

Effect of chitosan on stabilization of acetates-containing solution: A novel precursor for LiMn_2O_4 film deposition

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Received 11 September 2005; received in revised form 1 December 2005; accepted 15 December 2005

Available online 26 January 2006

Abstract

Due to the adequate viscosity of the chitosan-added precursor solutions, the films deposited from the chitosan-added precursor solution showed a higher deposition rate than the ones from the PVP-added solution under the same coating parameters. Furthermore, the chitosan-added precursor solution remained stable without any precipitation for at least 10 months. On the other hand, without the addition of chitosan, the precursor solution showed apparent precipitation after being stirred for 12 h. The enhanced stability of the precursor solution by the addition of chitosan is attributed to the complexation between metal ions and the $-\text{NH}_2$ groups of chitosan. And the electrochemical behavior for the deposited films calcined at 700°C for 1 h was also characterized by charge–discharge test. The result revealed that the film deposited from chitosan-containing precursor solution possesses an initial discharge capacity of 134 mAh g^{-1} and about 9% capacity loss after 50 charge/discharge cycles, which is better than the one deposited from chitosan-free precursor solution with an initial discharge capacity of 108 mAh g^{-1} and 24% capacity loss after 50 cycles. © 2006 Elsevier B.V. All rights reserved.

Keywords: LiMn_2O_4 ; Solid-state NMR; Thin film; Chitosan; Chelate

1. Introduction

Recently, thin-film solid-state batteries have attracted significant attention because they have been studied for various applications [1,2]. One of these applications is to serve as an independent power supply for microsensors, microelectronics and high-temperature semiconductor electronics, etc. Therefore, to develop long-lasting and high-energy efficient microbatteries is very important.

Spinel LiMn_2O_4 is a promising cathode material for microbatteries due to its high operating voltage, low cost and low toxicity. To date, LiMn_2O_4 thin films have been fabricated by the techniques such as pulse laser deposition [3], electrostatic spraying deposition [4], rf magnetron sputtering [5] and wet chemical deposition [6–9]. Among these methods, wet chemical deposition has the most advantages, including simple processing, easy control of stoichiometry and high deposition rate. However, it has also been found that the quality of the prepared LiMn_2O_4 films is strongly dependent on the nature of the precursor solu-

tion used. For example, when the aqueous solution containing metal acetates was spin-coated on the platinumized silicon substrates, homogeneous films could not be obtained, and droplets were just left on the substrate. This failure in the film deposition was mainly due to the poor wettability between the substrate and water with high surface tension (72.0 mN m^{-1}). Thus, absolute ethanol with a low surface tension of 21.9 mN m^{-1} was used to improve the wettability of the precursor solution. However, the ethanol solution containing metal acetates showed apparent precipitation after being stirred for 12 h. In order to eliminate the formation of the precipitates, the addition of an appropriate chelating agent was found to be effective in the stabilization of the ethanol solution containing lithium and manganese acetates and then beneficial to the deposition of LiMn_2O_4 films on a Pt-coated silicon substrate. For example, poly(vinylpyridine) (PVP) has been used as an additive to adjust the nature of the prepared precursor solutions [8,9]. Thus, the addition of PVP in the precursor solution was able to enhance the deposition of LiMn_2O_4 films.

Chitosan, a polysaccharide derived from crustacean and fungal chitin, is a non-toxic, tissue-compatible polymeric biomaterial. Chitosan can be dissolved in the aqueous solution with weak acid. Homogeneous polymeric membranes or films can be

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easily fabricated from the chitosan-containing aqueous solution by dipping or spin-coating. Thus, the objectives of this work were to (i) examine the effect of the addition of chitosan on the deposition of the LiMn_2O_4 films, (ii) elucidate the mechanism of chitosan addition on the stabilization of the lithium/manganese acetates-containing precursor solution and (iii) investigate the electrochemical performance of the LiMn_2O_4 film deposited from the chitosan-containing solution.

2. Experimental

2.1. Preparation of the precursor solutions

In this work, three sets of the precursor solutions were prepared. In the first set, the chitosan-containing precursor solution was prepared as follows: first, 0.125 g chitosan (Fluka, low viscous) was dissolved completely in 25 mL de-ionized water containing 1.5 mL acetic acid (CH_3COOH) (Fluka, 99.8%). Then, 0.025 mol lithium acetate ($\text{LiC}_2\text{H}_3\text{O}_2 \cdot 2\text{H}_2\text{O}$) (Alfa Aesar, 99%) and 0.05 mol manganese acetate ($\text{MnC}_4\text{H}_6\text{O}_4 \cdot 4\text{H}_2\text{O}$) (Fluka, 99%) were also dissolved in 25 mL ethanol ($\text{C}_2\text{H}_5\text{OH}$) (Fluka, 99.8%). Subsequently, the ethanol solution with acetates salts was poured into the aqueous solution containing chitosan.

