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Synthesis and characterisation of sponge-like carbon anode materials for lithium ion batteries

Jingjing Tang, Juan Yang, Xiangyang Zhou *

School of Metallurgy and Environment, Central South University, Changsha 410083, China

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ABSTRACT

Micro-sized carbon material with a unique sponge-like morphology has been fabricated by hydrothermal method coordinating etching process. When evaluate its electrochemical properties in lithium ion batteries, the sponge-like carbon structure exhibits very high specific capacity (around 1175 mAh g^{-1} after 140th cycle tested at the charge/discharge current density of 200 mA g^{-1}) and wonderful cyclability (about 117% retention is available when cycled back from very high current density of 800 mA g^{-1}) during the galvanostatic cycling, indicating it may be a promising candidate as anode material for Li-ion batteries.

1. Introduction

In the early 1990s, Sony succeeded in realizing the commercial application of the first rechargeable Lithium ion cell based on a carbon anode (petroleum coke) and a $LiCoO_2$ cathode [1]. Since then, lithium ion batteries have been identified as one of the most important and the greenest type of rechargeable batteries. At present, graphitic carbon anodes are often employed in lithium ion batteries which can avoid the problem of Li dendrite formation by the reversible intercalation of Li into the carbon host lattice and guarantee good cyclability and safety [2]. However, the limited theoretical capacity of 372 mAh g^{-1} drives extensive research focusing on developing alternative anode materials to realize a high specific capacity and good cycling ability. Among them, hard carbons are found promising due to their appealing properties, such as higher specific capacity and long durability [3,4].

In this paper, sponge-like carbon (SPC) anode material has been prepared via template synthesis process. When employed as anode material for lithium ion batteries, the SPC anode material shows high discharge capacity and good cyclic performance.

2. Experimental

Material preparation and characterization: First, 2 g of Co $(NO_3)_2 \cdot 6H_2O$ was dissolved into 100 ml of continuously stirred isopropyl alcohol–water (1:1, v/v) solution at room temperature. 2 ml of ammonia solution ($NH_3 \cdot H_2O$, 25 wt%) was subsequently added drop by drop at a time interval of 2 h under vigorous stirring. The reaction was allowed to proceed for a further 12 h and the resulting Co_3O_4 powder was collected and washed with water. Then, silica coating process was carried out to synthesis Co_3O_4/SiO_2 composites as previously reported [5]. 0.85 g of as-prepared Co_3O_4/SiO_2 products, 4.2 g glucose, 0.28 g polyvinylpyrrolidone (PVP) were dissolved in 220 ml deionized water under stirring and then ultrasonicated for 0.5 h. The mixture was heated at 180 °C for 6 h in a sealed Teflon-lined autoclave. The dark brown products were collected by suction filtration with absolute ethyl alcohol and deionized water, and dried at 80 °C. The as-synthesized samples were further annealed in Ar atmosphere at 900 °C for 2 h. After been immersed in dilute hydrofluoric acid for 3 h, SPC powder was finally obtained after filtering, washing and drying. For comparison, hollow carbon spheres (HCS) were synthesized under the same conditions without the addition of Co_3O_4.

Material characterization: The morphologies of the materials were observed by field emission scanning electron microscopy (NOVA NANO SEM230) and field emission transmission electron microscopy (FETEM, JEM-2100 F). Chemical analysis was performance using an EDAX system interfaced to the FETEM. Structure characterizations were performed by X-ray diffraction (XRD, Rigaku-TTRIII, Cu Kα) at a scanning rate of 10 deg min^{-1} and Raman spectroscopy (LabRAM Hr800).

Electrochemical measurement: The working electrodes were prepared by mixing active material, acetylene black and polyvinylidene at a weight ratio of 8:1:1 and pasted on pure copper foil. Standard 2025 coin cell was assembled in an ultra pure argon filled glove box for electrochemical tests by employing a lithium foil as the counter electrode and 1 M $LiPF_6$ in ethylene

* Corresponding author. Tel./fax: +86 731 8883 6329.
E-mail address: hncsxyzhou@163.com (X. Zhou).

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carbonate/dimethyl carbonate (1:1) as the electrolyte. Galvanostatic charging/discharging was performed on LAND CT-2001 A in the potential range of 0.01–3.2 V versus Li/Li$^+$ at a current density of 200 mA g^{-1}.

