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Hollow microspheres of NiO as anode materials for lithium-ion batteries

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ABSTRACT

NiO hollow spheres are prepared by heating the NiCl₂/resorcinol-formaldehyde (RF) gel in argon at 700 °C for 2 h, and subsequently in oxygen at 700 °C for 2 h. X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) are employed to characterize the structure and morphology of the as-prepared NiO hollow spheres. These hollow spheres have a diameter of about 2 μ m, which are composed of NiO particles of about 200 nm. The electrochemical properties of these NiO hollow spheres are investigated to determine the reversible capacity and cycling performance as anode materials for lithium-ion batteries, and the advantages of their hollow spherical morphology to the electrochemical performance are discussed.

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1. Introduction

3d transition-metal oxides, including FeO, CoO, NiO, Cu₂O, and their high valence oxides or mixed oxides, exhibit capacities over 700 mAh g^{-1} , which are twice higher than the traditional carbon materials, are promising alternatives to carbon as anode materials for lithium-ion batteries [1-7]. However, for many unmodified 3d transition-metal oxides, their capacities often reduce very quickly during the repeated charge-discharge cycling. So in recent years, much research work is focused on improving their electrochemical performance, and many methods are invented. For example, forming composites with conductive materials such as carbon [8,9] is a very common and useful method, but this method often reduces the mass specific capacity. So preparing materials with special morphology such as porous structure [10–13], nanoarrays [14,15], microspheres [16-20] and some others [21] to enhance the electrochemical performance has attracted much attraction. For example, hollow spherical materials often exhibit good electrochemical performance, mainly due to their large specific surface area, short diffusion length of Li⁺, good electrical contact and conductivity, or good ability of buffering the volume change during the electrochemical reactions.

Hollow spherical metal oxides can be prepared using carbon spheres as the template [22,23]. In the present work, Ni/carbon composite microspheres are prepared by calcining NiCl₂/RF gel in argon, and then used as the template to prepare NiO hollow microspheres. These NiO hollow microspheres are assembled with many NiO particles, and their electrochemical properties are investigated to determine the capacity and cycling performance as anode materials for lithium-ion batteries.

2. Experimental

The synthetic procedure is described in Scheme 1. In a typical synthesis, $10 \text{ g NiCl}_2 \cdot 6\text{H}_2\text{O}$, 6.5 g resorcinol, and 9 mL 37% formalde-hyde was dissolved in 100 mL deionized water. Adjust pH with concentrated hydrochloric acid until it reached 1.0. The mixture was sealed with a layer of PE film and placed in a water bath at 85 °C for 3 h to produce a NiCl₂/resorcinol-formaldehyde (RF) gel, and then the gel was dried in an oven at 85 °C for 24 h. Subsequently, the dried gel was transferred to a quartz tube furnace and calcined at 700 °C for 2 h under flowing argon, and this carbonization process produced Ni/carbon composite microspheres. When the Ni/carbon composite was finally heated to 700 °C and maintained for 2 h under oxygen atmosphere, the carbon spheres template was burnt out completely and NiO hollow microspheres were obtained.

The structure and morphology of the materials were characterized by X-ray diffraction (XRD, Rigaku D/max-rA), scanning electron microscopy (SEM, FEI Sirion-100), and transmission electron microscopy (TEM, JEOL, JEM200CX).

The working electrodes were prepared by coating the slurry consisted of 80 wt% active materials, 12 wt% acetylene black, and 8 wt% polyvinylidene fluoride (PVDF) dissolved in N-methyl pyrrolidinone (NMP) on copper foil. The electrodes were dried at 95 °C for 12 h in vacuum and then pressed under 20 MPa. Half cells were assembled in an argon-filled glove box using Li foil as counter electrode, and polypropylene film as separator. The electrolyte

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Scheme 1. Schematic representation of synthetic procedure.

was a mixed solution of ethylene carbonate (EC) and diethyl carbonate (DEC) containing 1 mol L⁻¹ LiPF₆. The cells were galvanostatically discharged and charged using different current densities over a potential range of 0.02–3.0 V. Cyclic voltammetry (CV) measurements of the electrodes were carried out on a CHI660C electrochemical workstation at a scan rate of 0.1 mV s⁻¹ between 0 and 3 V.

