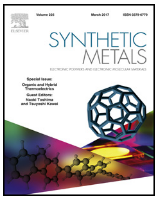
Synthetic Metals 226 (2017) 39–45

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



Research paper

One-step synthesis of ZnO/N-doped carbon/Cu composites for high-performance lithium ion batteries anodes

Junfei Duan[a], Song Yuan[a], Chao Zhu[a], Zhaoyong Chen[a,*], Guanhua Zhang[b], Huigao Duan[b], Lingjun Li[a], Zhiying Zhu[a]

[a] School of Materials Science and Engineering, Changsha University of Science and Technology, Changsha, 410004, Hunan Province, China
[b] School of Physics and Electronics, Hunan University, Changsha, Hunan 410082, China

ARTICLE INFO

Article history:
Received 22 October 2016
Received in revised form 4 January 2017
Accepted 12 January 2017
Available online 5 February 2017

Keywords:
Zinc oxide
N-doped carbon
Cu nanoparticles
Anode materials
Lithium ion batteries

ABSTRACT

Developing the advanced electrode materials with large capacity, low cost, high-rate capability and long cycle stability for lithium ion batteries (LIBs), is still a challenge and hot-topic today. Herein, ZnO/N-doped carbon/Cu composites (ZnO/NC/Cu) with different ZnO loading amounts are first synthesized by a simple pseudo-solid-state method only using the copper phthalocyanine as carbon, nitrogen and copper sources. In a typical massive-like structure, ZnO and Cu nanoparticles distribute randomly and are well surrounded by amorphous carbon. Benefiting from the advantages of intrinsic architecture, as LIBs anodes, ZnO/NC/Cu (1:1) exhibits a large specific capacity of 602 mAh g^{-1} at a current density of 100 mA g^{-1}, keeps a high up to 96% capacity retention even after 100 cycles vs the 2nd cycle, and presents high rate capability. It could be inferred that appropriated amount of ZnO, the modification of copper nanoparticles and N-doped carbon framework are mainly responsible for those encouraging electrochemical performances of ZnO/NC/Cu composites.

1. Introduction

Lithium ion batteries (LIBs) are facing new challenges for the extensive applications in smart mobile phone and electric vehicles, because the relatively low energy density and poor rate capability can not meet the increasing requirements [1–4]. Hence, considerable efforts have been devoted to develop substitutable electrode materials with large specific capacity, low cost, high-rate capability and long cycle stability. Transition metal oxides have been attracted in recent years as LIBs anodes due to their high specific capacity in comparison with the commercial graphite anodes (theoretical specific capacity: 372 mAh g^{-1}) [5–7]. ZnO is one of the most promising candidate anodes due to the high theoretical capacity (978 mAh g^{-1}), low cost and environmental benignity [8,9]. However, its practical application is still hampered by the poor cycling stability, which arises from its poor conductivity and drastic volume change during lithiation/delithiation [10]. At present, mainly two effective strategies have been made to circumvent these drawbacks. One is synthesizing nano-structure morphology to shorten the lithium ions diffusion length and alleviate the volume change during lithiation/delithiation, such as quantum dots [11–13], nanorods [14,15], nanosheets [16–18] and hierarchical structure constructed by nanocrystals [19–21], therefore enhances the electroactivity and mechanical stability. Another is coating conductive materials on ZnO surface to increase the conductivity and restrict the volume change during ion intercalation/deintercalation, such as carbon [22–27], metal (Ag [28,29], Cu [30,31], Ni [32]) and metal oxide (NiO [21,33], TiO_2 [34,35], SnO_2 [36–38]), leading to enhanced rate capability and cycle performance. Recently, it is demonstrated that incorporation of nitrogen heteroatoms and/or non-noble metals into nanostructured materials of metal oxide can greatly improve the cycling performance and rate capacity of metal-oxide based electrode materials due to the improvement in electronic conductivity [39–42]. Despite these progresses, in most cases, the material preparation process is difficult to scale up for low-cost volume manufacturing.

