Nanostructured LiNi_{0.5}Mn_{1.5}O_{4} Thin Films Prepared by Low-Temperature Pulsed Laser Deposition for Microbatteries

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ABSTRACT

Nanostructured LiNi_{0.5}Mn_{1.5}O_{4} thin films have been prepared on the stainless steel substrates and SiO₂/Si substrates by low-temperature pulsed laser deposition (PLD). Thin film samples were characterized by X-ray diffraction, Raman spectroscopy, field emission scanning electron microscopy, and X-ray photoelectron spectroscopy. It was found that the low-temperature PLD prepared LiNi_{0.5}Mn_{1.5}O_{4} thin films are composed of nanocrystallines with well-dispersed nanoflakes on top. XPS results indicate partial Mn in the film exist in 3+ oxidation state. The electrochemical behavior of the low-temperature PLD prepared LiNi_{0.5}Mn_{1.5}O_{4} thin films were investigated by cyclic voltammetry and galvanostatic charge/discharge. The LiNi_{0.5}Mn_{1.5}O_{4} thin film electrode exhibited a reversible capacity of about 50 μA h/cm² μm, which is comparable to the reported values for other thin film cathodes. In addition to large capacity, the thin film electrode also exhibited excellent cycling stability, making it promising for application in microbatteries.

KEYWORDS: LiNi_{0.5}Mn_{1.5}O_{4} Thin Films, Thin Film Microbatteries, Cathode Material, Low-Temperature, Pulsed Laser Deposition.

1. INTRODUCTION

All-solid-state thin film Li-ion microbatteries have attracted great attention due to their potential applications as power sources for micro- and nanodevices, such as microsensors, implantable medical devices, smart cards, and nanoelectromechanical systems.¹,² To realize thin film microbatteries for various applications, the development of a high-quality cathode film with high energy density, good reversibility, stable working voltage, and low cost is imperative. Previous works on developing thin film cathodes have been focused on LiCoO₂ thin film electrodes due to its high capacity, good cycling stability, and good rate capability, which make it promising as thin film cathode for microbatteries.³ However, to further improve the energy density of thin film microbatteries, alternative thin film cathodes with larger capacity or higher working voltage need to be developed. Several research groups have reported transition metal substituted spinel (LiM_{x}Mn_{2−x}O₄, M = Ni, Co, Cu, etc.) with high working voltages around 5 V.⁴⁵ Among them, LiNi_{0.5}Mn_{1.5}O₄ is particularly interesting due to its high capacity, good cycling stability, and good rate capability, which make it promising as thin film cathode for microbatteries.⁶ LiNi_{0.5}Mn_{1.5}O₄ thin films can be prepared by various methods, including radio frequency (RF) sputtering,⁸ pulsed laser deposition (PLD),⁹ and spin coating.¹⁰ Among them, PLD is a powerful and easy method for producing high quality and dense films without post-deposition annealing.

Most of the previous studies have been focused on the electrochemical properties of high-temperature processed LiNi_{0.5}Mn_{1.5}O₄ thin films. However, the high-temperature process is not suitable for the integration of microbatteries in complementary metal-oxide-semiconductor (CMOS) circuits.¹¹ Therefore, decreasing the processing temperature and shortening the time of deposition at high-temperature for thin film preparation become very important for future application of thin film microbatteries for microelectronic devices.¹² In this work, LiNi_{0.5}Mn_{1.5}O₄ thin films have been prepared by PLD at a low substrate temperature of 400 °C. The low-temperature PLD prepared LiNi_{0.5}Mn_{1.5}O₄ thin film exhibited large reversible capacity and good cycling stability, making it promising as thin film cathode for the next-generation thin film microbatteries with high energy density.
2. EXPERIMENTAL DETAILS

A Lambda Physik KrF excimer laser (λ = 248 nm, pulse width = 25 ns) was used for the thin film deposition. For PLD, the laser fluence and repetition rate were controlled at 2 J cm⁻² and 10 Hz. The targets for PLD were prepared by synthesizing a mixture of MnO₂ 99.9% (Alfa Aesar), NiO 99% (Alfa Aesar), and LiOH 98% (Merck) at 750 °C in air for 24 h. The target-substrate distance was kept at 40 mm, and the vacuum chamber was evacuated to a base pressure less than 1 × 10⁻⁵ Torr. LiNi₀.₅Mn₁.₅O₄ thin films were deposited on the stainless steel (SS) and SiO₂/Si substrates at a low substrate temperature of 400 °C under an oxygen partial pressure of 200 mTorr for 40 min. LiNi₀.₅Mn₁.₅O₄ thin films deposited on the SiO₂/Si substrates were only used for estimating the growth rate and thin film thickness.

