

## Thin-film lithium-ion battery derived from $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ sintered pellet

XIAO Zhuo-bing(肖卓炳), MA Ming-you(麻明友), WU Xian-ming(吴显明),  
HE Ze-qiang(何则强), CHEN Shang(陈 上)

College of Chemistry and Chemical Engineering, Jishou University, Jishou 416000, China

Received 24 November 2005; accepted 20 March 2006

**Abstract:** Thin-film lithium-ion battery of  $\text{LiMn}_2\text{O}_4/\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3/\text{LiMn}_2\text{O}_4$  was fabricated using  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  sintered pellet as both substrate and electrolyte.  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  sintered pellet was prepared by sol-gel technique, and the thin-film battery was heat-treated by rapid thermal annealing. Phase identification, morphology and electrochemical properties of the components and thin-film battery were investigated by X-ray diffractometry, scanning electron microscopy, electrochemical impedance spectroscopy and galvanostatic charge-discharge experiments. The results show that  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  possesses a electrochemical window of 2.4 V and an ionic conductivity of  $1.2 \times 10^{-4}$  S/cm. With  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  sintered pellet as both substrate and solid electrolyte, the fabricated thin-film battery with an open circuit voltage of 1.2V can be easily cycled.

**Key words:**  $\text{LiMn}_2\text{O}_4$ ;  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ ; solid electrolyte; lithium ion battery; thin-film battery; sintered pellet

### 1 Introduction

All-solid-state thin-film batteries have drawn a lot of attention due to their many possible applications, such as smart cards, CMOS-based integrated circuits and microdevices[1–11]. However, most of thin-film batteries employ substrate, which makes the fabrication of thin-film battery inconvenient.

In the synthesis of  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  sintered pellet, although the pressure to press  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  powders into pellet is not high and no sintering additive is added, the sintered pellets possess strong intensity and are not easy to break. This makes it important to prepare a kind of thin-film battery using this sintered pellet as both substrate and electrolyte.

The average ionic conductivity of LIPON (lithium phosphorus oxynitride) thin film is about  $2.3 \times 10^{-6}$  S/cm[12] and that of  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  is  $7 \times 10^{-4}$  S/cm[13]. So the resistance of 300  $\mu\text{m}$ -thick  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  sintered pellet (thickness of most substrates is about 300  $\mu\text{m}$ ) is almost the same as that of 1  $\mu\text{m}$ -thick LIPON thin film if their surface areas are the same. Therefore, compared with most other thin-film lithium-ion batteries which employ substrate and electrolyte of LIPON film, the thin-film lithium-ion

battery using  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  sintered pellet as both substrate and solid electrolyte will not increase the internal resistance and the thickness of thin-film battery, but make the fabrication of thin-film battery simpler because this kind of thin-film battery no longer needs extra substrate.

Based on the above considerations, the fabrication of thin-film lithium-ion battery of  $\text{LiMn}_2\text{O}_4/\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3/\text{LiMn}_2\text{O}_4$  was carried out to investigate the feasibility of the thin-film battery using  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  sintered pellet as both substrate and electrolyte.

### 2 Experimental

#### 2.1 Preparation of $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ sintered pellet

Dissolved stoichiometric amount of  $\text{Li}(\text{CH}_3\text{COO}) \cdot 2\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$ . Dripped  $\text{PO}(\text{OC}_4\text{H}_9)_4$  and  $(\text{Ti}(\text{OC}_4\text{H}_9)_4)$  into the mixture under constant stirring. Then added several drops of deionized water into the solution and the solution was finally dried at 140 °C for 4 h to form  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  gel. The gel was first calcined at 900 °C for 2 h and then grounded into fine powder. With addition of a small amount of 3% polyvinyl-alcohol solution as binder, the fine powder was then pressed into

pellets at pressure of 50 MPa. Finally the pellets were calcined at 900 °C for 2 h.