Herein, we report a facile, direct one-step route for the synthesis of ZnO/N-doped carbon/Cu (ZnO/NC/Cu) composites by a simple pseudo-solid-state method only using copper phthalocyanine (CuPc) as carbon, nitrogen and copper sources. In this composite, ZnO nanocrystals are well decorated with Cu nanoparticles and surrounded by N-doped carbon framework. Such structure achieves the synergism of short ion diffusion

---

* Corresponding author.
E-mail address: chenzhaoyongcioc@126.com (Z. Chen).

http://dx.doi.org/10.1016/j.synthmet.2017.01.010
0379-6779/

length, high conductivity and stable structure, and thus results in high electrochemical performance as anodes materials of LIBs.

2. Experimental section

2.1. Synthesis of ZnO/NC/Cu composites

CuPc (95%, AR), ZnO nanocrystals (99.9%, 30 ± 10 nm), normal-sized ZnO (99%, AR) and other reagents were purchased from Alfa Aesar and used as received without purification. In a typical synthesis, CuPc (0.58 g) and ZnO (0.58 g) were mixed well using mortar to get the precursor. Subsequently, the mixture precursor was annealed at 580 °C under Ar gas flow with a heating rate of 5 °C min^{-1}, and kept for 4 h to get ZnO/NC/Cu (1:1, mass ratio of ZnO/CuPc). Similarly, ZnO/NC/Cu with different ZnO mass loading could also be obtained by varying the ZnO/CuPc mass ratio (1:2 and 2:1). For comparison, we also synthesized NC/Cu hybrid under identical reaction condition except adding the ZnO.

2.2. Characterizations

The obtained samples were investigated by X-ray diffraction (Philips X'pert Pro X-ray diffractometer), scanning electron microscopy (SEM, Hitachi S-4800), and transmission electron microscopy (TEM, JEOL, JEM 2100). Thermal gravimetric analysis (TGA) were performed using a Perkin-Elmer Pyris I instrument at a heating rate of 10 °C min^{-1} under an air atmosphere in the range of 100–1000 °C. Raman spectra were recorded with a Renishaw 1000 spectrometer using a 632.8 nm He-Ne laser operating at 2 mW. X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI 5000 Versa probe system, using monochromatic Al Kα radiation (1486.6 eV) operating at 25 W. The electrical conductivity was measured by a RTS-9 four-point probe tester.

2.3. Electrochemistry measurements

Electrochemical measurements were performed using 2032 type coin cells. The working electrode slurry consisted of active material (70 wt%), conducting carbon (20 wt%) and polyvinyldifluoride (PVDF, 10 wt%) in N-methylpyrrolidone (NMP). The above slurry was coated onto a copper foil current collector (1 cm^2 area, the mass loading: 1.0–1.3 mg) and dried in vacuum at 110 °C. The electrolyte was 1 M $\mathrm{LiPF_6}$ in an ethylene carbonate and diethyl carbonate (EC/DMC, 1:1 vol) mixture, and Celgard 2500 separator was used. Coin cells were assembled in an argon-filled glove-box and Li foil was taken as the counter electrode. Electrochemical tests were carried out using an automatic galvanostatic charge-discharge unit, Land CT2001 battery cycler, between 0.01-3.0 V versus Li electrode at room temperature. The specific capacity of charge/discharge was calculated from equation C = I*t/m, where *I* is the given current, *t* the charge or discharge time, *m* the quality of active materials. The electrochemical impedance spectroscopy (EIS) measurement were conducted by an electrochemical analyzer (CHI660a, Shanghai Chenhua, China), The amplitude voltage is 5 mV and frequency range is 10^{-3}–10^{5} Hz. Cyclic voltammograms (CV) profiles were obtained in the range of 0.01–3.00 V at a scan rate of 0.2 mV s^{-1} with CHI660a. All the electrode capacities were calculated by using the total of active material including ZnO, carbon and Cu.

3. Results and discussion

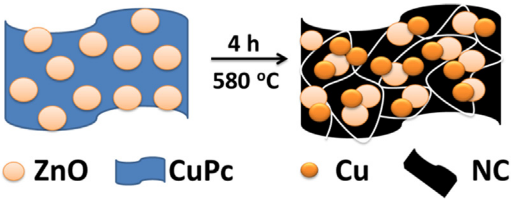


Fig. 1. The schematic illustration of synthesis of ZnO/NC/Cu composites.