Structure and crystallinity of low-temperature PLD prepared LiCoO₂ thin films were investigated with a Shimadzu XRD-6000 X-ray diffractometer (XRD) with Cu Kα radiation. Data were collected in the 2θ range of 10–70° at a scan rate of 2°/min. Raman spectroscopy measurements were carried out using a Jobin-Yvon T64000 micro-Raman system equipped with a charge-coupled device detector. The surface morphology of LiNi₀.₅Mn₁.₅O₄ thin film samples were characterized using a Hitachi S-4100 field emission scanning electron microscopy (FESEM). X-ray photoelectron spectroscopy (XPS) analysis was performed on the thin film with a VG ESCALAB MK spectrometer using Al Kα radiation (1486.6 eV). An analyzer with a pass energy of 20 eV was adopted, and a C 1s peak at 284.6 eV due to adventitious carbon was used as an internal reference.

The electrochemical properties of the low-temperature PLD prepared thin films were investigated by cyclic voltammetry (CV) and galvanostatic charge/discharge measurements. All electrochemical measurements were carried out on the Li/LiNi₀.₅Mn₁.₅O₄ cells fabricated in the glove box. The laboratory-made Swagelok-type cells consist of a Li metal foil counter electrode, a LiNi₀.₅Mn₁.₅O₄ thin film working electrode, and 1 M LiPF₆ in ethylene carbonate/diethyl carbonate (1/1, vol%) as the electrolyte. CV measurements were carried out in the voltage range between 3.5 and 5 V with a scan rate of 0.2 mV/s. Galvanostatic charge–discharge measurements were carried out in a potential range between 3 and 5 V at a constant current density of 20 μA/cm² using LAND CT2001A electrochemical workstation at room temperature.

3. RESULTS AND DISCUSSION

Figure 1(a) shows the XRD spectra of the LiNi₀.₅Mn₁.₅O₄ target and the low-temperature PLD prepared LiNi₀.₅Mn₁.₅O₄ thin film. All diffraction peaks of the target can be indexed based on a spinel structure with space group Fd-3m. In this spinel-framework structure, the oxygen ions at the 32e sites form the cubic-close packing, in which Li atoms occupy the octahedral interstices (16 sites). The diffraction peaks of the LiNi₀.₅Mn₁.₅O₄ thin film can be indexed based on the XRD spectrum of the target. The strong peak at about 19° can be indexed as (111) reflection while other small peaks can be attributed to (311), (222), (333), and (440) reflections, respectively. Compared to the highly crystallized target, the main peak (111) of the film is much broader and weaker, which is probably due to the small crystallite size and low crystallinity in nanocrystalline film as usually observed in nanomaterials. Figure 1(b) shows Raman spectrum of the low-temperature PLD prepared LiNi₀.₅Mn₁.₅O₄ thin film, which matches well with the known reported spectrum for the disordered cubic structure. According to recent group theory analysis, the Raman active vibrational modes of spinel LiNi₀.₅Mn₁.₅O₄ include the symmetrical stretching mode (A₁g), symmetrical deformation mode (E₁g) and three symmetrical bending modes (F₂g). The Raman bands located at 632 and 604 cm⁻¹ are assigned as the A₁g and E₁g modes corresponding to the Mn–O stretching. The Raman bands located at 501 and 421 cm⁻¹ can be assigned as the F₂g and E₁g modes corresponding to the Ni–O stretching. The XRD result agrees well with
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Fig. 2. (a)–(c) FESEM images of the low-temperature PLD prepared LiNi_{0.5}Mn_{1.5}O_4 thin film on the SS substrate at various magnifications (Inset is the EDX spectrum of the film). (d) Cross-section FESEM image of the low-temperature PLD prepared LiNi_{0.5}Mn_{1.5}O_4 thin film on the SiO_2/Si substrate.

the Raman result, indicating phase pure LiNi_{0.5}Mn_{1.5}O_4 thin film has been successfully prepared by PLD at low-temperature.

