Materials Research Bulletin 63 (2015) 112–115

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Short communication

The fabrication of foam-like 3D mesoporous NiO-Ni as anode for high performance Li-ion batteries

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ARTICLE INFO

Article history:
Received 25 March 2014
Received in revised form 24 September 2014
Accepted 5 October 2014
Available online 13 October 2014

Keywords:
A. Microporous materials
D. Electrochemical measurement
D. Energy storage

ABSTRACT

Foam-like three dimensional mesoporous NiO on Ni foam was fabricated via facile hydrothermal etching and subsequent annealing treatment. The porous NiO consists of a large number of nanosheets with mean thickness about 50 nm, among which a large number of mesoscopic pores with size ranges from 100 nm to 1 μm distribute. The electrochemical performance of the as-prepared NiO-Ni as anode for lithium ion battery was studied by conventional charge/discharge test, which shows excellent cycle stability and rate capability. It exhibits initial discharge and charge capacities of 979 and 707 mA h g^{-1} at a charge/discharge rate of 0.7 C, which maintain of 747 and 738 mA h g^{-1} after 100 cycles. Even after 60 cycles at various rates from 0.06 to 14 C, the 10th discharge and charge capacities of the NiO-Ni electrode can revert to 699 and 683 mA h g^{-1} when lowering the charge/discharge rate to 0.06 C.

1. Introduction

Based on a novel electrochemical reaction mechanism $2y\,Li^+ + 2y\,e^- + Me_xO_y \leftrightarrow x\,Me + y\,Li_2O$, transition metal oxides (TMOS) show theoretical capacity as high as 500–1000 mA h g^{-1}, which endow them with potential applications in lithium ion batteries [1–4].

Among them, NiO anode has been widely researched due to its high theoretical capacity of 718 mA h g^{-1}, low cost, environment friendly and abundance [5–9]. However, the low electrical conductivity (less than $10^{-13}\,\Omega^{-1}\,cm^{-1}$ at room temperature) is a disadvantage for the application as anode for lithium ion batteries. In addition, the volume variation in cycling is another challenge for NiO, which leads to the destruction of the original morphology, worsening the electrochemical performance. Fabrication of nano-sized NiO on electric substrate is an efficient way to improve the electronic conductivity of NiO, which is beneficial to improve the reaction kinetics of NiO. Meanwhile, porous architecture usually shows specific physical and chemical properties owing to its big surface area, which has potential application in lithium ion batteries, gas sensor, and catalysis [10–12]. By now, much work on the preparation of porous architecture of NiO on electric substrate has been done, which shows attractive electrochemical performance as anodes for lithium ion batteries. For example, Wang et al. fabricated NiO nanoparticles on porous Ni foam via a thermal treatment method, which shows capacity retention higher than 93% after 30 cycles [13]. Varghese et al. deposited NiO nanowalls on Ni foil via a plasma assisted oxidation method, which exhibits low capacity fading of 7% from the 2nd to 40th cycle [14]. Wang et al. reported the preparation of NiO nanocone on Ni foam via an electrochemical deposition method with subsequent oxidation treatment and NiO nanosheet networks on Ni foam via solvothermal method with subsequent annealing, which shows charge and discharge capacities higher that the theoretical capacity [15,16]. Wu et al. fabricated NiO nanoflakes on Cu foam via a chemical method and subsequent annealing, which shows discharge capacity of 720 mA h g^{-1} after 20 cycles [17]. Ni et al. reported the preparation of NiO nanowalls on Ni foam via graft growth and in situ methods, which show stable charge and discharge capacities over 100 cycles [18,19].

Here in this paper, we report the preparation of novel foam-like 3D mesoporous NiO on 3D microporous Ni foam via a facile hydrothermal etching and subsequent annealing. The electrochemical performance of the as-synthesized NiO-Ni as anode for lithium ion batteries was studied, which shows good cycle stability and rate capability, endowing it with potential application in lithium ion batteries.

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http://dx.doi.org/10.1016/j.materresbull.2014.10.023
0025-5408/

2. Experimental

2.1. Sample preparation

Ni foam with pore size of 100 PPI, surface density of 380 g m^{-2} and thickness of 1.5 mm was purchased from Changsha Lyrun New Material corporation. Before sample preparation, Ni foams were firstly put into diluted hydrochloric acid until the solution changes into pea green to eliminate the surface oxide layer. Then, it was washed with distilled water several times to remove the rudimental Cl^-. The washed Ni foam was placed into a 50 ml teflonlined autoclave, distilled water and 0.5 ml HF was subsequently added to 80% of the capacity. The autoclave was sealed and placed in an oven, heated at 90 °C for 10 h. After the reaction, the autoclave was cooled in air. The treated Ni foam was annealed in air at 350 °C for 5 h to obtain NiO-Ni. For measuring the weight of active NiO on Ni, the NiO-Ni was washed in diluted hydrochloric (V_{HCl}:V_{H_2O} = 1:10) to remove the surface NiO and then dried. $m_{NiO} = \Delta m$, where Δm is the weight of Ni foam before and after washing.

2.2. Structure and morphology characterization

The structure and morphology of the resulting products were characterized by X-ray powder diffraction (Rigaku Ultima IV Cu Kα radiation $\lambda = 1.5406$ Å) and field-emission scanning electron microscopy (FE-SEM JSM 7500F, JEOL).

