Investigation of anode materials for lithium-ion batteries

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7.1 Introduction

Rock salt structured MO-type (M = Fe, Co, Ni, Cu) transition metal oxides react reversibly with lithium in a lithium cell below 1.5 V (Poizot et al. 2000). It has been reported that the MO type oxides demonstrate large capacity (700 mAh/g), long cycle life, and high recharging rates. These brilliant properties make them promising candidates for use as anode materials for Li-ion batteries (Poizot et al. 2002). Among them, nickel oxide is an interesting material due to its applications in diverse fields, including catalysis (Sheela et al. 1995), electrochromic films (Chigane and Ishikawa, 1992; Yoshimura et al. 1995), fuel cell electrodes (Tomczyk et al. 1993; Makkus et al. 1994), gas sensors (Alcock et al. 1992; Kumagai, et al. 1996), smart windows (Ferreira et al. 1996; Scarminio et al. 1992; Fantini et al. 1996), and lithium ion batteries (Chiu et al. 2005; Wang and Qin, 2002). Many methods have been used to prepare NiO, such as calcinations of almost any nickel compounds in air, physical and chemical vapor deposition, and the sol-gel process (Jiao et al. 2003; Yang et al. 2005). Considerable efforts have also been made in the synthesis of one-dimensional (1D) nanostructured NiO materials because of their intriguing properties and unique applications. Wang et al. (2002d) synthesized single crystal cubic NiO nanorods by a simple thermal decomposition approach. Matsui et al. (2001) made nickel oxide nanoribbons in the cavities of carbon nanotubes. Polycrystalline NiO nanowires have been synthesized by an electrochemical deposition method (Lin et al. 2003), while single crystal NiO
nanowires have been prepared via a wet chemical method, a molten salt assisted oxidation route, and a sol-gel process (Xu et al. 2003; Zhan et al. 2003).

In this part, we report a simple aqueous solution method used in combination with calcination to fabricate spherical clusters of NiO nanoshafts. For comparison, NiO nanoparticles made by calcining Ni(OH)$_2$ nanopowder were also prepared. Although NiO nanopowders, nanotubes, and thin films have been reported recently as anode materials for lithium ion batteries (Chiu, et al. 2005; Wang and Qin, 2002e), NiO spherical particles composed of nanoshafts have not been reported to the best of our knowledge. Since both the morphology and the particle size of transition-metal oxides (MO, where M is Fe, Co, Ni, Cu or Mn) have an influence on their anode performance (Li, et al. 2005b), this investigation on the spherical clusters of NiO nanoshafts has some significance. The advantages of the spherical clusters of NiO nanoshafts as anode materials for lithium ion batteries are not only the extremely large surface area, but also that, it is easy for the lithium ions to diffuse along the direction of the nanoshafts.

The electrochemical performance of the as-prepared spherical clusters of NiO nanoshafts and NiO nanoparticles as anode materials for lithium ion batteries was systematically investigated by using cyclic voltammetry and charge/discharge methods. The results show that spherical clusters of NiO nanoshafts are promising materials for application in rechargeable lithium-ion batteries.
7.2 Synthesis and characterization of NiO nanoshfts

Spherical clusters of NiO nanoshfts were synthesized by decomposing (at 280 °C in air) spherical Ni(OH)$_2$ precursors. The preparation of the precursor is the most crucial step in the synthesis procedure. First, nickel sulfate was dissolved in distilled water, then NH$_3$. H$_2$O was added to the NiSO$_4$ solution as a complexing agent. The pH was adjusted to 11-12. After that, sodium hydroxide solution was dropped into the reaction solution very slowly, and precipitation was induced. The temperature of the reaction solution was maintained at about 45°C, while the reaction solution was continuously stirred. Throughout this operation, the pH and temperature of the reaction solution were rigidly kept at values within the above-mentioned ranges. Thus, spherical Ni(OH)$_2$ particles were yielded. The next step consisted of the calcination of the Ni(OH)$_2$ precursors. In order to preserve the morphology of the precursors, we needed to optimize the calcination parameters. TGA/DTA analysis on the precursors was conducted at a heating rate of 5°C min$^{-1}$ in air. The TGA/DTA curves showed that the decomposition of the hydroxide precursor occurs between 240 and 320 °C. Therefore, in our work, we chose to calcine the precursor at 280 °C for 2 h in air. NiO nanoparticles were also prepared for comparison. NiO nanoparticles were prepared by grinding a stoichiometric amount of Ni(OAc)$_2$·4H$_2$O with KOH and the appropriate amount of citric acid in an agate mortar at room temperature for about half an hour. Then the products were washed with distilled water, treated in an ultrasonic bath with ethanol, and centrifuged. After that, the samples were dried at 80 °C in vacuum for 4 h, and a light green Ni(OH)$_2$ powder was obtained, which was then sintered at 350 °C for 2 h.
Fig. 7-1 XRD patterns of the as-prepared NiO materials.

