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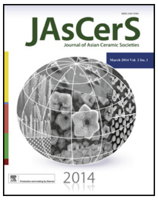

Preparation of $Li_4Ti_5O_{12}$ electrode thin films by a mist CVD process with aqueous precursor solution

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ABSTRACT

Spinel $Li_4Ti_5O_{12}$ thin films were prepared by a mist CVD process, using an aqueous solution of lithium nitrate and a water-soluble titanium lactate complex as the source of Li and Ti, respectively. In this process, mist particles ultrasonically atomized from a source aqueous solution were transferred by nitrogen gas to a heating substrate to prepare thin films. Scanning electron microscopy observation showed that thin films obtained by this process were dense and smooth, and thin films with a thickness of about 500 nm were obtained. In the X-ray diffraction analysis, formation of $Li_4Ti_5O_{12}$ spinel phase was confirmed in the obtained thin film sintered at 700 °C for 4 h. The cell with the thin films as an electrode exhibited a capacity of about 110 mAh g^{-1}, and the cell showed good cycling performance during 10 cycles.

1. Introduction

In the last few years, an interest has developed in the thin-film microbattery for use in micropower sources for RF-IC tags, smart cards, medical devices, microelectric mechanical systems, wireless sensors and so on [1]. For the fabrication of thin film batteries, physical vapor (PVD) processes, such as sputtering and pulsed laser deposition (PLD) process, have been used [1–7]. Solution processes like sol–gel process have also been proposed to prepare electrode and electrolyte thin film for lithium ion battery materials [8,9]. Solution processes contribute to system simplicity, low-cost deposition and large area coating. In addition, chemical compositions of thin films can be easily controlled, and rather thick films are easily obtained. Thus, the solution processes are very attractive for the development of thin film batteries.

From the viewpoint of the load to the environment, an aqueous solution process is more favorable. A “mist CVD process” is known to be a thin film formation process using aqueous solution [10]. In this process, aqueous solution of starting materials is ultrasonically atomized to form mist particles with a size of about 3 μm, and mists are transferred by a carrier gas to the substrate to form thin films [10,11]. This process is carried out at atmospheric conditions, and aqueous solutions can be used for the source. Thus, this process possesses advantages of safety, cost-effectiveness, light load to the environment, multiplicity of applying to a lot of materials. In our previous study, we showed that spinel $LiMn_2O_4$ thin films were successfully prepared as cathode material for lithium ion battery by the mist CVD process [11].

On the other hand, spinel $Li_4Ti_5O_{12}$ has been very important negative electrode materials for lithium ion batteries because of the several advantages such as good cycle performance, no volume change during the charge–discharge and its excellent reversibility with a theoretical specific capacity of 175 mAh g^{-1} [7,12,13]. This material was successfully used as the negative electrode coupled with high potential positive electrode materials ($LiMn_2O_4$ or $LiCoO_2$) to provide a cell with an operating voltage of about 2.5 V [13,14]. Thin film of spinel $Li_4Ti_5O_{12}$ is also very attractive for all-solid-state thin film batteries. Preparation of $Li_4Ti_5O_{12}$ thin films by a sol–gel process has been reported with different approaches. For example, Rho and Kanamura [9] have reported the preparation of rather thick $Li_4Ti_5O_{12}$ films using Ti- and Li alkoxides with poly(vinylpyrrolidone), and Haetge et al. [15] have reported the preparation of mesoporous $Li_4Ti_5O_{12}$ thin films using Ti-alkoxide, lithium acetate and poly(ethylene-co-butylene)-block-poly(ethylene oxide) diblock copolymer. We have also reported the preparation of $Li_4Ti_5O_{12}$ thin films by a sol–gel process using titanium isopropoxide and lithium acetate

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as precursors [16,17], and effects of Li/Ti ratio [16] or the thermal treatment [17], on the phase composition, structure and electrochemical behavior, were studied. Nevertheless, development of an aqueous solution process for the preparation of $Li_4Ti_5O_{12}$ thin films is still important, because an aqueous solution process possesses advantages of safety, cost-effectiveness, and light load to the environment.

In the present study, $Li_4Ti_5O_{12}$ thin films were prepared by the mist CVD process using aqueous solution of starting materials, and the electrochemical behavior of the obtained $Li_4Ti_5O_{12}$ thin films on Au substrate was examined.