In the second set, two kinds of PVP powders with a molecular weight (MW) of 10,000 (Sigma) and 360,000 (Fluka) were used. The preparation of the PVP-containing precursor solutions follows the procedure reported by Rho et al. [8,9]. 0.125 g PVP powder, 1.5 mL acetic acid and 0.025 mol lithium acetate were successively dissolved in 25 mL ethanol. Afterwards, 0.05 mol manganese acetate and 25 mL de-ionized water were also added to the precursor solution.

Both chitosan-added and PVP-added precursor solutions were stirred continuously for 12 h. Finally, two colorless and transparent solutions were obtained.

In the final set, to prepare a precursor solution without chitosan and PVP for the sake of comparison, 0.025 mol lithium acetate and 0.05 mol manganese acetate were also dissolved in 50 mL ethanol or 25 mL/25 mL ethanol/water mixed solution. At first, these solutions were clear and transparent. However, they gradually got turbid after being stirred continuously for 12 h, and finally a lot of precipitates were formed.

The three sets of precursor solutions were employed as a coating solution for the deposition of thin-film cathodes.

2.2. Viscosity measurement

The viscosity of the precursor solutions were measured at 25 °C using a viscosimeter (BROOKFIELD DV II+ Pro) at a shear rate of 100 s^{-1} .

2.3. Characterization of the deposited films

Thin films were deposited on a Pt-coated silicon substrate by spin-coating the well-prepared precursor solutions at a rotation speed of 4500 rpm. The coating procedure was repeated several times when a thicker film was needed.

FT-IR spectra of the as-deposited films were obtained from a Fourier transform infrared spectrometer (Thermo Nicolet NEXUS 470).

The dried precursor films were scraped off from the silicon substrate and used as the sample for the solid-state NMR analysis. Solid-state ^7Li NMR spectra were recorded with a Bruker AVANCE 400 NMR spectrometer, operating at 155.5 MHz. Typical NMR experimental conditions were as follows: $\pi/2$ pulse length, 4 μs ; recycle delay, 1 s. Chemical shifts were externally referenced to the LiCl solution at 0.0 ppm.

Furthermore, the deposited precursor films were heat-treated to obtain LiMn_2O_4 films under a two-step annealing procedure at 300 and 700 °C for 1 h, respectively. The thickness of the calcined films was measured by a profilometer (Tencor α -500 surface profiler). The phase identification of the calcined films was characterized by glancing angle X-ray diffraction (GXR). The patterns were recorded on a Rigaku D/MAX 2500 diffractometer with $\text{Cu K}\alpha$ radiation at a glancing incident angle of 1°. The detected diffraction angle (2θ) was scanned from 15° to 70° with a speed of 4° min^{-1} . The microstructure of the prepared films was examined using a scanning electron microscope (SEM, Hitachi S-3000N).

2.4. Charge–discharge tests

Electrochemical measurements were carried out with a two-electrode glass cell where metallic lithium was used as the counter electrode, and a mixed solution of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1, v/v) containing 1 M LiPF_6 (Mitsubishi Chemical) as the electrolyte. Charge–discharge cycling experiments were performed over the voltage range of 3.2–4.3 V under 1C rate and recorded with an automated battery cycle-life tester (Arbin BT2043). All cell assembly was performed in a grove-box filled with purified argon.

3. Results and discussion

3.1. Effect of the addition of chitosan and PVP on the viscosity of the precursor solutions

According to Rho et al.'s works [8,9], they found that the viscosity of the prepared precursor solutions is dependent on the molecular weight of PVP added, and the viscosity of the solutions strongly influences the nature of the deposited thin films. Thus, the effect of the addition of chitosan on the viscosity of the prepared precursor solutions was compared with ones with PVP addition. A viscosimeter was employed to measure the viscosity of the precursor solutions. The results of the viscosity measurements are shown in Fig. 1. In the case of the PVP-added solution, it can be seen that the viscosity of the prepared precursor solutions is related to the molecular weight of PVP added. The greater the MW of PVP added, the higher the viscosity of the prepared precursor solution. However, the viscosity of both PVP-containing solutions is lower than that of the ones containing chitosan. It was found that when 0.25 g chitosan was added, the viscosity of the precursor solution increased to

