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Facile ammonia-induced fabrication of nanoporous NiO films with enhanced lithium-storage properties

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ABSTRACT

Nanoporous NiO films directly grown on the foam Ni are fabricated via a facile ammonia-induced route. As anode materials for lithium-ion batteries, nanoporous NiO films exhibit an outstanding rate capacity of 280 mAh·g^{-1} at 10 *C* rate and high reversible capacity of 543 mAh·g^{-1} after 100 cycles at 0.2 *C* rate. The fabrication strategy offers a novel approach to fabricate other thin film materials.

1. Introduction

With the ever-going demand for high power lithium-ion batteries (LIBs) as the prime candidates for electric vehicles (EV) and hybrid electric vehicles (HEV), as the transition-metal oxides, NiO is one of the most appealing anode materials with a theoretical capacity of 718 mAh·g^{-1} and improved safety than graphite [1,2]. However, its practical application is frustrating owing to the low rate performance caused by kinetic limitations and poor cycling stability that resulted from the huge volume variation during the discharge–charge process [3]. Recently, nanostructured NiO anodes have attracted great interest in virtue of their easier ions and electron transport and larger electrode/electrolyte contact area. Various NiO nanostructures [4] such as nanoplates [5], nanotubes [6], nanoflowers [7], nanosheet-based microspheres [8] and nanostructured thin films [9,10] have been studied in recent years. Hereinto, nanostructured thin films are regarded as promising nanoarchitectured electrodes for LIBs consisting of active nanomaterials directly connected to the substrate which could enhance the electrical contact between the substrate and active materials, shorten diffusion lengths for lithium ion, and keep the structural stability, leading to excellent electrochemical performance [9,10].

Generally, strategies for fabricating nanostructured NiO films mainly include template assisted deposition [11], RF plasma assisted oxidation [9], electrodeposition [12], electrostatic spray deposition [13], chemical bath deposition [14], etc. All these approaches require expensive template, complicated procedures, special equipment, or diversified additives. In this work, we report a facile ammonia-induced route to grow nanoporous NiO films on the foam Ni substrate, wherein neither template nor surfactants are employed. The as-prepared nanoporous NiO films with a well-defined unique porous structure exhibit enhanced lithium-storage properties.

2. Experimental

Nanoporous NiO films (S1) were fabricated as follows: first, foam Ni (diameter 1.4 cm, 1.54 cm^2) was rinsed ultrasonically with ethanol, and dried at room temperature. Then, foam Ni was immersed into 1.0 M (mol·L^{-1}) ammonia solutions for 4 days, and finally heated at 500 °C for 4 h in air. In comparison, NiO films (S2) were gained by directly heating foam Ni at 500 °C for 4 h. According to the literature [15], the mass of a piece of S1 and S2 was ~0.6 and 1.0 mg, respectively. All samples were characterized by X-ray diffraction (XRD, Rigaku D/max-γB), Fourier transform infrared (FTIR, Nicolet iS10), differential scanning calorimetry (DSC-60), scanning electron microscopy (SEM, Hitachi S4800) and transmission electron microscopy (TEM, Tecnai G^2 F30). The pore size analysis was calculated by the software of SEM image analysis (Nano Measurer System, 1.2.5).

Electrochemical behaviors of NiO films S1 and S2 were measured via CR2025 coin-type test cells assembled in a dry argon-filled glove box. NiO films were used as working electrodes, two porous polypropylene films as a separator, 1 M LiPF$_6$ in ethylene carbonate, diethyl carbonate and ethylmethyl carbonate (EC/DMC/EMC, 1:1:1 vol) as electrolyte, and Li foil as the counter and reference electrodes, respectively. Cells were aged for 8 h before measurement. Galvanostatic

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discharge/charge was performed at various rates from 3.0 to 0.02 V (vs. Li^+/Li) on BTS battery testing system.

3. Results and discussion

The ammonia-induced route to fabricate nanoporous NiO films shown in Fig. 1A, involves the complexation, decomposition and oxidation processes, which were different from the process of heating oxidization growth [10,16]. From the FTIR spectra of ammonia solutions in Fig. 1B, strong bands at 3460, 1640 and 442 cm^{-1} can be observed, corresponding to vibrations of $V(Ni(NH_3)_x, NH_3)$, $V(H_2O)$ and V(Ni–N), respectively [17,18]. Fig. 1C displays DSC analyses of the Ni immersed in ammonia solutions for 4 (a) and 0 (b) days. Apparently, a sharp peak was at ~56 °C, corresponding to the volatilization of the ammonia molecule absorbed physically on the Ni surface. The broad peak at ~380 °C could be attributed to the transformation from nickel–ammonia complexation $Ni(NH_3)_x$ [19,20] to active Ni nanoparticles and release of nitrogen-related gas [21]. It was indicated that $Ni(NH_3)_x$ contributed to nanoporous NiO films. While immersed in the ammonia solution, the Ni surface underwent a complicated nickel–ammonia complexing reaction and generated $Ni(NH_3)_x$. With the increase of the heating temperature, $Ni(NH_3)_x$ was decomposed, translated into active Ni nanoparticles, quickly oxidized into NiO nanoparticles in heating air, and finally cumulate to nanoporous NiO films.