2. Experimental procedure

$Li_4Ti_5O_{12}$ electrode thin films were prepared by the mist CVD process, using the precursor aqueous solution, on a silica glass or Au plate. It has been reported that TiO_2 (anatase) electrode thin films can be prepared from aqueous solution of peroxo-titanium complex as a precursor solution by using a spray pyrolysis process [18]. In this study, titanium(IV)bis(ammonium lactato)dihydroxide (Aldrich, 50 wt.% solution in water) was used as the water soluble starting material. Aqueous solution of 0.02 M lithium nitrate (Wako Chemicals, Japan) and 0.025 M the titanium lactate complex was used as the source of Li and Ti, respectively. The solution was ultrasonically atomized, and the mist particles including Li and Ti precursor with the water solvent were transferred onto a heated substrate through a linear shaped nozzle by N_2 carrier gas at a flow rate of 8 L min^{-1} (the apparatus was provided by TOUKI Co. Ltd., Japan). The substrate was placed on a heating stage, and the temperature of the stage was 400 °C. The distance between the substrate and the nozzle was about 1 mm. The stage was scanned at a speed of 0.05 mm s^{-1}, and the scanning process was repeated for 10–96 times. The obtained thin films were further heat-treated at 700 °C for 1 or 4 h.

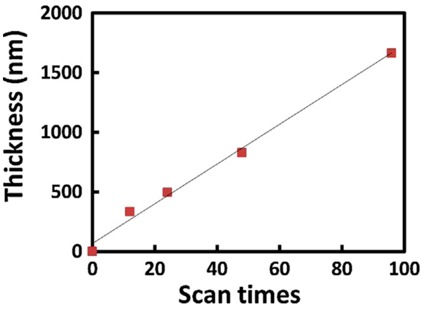

Fig. 1. Thickness of deposited Li_2O–TiO_2 system films on quartz substrate versus number of scan at 400 °C.

The film surface was examined using a scanning electron microscopy (SEM, JSM-5300, JEOL). X-ray diffraction (XRD) patterns were recorded using an X-ray diffractometer (XRD-6000, Shimadzu) with Cu Kα radiation.

Electrochemical behavior of the $Li_4Ti_5O_{12}$ thin film prepared on Au substrate was examined by a three-electrode beaker cell using Li as the counter and reference electrodes, and 1 M $LiPF_6$ in a mixed solvent of EC and DEC as liquid electrolyte.

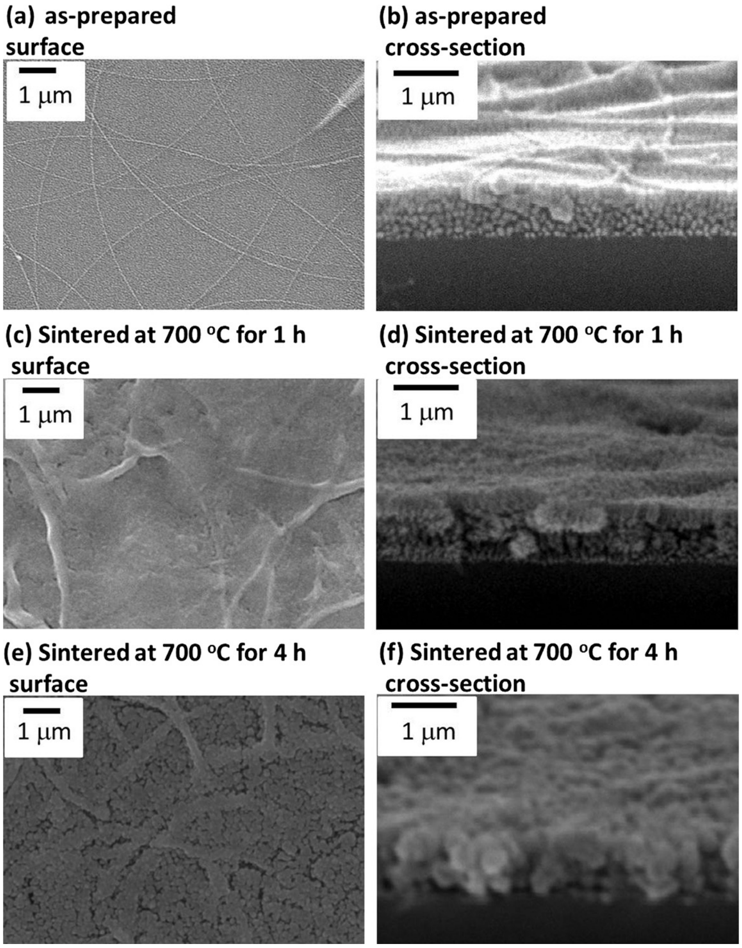

Fig. 2. SEM images of the as-prepared film with the substrate temperature of 400 °C, and that of the films obtained by the heat treatment at 700 °C for 1 or 4 h.