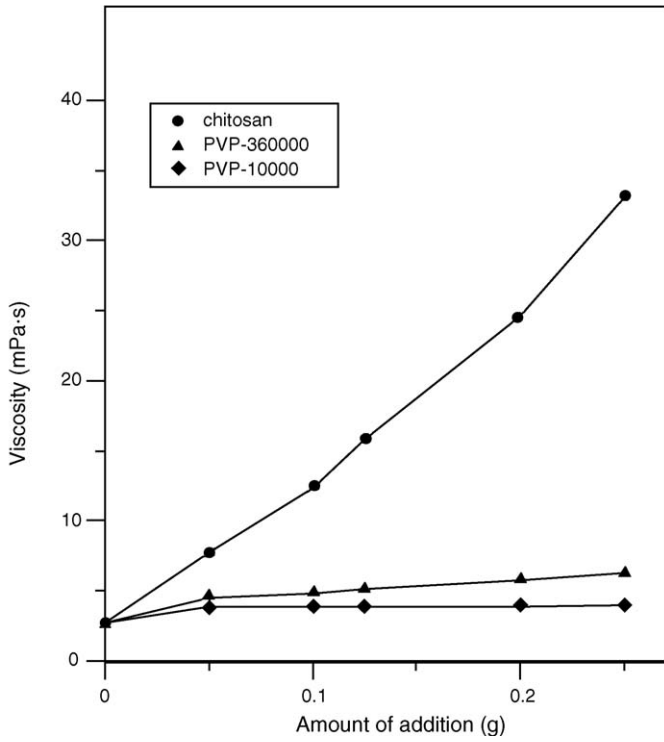


Fig. 1. Dynamic viscosity of the precursor solution plotted as a function of the amount of chitosan and PVP.

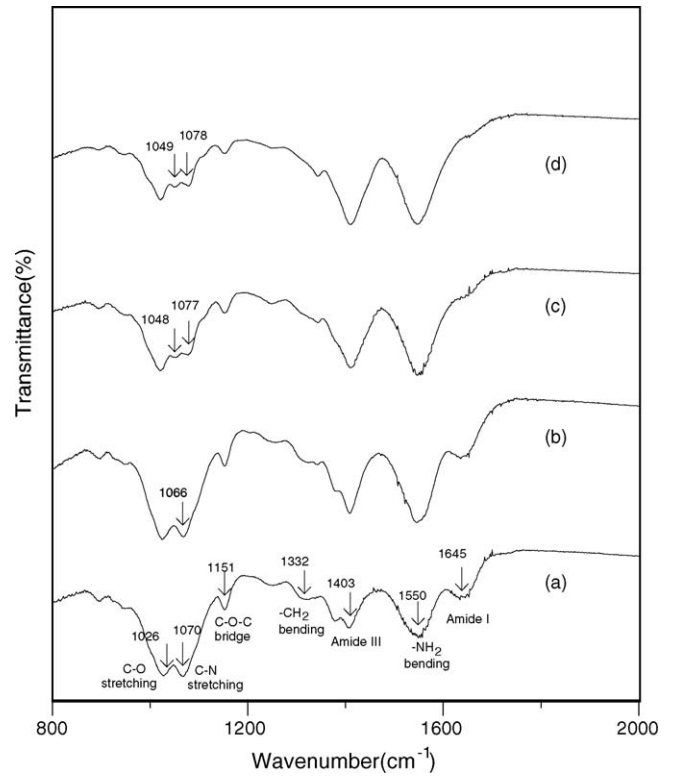


Fig. 3. FT-IR spectra of (a) chitosan, (b) lithium acetate–chitosan, (c) manganese acetate–chitosan and (d) lithium/manganese acetates–chitosan precursors in the wavenumber range from 800 to 2000 cm^{-1} .

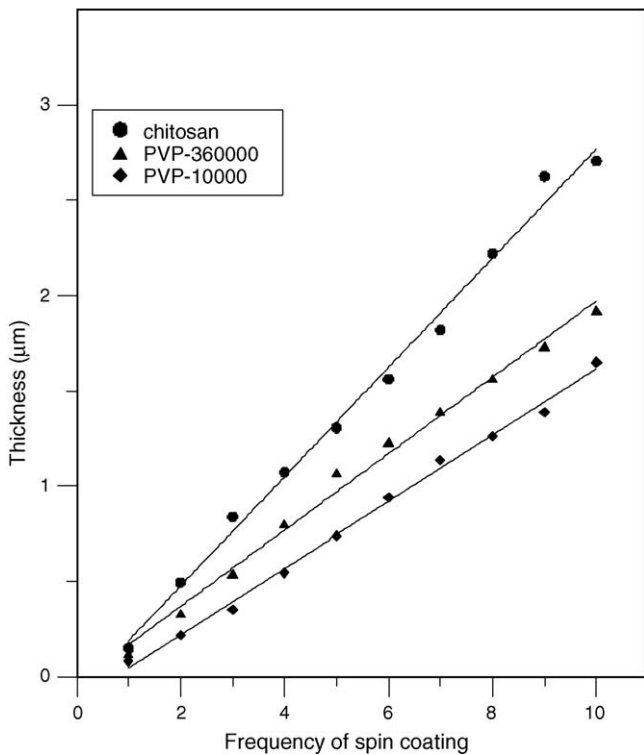


Fig. 2. Dependence of the thickness of the deposited LiMn_2O_4 film plotted as a function of coating time.