## 2.2 Preparation of $\text{LiMn}_2\text{O}_4$ precursor solution

Dissolved stoichiometric amount of lithium acetate and manganese acetate in a small amount of deionized water under heating. Added 2-methoxyethanol to adjust the viscosity and wetting property of the solution. Removed dust and other suspended impurities from the solution by filtering through 0.2  $\mu\text{m}$  syringe filters and thus obtaining the  $\text{LiMn}_2\text{O}_4$  precursor solution.

## 2.3 Preparation of $\text{LiMn}_2\text{O}_4/\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3/\text{LiMn}_2\text{O}_4$ thin-film lithium-ion battery

After 2 mm-thick  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  sintered pellet was polished with 800 grade emery paper(a thick  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  sintered pellet was employed to avoid the short circuit of the thin-film battery by the soaking of  $\text{LiMn}_2\text{O}_4$  precursor throughout the whole pellet),  $\text{LiMn}_2\text{O}_4$  precursor solution was deposited by spin coating on both sides of the sintered pellet and then heated up to 350 °C in air at the heating rate of 10 °C/min and maintained at 350 °C for 20 min. In order to minimize the interfacial reaction between  $\text{LiMn}_2\text{O}_4$  and  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ , the thin-film battery was annealed in a rapid thermal annealing system at 750 °C in air for 2 min.

In order to confirm that  $\text{LiMn}_2\text{O}_4$  thin film was formed under the above synthesis conditions,  $\text{LiMn}_2\text{O}_4$  precursor solution derived  $\text{LiMn}_2\text{O}_4$  thin films deposited on Si substrate was prepared under the same synthesis conditions as that of the preparation of  $\text{LiMn}_2\text{O}_4/\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3/\text{LiMn}_2\text{O}_4$  thin-film lithium-ion battery.

## 2.4 Measurements

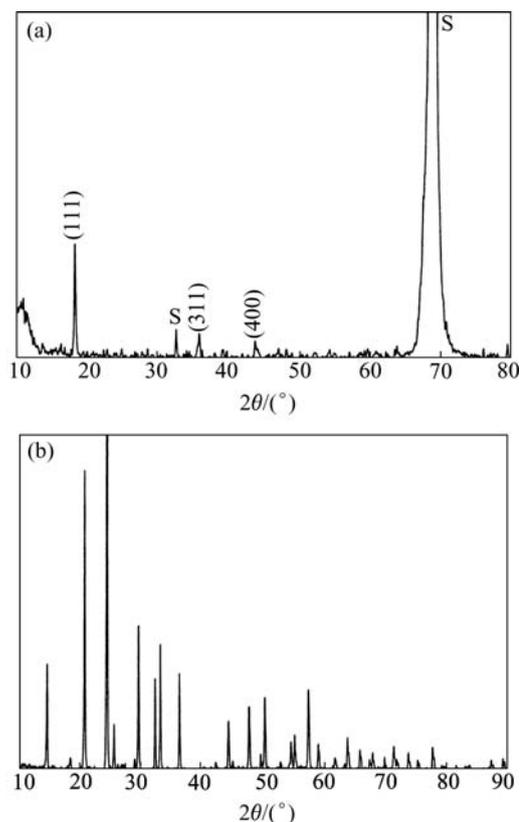
Phase identification of the  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  powders and  $\text{LiMn}_2\text{O}_4$  thin film were performed with Rigaku D/MAX-gA X-ray diffractometer. The morphology of  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  pellet was studied by JSM 5600LV scanning electron microscopy. For the measurements of the electrochemical window of  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ ,  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  thin film deposited on Pt-Coated Si substrate (Pt acts as current collector) was placed in an open beaker cell containing 1 mol/L  $\text{LiPF}_6$  dissolved in ethylene carbonate(EC) and dimethyl carbonate (DMC)(1 : 1, volume ratio). Lithium metal was used as both counter and reference electrodes.  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  thin film was prepared as follows: a Pt-coated Si substrate was dipped into  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  precursor solution and then taken out and followed by heat treatment at 900 °C for 2 h at a heating rate of 8 °C/min.

