Journal of Energy Chemistry xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Energy Chemistry

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

http://www.journals.elsevier.com/journal-of-energy-chemistry/

Fabrication and application of hierarchical mesoporous $MoO_2/Mo_2C/C$ microspheres

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ARTICLE INFO

Article history:
Received 23 June 2017
Revised 8 August 2017
Accepted 4 September 2017
Available online xxx

Keywords:
Lithium ion batteries
Anode materials
$MoO_2/Mo_2C/C$
Mesoporous
Polymer regulation

ABSTRACT

Hierarchical mesoporous $MoO_2/Mo_2C/C$ microspheres, which are composed of primary nanoparticles with a size of about 30 nm, have been designed and synthesized through polymer regulation and subsequent carbonization processes. The as-synthesized microspheres were characterized by XRD, Raman, SEM, TEM, XPS measurements and so on. It was found that polyethylene glycol acted as a structure-directing agent, mild reducing agent and carbon source in the formation of these hierarchical mesoporous $MoO_2/Mo_2C/C$ microspheres. Moreover, the electrochemical property of the microspheres was also investigated in this work. Evaluated as an anode material for lithium ion batteries, the hierarchical mesoporous $MoO_2/Mo_2C/C$ electrode delivered the discharge specific capacities of 665 and 588 mAh/g after 100 cycles at current densities of 100 and 200 mA/g, respectively. The satisfactory cycling performance and controllable process facilitate the practical applications of the hierarchical mesoporous $MoO_2/Mo_2C/C$ as a potential anode material in high-energy density lithium-ion batteries.

1. Introduction

To solve the grim problems of global warming and energy crisis in the 21st century, it is urgent to exploit the green sustainable energy sources. As one of the important green energy sources, lithium ion batteries (LIBs) have been widely applied in numerous fields including electronic devices, electric vehicles, state grid and energy storage devices due to its long-term cycle life, high energy density and appropriate cost [1–4]. Despite the current success, more research and improvement are quite necessary to satisfy the ever-growing demand and expand the applications of LIBs in future. Various cathode materials such as $LiFePO_4$, $LiNi_{0.5}Mn_{1.5}O_4$ and V_2O_5 have been extensively studied and made great progress in recent years [5–7]. For better matching with the cathode materials, considerable research has also been dedicated to develop new anode materials with high capacity, high density and satisfactory cycling stability, because the commercial graphite with limited theoretical specific capacity of 372 mAh/g can not meet the demand of advanced electric devices [8].

Among the numerous anode materials, transition metal oxides (e.g., Fe [9], Co [10] and Mo [11]) have drawn great research interest due to their high theoretical capacity, good safety and huge abundance. Significantly, compared with other transition metal oxides, molybdenum oxides have merits of high density, multiple valence states and rich chemistry, making them attractive anode materials for high performance LIBs [12–14]. Typically, molybdenum dioxide (MoO_2), as a promising anode material for LIBs, has triggered much attention owing to its high theoretical capacity (838 mAh/g), low electrical resistivity, high density (6.5 g/cm^3), and affordable cost [15–19]. Although it has excellent physicochemical properties, MoO_2 still possesses two crucial drawbacks before practical application. One weakness is sluggish kinetics performance resulting in limited redox conversion process of bulk MoO_2 [20–22]. The other weakness is huge volume change of MoO_2 during lithiation and delithiation processes leading to electrode pulverization and rapid capacity fading [23].

Therefore, various techniques have been employed to overcome these inadequacies. First, manipulation of nanostructured materials could increase the contact surface between the electrolyte and electrode, and shorten the diffusion distance of electrons and lithium ions, resulting in remarkably improved electrochemical performance versus the bulk counterpart [24–26]. Furthermore,

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https://doi.org/10.1016/j.jechem.2017.09.008

Please cite this article as: X. Li et al., Fabrication and application of hierarchical mesoporous $MoO_2/Mo_2C/C$ microspheres, Journal of Energy Chemistry (2017), https://doi.org/10.1016/j.jechem.2017.09.008

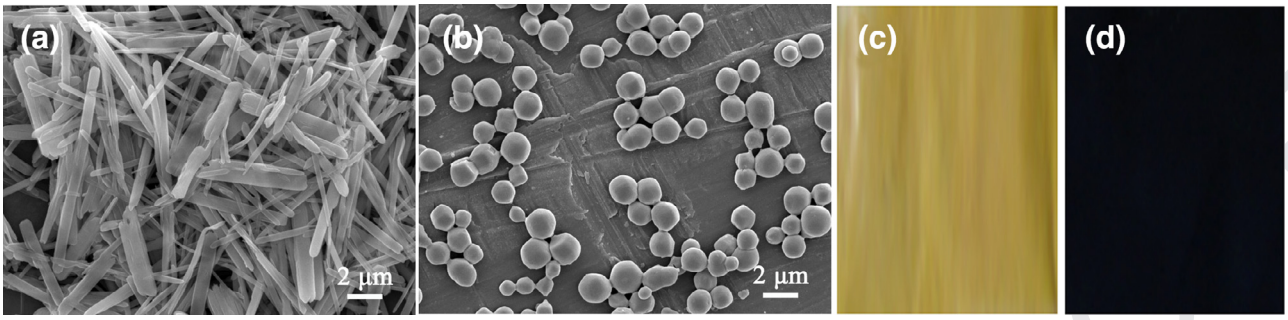

Fig. 1. SEM and color images of hybrid material obtained in the absence of PEG (a, c) and in the presence of PEG (b, d). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

introduction of carbon species in MoO_2 composite has been considered to counteract disintegration of the active material and enhance the electrical conductivity of the host material, achieving high rate capacity and long cycle life [27–33]. After this, in order to further improve the conductivity of active materials, Zhang and coworkers proposed using Mo_2C to modify MoO_2 material [34]. Mo_2C with a high specific conductance (1.02×10^2 S/cm) could decrease the resistance of electrode materials [35]. In addition, formation of hierarchical mesoporous structure is also generally expected to enhance the electrochemical performance of MoO_2. Hierarchical mesoporous structure could mitigate the drastic volume expansion and provide numerous open channels for the infiltration of electrolyte into electrode [36–39]. Therefore, taking advantages of hierarchical mesoporous structure and effective combination of MoO_2, Mo_2C, C components, a new anode material would be expected to exhibit high performance.