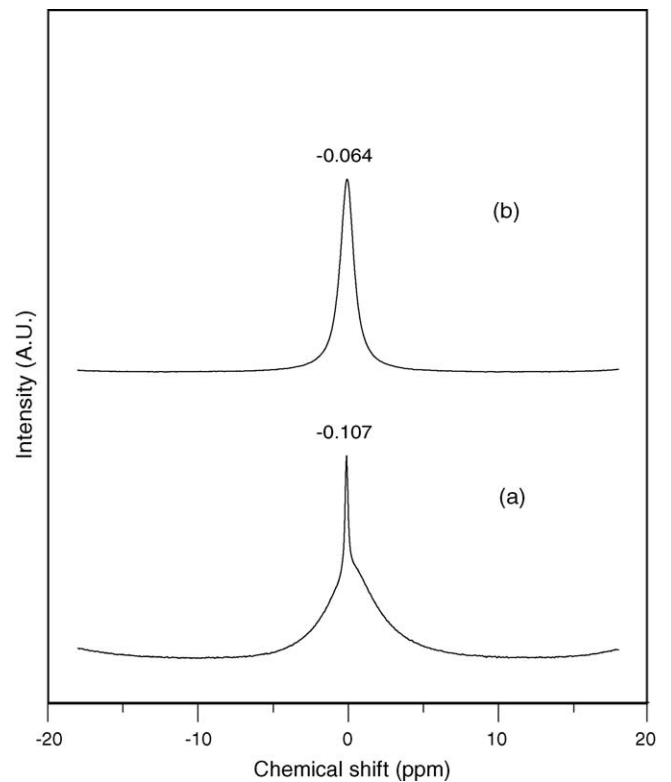


Fig. 4. ^7Li NMR spectra of (a) lithium acetate and (b) lithium acetate–chitosan precursor.

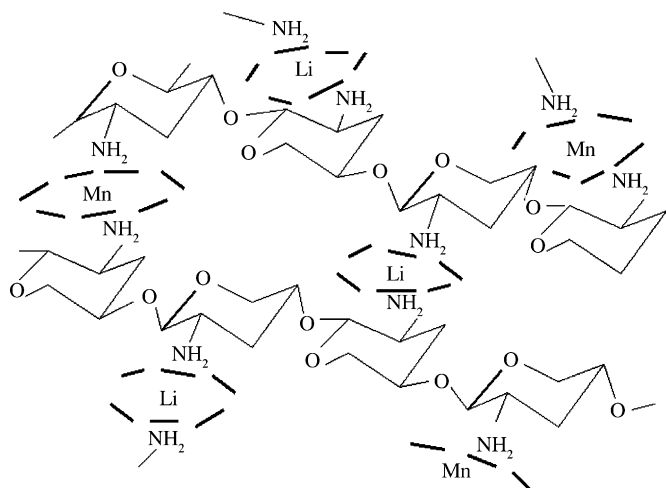


Fig. 5. Schematic illustration of the chelate mechanism between chitosan and Li/Mn ions.

33.1 mPa s, which is significantly higher than that of both PVP-containing precursor solutions (3.9 mPa s for the solution with MW ~ 10,000 and 6.3 mPa s for the one with MW ~ 360,000). Since a precursor solution with a higher viscosity may be beneficial to the deposition of a thicker film [8,9], the thickness of the prepared LiMn_2O_4 films deposited from the chitosan-added or PVP-added precursor solutions under the same coating parameters was compared. Fig. 2 shows the dependence of the thickness of the deposited LiMn_2O_4 films versus the frequency of coating under the rotation speed of 4500 rpm. Obviously, the thick-

ness of the prepared films increased with the coating number. After spin-coating for 10 times, the thickness of the deposited LiMn_2O_4 film from the chitosan-added precursor solution was about 2.7 μm . Thus, the average thickness of film obtained each time is 0.27 μm . This value is higher than that for either of the PVP-added precursor solutions, 0.16 μm for MW ~ 10,000 and 0.19 μm for MW ~ 360,000.

Based on the above-mentioned results, it may be concluded that the addition of chitosan in the precursor solution can enhance the efficiency of the deposition of LiMn_2O_4 films in comparison with the one containing PVP.

