Short communication

Electrochemical properties of layer-built cells

Min Park*, Hunjoon Jung, Sang-Im Yoo, John B. Bates, Seung-Ki Joo

School of Materials Science and Engineering, Seoul National University, #San 56-1, Shillim-dong, Gwanak-gu, Seoul 151-742, Republic of Korea

Abstract

Two differently-structured layer-built cells have been fabricated using screen-printed $LiMn_2O_4$ and metallic Li as the electrodes, and PEO-based polymer electrolytes. Two-cathode layer-built cells (cathode/electrolyte/anode/electrolyte/cathode) and two-anode layer-built cells (anode/electrolyte/cathode/electrolyte/anode) were prepared for this study. To evaluate the layer-built cells, electrochemical cycling and ac impedance test have been performed. Of the cells tested, the layer-built cells showed improvements in polarization losses.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Layer-built cell; Screen-printed $LiMn_2O_4$; Polymer electrolyte; AC impedance; Polarization loss

1. Introduction

The rapid progress in the micro-electronics industry and the miniaturization of electronic devices have prompted the development of all-solid-state thin film lithium secondary batteries as self-contained power sources in such devices.

Much research has been performed on a spinel $LiMn_2O_4$ [1–3] which is a substitute for $LiCoO_2$ [4–7] as the cathode material in lithium secondary batteries. $LiMn_2O_4$ has economical and environmental advantages because it is cheaper, less toxic and easier to prepare than $LiCoO_2$ [8–10]. Also it has a similar operating voltage range. However, the thin film $LiMn_2O_4$ cathode has some problems of structural instability and capacity decrease during charge/discharge cycling [11–13]. It is hard to get a useful thickness of the cathode for sufficient capacity by sputtering. Also sputter-deposited thin films are not suitable for layer-built cells because the cathode active materials are deposited only on one side. Accordingly, we used a screen-printing method [32,33] which improved capacity of the thin film batteries and made it possible to pattern both sides of electrode.

Many electrochemical properties change when the cells are layered [14–18]. To investigate these phenomena, we performed some electrochemical tests on two differently-structured layer-built cells. In this study, we prepared lithium polymer batteries using screen-printed cathodes, polymer electrolytes [19–24] and lithium metal anodes [25–31].

2. Experimental

The $LiMn_2O_4$ cathodes were fabricated by screen-printing. After $LiMn_2O_4$ powders (Aldrich) were mixed with binder and thinner, we milled this mixture using a three-roll miller. So that the paste had a uniform particle size and homogeneous composition for screen-printing. A stainless steel mesh was placed beneath a patterned silk screen and the paste was sprayed onto the screen. Then the paste was rolled. Heat treatment of the cathode at 400 °C led to removal of the binder and thinner in the paste. Subsequently, the cathodes were annealed at 750 °C in air to enhance adhesion between the cathode active materials and the mesh. Through these procedures, we obtained spinel $LiMn_2O_4$ cathodes, of which X-ray diffraction patterns matched the JCPDS profiles of $LiMn_2O_4$ (No. 35-0782) with good crystallinity. The thickness of the screen-printed cathode was 100 μm.

The Polymer electrolyte was based on PEO (polyethylene oxide, Aldrich, M.W. = 5,000,000). The PEO-based polymer electrolyte was prepared by following procedure. In advance, we prepared the liquid electrolyte which consisted of 1 M-lithium perchlorate ($LiClO_4$, Aldrich) in propylene carbonate (PC, Aldrich) and then PEO powders were added. In order to disperse the $LiClO_4$–PC liquid electrolyte in the PEO matrix properly, the mixture was stirred into the slurry. The slurry's

* Corresponding author. Tel.: +82 2 880 7442; fax: +82 2 887 8791.
  E-mail address: hyolee78@snu.ac.kr (M. Park).

viscosity was controlled by changing the amount of PEO powder. The film-type polymer electrolyte was prepared by casting this slurry onto a smooth-surfaced Teflon mould. Then, these film-type polymer electrolytes were dried in a vacuum for one day at room temperature. The thickness of polymer film was about 100 μm.

Li metal (Aldrich) was used as the counter and reference electrode. The Li metal anodes were deposited onto the Cu foils under vacuum from a thermal evaporation source. The Cu foils were used as current collectors without alloying.

Using these cathodes, electrolytes and anodes, two differently-structured layer-built cells and the reference cell having a normal structure were fabricated. The layer-built cells were assembled by sandwiching one electrode between two opposite electrodes with the film-type polymer electrolytes at their interfaces. The cells were assembled in an Ar-filled glove box and each assembly was clipped together. Each cell configuration is given in Table 1.

