研究简报

电化学沉积技术制备 $LiNiO_2$ 薄膜及表征

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关键词: 电化学沉积技术; $LiNiO_2$ 薄膜; 制备; 表征
中图分类号: O614; O484.1; TM912 **文献标识码**: A **文章编号**: 1001-4861(2006)10-1929-04

$LiNiO_2$ Thin Films: Preparation by Electrochemical Deposition Technique and Characterization

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Abstract: Well-crystallized $LiNiO_2$ thin films were prepared directly on nickel substrates in LiOH solution by constant current electrochemical deposition technique at 95 ℃. The as-prepared $LiNiO_2$ thin films were characterized by using XRD, SEM and XPS, and the results reveal that the as-prepared $LiNiO_2$ thin films are dense and uniform in surface and show hexagonal structure. The influence of processing parameters such as reaction temperature, duration, electrical current density as well as the concentration of LiOH solution on the structure and morphologies of as-prepared $LiNiO_2$ thin films were studied, and the preferable electrochemical processing conditions for preparing $LiNiO_2$ thin films were suggested.

Key words: electrochemical deposition technique; $LiNiO_2$ thin film; preparation; characterization

0 Introduction

The work on the Li-M-O oxides (M=transition metals) has intensified over the last years in view of their application as cathode materials in lithium-ion batteries. Studies have mainly focused on layered oxides of $LiNiO_2$, $LiCoO_2$ and spinel $LiMn_2O_4$ because of their attractive electrochemical properties[1~3]. As the miniaturization of electronic devices progresses, the need to develop suitable micro-battery systems as power sources for the microelectronic devices increases, so the fabrication of the lithiated intercalation cathode films has been intensively investigated recently. The original pioneer works have been performed mainly by using gas phase or vacuum system, such as chemical vapor deposition (CVD) and sputtering. These synthetic methods usually represent sophisticated equipment, requiring enormous energy consumption, expensive precursors as well as post-synthesis heat treatments. Generally speaking, all these techniques will result in environmental and economic problems.

收稿日期:2006-06-20。收修改稿日期:2006-08-10。
国家自然科学基金(No.50472103)和四川省教育厅自然科学基金(No.2004A090)资助项目。
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Therefore, it is important to develop a novel economical and environmental friendly process that can produce the desired lithiated intercalation cathode films on a chip. Electrochemical deposition technique seems to be able to fulfill the above needs[4-7].

This work is devoted to the preparation of the crystalline $LiNiO_2$ film directly from alkaline LiOH solution by using electrochemical deposition technique. The influence of processing parameters on the structure and morphologies of as-prepared $LiNiO_2$ thin films are also discussed. To our knowledge, no publication on this respect of the work has been available up to now.

1 Experimental

99.5% nickel metal substrate was used as anode (working electrode) and cathode (counter electrode), respectively. Prior to the electrochemical deposition, the nickel substrate was degreased in acetone with ultrasonic cleaner for 10 minutes, etched subsequently in dilute chromic acid (about 1 $mol \cdot L^{-1}$) for 20 hours, and then washed in distilled water with ultrasonic cleaner twice.

All electrochemical depositions were performed under galvanostatic conditions. In order to study the influence of processing parameters such as reaction temperature, duration, current density and the concentration of LiOH solution on the structure and morphologies of as-prepared $LiNiO_2$ thin films, a series of experiments were carried out. Some processing parameters are shown in Table 1.

The resultant phase of the as-deposited films was analyzed by using X-ray diffraction (XRD) method, the surfaces of the films were observed by using scanning electronic microscopy (SEM), and the compositions of the films were confirmed by X-ray photoelectron spectroscopy (XPS).

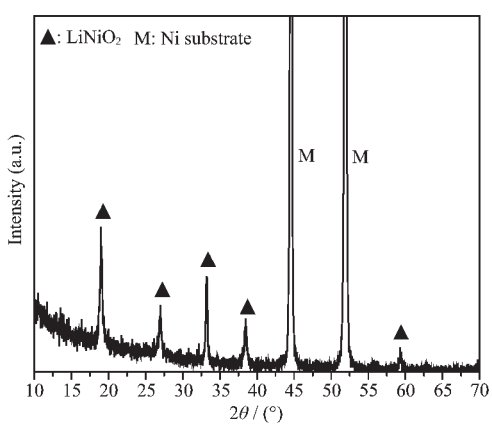
2 Results and discussion

Table 1 Processing parameters for preparing $LiNiO_2$ thin films by electrochemical technique

Temperature / ℃	Concentration of LiOH solution / ($mol \cdot L^{-1}$)	Current density / ($mA \cdot cm^{-2}$)	Reaction time / h
70	3.0	1.5	30
80	3.0	1.5	30
85	3.0	1.0	30
95	3.0	1.0	30
95	4.0	1.0	30
95	5.0	1.0	30

Fig.1 gives the XRD pattern of $LiNiO_2$ film prepared by electrochemical deposition technique at 95 ℃, which indicates that the films have single hexagonal feature of the layered type. The peak intensities and the lattice parameters agree well with the corresponding JCPDS cards.