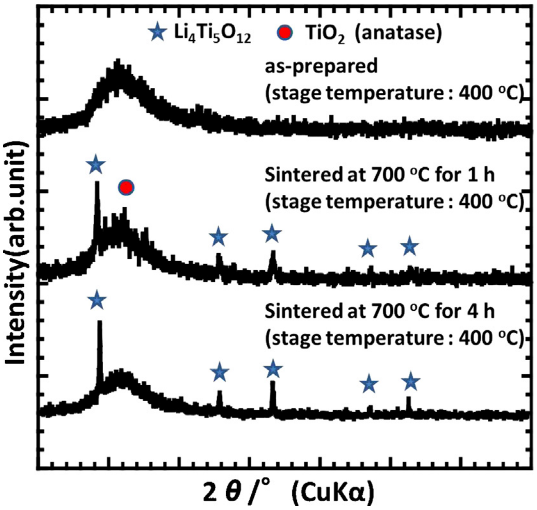

Fig. 3. XRD patterns of the as-prepared film with the substrate temperature of 400 °C, and that of the films obtained by the heat treatment at 700 °C for 1 or 4 h.

3. Results and discussion

Fig. 1 shows the relation between the film thickness and scan times with stage temperature of 400 °C. Thickness of the film increases with an increase in the scans, and was about 1.6 μm after 96 scans. Deposition time for 24 scans was about 80 min, and the thickness of the film after 24 scans was about 500 nm. Thus, the deposition rate of the mist CVD process at this condition is estimated to be about 6.3 nm min^{-1}.

Fig. 2 portrays SEM images of the as-prepared film with the substrate temperature of 400 °C (a and b), and that of the films obtained by the sintering at 700 °C for 1 h (c and d) and 4 h (e and f). The SEM observation of the cross-section of the films revealed that the thin films were dense. On the surfaces, string-like structures were observed. Formation of these string-like structures suggests that polymerized precursors were partly formed on the surface of the mists before drying, and such precursors were deposited on the film surface. In the surface and cross-section images, the growth in the grain sizes was observed by sintering at 700 °C, from several tens of nanometers in the 1 h-sintered samples to a few hundreds of nanometers in the 4 h-sintered samples.

Fig. 3 presents XRD patterns of the as-prepared film with the substrate temperature of 400 °C, and that of the films obtained by the sintering at 700 °C for 1 or 4 h. The halo pattern observed in all the samples is background from the SiO_2 glass substrate. In the as-deposited film obtained at substrate temperature of 400 °C, the precipitation of crystals was not confirmed, indicating that the as-deposited film is amorphous. With a sintering at 700 °C, $Li_4Ti_5O_{12}$ and very small amounts of TiO_2 were observed. However, the degree of crystallization in the films increased with an increase in the sintering time, and $Li_4Ti_5O_{12}$ single phase was obtained after sintering at 700 °C for 4 h. In lithium-containing oxides, loss of lithium with a high temperature heat-treatment is often observed. Thus, a heat-treatment at rather low temperatures is preferred to avoid the loss during heating. In the present process, $Li_4Ti_5O_{12}$ single phase was obtained after sintering at 700 °C for 4 h, and this sample was used for the electrochemical characterization.

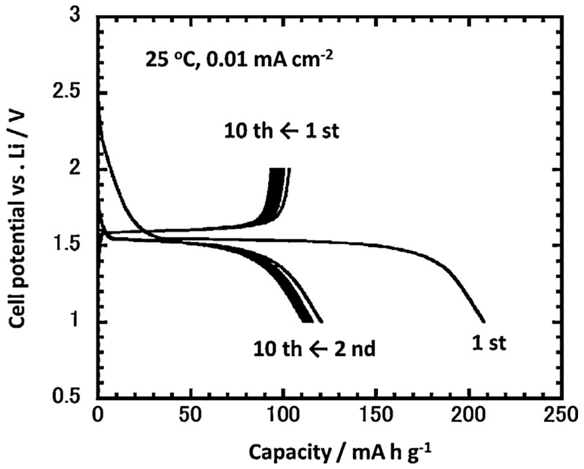

Fig. 4. Charge–discharge curves of a cell using the $Li_4Ti_5O_{12}$ thin film heat-treated at 700 °C for 4 h, up to the 10th cycle.

