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Synthesis of nickel oxide nanospheres by a facile spray drying method and their application as anode materials for lithium ion batteries

Anguo Xiao [*], Shibiao Zhou, Chenggang Zuo, Yongbing Zhuan, Xiang Ding

Department of Chemistry and Chemical Engineering, Hunan University of Arts and Science, Changde, Hunan 415000, China

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ABSTRACT

Fabrication of advanced anode materials is indispensable for construction of high-performance lithium ion batteries. In this work, nickel oxide (NiO) nanospheres are fabricated by a facial one-step spray drying method. The as-prepared NiO nanospheres show diameters ranging from 100 to 600 nm and are composed of nanoparticles of 30–50 nm. As an anode for lithium ion batteries, the electrochemical properties of the NiO nanospheres are investigated by cyclic voltammetry (CV) and galvanostatic charge/discharge tests. The specific reversible capacity of NiO nanospheres is 656 mA h g^{-1} at 0.1 C, and 476 mA h g^{-1} at 1 C. The improvement of electrochemical properties is attributed to nanosphere structure with large surface area and short ion/electron transfer path.

1. Introduction

In the past decades, 3d transition metal oxides (MO, where M is Fe, Co, Ni, and Cu) have been widely investigated as promising anodes for lithium ion batteries (LIBs) [1–5], because they have much higher capacities (two or three times) than that of graphite as well as smaller volume change than the alloy anodes [6–8]. Among the explored candidates, NiO has gained much more attentions due to its high theoretic capacity (718 mA h g^{-1}), non-toxicity, natural abundance, and low cost [9,10]. Albeit so many advantages, NiO still suffers from large volume expansion, thus resulting in large irreversible loss and fast capacity fading during the conversion reaction process [4,7], which severely limits its practical application. In order to overcome these issues, great efforts have been made to ameliorate the electrochemical capability of NiO, including nanostructuring of NiO [11–13], and surface modification with conductive layers [14–16]. Particularly, nanostructuring of NiO has been proven to be an effective method for enhancing the electrochemical performances. Researches have demonstrated that nanostructuring of NiO, usually porous NiO nanostructures [14,17,18], could effectively buffer the volume expansion avoiding the rapid capacity fading, leading to improved cycling performance, especially at high charge/discharge rates. Additionally, these porous structures can provide a very short diffusion pathway for lithium ion as well as large active surface, which leads to enhanced electrochemical properties [9,19,20].

Over recent years, various NiO nanostructures such as nanoparticles [21], nanoflakes [15,22], nanowalls [18,23], have been reported and applied for LIBs with enhanced properties. Inspired by these results, different from the above NiO nanostructures, in this work, we adopt a facile spray drying method for the preparation of NiO nanospheres composed of nanoparticles. The electrochemical properties of NiO nanospheres as anode of LIBs are investigated in detail. The developed method is useful for construction of other metal oxides for applications in supercapacitors and electrocatalysis.

2. Experimental

NiO nanospheres were prepared by a spray-drying method using $Ni(CH_3COO)_2 \cdot 4H_2O$ as starting materials. Nickel acetates and citric acid were measured with molar ratio (1:1) and dissolved in distilled water. The resulting solution was fed into a commercial spray-dryer to produce homogeneous precursor powders. The inlet air temperature was 220 °C, and the exit air temperature was kept in the range of 90–110 °C. The precursor powders were sintered in oxygen at 450 °C for 2 h to form NiO nanospheres.

The morphology and microstructure of products were characterized using scanning electron microscope (SEM, Hitachi S-4700), X-ray diffractometer (XRD, Rigaku D/max 2550 PC, Cu Kα) and transmission electron microscope (TEM, JEM 200CX at 160 kV and Tecnai G2 F20 at 200 kV).

The electrochemical measurements were performed using a coin-type half cell (CR 2025). The slurry consisted of 85 wt.% NiO nanospheres, 10 wt.% acetylene black and 5 wt.% polyvinylidene fluoride (PVDF) dissolved in N-methyl pyrrolidinone (NMP) was

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* Corresponding author. Tel.: +86 736 78186715; fax: +86 736 78186716.
E-mail address: hixiaoanguo@126.com (A. Xiao).

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pasted on copper foil with 12 mm in diameter. After dried at 90 °C for 24 h in vacuum, test cells were assembled in an argon-filled glove box with the metallic lithium foil as both the reference and counter electrodes, 1 M $LiPF_6$ in ethylene carbonate (EC)–dimethyl carbonate (DME) (1:1 in volume) as the electrolyte, and a polypropylene (PP) micro-porous film (Cellgard 2300) as the separator.

The galvanostatic charge/discharge tests were conducted on LAND battery program-control test system at rate 0.1 C in the voltage range of 0.01–3.0 V (versus Li/Li^+) at room temperature (25 ± 1 °C). Cyclic voltammetry (CV) and electrochemical impedance spectrum (EIS) were performed on CHI660C electrochemical workstation.