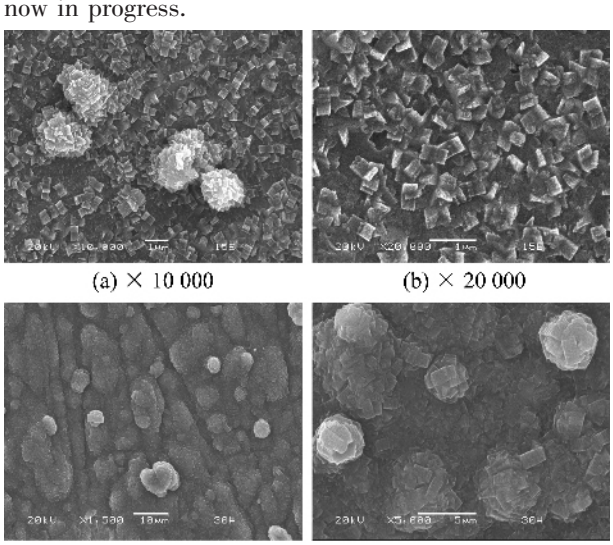
The scanning electronic micrographs of $LiNiO_2$ films prepared by electrochemical deposition technique in different concentration of LiOH electrolytes are displayed in Fig.2(a~d). It can be seen that the as-prepared $LiNiO_2$ films are well-crystallized, deposited densely and evenly, and the grains of $LiNiO_2$ films are cuboids in shape, the mean length of the grains is about 0.5~1 μm. Furthermore, Fig.2(c) and (d) show that some $LiNiO_2$ grains of the films are in the gathered sphere, this is an interesting and puzzling result. The probable reason is that the concentration of LiOH solution is too high in this



Temperature: 95 ℃; concentration of LiOH: 3 $mol \cdot L^{-1}$; current density: 1 $mA \cdot cm^{-2}$; reaction time: 30 h

Fig.1 XRD pattern of $LiNiO_2$ film prepared by electrochemical depositon

case, and the formation rate of $LiNiO_2$ grains is too fast, the $LiNiO_2$ grains can not be diffused immediately and effectively, thus resulting in the gathering of grains. And further studies for this are now in progress.



(a, b): 95 ℃, 3 mol·L^{-1} LiOH, 1 mA·cm^{-2}, 30 h
(c, d): 95 ℃, 5 mol·L^{-1} LiOH, 1 mA·cm^{-2}, 30 h

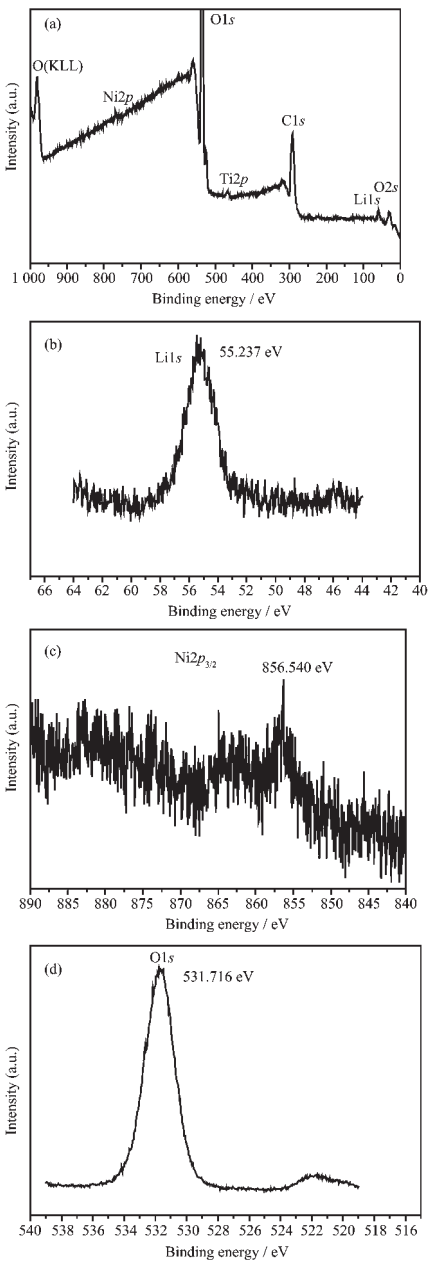
Fig.2　SEM micrographs of the surfaces of $LiNiO_2$ film prepared by electrochemical deposition

Fig.3(a) gives the wide-scan XPS spectrum of the as-deposited $LiNiO_2$ film in the binding energy range of 1 000~0 eV. All of the binding energies at varies peaks in Fig.3 are calibrated using the binding energy of *C*1*s*(285.0 eV). As shown in Fig.3(a), the as-deposited $LiNiO_2$ film contains Li, Ni, O, C and Ti elements, and no impurity element is detected in the spectrum up to 1 000 eV except for carbon (which may be caused by pump oil) and titanium (may be existed in nickel substrate).