3.2. Effect of chitosan addition on the stabilization of acetates-containing precursor solution

In addition to deposition rate, another merit of chitosan is that it is able to stabilize the lithium/manganese acetates-containing ethanol solution. As mentioned in the previous sections, a large amount of precipitate was observed after the ethanol solution containing acetates was stirred continuously for 12 h. On the other hand, the chitosan-added precursor solution showed better

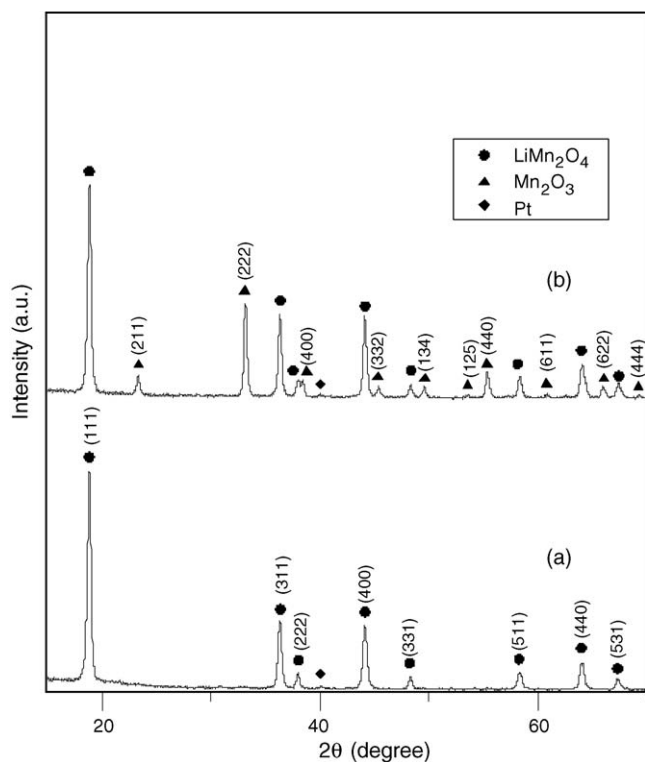


Fig. 6. GXR D traces of the films deposited from the acetates-containing precursor solutions (a) with and (b) without chitosan addition followed by heat-treatment at 700 °C for 1 h.

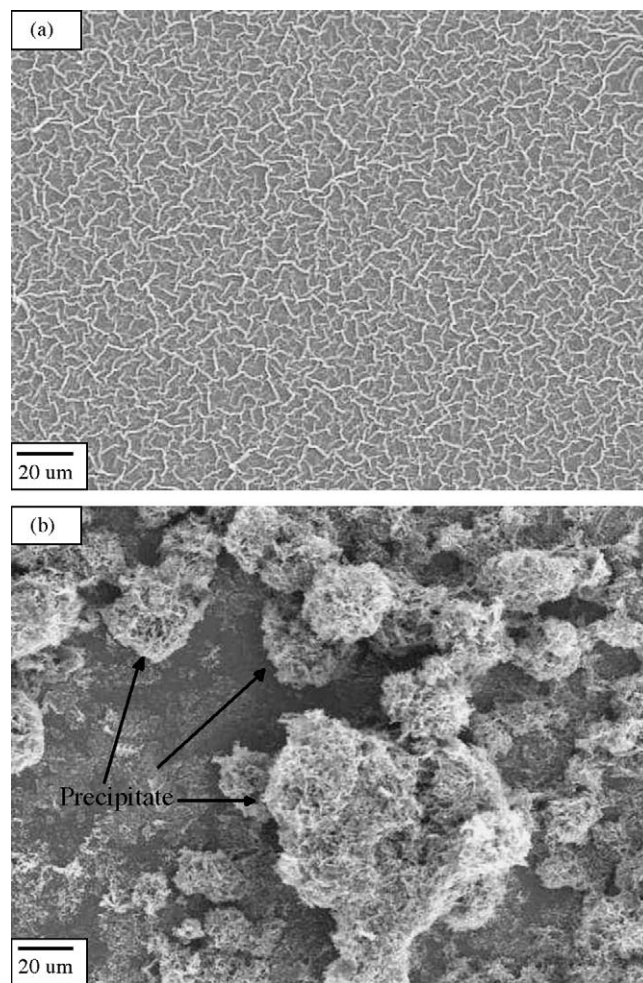


Fig. 7. SEM micrographs of the films deposited from the acetates-containing precursor solutions (a) with and (b) without chitosan addition followed by heat-treatment at 700 °C for 1 h.

stability with no formation of precipitate for 10 months. Thus, it is inferred that the enhanced stability of the precursor solution may be attributed to the addition of chitosan or water. In order to clarify the situation, a 25 mL/25 mL ethanol/water mixed solution dissolving 0.025 mol lithium acetate and 0.05 mol manganese acetate was prepared for comparison. It was found that such a chitosan-free precursor also showed precipitation after being stirred for 12 h. According to these results, the addition of chitosan indeed plays the determining role in the stabilization of the precursor solution containing acetates. Therefore, to examine the effect of chitosan addition on the stability of the prepared precursor, FT-IR and solid-state NMR spectroscopy were conducted.

