

Journal of ALLOYS AND COMPOUNDS

Journal of Alloys and Compounds 432 (2007) L22-L25

www.elsevier.com/locate/jallcom

Letter

The stability between perovskite $La_{2/3-x}Li_{3x}\Box_{1/3-2x}TiO_3$ (3x = 0.3) electrolyte and LiM_mO_n (M = Mn, Ni and Co) cathodes

Cheng-Lung Liao, Chung-Han Wen, Kuan-Zong Fung*

Department of Materials Science and Engineering, National Cheng Kung University, No. 1, Ta-Hsueh Road, Tainan 70101, Taiwan

Received 18 May 2006; received in revised form 3 June 2006; accepted 6 June 2006

Available online 11 July 2006

Abstract

Perovskite $La_{2/3-x}Li_{3x}\Box_{1/3-2x}TiO_3$ (LLT) exhibits high lithium-ion conductivity ($\sim 10^{-3}$ S cm⁻¹) is a potential material for using as solid-state electrolyte in all-solid-state lithium-ion microbatteries. Considering about the LLT and cathode films might undergo high-temperature heat treatment simultaneously, the stability and reaction in the interface of electrolyte and cathode become interesting points to be investigated. In this study, LLT powders were mixed with three kinds of cathodes and then annealed at 500–800 °C. The results indicated that the LLT electrolyte was extremely stable with spinel LiMn₂O₄ even after 800 °C heat treatment for 2 h. The commercial cathode material, HT-LiCoO₂, also shows good stability with LLT electrolyte after 700 °C annealing, but the structures of LLT and LiCoO₂ both showed slight damage after 800 °C heat treatment. Moreover, layered LiNiO₂ showed poor stability with LLT, and, it decomposed into NiO when annealing with LLT above 500 °C.

Keywords: Electrode materials; Electrolyte materials; X-ray diffraction; Perovskite LaLiTiO3

1. Introduction

All-solid-state lithium-ion microbattery, exhibits high energy density and good cycleability, is a promising alternative power storage in the recent applications of portable electronics, microelectronics, and implantation devices. For fabricating highperformanced all-solid-state lithium-ion microbatteries, it is an essential task to investigate and improve the properties of solid electrolyte. Generally, Li_{3.3}PO_{3.9}N_{0.17} (LIPON) with lithiumion conductivity about 10^{-6} S cm⁻¹ is the common electrolyte material that was first reported by Bates et al. [1,2]. However, LIPON still has some disadvantages such as sensitive to moisture and/or oxygen and difficult to fabricate reproduceably [3]. Consequently, it is extremely a crucial demand to investigate a new and stable solid-state electrolyte that exhibits high lithiumion conductivity and low electronic conductivity.

For the last few decades, perovskite $La_{2/3-x}Li_{3x}\Box_{1/3-2x}TiO_3$ (LLT) was investigated as a new electrolyte for all-solid-state microbatteries as a result of its high lithium-ion conductivity in bulk ($\sim 10^{-3}$ S cm⁻¹) [4,5]. It was reported that the lithium-ion

0925-8388/\$ - see front matter © 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2006.06.024 conductivity highly relatives to and varies with the concentrations of lithium-ions and A-site vacancies. Moreover, to be used as electrolyte in thin-film microbatteries, the thin-film fabrications and properties of LLT films were widely investigated recently [3,6–9]. Nevertheless, the stability between this perovskite material and cathodes during the thin-film fabrication should be an important concern. Because of the as-deposited LLT films exhibit amorphous structure [3,8,9] and as-deposited cathodes exhibit poor crystallinity. Therefore, LLT and cathode films have to undergo a heat treatment to enhance their crystallinities and properties. Therefore, the stability and reaction in the interface of electrolyte and cathode during the heat treatment are very important and would affect the properties of the microbatteries. Consequently, this study is focused on the stability and reaction between LLT and three kinds of common-used cathodes (LiNiO₂, LiCoO₂ and LiMn₂O₄) to probe into the feasibility of LLT as solid electrolyte and find out a suitable cathode for using with LLT electrolyte.

2. Experimental

The La_{0.57}Li_{0.3} $\Box_{0.13}$ TiO₃ (LLT), LiNiO₂, LiCoO₂, and LiMn₂O₄ powders were synthesized by solid-state reaction method from La₂O₃, TiO₂, Li₂CO₃, NiO, CoCO₃, and MnO₂ powders. After mixing the precursor, 6-h calcination was carried out at 1300 and 800 °C for electrolyte and cathodes, respectively.

^{*} Corresponding author. Tel.: +886 6 2757575x62903; fax: +886 6 2380208. *E-mail address:* kzfung@mail.ncku.edu.tw (K.-Z. Fung).