2.3. Electrochemical characterization

For fabricating of lithium ion battery, the as-prepared NiO-Ni foam discs were dried (120 °C, 24 h, vacuum). Coin-type cells (2025) of Li/1M $LiPF_6$ in ethylene carbonate, dimethyl carbonate, and diethyl carbonate (EC/DMC/DEC, 1:1:1 v/v/v)/NiO-Ni disc electrode with diameter of 14 mm were assembled in an argon-filled dry box (MIKROUNA, Super 1220/750, $H_2O < 1.0$ ppm, $O_2 < 1.0$ ppm). A Celgard 2400 microporous polypropylene was used as the separator membrane. The cells were tested in the voltage range between 0.02 and 3 V with a multichannel battery test system (LAND CT2001A). The Cyclic voltammetry (CV) measurement of the electrodes was carried out on a CHI660C electrochemical workstation at a scan rate of 0.2 mV s^{-1} between 0 and 3 V.

3. Results and discussion

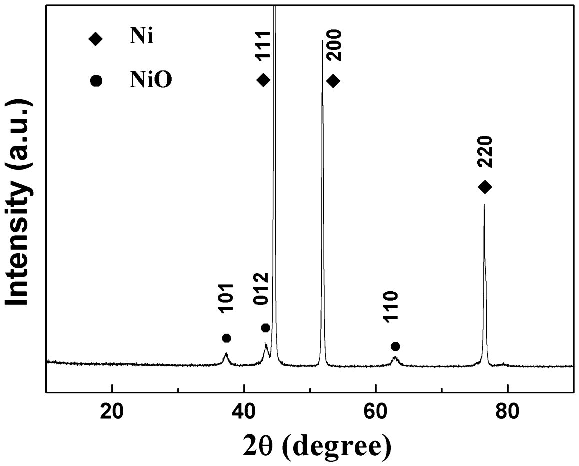

Fig. 1. XRD pattern of the obtained sample.

Fig. 1 is the XRD pattern of the as-prepared sample. It shows three typical diffraction peaks located at 44.5°, 51.9°, and 76.5°, which correspond to Ni (1 1 1), (2 0 0), and (2 2 0) faces, respectively (JCPDS, No. 04-0850). Diffraction peaks other than those of Ni, located at 37.4°, 43.3°, and 63.0°, respectively, can be ascribed to the (1 0 1), (0 1 2), and (1 1 0) faces of hexagonal NiO with lattice constant $a = 2.955$ Å and $c = 7.227$ Å, which is in accordance with JCPDS, No. 44-1159.

Fig. 2(a) is a low magnification SEM image of the obtained NiO-Ni. As seen, uniform film-like NiO is successfully grown on the surface of Ni foam, which shows porous architecture. High magnification SEM image of the NiO-Ni is shown in Fig. 2(b), which exhibits foam-like porous architecture with a large number of 3 dimensional (3D) pores with pore size ranges from 100 nm to 1 μm. As seen, the foam-like 3D porous architecture of NiO originates from the construction of a large number of NiO nanosheets with mean thickness about 50 nm, which interweave with each others in 3D space and form an integrated structure. The formation mechanism of the novel 3D mesoporous architecture of NiO is not clear by now, which may be relevant to the presence of HF, playing an etching effect in the hydrothermal process.

Galvanostatic charge/discharge cycling was carried out in the potential window of 0.02–3.0 V versus Li. Fig. 3(a) shows the initial three charge and discharge curves for the NiO-Ni electrodes at a charge/discharge rate of 0.7 C (1 C means accomplishing discharge or charge in an hour, 2.3 mg). An obvious plateau near 0.5 V in the initial discharge curve can be observed, which corresponds to the formation of solid electrolyte interface (SEI) and the reduction of NiO into Ni [9,13,20,21]. It becomes a sloping potential region from 1.7 to 0.8 V in the subsequent two discharge curves owing to the

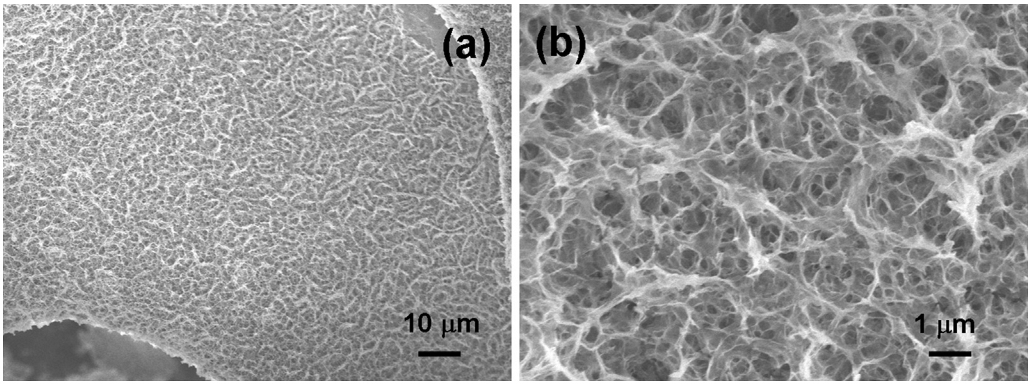

Fig. 2. SEM images of the NiO-Ni electrode with low (a) and high (b) magnification.