The spherical clusters of NiO nanoshfts were synthesized by decomposing spherical clusters of Ni(OH)$_2$ nanoshfts. Despite full conversion to the ordered cubic unit cell, the overall morphology of the spherical clusters of nanoshfts has remained. We believe that the main difference between our preparation method and other lies in the strict control of the speed at which the sodium hydroxide and ammonia aqueous solution are added, the PH values, and the reaction temperature. The NH$_3$, H$_2$O works as a complexing agent, helping to form one dementsional Ni(OH)$_2$ nanoshft structures, which is believed to be beneficial to formation of agglomerated particles with an overall spherical shape. The phase purity and crystallinity of the as-synthesized NiO materials were characterized by using x-ray diffraction (XRD). Fig. 7-1 shows the XRD patterns of the as-prepared spherical clusters of NiO nanoshfts and nanoparticles. All diffraction peaks can be perfectly indexed to cubic structure crystalline NiO, indicating that there is no impurity
in the NiO powder. The Bragg peaks of the spherical clusters of NiO nanoshafts are markedly broadened compared with those of the NiO nanoparticles, suggesting that very fine grain sizes and defects in the spherical clusters of NiO nanoshafts were produced in the synthesizing process. The crystallite size of NiO was calculated using the Scherrer equation, and the calculated crystallite size of NiO in the as-prepared spherical clusters of NiO nanoshafts and NiO nanoparticles are 6.73 and 10.71 nm, respectively.

Fig. 7-2 shows scanning electron microscope (SEM) images of the as-prepared spherical clusters of NiO nanoshafts. Fig. 7-2(a) is an overall view of the as-synthesized spherical clusters, from which it can be seen that the aggregated nanoshafts are spherical in morphology with particle sizes ranging from less than 3 μm to greater than 10 μm. Fig. 7-2(b) shows a typical surface image of the spherical particles at a higher magnification. This shows that the NiO nanoshafts are arranged randomly on the surface of the spherical particles. Fig. 7-2(c) shows the particle surface at an even higher magnification. The image of the primary NiO nanoshafts shows that the diameter of the shafts becomes smaller along the length of the particles until it finally forms nanoscale tips.
Fig. 7-2 SEM images of the spherical clusters of NiO nanoshafts (a) at low magnification, (b) at high magnification (surface of a spherical particle), (c) at higher magnification (surface of a spherical particle), and (d) in a cracked NiO spherical particle.

The interior of the spherical particles was also investigated (as shown in Fig. 7-3(d)). From the crack on the surface of the spherical particle, it can be seen that the nanoshafts also grow from the center of the spherical particles to their surface. It is worthwhile to point out that the spherical clusters of nanocrystals could also serve as effective confined templates for spherical nanostructures. The morphologies of these spherical clusters can be maintained even after thermal treatment at 1000 °C (Fig. 7-3). However, the primary NiO nanoshaft structure in the spherical particles is destroyed, and submicron-sized particles are formed. These submicron-sized particles are arranged in an ordered way (as
shown in Fig 7-3(b)), which reflects the original structure of the spherical particles before heat treatment. Fig. 7-3(c) is a bright-field TEM image of some NiO nanoshaft clusters. The material was ground in an agate mortar before TEM sample preparation. It is obvious that some nanoshaft structures have been destroyed during grinding. However, nanoshafts with lengths of 100-400 nm still can be observed. Fig. 7-3(d) shows a typical image of NiO nanoparticles, from which it can be seen that the sample is composed of nanoparticles with typical sizes of about 100 nm. Brunauer- Emmett-Teller (BET) nitrogen-adsorption measurements show that the specific surface areas of the NiO nanoshaft clusters and nanoparticles are 113 and 36 m$^2$/g, respectively.