3. Results and discussion

The crystallinity of carbon materials can be determined by XRD and Raman spectroscopy. Fig. 1a shows the XRD patterns of SPC and HCS. The characteristic (002) (20–30°) and (100) (40–45°) peaks of graphite are discernible in both carbon materials, which indicates the amorphous nature of obtained materials. Compared with HCS, SPC exhibits a stronger (002) peak, demonstrating the well-stacked graphene layers in the sample [6]. The d_{002} of SPC and HCS is about 0.37 nm and 0.38 nm, respectively. The larger interlayer spacing compared with pure graphite carbon (about 0.33 nm) is thought to be favorable for lithium insertion and extraction, retaining the structural stability of an electrode during cycles [7]. It is

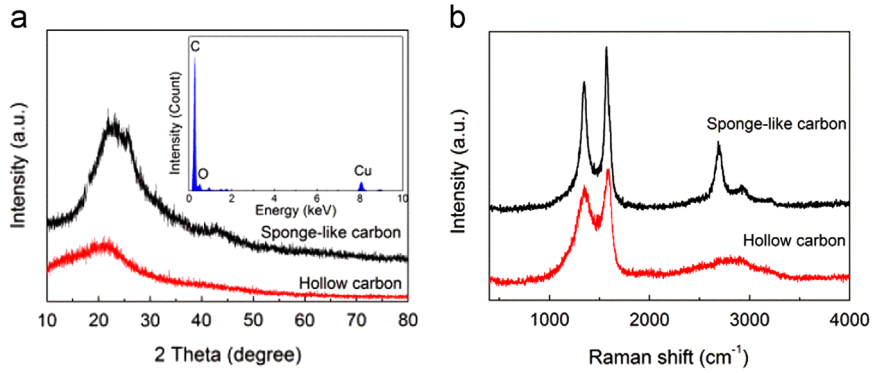

Fig. 1. (a) XRD patterns and (b) Raman spectra of samples. Insert is the EDS of SPC.

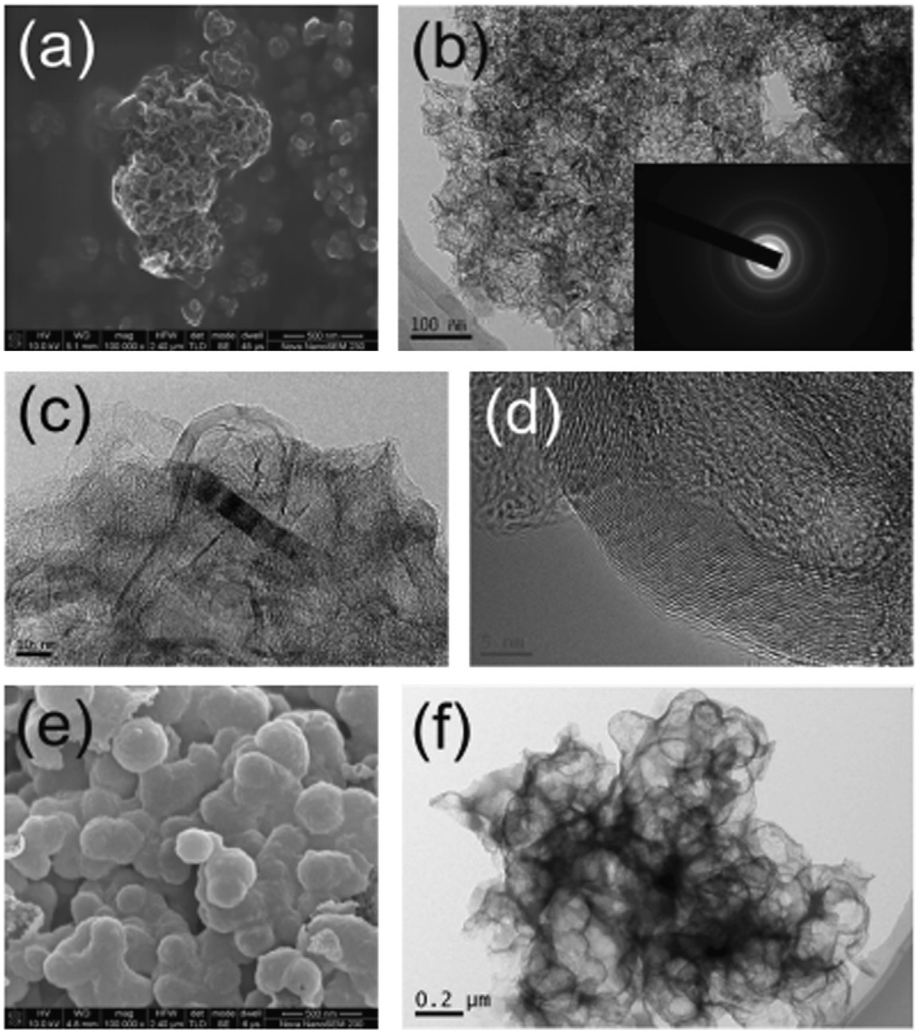

Fig. 2. (a) SEM and (b–d) TEM images of SPC, (e) SEM and (f) TEM images of HCS.