Fig. 4 shows the charge–discharge curves of a cell with the thin film heat-treated at 700 °C for 4 h using 1 M $LiPF_6$ in EC and DEC as an electrolyte, up to the 10th cycle. The current density employed in the present study was 0.01 mA cm^{-2}, and the cell was charged up to 2 V, and discharged to 1 V. The observed cycling curves are typical for the $Li_4Ti_5O_{12}$ electrode with a very flat plateau at 1.55 V. As clarified already, this plateau is owing to the coexistence of two active phases in the electrode, $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$ [12]. The electrochemical reaction can be written as:

$$Li_4Ti_5O_{12} + 3Li^+ + 3e^- \rightarrow Li_7Ti_5O_{12} \qquad (1)$$

According to reaction (1), the $Li_4Ti_5O_{12}$ has a theoretical capacity of 175 mAh g^{-1}. The initial charge capacity was about 110 mAh g^{-1} in this study, and the cell showed good cycling performance during 10 cycles. Discharge capacities of the thin films are rather small compared with the theoretical charge storage capacity. Lack of crystallinity, or lithium content, or poor electron conductivity can be a reason for the small capacity.

In the present study, we have shown the performance of $Li_4Ti_5O_{12}$ thin film prepared by the mist-CVD process. The mist-CVD process is shown to be effective to prepare an anode thin film with good cycle performance. The mist-CVD process in the present study only uses an aqueous solution of lithium nitrate and a titanium lactate complex as a precursor solution. Since this process is very simple, and can be conducted under the ambient atmosphere, this process is expected to be easily applied for thin films of other cathode, anode and electrolyte materials for lithium batteries.

4. Conclusions

We demonstrated that $Li_4Ti_5O_{12}$ thin films were prepared by using so called the “mist CVD process”, employing the aqueous solution of lithium nitrate and a water-soluble titanium lactate complex, as the precursor solution. SEM observation revealed that thin films obtained by this process were dense and smooth, and thin films with a thickness of about 500 nm were obtained. In the XRD measurement, precipitation of $Li_4Ti_5O_{12}$ with spinel structure was confirmed in the sintered at 700 °C film with substrate temperature of 400 °C. The cell with the thin films obtained by sintering at 700 °C for 4 h exhibited a capacity of about 110 mAh g^{-1}, and the cell showed good cycling performance during 10 cycles.

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References

[1] A. Patil, V. Patil, D.W. Shin, J.W. Choi, D.S. Paik and S.J. Yoon, Mater. Res. Bull., 43, 1913–1942 (2008).

[2] K.H. Hwang, S.H. Lee and S.K. Joo, J. Electrochem. Soc., 141, 3296–3299 (1994).
[3] B.J. Hwang, C.Y. Wang, M.Y. Cheng and R. Santhanam, J. Phys. Chem. C, 113, 11373–11380 (2009).
[4] A. Rougier, K.A. Striebel, S.J. Wen, T.J. Richardson, R.P. Reade and E.J. Cairns, Appl. Surf. Sci., 134, 107–115 (1998).
[5] N. Kuwata, J. Kawamura, K. Toribami, T. Hattori and N. Sata, Electrochem. Commun., 6, 417–421 (2004).
[6] N. Kuwata, N. Iwagami, Y. Tanji, Y. Masuda and J. Kawamura, J. Electrochem. Soc., 157, A521–A527 (2010).
[7] M. Hirayama, K. Kim, T. Toujigamori, W. Cho and R. Kanno, Dalton Trans., 40, 2882–2887 (2011).
[8] Y.H. Rho and K. Kanamura, J. Electroanal. Chem., 559, 69–75 (2003).
[9] Y.H. Rho and K. Kanamura, J. Solid State Chem., 177, 2094–2100 (2004).
[10] Y. Kamada, T. Kawaharamura, H. Nishinaka and S. Fujita, Jpn. J. Appl. Phys., 45, L857–L859 (2006).
[11] K. Tadanaga, A. Yamaguchi, A. Sakuda, A. Hayashi, M. Tatsumisago, A. Duran and M. Aparicio, Mater. Res. Bull., 53, 196–198 (2014).
[12] T. Ohzuku, A. Ueda and N. Yamamoto, J. Electrochem. Soc., 142, 1431–1435 (1995).
[13] K. Amine, I. Belharouak, Z. Chen, T. Tran, H. Yumoto, N. Ota, S.T. Myung and Y.K. Sun, Adv. Mater., 22, 3052–3057 (2010).
[14] D. Peramunage and K.M. Abraham, J. Electrochem. Soc., 145, 2609–2615 (1998).
[15] J. Haetge, P. Hartmann, K. Brezesinski, J. Janek and T. Brezesinski, Chem. Mater., 23, 4384–4393 (2011).
[16] J. Mosa, J.F. Velez, I. Lorite, N. Arconada and M. Aparicio, J. Power Sources, 205, 491–494 (2012).
[17] J. Mosa, J.F. Velez, J.J. Reinosa, M. Aparicio, A. Yamaguchi, K. Tadanaga and M. Tatsumisago, J. Power Sources, 244, 482–487 (2013).
[18] C. Natarajan, N. Fukunaga and G. Nogami, Thin Solid Films, 322, 6–8 (1998).