Fig. 3 shows FT-IR spectra for (a) chitosan, (b) lithium acetate–chitosan, (c) manganese acetate–chitosan and (d) lithium/manganese acetates–chitosan. The chitosan spectrum shows the characteristic absorption bands at 1070 cm^{-1} (C–N stretching), 1332 cm^{-1} ($-\text{CH}_2$ bending), 1403 cm^{-1} (Amide III), 1550 cm^{-1} ($-\text{NH}_2$ bending) and 1645 cm^{-1} (Amide I). The absorption bands at 1026 cm^{-1} (C–O stretching vibration) and 1151 cm^{-1} (anti-symmetric stretching of the C–O–C bridge) are characteristics of its saccharide structure [10–12]. For the lithium acetate–chitosan precursor, the difference in the C–N stretching vibration from chitosan was observed. The band located at 1070 cm^{-1} , assigned to the C–N stretching vibration, was shifted to the lower wavenumber of 1066 cm^{-1} after lithium acetate was added to the chitosan.

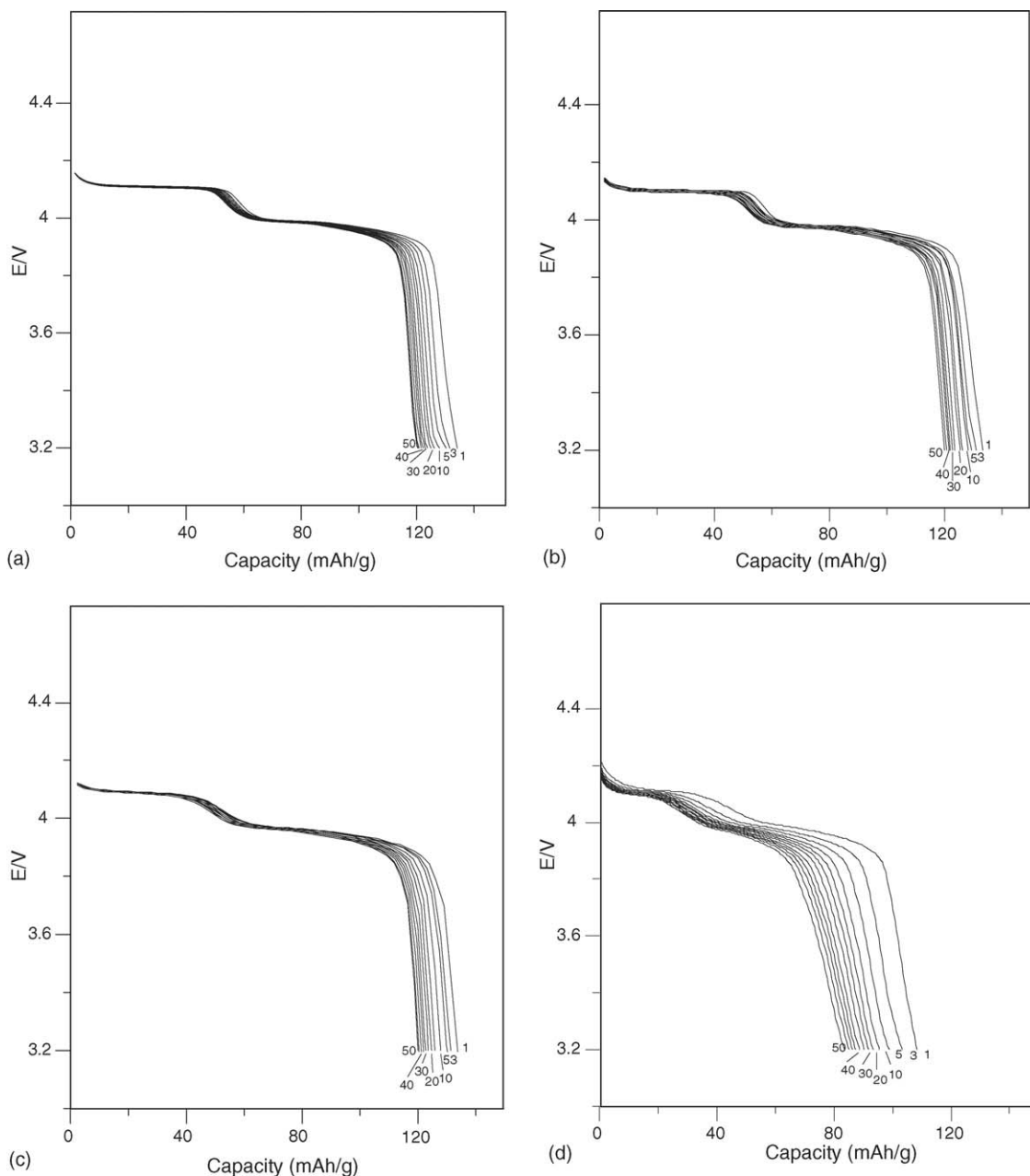


Fig. 8. Cycling discharge curves of Li/liquid electrolyte (LiPF_6)/ LiMn_2O_4 cell using the films deposited from the acetates-containing precursor solutions (a) with chitosan addition, (b) with PVP of MW $\sim 10,000$ addition, (c) with PVP of MW $\sim 360,000$ addition and (d) with no chitosan addition.