As schematically shown in Fig. 1, the ZnO/NC/Cu composites were simply prepared by annealing the CuPc and ZnO nanocrystals precursor under Ar gas flow. CuPc is abundant and low cost, which has been used to synthesize carbon nanotubes and graphitic carbon materials with high carbon yields (70–85 wt%) [43,44]. In this study, CuPc was simultaneously used as carbon, nitrogen and copper sources. In the anneal progress, CuPc sublime near 500 °C and the vapour decomposed into carbon and Cu metal nanoparticles when heated at 580 °C just above sublimation temperature under Ar [45], and the materials of Cu nanoparticles and N-doped carbon derived from CuPc would almost instantaneously decorate on the surface of ZnO to form ZnO/NC/Cu composites. It is worth noting that the carbon yields are usually higher than 80 wt%, which is very important for practical application [45]. This pseudo-solid-state approach is very simple and suitable for scale-up production of the ZnO/NC/Cu composites. For comparison, we also prepared the normal-sized ZnO/NC/Cu composite by using commercial normal-sized ZnO and CuPc precursor (1:1).

Figs. 2 and 3 shows the structural characterizations of obtained ZnO/NC/Cu samples. XRD patterns demonstrated the composites comprised of wurtzite crystal structural ZnO (JCPDS, No. 79-0206) and metallic Cu (JCPDS, No. 04-0836) (Fig. 2a) [31]. The diffraction peaks observed at 31.7, 34.4, 36.2, 47.4, 56.5, 62.9 and 67.9° can be identified as (100), (002), (101), (102), (110), (103) and (112) planes of ZnO, respectively, and the peaks at 43.2, 50.1 and 73.8 ° can be assigned to the (111), (200) and (220) planes of metallic Cu, respectively. It is clearly seen that the intensities of ZnO characteristic peaks increase with the increasing amount of ZnO. In Fig. 2b, Raman spectrum verified the composites also consisted of amorphous carbon, from the G-band and D-band at 1580 and 1342 cm^{-1} with an intensity ratio of 0.96 [46]. TGA results also demonstrated that the composites comprised of carbon (Fig. S1), and the carbon content was estimated about 21, 27 and 55 wt% for sample 2:1, sample 1:1 and sample 1:2, respectively.

The composition of the ZnO/NC/Cu composite (1:1) was further characterized by XPS, as shown in Fig. 3. The full XPS survey revealed that the composite was composed of element Zn, O, C, N and Cu (Fig. 3a), demonstrating the presence of N-doped carbon. The high resolution Zn 2p spectrum located at 1045.5 and 1021.4 eV exhibits two characteristic peaks (Fig. 3b), corresponding to Zn $2p_{1/2}$ and Zn $2p_{3/2}$ of ZnO, respectively. It is shown that the N 1 s spectrum can be fitted into three kinds of nitrogen species including quaternary N (~400.9 eV), pyrrolic or pyridonic N (~399.4 eV) and pyridinic N (~398.2 eV) (Fig. 3c). The quaternary N is graphitic N located inside the graphitic carbon plane and bonds with three sp^2 carbon atoms, the pyrrolic (pyridonic) and pyridinic N bond with two sp^2 carbon atoms [45]. In addition, the high resolution Cu 2p spectrum exhibited two characteristic peaks located at 952.2 and 932.4 eV (Fig. 3d), corresponding to Cu $2p_{1/2}$ and Cu $2p_{3/2}$ of Cu, respectively. There was no configuration satellite between Cu $2p_{1/2}$ and Cu $2p_{3/2}$, consistent with the XRD result.

The morphology of the ZnO/NC/Cu composites was observed by SEM and TEM, as shown in Figs. 4 and S4. From SEM images, the composites presented massive-like micro-particles with the size of 20–100 um in diameter (Fig. 4a and Fig. S2). The individual micro-particle was constructed by many secondary interconnected nanosheets (Fig. 4b), and the nanosheets consisted of ZnO and Cu