Then, in order to investigate the stability and reactions between LLT electrolyte and common-used cathodes, LLT and cathode powders were well mixed under 1:1 by weight and underwent heat treatments at 500–800 °C for 2 h. After heat treatment, the mixtures were analyzed by X-ray diffractometer (XRD) using Cu K α radiation (λ = 1.5418 Å). The conductivity variations of mixtures during heat treatment were also conducted by pellets (diameter 10 mm, thickness \approx 5 mm, CIP pressure = 2000 kg/cm²) of the mixed powders. The conductivity variations of pellets were measured from ambient temperature to 800 °C at a rate of 5 °C/min and then hold at 800 °C for 12 h.

3. Results and discussion

The reactions between LLT and cathode materials were investigated by XRD analysis. Fig. 1 shows the XRD patterns of asmixed, 500 and 600 °C-annealed mixtures of LLT and LiNiO₂. In Fig. 1(a), two well-defined phases of layered LiNiO₂ and perovskite LLT with superstructure peaks (superlattice) can be observed. Generally, the superlattices are attributed to the ordering of cation vacancies, and, the intensities of superlattices vary with lithium contents as a consequence of the cation disorder. After annealed the LiNiO₂ and LLT mixtures at 500 °C for 2 h, the intensity of LiNiO₂ and superlattice decreases obviously that can be observed in Fig. 1(b). Because the intensity of superlattice is decreasing with the increasing lithium content in LLT, therefore, it can be suggested that the decreasing intensity of superlattice in Fig. 1(b) is due to the lithium in LiNiO₂ diffuse into the LLT A-site vacancies. Moreover, it is well known that the layered LiNiO₂ exhibits poor structural stability when the stoichiometry shows lithium deficiency. Therefore, when lithiumions move out from the LiNiO₂ layered structure, the layered structure becomes unstable and might decompose into NiO is suggested. In addition, La₂Ti₂O₇ and NiO second phases were observed after 600 °C annealing for 2 h as shown in Fig. 1(c).



Fig. 1. XRD patterns of (a) as-mixed LiNiO₂ and La_{2/3-x}Li_{3x} $\Box_{1/3-2x}$ TiO₃ (3*x* = 0.3) powders, and heat treatment the mixtures at (b) 500 °C and (c) 600 °C for 2 h.

This result indicates that the reaction between LiNiO₂ and LLT at 600 $^{\circ}$ C was much acuter than that at 500 $^{\circ}$ C. The stability between LLT electrolyte and LiNiO₂ cathode is extremely poor.

In the case of LiCoO₂ and LLT mixtures, two well-defined phases of layered LiCoO2 and perovskite LLT are also observed in XRD pattern (Fig. 1(a)) of as-mixed sample. After the mixtures of LiCoO₂ and LLT annealed at 600 °C for 2 h, the XRD pattern (as shown in Fig. 2(b)) shows that the LLT was a little affected by LiCoO₂ due to the decreasing intensity of LLT reflections. Moreover, 700 °C-annealed mixtures show the similar result with 600 °C-annealed one. This result indicates that these two phases could maintain their structure even after 700 °C heat treatment. To compare with LiNiO₂, the stability between LiCoO₂ and LLT is better than that between LiNiO₂ and LLT. However, this stability is broken after 800 °C heat treatment. The decreasing intensity of LiCoO₂ and the formation of β -LLT second phase are observed. Finally, the mixtures of LiMn₂O₄ and LLTO was also underwent the same heat-treatment procedure. The XRD patterns (as shown in Fig. 3) show that there are no reactions between LiMn₂O₄ and LLT even after 800 °C heat treatment for 2 h. This result indicates that the stability of LiMn₂O₄ between LLT is much better than that of LiNiO₂ as well as than LiCoO₂.

Generally, to synthesize stable and stoichiometric $\rm LiNiO_2$ is much more difficult than $\rm LiCoO_2$ and $\rm LiMn_2O_4.$ In addi-



Fig. 2. XRD patterns of (a) as-mixed LiCoO₂ and La_{2/3-x}Li_{3x} $\Box_{1/3-2x}$ TiO₃ (3*x*=0.3) powders, and heat treatment the mixtures at (b) 600 °C, (c) 700 °C and (d) 800 °C for 2 h.



Fig. 3. XRD patterns of (a) as-mixed LiMn₂O₄ and La_{2/3-x}Li_{3x} $\Box_{1/3-2x}$ TiO₃ (3*x* = 0.3) powders, and heat treatment the mixtures at (b) 700 °C and (c) 800 °C for 2 h.

tion, the Gibbs energies for LiNiO₂, LiCoO₂, and LiMn₂O₄ formations from elements at 300 K are -514.96, -619.65, and -1315.61 kJ/mol can be estimated, respectively. It indicates that once the LiMn₂O₄ formed, the LiMn₂O₄ would be the most stable material among LiNiO₂, LiCoO₂, and LiMn₂O₄. In other words, it means that the LiNiO₂ is the most unstable cathode among three of them, and, it is the easiest cathode material to decompose and react with LLT electrolyte. Consequently, considering about a suitable cathode for LLT electrolyte, LiCoO₂ and LiMn₂O₄ might be the considerable ones.