Fig. 7-3 SEM images of the spherical NiO following calcination for 3 h at 1000 °C: (a) at low magnification, (b) at higher magnification, (c) TEM image of the NiO nanoshafts, and (d) SEM image of NiO nanoparticles.
7.3 Electrochemical properties of NiO nanoshfts

Fig. 7-4(a) shows cyclic voltammograms (CVs) of electrodes made from spherical clusters of NiO nanoshfts. For comparison, the CV curves of NiO nanoparticle electrode are also shown in Fig. 7-4(b).

![Cyclic voltammograms (CVs)](image)

Fig. 7-4 Cyclic voltammograms (CVs) of electrodes made with NiO: (a) nanoshft clusters and (b) nanoparticles.
The profiles of CV curves for both electrodes are similar, but differences between the first and subsequent cycles are found in the CV curves. A reduction peak ranging from 0.3-0.8 V in the first cycle corresponds to the initial reduction of NiO to metallic Ni nanoparticles and the formation of a partially reversible SEI layer. In the subsequent cycles, the reduction peak becomes broad and is composed of a main peak at around 0.98 V and a low-density shoulder peak near 1.3 V. In the oxidation scan, two broad peaks are well resolved at about 1.3 V and 2.2 V. The two pairs of redox peaks indicate that there are two sets of faradaic reaction involved. The well-known mechanisms for these reactions are the reversible reaction of NiO ↔ Ni/Li$_2$O and the partial composition/decomposition of the polymeric coating on the NiO surface (Laruelle et al. 2002; Dolle et al. 2002). By carefully comparing the CV curves of spherical clusters of NiO nanoshfts with those of NiO nanoparticles, it was found that the potential and the current densities of the peaks are different. The results describing the features of the second cycle CV curves are summarized in Table 7-1.

Table 7-1. Reduction potentials ($E_{r1}$, $E_{r2}$), oxidation potential ($E_{o1}$, $E_{o2}$), and the corresponding current densities of the electrodes made with NiO nanoshft clusters and nanoparticles in the second cycle cyclic voltammogram curves.

<table>
<thead>
<tr>
<th>NiO electrode</th>
<th>Potential Values (V)</th>
<th>Current densities (mAcm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{r1}$</td>
<td>$E_{r2}$</td>
</tr>
<tr>
<td>Nanoshft clusters</td>
<td>1.378</td>
<td>0.994</td>
</tr>
<tr>
<td>Nanoparticles</td>
<td>1.287</td>
<td>0.979</td>
</tr>
</tbody>
</table>
From Table 7-1, it is found that in the second cycle, the current densities for the nanoshaft cluster electrode are much larger than for the nanoparticle electrode, revealing higher capacity and faster kinetics for the Ni\textsuperscript{2+}/Ni transformation in the nanoshaft cluster electrode. In addition, for the nanoshaft cluster electrode, the potential difference between $E_{o2}$ and $E_{r2}$ ($2.245-0.994 = 1.251$ V), which corresponds to the redox reaction NiO $\leftrightarrow$ Ni/Li\textsubscript{2}O, is smaller than that of the nanoparticle electrode ($2.274-0.979 = 1.295$ V), indicating the higher reversibility and better stability of the nanoshaft cluster electrode. A decrease in the individual peak intensity and integral areas for $E_{o2}$ and $E_{r2}$ with cycling are also observed for both electrodes, with $E_{o2}$ shifting to higher potential while $E_{r2}$ shifts to a lower potential. The decrease in the peak density and integral areas results from the irreversible capacity losses due to the incomplete redox reaction. The increase in the potential difference ($E_{o2} - E_{r2}$) with cycling indicates degradation of the electrodes. However, the shape of the CV curves in the following cycles remained similar to those in the second cycle, suggesting reversible reduction and oxidation of the NiO electrode materials.

