading and poor reaction kinetics are often caused by the low electrical conductivity, slow lithium-ion diffusion, and large volume changes of ZnO during repeated charge/discharge processes. To overcome these drawbacks, N-doped carbon-coated ZnO microstructures are synthesized through a facile hydrothermal reaction and the subsequent calcination process using citric acid and urea as carbon and nitrogen sources, respectively. The ZnO sample has a hierarchical skein-shaped morphology and exhibits a higher discharge capacity of about 1047 mA h g^{-1} after 100 cycles at a 0.1 C rate in the 0.01–3.0 V voltage range, compared to those of bare ZnO and carbon-coated ZnO samples (about 42 and 341 mA h g^{-1} after 100 cycles, respectively).

1. Introduction

Lithium-ion batteries (LIBs) have been widely used as major energy-storage tools for small portable electronic devices such as laptops, mobile phones, and digital cameras, due to their high operating voltages, large energy densities, and long cycle lives [1–3]. Despite these advantages, meeting the growing demands of higher reversible capacities and energy densities for transportation applications, such as in electric and hybrid-electric vehicles, remains a challenge [4,5]. One of the most effective approaches to solving this problem involves the use of noble electrode materials with larger capacities than those of conventional electrodes. Graphite is the most widely used anode in commercial LIBs; however, its low theoretical capacity of about 372 mA h g^{-1} has catalyzed the development of alternative anode materials. Recently, transition metal oxides, such as Fe_3O_4, Co_3O_4, CuO, and NiO, have attracted significant levels of attention due to their safer operating voltages and higher theoretical capacities (about 674–924 mA h g^{-1}) compared to those of graphite [6–9]. In particular, ZnO is advantageous because of its natural abundance, low cost, and theoretical capacity of about 978 mA h g^{-1} through both conversion ($ZnO + 2Li^+ + 2e^- \rightarrow Zn + Li_2O$) and alloying ($Zn + xLi^+ + xe^- \rightarrow Li_xZn\,(x \le 1)$) reactions [10,11]. However, ZnO suffers from low electrical and ionic conductivities as well as large volume changes during charging and discharging processes, resulting in unsatisfactory electrochemical performance that includes serious capacity fading and slow reaction kinetics.

In order to overcome these problems, many approaches, including the use of smaller particles and morphological tailoring, have been investigated in attempts to shorten the migration path of lithium ions and to cope with the severe volume changes of the ZnO electrodes during cycling [11–15]. However, adverse side reactions are difficult to avoid due to increases in the direct contact area of the electrode surface with the electrolyte, and the reduction in the tap density of the electrode. On the other hand, ZnO has been hybridized, mainly with conductive metals [16–20] and/or carbon materials [21–29], in order to improve the electrical conductivities of ZnO electrodes. In particular, ZnO/reduced graphene oxide and ZnO/porous carbon materials show noticeable improvements in electrochemical performance [21,25,27–29]. However, it is difficult to form an effective electrical network of ZnO particles with small amounts of carbon. For example, the synthesis of nano-sized ZnO/graphene composites using the high energy ball-milling technique can result in structural defects in the ZnO electrode [27]. Impregnation of a ZnO precursor into porous carbon is also frequently

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https://doi.org/10.1016/j.jallcom.2018.09.198
0925-8388/

accompanied with the formation of ZnO aggregates outside of the pores [21,30]. Recently, Zn^{2+} or ZnO/organic composites have been used as precursors to ZnO/C composites that effectively intermix ZnO particles and the carbon matrix [17,25,31–36]. In addition, the use of N-doped carbon materials has also been actively explored due to the benefits associated with the increased electronegativity of nitrogen, and the presence of electron-donating functional groups [30,36–38]. However, achieving concurrent ZnO hybridization with the carbon matrix and control of hierarchical morphology remains challenging.

Herein, we report an effective approach for the synthesis of skein-shaped ZnO/N-doped carbon microstructures using a simple hydrothermal reaction in the presence of citric acid ($C_6H_8O_7$) and urea ($CO(NH_2)_2$), with subsequent carbonization, as shown in Scheme 1. Here, citric acid and urea were used as the carbon and nitrogen sources, respectively; they are reacted to form a polymer matrix bearing sufficient hydroxyl and amino groups that strongly coordinate Zn^{2+} ions and embed the subsequently formed ZnO particles [39,40], in the same manner as a binding agent, resulting in skein-like ZnO/N-doped carbon microspheres. In addition, these adsorptive interactions facilitate the establishment of intimate contacts between ZnO nanoparticles and the conductive N-doped carbon matrix, which is formed by the thermal decomposition of the polymeric matrix during the subsequent reductive annealing process. The ZnO particles enwrapped by conductive N-doped carbon exhibit significantly improved electrochemical properties, including cycling stability, reversible capacity, and rate capability.