For both manganese acetate–chitosan and lithium/manganese acetates–chitosan precursors, the splitting of the band corresponding to the C–N stretching vibration was also observed. These results clearly indicate that the -NH_2 groups in chitosan were involved in complexation after chitosan was added to the lithium and/or manganese acetates.

Fig. 4 shows ^7Li NMR spectra of lithium acetate and lithium acetate–chitosan precursor. For lithium acetate, the ^7Li signal was recorded at -0.107 ppm with respect to the aqueous LiCl solution. This peak corresponds to the interaction between the lithium ion and the carboxylic ligand in acetate. However, the ^7Li signal shifted from -0.107 to -0.064 ppm after lithium acetate was added to the chitosan. This indicates that a new bond was formed between the lithium ion and chitosan.

According to these results of both FT-IR and NMR analyses, it is inferred that lithium/manganese ions in acetates were dissociated from carboxylic groups and subsequently coordinated with the amino groups of chitosan. The structure for the lithium/manganese acetates–chitosan precursor is proposed and shown in Fig. 5. Due to the chemical bonding between chitosan and lithium/manganese ions, the precursor solution composed of lithium/manganese acetates and chitosan shows better stability in comparison with the chitosan-free one.

3.3. Effect of chitosan addition on the formation of pure LiMn_2O_4 films

The GXRD traces of the films deposited from the acetates-containing precursor solutions with and without chitosan addition followed by heat-treatments at 700°C for 1 h are shown in Fig. 6. In the case of the sample deposited from the chitosan-added precursor solution (Fig. 6(a)), the observed peaks located at $2\theta = 18.65^\circ$, 36.13° , 43.97° and 63.91° are consistent with (1 1 1), (3 1 1), (4 0 0) and (4 4 0) reflections of LiMn_2O_4 lattice (JCPDS 89-0118). On the other hand, for the sample deposited from the chitosan-free precursor solution, in addition to the spinel LiMn_2O_4 phase, some other peaks at $2\theta = 23.34^\circ$, 33.18° , 38.46° and 55.38° were also observed, as is seen in Fig. 6(b). These extra peaks are assigned to (2 1 1), (2 2 2), (4 0 0) and (4 4 0) reflections of Mn_2O_3 lattice (JCPDS 78-0390).

Moreover, SEM was also employed to observe the morphology of the deposited films heated at 700°C for 1 h. Fig. 7(a) shows that a relatively dense film without cracking was formed when the chitosan-added precursor solution was used. However, the films deposited from the chitosan-free precursor solution showed numerous cotton-like precipitates.

According to the results of both GXRD and SEM, the addition of chitosan can indeed stabilize the lithium/manganese acetates-containing precursor solution and is also helpful for the deposition of a single-phase and crack-free LiMn_2O_4 film.

3.4. Charge–discharge tests

Electrochemical charge–discharge behaviors of the deposited LiMn_2O_4 films were investigated using a metal Li/liquid electrolyte (LiPF_6)/ LiMn_2O_4 cell. These films were heat-treated at 300 and 700°C for 1 h, respectively. Fig. 8(a) illustrates the

typical discharge curves of the deposited LiMn_2O_4 cathode prepared from chitosan-added precursor solution. There was an initial discharge capacity of 134 mAh g^{-1} and about 9% loss in the discharge capacity was observed after 50 charge/discharge cycles. The discharge curves of the deposited LiMn_2O_4 films from the precursor solutions containing PVP with MW $\sim 10,000$ and MW $\sim 360,000$ are also shown in Fig. 8(b and c). It can be seen that their electrochemical performances are nearly similar to that of the film prepared from the chitosan-containing precursor. These results indicate that the addition of chitosan or PVP in the precursor solution has little difference on the electrochemical properties of the resultant LiMn_2O_4 films. According to the published literatures [13–16], the thermal decomposition of chitosan and PVP occurs at about 300°C . Thus, it is inferred that a heat-treatment of 700°C in this work would lead to the complete removal of chitosan or PVP in the precursor films. Thus, these LiMn_2O_4 films prepared from either the chitosan-added or PVP-added precursor solutions exhibit no discernible difference in the electrochemical behaviors. However, for the film deposited from the chitosan-free precursor solution, a discharge capacity of 108 mAh g^{-1} in the first run was obtained