The narrow-scan XPS spectra for Li, Ni and O elements of the as-prepared $LiNiO_2$ film are given in Fig.3(b~d), respectively. It can be seen that the Li1s band in the $LiNiO_2$ film appears at 55.237 eV, the Ni2$p_{3/2}$ band in the $LiNiO_2$ films is observed at 856.540 eV, the O1*s* band of as-deposited film locates at 531.716 eV, and the results are consistent with those reported in the literature[2]. The results reveal that the presence of Li, Ni and O elements in the surface of the films, and confirm that the valence of Li, Ni and O elements are +1, +3 and −2, respectively. Therefore, the above data strongly support that the actually prepared films are $LiNiO_2$ films.

The electrochemical formation mechanisms of the $LiNiO_2$ films can be described as follows.

In alkaline LiOH solution, Ni substrate and OH^- can react on nickel electrode and form NiO_2^- by



(a) Wide-scan XPS spectrum of the surface of $LiNiO_2$ film; (b, c, d) Narrow-scan XPS spectra of Li, Ni and O of $LiNiO_2$ film respectively
Temperature: 95℃; concentration of LiOH: 3 mol·L^{-1}; current density: 1 mA·cm^{-2}; reaction time: 30 h

Fig.3　X-ray photoelectron spectra of $LiNiO_2$ film prepared by electrochemical depositon

anodic oxidation:

$$Ni + 3OH^- \rightarrow NiO_2^- + H_2O + H^+ + 3e^- \quad (1)$$

Then, the produced NiO_2^- reacts with Li^+ in the solution to form the film on the substrate:

$$Li^+ + NiO_2^- \rightarrow LiNiO_2 \quad (2)$$

From expressions (**1**) and (**2**) one can see that the growth of the $LiNiO_2$ films includes both of the electrochemical reaction and solution reaction, where reaction (**1**) is electrochemical reaction and reaction (**2**) is solution reaction. The electrochemical reaction is a faradic process accompanied by charge transfer between the solution and electrode, which is controlled by current density. Whereas the solution reaction is a non-faradic process that is not accompanied by charge transfer but mainly controlled by the reaction temperature and the concentration of the electrolyte.

Under the feasible adscititious current density and reaction temperature, reaction (**1**) can easily take place and produce NiO_2^- species; moreover, the larger the current density and the higher the reaction temperature, the quicker the speed of reaction (**1**) (i.e. the speed of NiO_2^- species formation). We have found that when reaction temperature is below 70 ℃, $LiNiO_2$ film can not be formed in this case, no matter how to aggrandize current density and/or elongate reaction time, there is not any film formed.

On the other hand, reaction (**2**) is a reversible process, which exists in the competition between the formation and dissolution of $LiNiO_2$ grains. When the temperature is rising up, the solubility of the formed $LiNiO_2$ grains would be increased, which affects the crystallization of the grain units and growth of $LiNiO_2$ grains, leading to the surface structure and the poor grain of the film. Especially, when the reaction temperature exceeds 100 ℃, LiOH solution would boil, and the $LiNiO_2$ film can not be formed as well. Therefore if the formation speed of NiO_2^- species is consistent with the growth speed of $LiNiO_2$ grains, the well-crystallized and dense $LiNiO_2$ films can be prepared by electrochemical deposition technique at a proper reaction conditions.

When the electric current density is too low (below 0.5 $mA \cdot cm^{-2}$), the speed of the NiO_2^- species formation will be very slow and then the $LiNiO_2$ film can not be prepared. Whereas when the current density is too high, the speed of NiO_2^- species formation will be very fast, and the $LiNiO_2$ grains can not be diffused immediately and effectively, resulting in the gathering of grains.

3 Conclusions

Electrochemical deposition technique is an environmentally conscious method, which can provide a simple and inexpensive way to prepare crystalline oxide films on metal substrate without any heat treatment. The highly crystallized $LiNiO_2$ films were prepared directly on nickel metal substrates in LiOH solution by electrochemical deposition technique. The reaction temperature and current density affect the crystallization and the growth of $LiNiO_2$ grains, the optimum parameters for electrochemical reaction are suggested as reaction temperature of 95 ℃, current density of 1 $mA \cdot cm^{-2}$, LiOH solution concentration of 3 $mol \cdot L^{-1}$ and electrochemical treatment duration of 30 h.

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