2. Experimental section

2.1. Sample preparation

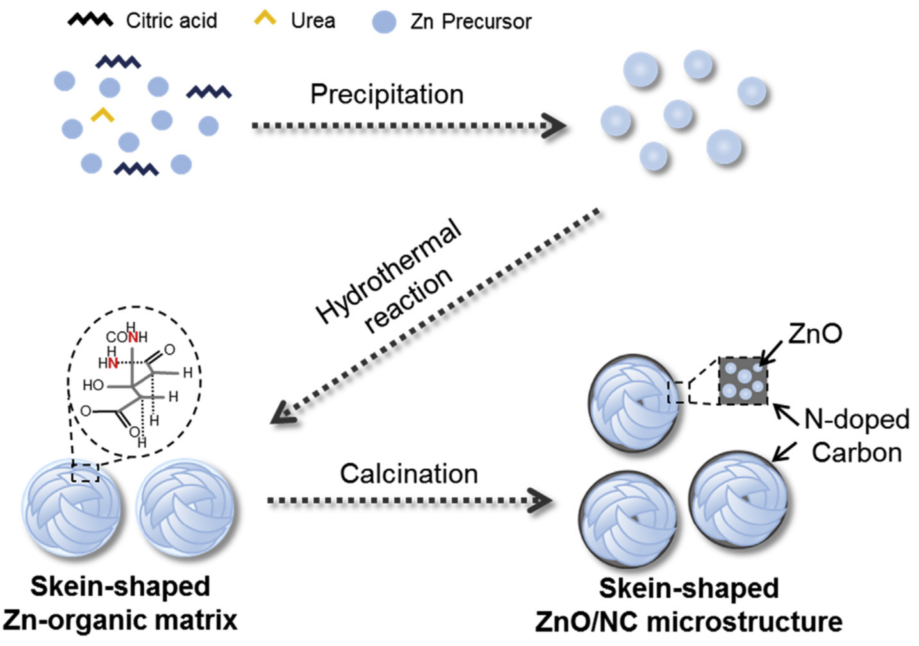
The ZnO/NC sample was prepared by adding 10 mL of a 0.05 M urea solution (Sigma, ≥98%) and 10 mL of a 0.3 M $Zn(NO_3)_2 \cdot 6H_2O$ solution (Sigma, 98%) dropwise to 10 mL of a 0.1 M citric acid solution (Sigma, ≥99.5%). The pH of the mixture was adjusted to 8.5 with 1 M NH_4OH solution, after which it was transferred to a 50-mL Teflon-lined stainless steel autoclave reactor and heated at 180 °C for 10 h. The formed white precipitation was collected by filtration, washed with distilled water, and dried at 80 °C. The powder sample was finally heated to 600 °C at a rate of 5 °C/min under a flow of Ar (50 mL/min), and calcined at that temperature for 2 h. The ZnO/C sample was additionally synthesized by the same procedure but in the absence of urea, and the bare ZnO sample was synthesized in the same manner, but in the absence of both citric acid and urea.

2.2. Material characterization

The structural phase of each sample was examined by X-ray diffraction (XRD) using a Rigaku benchtop X-ray diffractometer (Cu Kα radiation, $\lambda = 1.5418$ Å). Field-emission scanning electron microscopy (SEM, Hitachi S-4200) and transmission electron microscopy (TEM, JEOL JEM-2011) were used to examine sample morphology and particle size. Elemental maps were acquired by energy-dispersive X-ray spectroscopy (EDS, Hitachi S-4200). Cycled samples were subjected to SEM and TEM after disassembly of the coin cell, electrode washing with dimethyl carbonate, and drying in an Ar-filled glove box. Pore volumes and Brunauer-Emmett-Teller (BET) surface areas were determined using a Micromeritics ASAP 2010 gas-sorption analyzer. Pore-size distributions were determined by the Barrett–Joyner–Halenda (BJH) method. Thermogravimetric analysis (TGA) was conducted with a SETSYS Evolution (SETARAM) thermogravimetric analyzer over the 20–800 °C range at a heating rate of 10 °C/min in air. Fourier-transform infrared (FT-IR) spectroscopy was performed using a JASCO FT/IR-4600 spectrometer over the 400–4000 cm^{-1} wavelength range. The carbon and nitrogen contents of the samples were measured by TGA and elemental analysis (EA, Flash EA 1112). X-ray photoelectron spectroscopy (XPS) was performed using a Theta Probe AR-XPS system. UV–vis spectra were measured by JASCO V-770.

2.3. Electrochemical experiments

Working electrodes were prepared by mixing the ZnO compound, acetylene black (MTI), and poly(vinyldifluoride) (PVDF) binder in *N*-methylpyrrolidine (NMP, Aldrich) in a 7:2:1 (w/w)



Scheme 1. Schematic illustration of the preparation of skein-shaped ZnO/NC microstructure.