3. Results and discussion

SEM images of NiO samples prepared by the spray drying method are shown in Fig. 1a and b. Observe that the obtained NiO samples show typical spherical structures with diameters from 100 to 600 nm. The mean diameter is about 450 nm. The NiO nanospheres are composed of nanoparticles of 30–50 nm. Fig. 1c presents the TEM image of NiO nanopsheres. The nanospheres with mean diameter of 450 nm is clearly verified by the TEM result. The high-resolution TEM (HRTEM) image (Fig. 1c) provides more detailed structure information of the NiO nanopsheres. The secondary nanoparticles of 30–50 nm are also demonstrated in the inset of Fig. 1c. Moreover, the measured spacing between two adjacent lattices is 0.24 nm, which is consistent with the (1 1 1) planes of cubic NiO phase (JCPDS 47-1049). This is supported by the XRD powder pattern shown in Fig. 1d. The samples show typical diffraction peaks at 37.3, 43.3, 62.9, 75.4, 79.1° (Fig. 1d), which correspond to (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) crystal planes of cubic NiO phase (JCPDS 47-1049). In addition, no impurity peaks are observed, implying the purity of samples. Based on the above results, it can be concluded that the crystalline NiO nanospheres can be successfully prepared by the spray drying method.

To check the application for electrochemical energy storage, we investigated its ability to reversibly react with lithium as an anode for LIBs. The cyclic voltammogram (CV) of the NiO nanospheres electrodes measured between 0 and 3 V (versus Li^+/Li) at the 2nd cycle at a scanning rate of 0.1 mV s^{-1} is shown in Fig. 2a. For the NiO nanospheres electrodes, the reduction peak located at 0.94 V corresponds to the decomposition of NiO into Ni, and the formation of amorphous Li_2O and the SEI. The two oxidation peaks located at about 1.59 and 2.28 V can be attributed to the decomposition of the SEI and Li_2O, and reformation of NiO, respectively [11,12]. Fig. 2b shows the first two galvanostatic charge/discharge curves for NiO nanospheres electrodes at different current rates between 0.01 and 3.0 V. The initial discharge capacity of the NiO nanospheres electrodes is 968 mA h g^{-1} at 0.1 C, 862 mA h g^{-1} at 0.5 C and 786 mA h g^{-1} at 1 C, respectively. Accordingly, the first charge capacity is 654 mA h g^{-1} at 0.1 C, 554 mA h g^{-1} at 0.5 C and 476 mA h g^{-1} at 1 C, respectively. The corresponding initial coulombic efficiency is about 67.5, 64.2, and 62%, respectively. These obtained values are higher and comparable than other NiO powder electrodes including nanoparticles [21], and microspheres [24], but lower than NiO films such as nanoflake/nanowall films [14,18]. Notice that the first discharge capacity is higher than the theoretical capacity of 718 mA h g^{-1}, which can be attributed to be the formation of solid electrolyte interface (SEI) films on the NiO nanospheres during the discharge process [1,2], which happens in all 3d transition metal oxides, including NiO [15,25], Co_3O_4 [3,9], Fe_2O_3 [26,27], CoO [1], CuO [28]. Meanwhile, recently, Hu et al. [29] and co-workers have done a careful research about the additional capacity of metal oxides. It is indeed found that the additional capacity may come from reversible SEI formation, and the formation of LiOH and its subsequent reversible conversion to Li_2O and LiH.

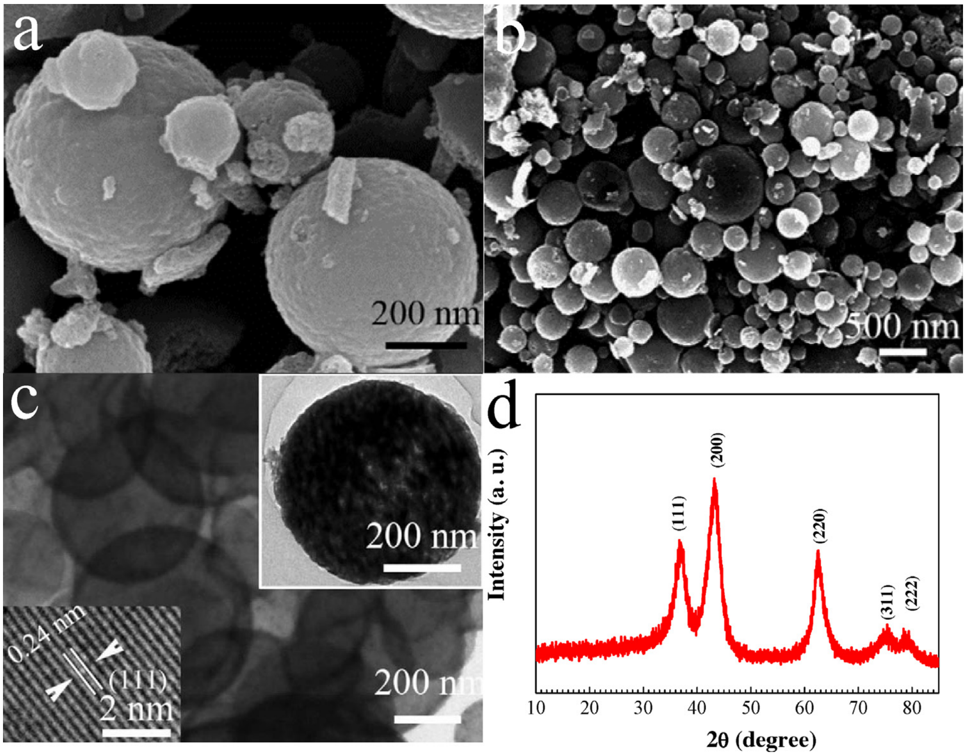

Fig. 1. (a and b) SEM images of NiO nanospheres prepared by a spray drying method. (c) TEM image of NiO nanospheres (fine structure and high-resolution TEM image in insets). (d) XRD pattern of NiO nanospheres.