In this study, utilizing the mild polymer regulation process followed by calcination treatment, we have successfully fabricated hierarchical mesoporous $MoO_2/Mo_2C/C$ microspheres constructing from primary nanoparticles for the first time. The phase, morphology and texture of the as-made sample were carefully investigated and the function of the polyethylene glycol (PEG) polymer for fabricating the hierarchical mesoporous microspheres was explored by means of the various characterization methods such as X-ray diffraction, high-resolution TEM, X-ray photoelectron spectroscopy, Brunauer–Emmett–Tellet and so on. The successfully prepared $MoO_2/Mo_2C/C$ microspheres were fabricated into anode for LIBs and its electrochemical performance was systematically examined. It was found that the fabricated anode for LIBs exhibited excellent Li-storage behavior. At current densities of 100 and 200 mA/g, the discharge specific capacities of 665 and 588 mAh/g were still retained over 100 cycles, respectively. Undoubtedly, this work provides a simple and mild method for the preparation of $MoO_2/Mo_2C/C$ with enhanced electrochemical performance. It is speculated that the excellent electrochemical performance of the prepared microspheres could be attributed to the efficient combination of MoO_2, Mo_2C and C in $MoO_2/Mo_2C/C$ composite.

2. Experimental

2.1. Synthesis of $MoO_2/Mo_2C/C$ microspheres

40 ml of H_2O_2 (30 wt%) aqueous solution was slowly added into a flask containing 4.78 g of molybdenum powder with continuous stirring in an ice-water bath to form a clarified and orange-yellow peroxomolybdate solution. After that, 10 g of PEG polymer was dissolved into 60 ml of deionized water to form a PEG water solution. Then, the PEG and peroxomolybdate aqueous solutions were mixed well and subsequently heated at 70°C for 16 h. The obtained blue precipitation was collected by centrifuging, washed with deionized water and dried at vacuum freezing drying oven. Finally, the sample was further calcined at 700 °C for 1 h in N_2 atmosphere to obtain the final $MoO_2/Mo_2C/C$ product.

2.2. Characterization

The phase of the material was determined by X-ray diffraction (XRD) collected on an X-ray powder diffractometer (Empyrean, Netherlands) with Cu *Kα* (λ = 1.5406 Å) radiation. In order to investigate the quality of carbon, Raman spectroscopy was recorded on an HR800 Raman microspectrometer (JOBIN YVON, France) and the excitation wavelength was 532 nm. The content of total carbon was determined by CS elemental analysis (CS-2800) based on pulse heating-infrared thermal conductivity. The morphology and dimension of the sample were characterized by a field emission scanning electron microscopy (FESEM, JSM-7610F). Transmission electron microscopy (TEM, JEM-2100F) and high-resolution TEM (HRTEM) equipped with an energy dispersive X-ray spectroscopy (EDX) were carried out to examine the detailed morphology and microstructure of the $MoO_2/Mo_2C/C$. Nitrogen adsorption-desorption measurement was employed to analyze the surface area and pore size distribution of the sample using an automated adsorption apparatus (NOVA3200e) at 77 K. X-ray photoelectron spectroscopy (XPS) measurement using Thermo Fisher (ESCALAB 250Xi) with a monochromatic Al *Kα* X-ray source was carried out to identify the surface oxidation state and chemical composition of the $MoO_2/Mo_2C/C$ microsphere.

2.3. Electrochemical measurement

The working electrode was firstly prepared by adequately dispersing the as-prepared $MoO_2/Mo_2C/C$ active material (70 wt%), acetylene black (20 wt%) and poly (vinylidene fluoride) binder (10 wt%) in N-methylpyrrolidone solvent to form a homogeneous slurry. Subsequently, the slurry was uniformly coated on a Cu foil and dried at 60 °C for 12 h to remove the solvent. Finally, the electrode material was cut into disks with a diameter of 14.0 mm and then dried at 120 °C in vacuum for 12 h. The average mass loading of $MoO_2/Mo_2C/C$ composite in the electrode was about 1–1.2 mg/cm^2. The counter electrode was pure lithium foil. The cell separator was polypropylene microporous film. In addition, the electrolyte was 1 mol/l $LiPF_6$ dissolved in a 1:1 (v/v) mixture of dimethyl carbonate (DMC) and ethylene carbonate (EC). A CR2025 coin-type half-cell was assembled in an argon-filled glove box with both oxygen and moisture contents below 1.0 ppm. The galvanostatic charge and discharge tests were recorded on a CT2001A LAND testing instrument (Wuhan Land Electronics Co., Ltd, China) with a voltage range of 0.01–3.0 V. Electrochemical impedance spectroscopy (EIS) (0.01 Hz–100 kHz, 5 mV) and cyclic voltammetry (CV) (0.01–3.0 V, 0.2 mV/s) were measured on an electrochemical workstation at room temperature.

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