Figure 2 shows the FESEM images of the low-temperature PLD prepared LiNi_{0.5}Mn_{1.5}O_4 thin film. As shown in Figures 2(a)–(c), the film exhibits a rough surface morphology and consists of two types of grains. On the top of the film, flake shaped larger grains about 200 to 300 nm are uniformly dispersed, creating a rough surface. The bottom of the film is composed of smaller grains about 20 to 30 nm in size. In our previous study, the high-temperature PLD prepared LiNi_{0.5}Mn_{1.5}O_4 thin film developed different surface morphology.9 The 600 °C deposited LiNi_{0.5}Mn_{1.5}O_4 thin film was composed of well-defined grains with uniform size about 200–300 nm, exhibiting a very smooth surface. The grain shape reflects the spinel structure with a high proportion of octahedral or pseudo-polyhedral forms with well-defined edges and facets. However, the grains of the low-temperature PLD prepared LiNi_{0.5}Mn_{1.5}O_4 thin film do not exhibit octahedral shape and develop well-defined grain boundaries, probably indicating a lower degree of crystallinity compared to the high-temperature deposited LiNi_{0.5}Mn_{1.5}O_4 thin film. The Ni/Mn molar ratio is estimated to be about 0.25 according to the energy-dispersive X-ray spectroscopy (EDX) result (Inset in Fig. 2(a)). Figure 2(d) shows the cross-section FESEM image of a LiNi_{0.5}Mn_{1.5}O_4 thin film deposited on the SiO_2/Si substrate. The thickness of the film is estimated to be about 300 nm and the thin film growth rate is about 7.5 nm/min.

XPS analysis was carried out to investigate the composition and the oxidation states of Ni and Mn in the low-temperature PLD prepared LiNi_{0.5}Mn_{1.5}O_4 thin film. The high-resolution XPS spectra for Mn 3s, Li 1s, Ni 2p, Mn 2p and O 1s are shown in Figure 3. Due to the similar binding energy (BE), both Mn 3s and Li 1s XPS spectra are shown in Figure 1(a). The low intensity/background ratio of the Li 1s emission peak results from its low scattering coefficient towards X-rays.17 The fitting of Li 1s spectrum gives a BE of 54.2 eV, which is in good agreement with the values reported in other Li transition metal oxides.18 The Mn 3p XPS spectrum can be deconvoluted into two components. The intense one located at 50.1 eV is assigned to Mn^{4+} and the minor one at 48.6 eV is assigned to Mn^{3+}. As shown in Figure 2(b), the Ni 2p_{3/2} XPS spectrum can be best fitted with one peak with a binding energy of 854.2 eV, indicating almost all Ni in the film exist in 2+ oxidation state. The Ni 2p_{3/2} XPS spectrum also exhibits the characteristic satellite peak with the BE at 860.4 eV, which is probably due to the multiple splitting in the energy levels of the Ni-oxides.19 Similar to the Mn 3s XPS spectrum, the deconvolution of the Mn 2p_{3/2} spectrum also gives two components at 642.1 eV and 641.2 eV, respectively. The major component at 642.1 eV corresponds to the Mn^{4+} and the minor one at 641.2 eV corresponds to the Mn^{3+}. Formation of Mn^{3+} in the film is probably induced by the oxygen loss during the thin film deposition, which is also found in the LiNi_{0.5}Mn_{1.5}O_4 powders. Once the oxygen deficiency takes place, the average valence of manganese will decrease owing to the charge balance compensation, resulting in the reduction of some Mn from...
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Fig. 3. (a) Mn 3s and Li 1s, (b) Ni 2p, (c) Mn 2p and (d) O1s XPS high resolution spectra of the low-temperature PLD prepared LiNi$_{0.5}$Mn$_{1.5}$O$_4$ thin film on the SS substrate.

4+ to 3+. The O 1s XPS spectrum shows a complex profile with a major component located at 529.6 eV, corresponding to the Mn(Ni, Li)−O bonds. The components at higher binding energies of 531.2 and 532.8 eV with lower intensity are typically associated to either OH$^-$ groups, O$_2^-$ or the multiplicity of physisorbed and chemisorbed water on and into the surface.$^{20}$