Gold was deposited on both sides of  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}$ -

$(\text{PO}_4)_3$  sintered pellet and  $\text{LiMn}_2\text{O}_4/\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3/\text{LiMn}_2\text{O}_4$  sandwich by direct current sputtering to carry out electrochemical measurements. The ionic conductivity of  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  was measured by electrochemical impedance spectroscopy in the frequency range from 100 kHz to 1 Hz. The galvanostatic charge and discharge measurements of  $\text{LiMn}_2\text{O}_4/\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3/\text{LiMn}_2\text{O}_4$  thin-film battery were conducted in the voltage range 0.5 to 1.6 V.

## 3 Results and discussion

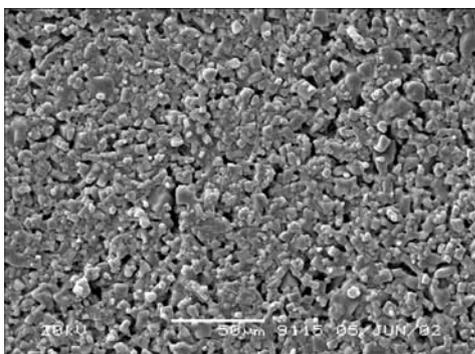
The X-ray diffraction patterns of the  $\text{LiMn}_2\text{O}_4$  thin film and  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  powders are shown in Fig.1. Three peaks at diffraction angles of 18.61°, 36.09°, and 43.87° can be observed in Fig.1(a), which correspond to the (111), (311) and (400) reflections of spinel  $\text{LiMn}_2\text{O}_4$ , indicating that the prepared thin film is  $\text{LiMn}_2\text{O}_4$ . In Fig.1(b) all the diffraction peaks agree well with the reported results of the bulk material of the  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ [14, 15], suggesting that the powders are  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ .



**Fig.1** X-ray diffraction patterns of  $\text{LiMn}_2\text{O}_4$  thin film and  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  powders: (a)  $\text{LiMn}_2\text{O}_4$  thin film on Si substrate(peaks marked with S belongs to the substrate); (b)  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  powders

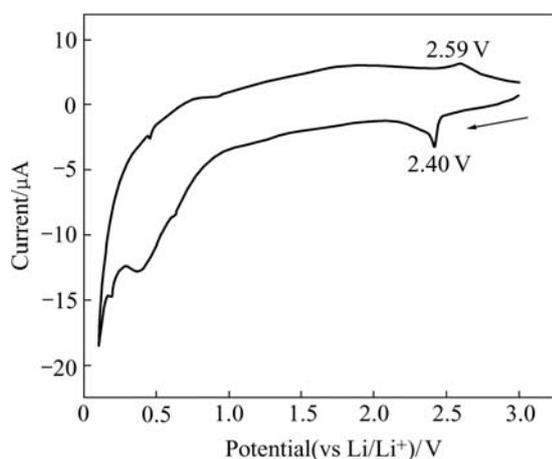
Fig.2 shows the SEM image of  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  sintered pellet. It can be seen from Fig.2 that the sintered

pellet is relatively dense although the pressure to press the  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  powders into the pellet is not high and no sintering additive is added.



**Fig.2** SEM image of  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  sintered pellet

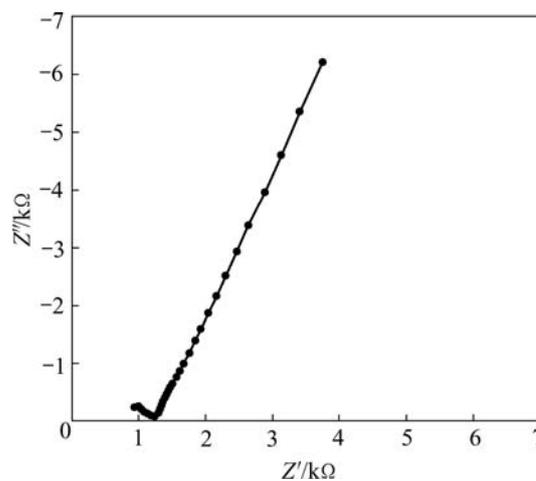
Electrochemical window of the electrolyte is an important factor for its practical application, especially in the field of batteries. Some difficulty exists in measuring the electrochemical window of  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  by using working electrode made up of  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  powders, i.e., no redox peaks can be observed in the cyclic voltammogram even at slow rate. This may be caused by the poor electronic conductivity of  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  (The electronic conductivity is about  $10^{-11}$  S/cm in our preliminary studies) and the thick electrode made up of  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  powders, i.e., the poor electronic conductivity and relatively thick working electrode make it hard to observe the current response (redox peaks) in the cyclic voltammogram. So  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  thin film was used to carry out the measurement. Fig.3 shows the cyclic voltammogram of the sol-gel derived  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  thin film recorded at a scan rate of 1 mV/s. The figure shows the voltages (vs.  $\text{Li}/\text{Li}^+$ ) corresponding to the redox peaks are about 2.4 V, which agrees well with the value of the  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  powder tested by coulometric titration [14],