3. Results and discussion

3.1. Characterization of NiO hollow spheres

When NiCl₂/RF gel was heated at 700 °C in argon, the gel was undergoing a carbonization process and NiCl₂ was reduced to Ni metal. Fig. 1(a) shows the XRD pattern of the product after this carbonization process. The peaks at 44.4°, 51.7°, and 76.3° can be assigned to the (111), (200), and (220) reflections of cubic Ni, respectively. After subsequently heated at 700 °C in oxygen, the carbon was burnt out completely and Ni was oxidized to NiO. This is confirmed in the XRD pattern (Fig. 1(b)), in which the peaks at 37.2°, 43.3°, 62.8°, 75.5°, and 79.4° can be assigned to the (111), (200), (220), (311), and (222) reflections of cubic NiO, respectively.

Microspheres were obtained after the carbonization of NiCl₂/RF gel in argon, as shown in Fig. 2(a). These spheres should be Ni/C composite spheres, and their diameter is about 2 μ m. After calcined in oxygen, the product remains the spherical morphology, as shown in Fig. 2(b), and the diameter of these NiO spheres is still about 2 μ m, but their surface becomes much rougher. According to the high magnified image of a sphere inserted in the lower right corner, it can be seen that the NiO sphere is constructed of many NiO particles. From the TEM image of a NiO sphere, shown in Fig. 3(a), it is obviously that the sphere is hollow, with the shell of 300–500 nm in thickness. Fig. 3(b) shows the TEM image of some particles peeled off from the spheres by an ultrasonic process. It can be seen that the sizes of these NiO particles are about 200 nm.

3.2. Electrochemical performance of NiO hollow spheres

The as-prepared NiO hollow microspheres were used as anode materials for lithium-ion batteries and their electrochemical per-



Fig. 1. XRD pattern of (a) Ni/C composite prepared by calcining NiCl₂/RF gel in argon, and (b) NiO prepared by calcining Ni/C composite in oxygen.



Fig. 2. SEM images of (a) Ni/C composite spheres and (b) NiO spheres.

formance were tested. Fig. 4 shows the cyclic voltammograms of a NiO/Li cell at a scan rate of $0.1 \,\mathrm{mV \, s^{-1}}$ in the potential range of 0-3 V. In the first reduction process, a strong reduction peak at 0.6 V is observed, corresponding to the first electrochemical reaction NiO + 2Li \rightarrow Ni + Li₂O, and the formation of the SEI layer, which is a polymeric gel-like layer which contains ethylene-oxide-based oligomers, LiF, Li₂CO₃, and lithium alkyl carbonate (ROCO₂Li) [7]. In the first oxidation process, two oxidation peaks are found at 1.6 and 2.3 V. The weak peak at 1.6 V should correspond to the dissolution of the organic SEI layer [3,5], and the strong peak at 2.3 V corresponds to the charge reaction $Ni + Li_2O \rightarrow NiO + 2Li$. However, the second curve is different from the first one, in which the reduction peak becomes weaker, and shifts to 1.2 V, exhibiting a smaller polarization. The curve of the third cycle is very similar to the second one, indicating the reversibility of the cell gets better since the second cycle.

Fig. 5 shows the discharge and charge curves for the first three cycles and the 45th cycle of the NiO/Li cell measured between 0.02 and 3.0 V at a current density of 100 mA g⁻¹. In the first discharge, there is a quick potential drop to 0.6 V at first, followed by a long flat plateau at 0.6 V, which corresponds to the convention reaction NiO+2Li \rightarrow Ni+Li₂O. The sloping part in the end of the discharge curve between 0.6 and 0 V corresponds to the formation of the SEI layer [6]. However, starting from the first charge, the charge and discharge plateaus are not obvious. There are two slops around 1.6 and 2.3 V in each charge curve, and the slop in each discharge curve is around 1.2 V. Smaller potential hysteresis indicates that the electrode reactions become more reversible since the second cycle. It is known that the theoretical capacity of NiO is 718 mAh g⁻¹, which is calculated from the electrode reaction NiO+2Li \Rightarrow Ni+2Li₂O. However, it can be seen in the curve that the first discharge capacity of



Fig. 3. TEM images of (a) a NiO hollow sphere and (b) NiO particles peeled off from the spheres.