Fig. 2A shows XRD patterns for NiO films S1 and S2. Removing strong peaks of the cubic crystal Ni (JCPDS card no. 65-2865), the broad peaks can be indexed as the face-centered cubic crystalline NiO in good agreement with the standard data JCPDS card no. 47-1049, suggesting that NiO films have grown on the Ni surface. Fig. 2B–D displays SEM images of S1. The low magnification image (B) indicates that foam Ni was constructed by Ni wires, which played the role of an electronic conductive path [22]. Viewed from the top and side of the Ni pore wall (Fig. 2C–D), nanoporous NiO films are perpendicular to the Ni pore wall with the thickness of 400–500 nm and composed of nanoparticles, which cumulate to the well-defined unique porous structure with an average pore size ca. 43 nm, according to the calculation of SEM image analysis software (Fig. 2E). Moreover, the TEM image (Fig. 2F) further demonstrates that NiO nanoparticles are polycrystalline with a grain size of 30–60 nm. For comparison, the kind of NiO films (S2, in Fig. 2G–I) with polycrystalline nature fabricated by directly heating foam Ni, consists of nanoparticles of ca. 100–150 nm, and has lots of loose porous structure with an average pore size of ca. 77 nm.

As anodes of high power LIBs, charge–discharge curves of nanoporous NiO films at 0.2 *C* (1 *C* = 718 $mA\cdot g^{-1}$) rate are shown in Fig. 3A. In the first discharge process, the constant slopes between 0.65 and 0.2 V indicate the conversion reaction between NiO and lithium [2]. The initial discharge and charge capacity are 1033.6 and 636.9 $mAh\cdot g^{-1}$, respectively. The initial irreversible capacity loss of 38.4% may result from interfacial lithium storage, inevitable formation of solid electrolyte interface (SEI layer) and organic conductive polymer [23]. Remarkably, from the second cycle onwards, nanoporous NiO films exhibit no capacity.

Fig. 3B shows high reversible capacities of nanoporous NiO films at different rates from 0.2 *C* to 10 *C*. Reversible capacity decreased slowly with increase in the discharge/charge rate. Outstanding capacities of 635 and 280 $mAh\cdot g^{-1}$ could be obtained at 0.2 *C* and 10 *C* rates, respectively. While the rate returned to 0.2 *C*, nanoporous NiO films can still deliver a reversible capacity of 601 $mAh\cdot g^{-1}$. Additionally, as shown in Fig. 3C, nanoporous NiO films exhibit a high reversible capacity of 543 $mAh\cdot g^{-1}$ after 100 cycles at 0.2 *C* rate. For comparison, Fig. 3D presents cycling stability of nanoporous NiO films S1 and NiO films S2. Reversible discharge capacity of S1 was 534 $mAh\cdot g^{-1}$ with capacity retention of 90.2% after 100 cycles at 0.5 *C* rate, and that of S2 was merely 432 $mAh\cdot g^{-1}$ with capacity retention of 60.0% after 100 cycles. It was indicated that the porous structure of nanoporous NiO films was considerably mechanically stable.

Compared to literature [21,24], nanoporous NiO films exhibited higher electrochemical performance, attributing to advantages of the well-defined unique nanoporous structure. First, the nanoporous structure that connected directly to the foam Ni has good contact with the substrate, facilitating electrons flowing from the substrate to NiO films, benefiting electrolyte penetration, and shortening diffusion paths for lithium ion. Second, the highly porous structure enlarges the efficient contact surface between active materials and electrolyte, providing more active sites for lithium-storage. Third, nanoporous structure possesses favorably morphological stability and accommodates the strain of the volume change during the charge–discharge process.

4. Conclusions

In conclusion, we have developed a facile ammonia-induced route to grow nanoporous NiO films on the foam Ni. Nanoporous

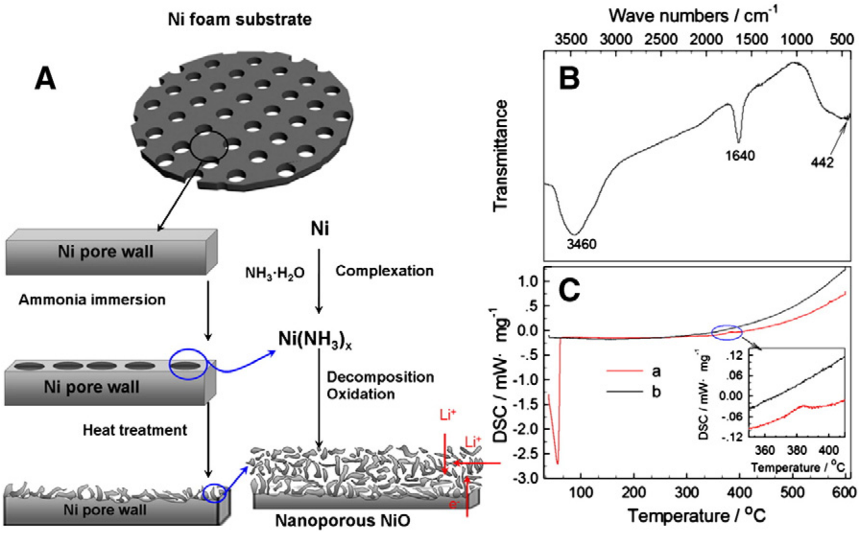

Fig. 1. (A) Schematic illustration of the formation process of nanoporous NiO films. (B) The FTIR spectra of ammonia solutions, where foam Ni was immersed for 4 days. (C) DSC curves for heating oxidation of foam Ni immersed in 1 M ammonia solutions for 4 (a) and 0 (b) days at 2 $°C\cdot min^{-1}$ in air.