**Fig.3** Cyclic voltammogram of  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  thin film recorded at scan rate of 1 mV/s

indicating that  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  possesses a wide electrochemical window.

The electrochemical impedance spectroscopy of the  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  sintered pellet is shown in Fig.4, as observed from this figure, the spectrum consists of an incomplete semicircle and an inclined line. The incomplete semicircle is caused by the insufficient upper limit of 100 kHz for Electrochemical Workstation CHI660A. From the intercept of the inclined line in the diagram the ionic conductivity can be estimated to be  $1.2 \times 10^{-4}$  S/cm.

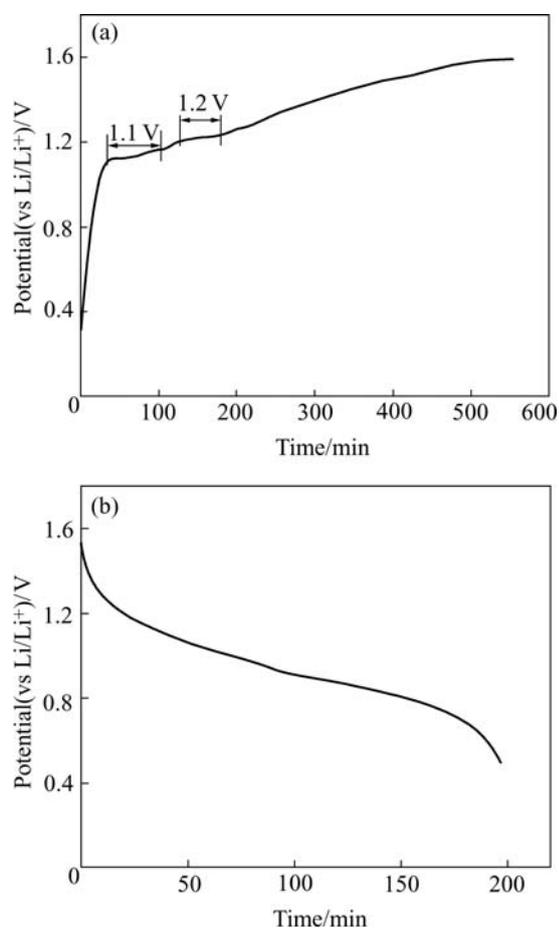


**Fig.4** Electrochemical impedance spectroscopy of  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  sintered pellet