Figure 4 shows the typical CV curve of the low-temperature PLD prepared LiNi$_{0.5}$Mn$_{1.5}$O$_4$ thin film electrode in the voltage range between 3.5 and 5 V at a scan rate of 0.2 mV/s. For both cathodic and anodic scans, three redox peaks can be observed, indicating good reversibility for Li intercalation/deintercalation. The high voltage peaks at 4.7 (A2) and 4.8 V (A3) on charge, and at 4.6 (C2) and 4.7 V on discharge may correspond to the distinct redox reactions of Ni$^{2+}$/Ni$^{3+}$ and Ni$^{3+}$/Ni$^{4+}$. As suggested by Dahn et al. the electrode potential of LiMn$_2$O$_4$ could be enhanced from 4 to 4.7 V by a partial substitution of Mn ions in LiMn$_2$O$_4$. Previous study on UV photoelectron spectroscopy indicates the energy of 3$d$ level for Ni$^{2+}$ ion and Ni$^{3+}$ ion in a low spin state is lower than that of Mn$^{3+}$ ion in a high spin state. Such a difference between energies for 3d levels leads to a higher electrode potential of LiNi$_{0.5}$Mn$_{1.5}$O$_4$. For the LiMn$_2$O$_4$ electrode, Li intercalation/deintercalation take place with the redox reaction of Mn$^{3+}$/Mn$^{4+}$ at about 4 V. The small redox peaks at about 4 V in Figure 4 should correspond to the redox reaction of Mn$^{3+}$/Mn$^{4+}$, which indicates the existence of a small amount of Mn$^{3+}$ ions in the film. For stoichiometric LiNi$_{0.5}$Mn$_{1.5}$O$_4$, all Ni exist in the 2+ oxidation state and all Mn exist in the 4+ oxidation state, resulting in the absence of 4 V peaks in CV curves. The CV behavior of the low-temperature PLD prepared LiNi$_{0.5}$Mn$_{1.5}$O$_4$ thin film electrode agrees well with that of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ composite electrodes from previous literature reports.$^{21}$

Agreeing well with the XPS analysis, oxygen deficiency exists in the film, leading to a small amount of Mn$^{3+}$ ions.

Figure 5(a) shows the first charge/discharge curves of the low-temperature PLD prepared LiNi$_{0.5}$Mn$_{1.5}$O$_4$.
thin film electrode between 3 and 5 V at a current density of 20 \( \mu \text{A/cm}^2 \). Three voltage plateaus for both charge and discharge curves can be observed, agreeing well with the redox peaks in the CV curve. However, compared with the charge/discharge curves of the high-temperature deposited \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) thin film electrode, the charge/discharge voltage plateaus of the low-temperature PLD prepared \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) thin film electrode are 52.9 and 49.4 \( \mu \text{A/cm}^2 \), respectively, with a coulombic efficiency of about 93%. The reversible capacity of the low-temperature PLD prepared \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) thin film electrode is relatively lower compared to the high temperature deposited \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) thin film electrode (\( \sim 60 \mu \text{A/cm}^2 \) \( \mu \text{m} \)) due to its lower degree of crystallinity.\(^{5}\) The \( \text{Li/} \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) cell with a thin film electrode was cycled between 3 and 5 V at a current density of 20 \( \mu \text{A/cm}^2 \) for 50 cycles. The cycle performance of the low-temperature PLD prepared \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) thin film electrode is shown in Figure 5(b). After 50 cycle, the retained reversible capacity of the thin film electrode is about 91% of its initial reversible capacity, indicating good cycling stability for the low-temperature PLD prepared \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) thin film electrode. Although the low-temperature PLD prepared \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) thin film electrode can deliver relatively lower reversible capacity compared to the high-temperature PLD prepared \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) thin film electrode, its reversible capacity is still comparable to those of other high-temperature deposited thin film cathodes, such as \( \text{LiCoO}_2 \) and \( \text{LiMn}_2\text{O}_4 \).\(^{23,24}\) Moreover, the low-temperature processing is highly compatible for circuit integration, making thin film microbatteries have great potential for application in microelectronic devices.

4. CONCLUSION

Fig. 5. (a) The initial charge/discharge curves of a low-temperature PLD prepared \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) thin film electrode between 3 and 5 V at a constant current density of 20 \( \mu \text{A/cm}^2 \). (b) Cycle performance of a low-temperature PLD prepared \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) thin film electrode at constant current density of 20 \( \mu \text{A/cm}^2 \) for 50 cycles.

Phase pure \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) thin films have been successfully prepared by low-temperature PLD. Structural and surface morphology characterizations indicate the low-temperature PLD prepared \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) thin film has a lower degree of crystallinity and smaller grain size compared to the high-temperature PLD prepared \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) thin film. XPS results indicate partial Mn in the low-temperature PLD prepared \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) thin film exist in 3+ oxidation state, which is probably due to the oxygen loss during thin film deposition. The low-temperature PLD prepared \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) thin film electrode exhibited a large reversible capacity up to 50 \( \mu \text{A h/cm}^2 \) \( \mu \text{m} \), which is comparable to the reversible capacity of other thin film cathodes prepared at high-temperatures. In addition to large reversible capacity, the low-temperature PLD prepared \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) thin film electrode also exhibited good cycling stability, making it promising for application in thin film microbatteries.

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References and Notes

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