There is another experiment to investigate the reactions between LLT and $\text{LiM}_m O_n$. The mixtures of LLT and $\text{LiM}_m O_n$ were shaped into pellets and conducted the variation of conductivity. The conductivity versus test time plot is showed in Fig. 4. In this figure, step 1 is for heating the specimens to 800 °C under a constant rate (5 °C/min), and, step 2 is for holding the temperature at 800 °C. Because of the conductivity of cathodes and electrolyte are about 10^{-2} and 10^{-6} S cm⁻¹, therefore, the conductivity variation of this test could be just attributed to cathode materials and the conductivity contribution of LLT could be ignored. It can be observed that the conductivities of LiNiO₂+LLT, LiCoO₂+LLT, and LiMn₂O₄+LLT specimens increasing with the increasing temperature that are reasonable variation for ceramics. However, the conductivity of LiNiO₂ + LLT was dropping quickly over 500 $^{\circ}$ C in step 1. This result can be connected with the XRD result due to the decomposition of LiNiO₂ into NiO. The defect equation for the formation of LiNiO₂ can be written as follows:





Fig. 4. The conductivity variations of the electrolyte and cathode mixtures.

When lithium-ions move into the LLT A-site vacancies, the lithium content in layered LiNiO_2 is decreasing. Therefore, the equation tends to go to left side to form NiO and results in the decreasing conductivity. But for $\text{LiCoO}_2 + \text{LLT}$ and $\text{LiMn}_2\text{O}_4 + \text{LLT}$, these two systems didn't show obviously changes in conductivity due to the LiMn_2O_4 and LiCoO_2 phases still existed in the mixture. From the results of XRD and conductivity test, LiMn_2O_4 is the most stable cathode among LiNiO_2 , LiCoO_2 , and LiMn_2O_4 to be used with LLT electrolyte. In other words, LLT can be used as high-performanced electrolyte when choosing a suitable cathode such as LiMn_2O_4 .

4. Conclusion

Three kinds of cathodes, LiNiO₂, LiCoO₂, and LiMn₂O₄, were reacted with $La_{2/3-x}Li_{3x}\Box_{1/3-2x}TiO_3$ (3x = 0.3) electrolyte to investigate the stability between cathode and electrolyte. The LiMn₂O₄ showed well stability with LLT electrolyte even after 800 °C heat treatment. LiCoO₂ + LLT system can remain stable at 700 °C, but a second phase β -LLT was observed after 800 °C heat treatment. The LiNiO₂ showed poor stability with LLT electrolyte, it decomposed into NiO obviously with a La₂Ti₂O₇ phase formation from LLT after annealing above 500 °C. Consequently, for the application in thin-film microbattery, LiMn₂O₄ cathode with LLT electrolyte might be the appropriate choice for the demand of high-temperature annealing.

Acknowledgement

This work was supported under the grant no. NSC94-2120-M-006-002 by National Science Council (NSC), Taiwan.

References

- J.B. Bates, G.R. Gruzalski, N.J. Dudney, C.F. Luck, X.H. Yu, S.D. Jones, Solid State Technol. 36 (1993) 59.
- [2] J.B. Bates, G.R. Gruzalski, N.J. Dudney, C.F. Luck, X.H. Yu, Solid State Ionics 70/71 (1994) 619.
- [3] J.-K. Ahn, S.-G. Yoon, Electrochim. Acta 50 (2004) 371.
- [4] Y. Inaguma, L. Chen, M. Itoh, T. Nakamura, T. Uchida, M. Ikuta, M. Wakihara, Solid State Commun. 86 (1993) 689.
- [5] A.G. Belous, G.N. Novitskaya, S.V. Polyanetskaya, Yu.I. Gornikov, Inorg. Mater. 23 (1987) 412.
- [6] J.-K. Ahn, S.-G. Yoon, Electrochem. Solid State Lett. 8 (2005) A75.
- [7] K. Kitaoka, H. Kozuka, T. Hashimoto, T. Yoko, J. Mater. Sci. 32 (1997) 2063.
- [8] J.-K. Ahn, S.-G. Yoon, C.S. Kim, J. Vac. Sci. Technol. B 23 (2005) 2089.
- [9] S.-I. Furusawa, H. Tabuchi, T. Sugiyama, S. Tao, J.T.S. Irvine, Solid State Ionics 176 (2005) 553.