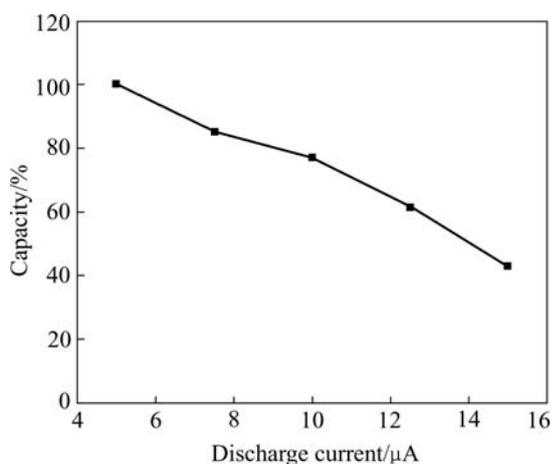
The battery with surface area of  $0.8 \text{ cm}^2$  exhibits an open circuit voltage of approximately 1.2 V at ambient temperature. Fig.5 shows the galvanostatic charge and discharge curves of  $\text{LiMn}_2\text{O}_4/\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3/\text{LiMn}_2\text{O}_4$  thin-film lithium-ion battery conducted at a current of  $5 \mu\text{A}$ . Two voltage plateaus can be observed at about 1.1 and 1.2 V in the charge curve, which is the characteristics of  $\text{LiMn}_2\text{O}_4$ . But no obvious voltage plateau can be seen in the discharge curve. It apparently shows that the thin-film battery has a large irreversible capacity, but in fact it is not the case because the battery only delivers very little capacity from 1.5 to 1.3 V in the discharge curve, i.e. the charge from 1.3 to 1.6 V contributes very little capacity to the battery.

The capacity as a function of discharge current is shown in Fig.6 (it is assumed that the capacity of the battery discharging at  $5 \mu\text{A}$  is 100%). As shown in Fig.6, the capacity decreases as the discharge current increases. The extent of the capacity reduction is higher than that of the battery using powder materials as electrodes, which is caused by the higher internal resistance of thin-film battery. Contrary to the battery using liquid electrolyte and electrodes containing electronic materials, thin film battery employs the solid electrolyte and electrode material which does not contain electronic materials.

Therefore, thin-film battery possesses higher internal resistance, leading to faster capacity decrease with the increase of the discharge current.



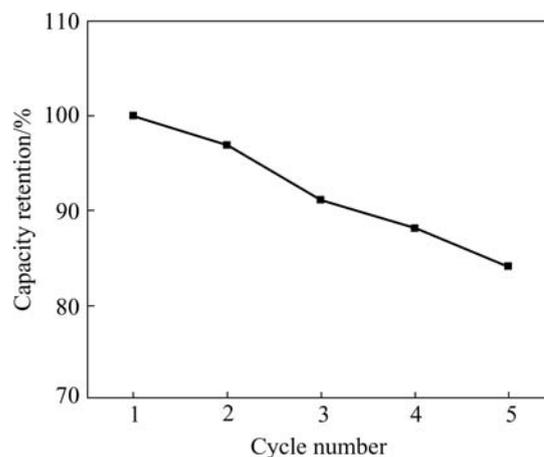
**Fig.5** Charge and discharge curves of  $\text{LiMn}_2\text{O}_4/\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3/\text{LiMn}_2\text{O}_4$  thin-film battery: (a) Charge curve; (b) Discharge curve



**Fig.6** Capacity variation of thin-film battery with discharge current

Fig.7 shows the cycling behavior of  $\text{LiMn}_2\text{O}_4/\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3/\text{LiMn}_2\text{O}_4$  thin-film battery carried out at current of 10  $\mu\text{A}$ . As observed in Fig.7, the

capacity decreases with the increase of the cycle number, and the capacity loss per cycle is about 3.2%. The capacity loss is a bit higher than that in Ref.[16]. The reason is that both the cathode and anode are  $\text{LiMn}_2\text{O}_4$ , which can cause the formation of  $\text{Li}_2\text{Mn}_2\text{O}_4$  and the occurrence of Jahn-Teller effect, thus leading to rapid capacity loss.



**Fig.7** Cycling behavior of  $\text{LiMn}_2\text{O}_4/\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3/\text{LiMn}_2\text{O}_4$  thin-film battery

## 4 Conclusions

A novel thin-film lithium-ion battery was fabricated by using  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  sintered pellet as both substrate and electrolyte. Although the thickness of  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  sintered pellet is more than 2 mm and the pressure to prepare the powders into pellets is only 50 MPa, the thin-film battery with an open circuit voltage of 1.2 V can be easily cycled. The thin-film battery using  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  sintered pellet as both substrate and electrolyte not only makes the fabrication of thin-film lithium-ion battery much simpler but also makes the operating voltage of the thin-film battery up to 2.4 V. This kind of thin-film lithium-ion battery can be commercialized if improved conditions, proper methods and techniques were available and used.