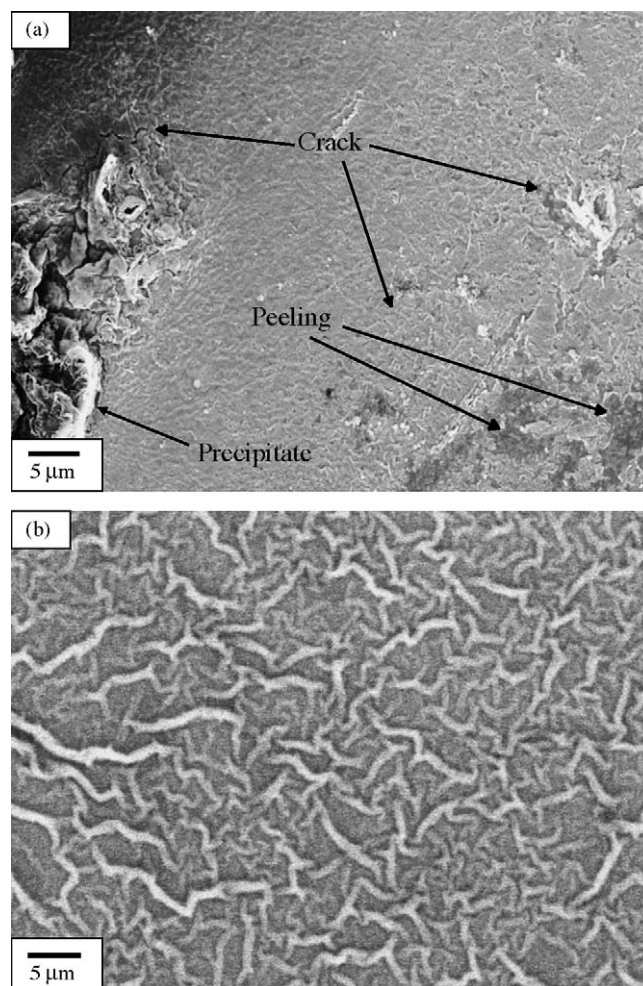


Fig. 9. Typical microstructures of the thin-film cathodes deposited from the (a) chitosan-free and (b) chitosan-added precursor solutions containing acetates after 50 charge/discharge cycles.

(Fig. 8(d)). This reduction of capacity is due to the presence of the electrochemically non-active Mn_2O_3 phase, as is evidenced in Fig. 6. Moreover, a significant discharge capacity loss of 24% after 50 cycles was also observed for the thin-film cathode prepared from the chitosan-free precursor solution. Based on the published works of Ohzuku et al. [17] and Xia and Yoshio [18], it was shown that about 3% variation in lattice volume took place during Li ion (de)intercalation process in $\text{Li}_x\text{Mn}_2\text{O}_4$. Thus, it is inferred that the adhesion between the deposited film and substrate plays an important role in the capacity retention. A strong adhesion is able to tolerate the expansion–extraction of the deposited film in volume during Li ion (de)intercalation and could result in a lesser discharge capacity loss. Fig. 9 shows the microstructure of the prepared thin-film cathodes after being charged/discharged for 50 cycles. Numerous cracks and peeling were observed on the films prepared from the chitosan-free precursor solution after 50 charge/discharge cycles, as indicated by the arrows in Fig. 9(a). This revealed that the poor adhesion between the substrate and the thin-film cathodes deposited from the chitosan-free precursor solution led to an increased capacity loss (24% after 50 cycles). On the other hand, Fig. 9(b) shows that the films deposited from the chitosan-containing precursor solution exhibited a good adhesion to the substrate. Thus, a better capacity retention of about 91% after 50 cycles for the films deposited from the chitosan-containing precursor solution was obtained.

4. Conclusions

In this work, the addition of chitosan in the precursor solution was found to be an effective method for the deposition of LiMn_2O_4 films. Furthermore, the chitosan addition can eliminate the formation of the precipitates in the precursor solution containing lithium/manganese acetates. A chitosan-added precursor solution remained stable without any precipitation for 10 months. Due to the chemical bonding between chitosan and cations, Li/Mn ions can be homogeneously distributed in the precursor solution at a molecular scale. Such a precursor solution is beneficial for the deposition of a single-phase LiMn_2O_4 film on a Pt-coated silicon substrate. The charge–discharge test also showed that the prepared thin-film cathode deposited from

the chitosan-added precursor solution exhibited a higher initial discharge capacity of 134 mAh g^{-1} and better capacity retention of 91% after 50 charge/discharge cycles in comparison with the performance of the film from the chitosan-free precursor solution. Thus, the lithium/manganese acetates-containing precursor solution with chitosan addition is a unique and appropriate way to prepare a dense and single-phase LiMn_2O_4 film.

Acknowledgement

Financial support by the National Science Council of the Republic of China under grant NSC 93-2120-M-006-004 is gratefully acknowledged.

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