The voltage-specific capacity profiles of the NiO/Li cells were obtained using constant current charge/discharge measurements. Fig. 7-5 shows the first two charging/discharging curves of the electrodes made from NiO nanoshaft clusters and nanoparticles, which were measured between 0.01 and 3.0 V vs Li/Li\textsuperscript{+} at a current density of 50 mA/g and room temperature. In the first discharge, the potential drops rapidly to reach a well-pronounced plateau at about 0.7 V, followed by a gradual decrease to 0.01 V. The discharge capacity delivered is above 1300 mAh/g, which is higher than the theoretical capacity (718 mAh/g).
Fig. 7-5 Charge/discharge curves of the electrodes made with the as-prepared (a) NiO nanoshift clusters and (b) NiO nanoparticles.
It is possible that the extra capacity was contributed by the formation of a polymer-like SEI (Laruelle et al. 2002; Dolle et al. 2002). The well-resolved oxidation peak ($E_{o1}$) in the CV curves (Fig. 7-4) is evidence for this. The first charge proceeds with a higher voltage and less capacity. In the second discharge, the plateau appears at about 1.1 V, which is related to the reduction process $E_{r2}$ in Fig. 7-4. The subsequent charge plateaus appear at about 1.3 and 2.2 V, which correspond to the two oxidation peaks ($E_{o1}$ and $E_{o2}$) in Fig. 7-4. By careful comparison, it is found that the discharge curves of the nanoshaft cluster electrode exhibit a higher discharging voltage and a longer plateau than those of the nanoparticle electrode, indicating a higher power-output behavior.

Fig. 7-6 Capacity as a function of cycle number for the electrodes made with the as-prepared NiO nanoshaft clusters and the NiO nanoparticles.

Fig. 7-6 shows the curves of specific capacity versus cycle number for the electrodes made from NiO nanoshaft clusters and nanoparticles. Generally, the reversible capacity
decreased with cycling. The capacity fading rate became faster after 16 cycles. After 30 cycles, the nanoshaft cluster and nanoparticle electrodes maintained 410 and 203 mAh/g, corresponding to about 47.8% and 26.9% of the initial capacity, respectively, indicating that the morphology has an influence on the electrode cycling stability.

By comparing the electrochemical behavior of the as-prepared NiO electrode with other reported transition metal oxide electrodes, such as CoO, CuO, Co$_3$O$_4$ and Fe$_2$O$_3$, it is found that the cycling performance of the as-prepared NiO electrode (with capacity after 20 cycles 64.1% of the initial capacity) is comparable to that of Fe$_2$O$_3$ nanotube electrode (62.9%) (Chen, et al. 2005), while the capacity decays faster than CoO, CuO or Cu$_2$O electrode. However, the as-prepared NiO electrode has a higher reversible capacity than CuO and Cu$_2$O, and it is less expensive than CoO and Co$_3$O$_4$. The charge/discharge curves of the MO electrodes (M=Co, Ni, Fe, ect.) show some similarities. During the first discharge, the potential rapidly drops to a plateau, and then continuously decreases down to lower potential. The second discharge curve differs significantly from the first one, indicating structural or textural modifications. Poizot et al. have proposed a new electrochemical mechanism for these transition-metal oxide electrodes, which can be written as:

$$M_xO_y + 2y \text{Li} \leftrightarrow y\text{Li}_2O + xM$$

During the discharge, the $M_xO_y$ particles are reduced into highly dispersed metallic nanoparticles and Li$_2$O, but the overall shape of the starting particle is preserved. During the subsequent charge, the Li$_2$O matrix decomposes and M nanoparticles convert back to $M_xO_y$ nanograins.
According to the results presented above, the electrochemical performance of electrodes made with spherical clusters of NiO nanoshafts is better than that of nanoparticle electrodes. This may be due to the high surface-to-volume ratio of the spherical clusters of NiO nanoshafts. The highly nanoporous structure of the spherical clusters contributes to a higher specific surface area (113 m$^2$/g), making the electrochemical reaction with lithium more effective. On the other hand, the nanoshaft structures are favorable for the diffusion of lithium ions, providing more active sites. In addition, the spherical cluster structure may inhibit aggregation of Ni crystals to some extent, relieving the stress caused by volume change during the charge/discharge cycles and thereby suppressing the degradation of the NiO electrode. Further study by transmission electron microscopy (TEM) is necessary to verify this assumption. This aspect of the work is ongoing in our laboratory, and the results will be published elsewhere.

7.4 Conclusion

Spherical clusters of NiO nanoshafts were successfully prepared by chemical precipitation followed by precursor decomposition at 280 °C in air. Electrochemical measurements showed that the as-prepared nanoshaft cluster electrodes could be charged and discharged reversibly with high capacities and superior cycling reversibility. In view of this special structural arrangement, it is proposed that redox reactions with Li could be more efficiently conducted with the spherical NiO nanoshaft clusters than with their nanocrystalline counterparts. The enhanced electrochemical character of nanoshaft cluster electrodes arises from their relatively high specific surface areas and easier
lithium diffusion. Therefore, spherical clusters of NiO nanoshfts are promising materials for application in rechargeable lithium-ion batteries.