## References

- [1] YOON Y S, KIM J S, CHOI S H. Structural and electrochemical properties of vanadium oxide thin films grown by d.c. and r.f. reactive sputtering at room temperature[J]. *Thin Solid Films*, 2004, 460: 41–47.
- [2] TAO Y, CHEN Z, ZHU B, HUANG W. Preparation of preferred oriented  $\text{LiCoO}_2$  thin films by soft solution processing[J]. *Solid State Ionics*, 2003, 161: 187–192.
- [3] WEST W C, WHITACRE J F, LIM J R. Chemical stability enhancement of lithium conducting solid electrolyte plates using sputtered LiPON thin films[J]. *J Power Sources*, 2004, 126: 134–138.
- [4] EFTEKHARI A. Fabrication of 5 V lithium rechargeable micro-battery[J]. *J Power Sources*, 2004, 132: 240–243.
- [5] WU X M, LI X H, XU M F, ZHANG Y H, HE Z Q, WANG Z. Preparation of  $\text{LiMn}_2\text{O}_4$  thin films by aqueous solution deposition[J]. *Materials Research Bulletin*, 2002, 37: 2345–2353.

- [6] KIM M K, PARK K S, SON J T, KIM J G, CHUNG H T, KIM H G. The electrochemical properties of thin-film  $\text{LiCoO}_2$  cathode prepared by sol-gel process[J]. *Solid State Ionics*, 2002, 152/153: 267-272.
- [7] NAGASUBRAMANIAN G, DOUGHTY D H. Electrical characterization of all-solid-state thin film batteries[J]. *J Power Sources*, 2004, 136: 395-400.
- [8] WU X M, LI X H, WANG Z, XIAO Z B, LIU J B, YAN W B. Characterization of solution-derived  $\text{LiMn}_2\text{O}_4$  thin films heat-treated by rapid thermal annealing[J]. *Materials Chemistry and Physics*, 2004, 83: 78-81.
- [9] LEE J H, HAN K S, LEE B J, SEO S I, YOSHIMURA M. Fabrication of  $\text{LiCoO}_2$  films for lithium rechargeable microbattery in an aqueous solution by electrochemical reflux method[J]. *Electrochimica Acta*, 2004, 50: 467-471.
- [10] BATES J B, DUDNEY N J, NEUDECKER B, UEDA A, EVANS C D. Thin-film lithium and lithium-ion batteries[J]. *Solid State Ionics*, 2000, 135: 33-35.
- [11] SHUI J L, JIANG G S, XIE S, CHEN C H. Thin films of lithium manganese oxide spinel as cathode materials for secondary lithium batteries[J]. *Electrochimica Acta*, 2004, 49: 2209-2213.
- [12] ZHAO S, FU Z, QIN Q. A solid-state electrolyte lithium phosphorus oxynitride film prepared by pulsed laser deposition[J]. *Thin Solid Films*, 2002, 415: 108-113.
- [13] TAKADA K, TANSHO M, YANASE I, INADA T, KAJIYAMA A, KOGUCHI M, KONDO S, WATANABE M. Lithium ion conduction in  $\text{LiTi}_2(\text{PO}_4)_3$ [J]. *Solid State Ionics*, 2001, 139: 241-247.
- [14] BIRKE P, SALAM F, DÖRING S, WEPPNER W. A first approach to a monolithic all solid state inorganic lithium battery[J]. *Solid State Ionics*, 1999, 118: 149-157.
- [15] BEST A S, FORSYTH M, MACFARLANE D R. Stoichiometric changes in lithium conducting materials based on  $\text{Li}_{1-x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ : impedance, X-ray and NMR studies[J]. *Solid State Ionics*, 2000, 136/137: 339-344.
- [16] HIDEAKI O, YOJI S. Characteristics of  $\text{Li/MoO}_{3-x}$  thin film batteries[J]. *Solid State Ionics*, 2001, 144: 59-64.

(Edited by LONG Huai-zhong)