NiO hollow spheres is 1100 mAh g^{-1} , much higher than the theoretical value. The extra capacity should come from the growth of the gel-like SEI layer on the surface of the particles during the first discharge [6]. The first charge capacity is 620 mAh g^{-1} , and the second discharge capacity is 700 mAh g^{-1} . Since the second cycle, the curves are similar, but the capacity is gradually decreases. Until the 45th cycle, the discharge and charge capacities remain 560 and 490 mAh g⁻¹, respectively. The discharge and charge capacities for each cycle are plotted in Fig. 6. It can be calculated that 80% of



Fig. 4. Cyclic voltammograms for NiO/Li cell at a scan rate of 0.1 mV s^{-1} . The cycle numbers are marked in the graph.



Fig. 5. The discharge and charge curves of the NiO/Li cell at a current density of 100 mA g^{-1} . The cycle numbers are indicated in the graph.

the reversible capacity remains after 45 cycles. The cycling performance of these NiO hollow microspheres is much better than NiO irregular particles and NiO solid spheres prepared in our previous work [24,25].

The rate capability of the NiO/Li cell was also investigated and the results are shown in Fig. 7. When cycled at the current density of 200 mAg^{-1} for the first 10 cycles, the final discharge and charge capacities are 635 and 535 mAh g⁻¹, respectively. Then the current density increases to 500 mAg^{-1} , and the end capacities are $520 \text{ and } 450 \text{ mAh g}^{-1}$. After that, the current density reaches to 1000 mAg^{-1} , and the capacities are 275 and 240 mAh g⁻¹. Subsequently, the current reduces to 100 mA g^{-1} , and the capacities are up to 580 and 510 mAh g⁻¹. When the current density returns back to 200 mA g^{-1} at last, the final capacities are 520 and 470 mAh g⁻¹.

As compared to many NiO irregular particles and NiO dense solid spheres [18,24,25], the NiO hollow microspheres exhibit better electrochemical performance. The hollow spherical morphology of NiO has many advantages to its electrochemical performance. In the hollow spheres, both the two sides of the shell can be immersed in the electrolyte, leading to a larger specific surface area and a shorter diffusion length of Li⁺. So the electrochemical reactions of the NiO hollow spheres can proceed much more quickly and completely, and thus they exhibit higher capacity and better rate capability. According to the SEM and TEM images, the NiO hollow spheres are assembled by many NiO particles, and these particles contact



Fig. 6. Cycling performance of NiO/Li cell at a current density of 100 mA g⁻¹.



Fig. 7. The specific capacities of NiO/Li cell cycled at different current densities.

well with each other, leading to good electric contact during the electrochemical reaction. Furthermore, the hollow spheres have good ability of accommodating the large volume change during the discharge and charge reaction and thus alleviate the pulverization process. The good conductivity and the alleviated pulverization lead to the good cycling performance of NiO hollow spheres.

4. Conclusions

NiO hollow spheres are prepared by calcining the NiCl₂/RF gel in argon and subsequently in oxygen. SEM and TEM images show that these hollow spheres are assembled by NiO particles with sizes of about 200 nm. Electrochemical test shows that these spheres deliver discharge and charge capacities of 560 and 490 mAh g⁻¹ after 45 cycles at the current density of 100 mA g⁻¹, and also exhibit good rate capability. The NiO hollow microspheres can offer large specific surface area, good electric contact among the particles, and good tolerance of volume change, which are benefit for their electrochemical performance.

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