The cells were evaluated using a WonATech WBCS 3000 battery cycling analyzer. Initially each cell was charged at constant current and then held 4.05 V until the current decreased to <1 μA. The cells were discharged at constant current to a 3.5 V cut-off voltage. The current density was 100 μA cm^{-2}.

To consider the kinetics of the cell reactions, we examined the ac impedance spectroscopy of each cell using Zahner IM5d. We carried out the ac impedance tests within a frequency range of 1 mHz to 1 MHz. The applied amplitude was 10 mV and the cell voltage was fixed at 4 V. All these experiments were performed in a high purity Ar-filled glove box. The moisture and the oxygen in a glove box were maintained below 1 ppm.

3. Result and discussion

The schematic drawings of each cell configuration are shown in Fig. 1. The normal cell (Cell A) consists of one cathode and one anode. On the other hand, a two-cathode layer-built cell (Cell B) was assembled by sandwiching one anode between two-cathodes. A two-anodes layer-built cell (Cell C) was assembled by sandwiching one cathode between two-anodes. We expected that the layer-built cells could improve the contact resistance of the cell because of the structural advantage that there is a doubled effective area for diffusion of Li ions. Also, we expected that Cell B may show a doubled capacity, considering that volume of the cathode active materials was increased and Cell C may show a stable plateau region because Li ions could move in two directions within the screen-printed cathode. To make the cathode active materials react sufficiently, we set the anode area about 20% wider than the cathode area. The cross-section area of the cell was 1 cm^2.
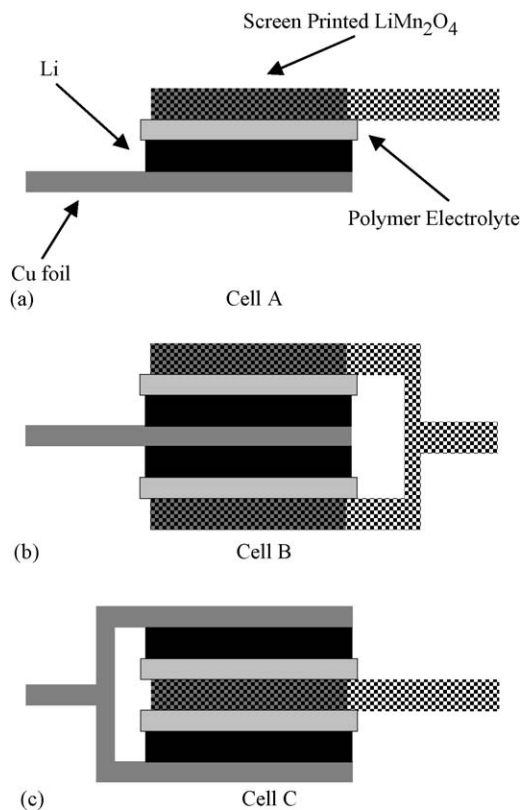

Fig. 1. Schematic drawings of cell structures: (a) Cell A; (b) Cell B; (c) Cell C.

The Nyquist plots of each cell are shown in Fig. 2 . The electrolyte resistance (R_{el}), the contact resistance (R_c) and the charge transfer resistance (R_{ct}) of Cell A were about 100, 180 and 370 Ω, respectively. We took these values as a reference. Cell B shows somewhat different values of R_{el}, R_c and R_{ct} which are approximately 50, 100 and 200 Ω. Cell C shows approximately 45, 120 and 320 Ω, respectively. Within experimental error, both Cell B and Cell C show about half the values of R_{el} and R_c compared with the reference, respectively. Cell B shows about half the
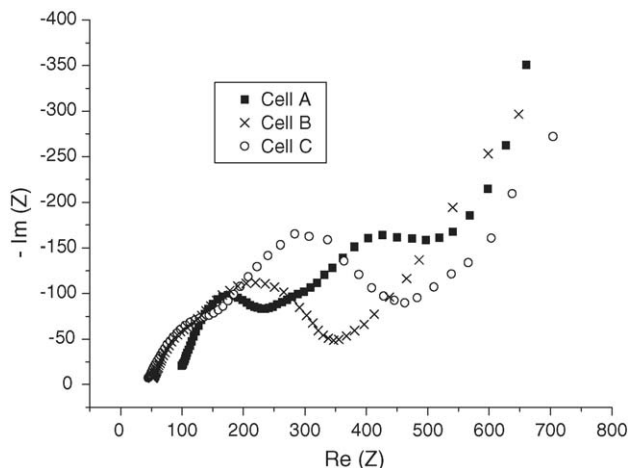

Fig. 2. AC impedance spectroscopy of each cell. Each test was conducted at 4 V.

Table 2
All electrochemical measurement data

	Cell A: reference	Cell B (ratio)	Cell C (ratio)
Electrolyte resistance	100 Ω	50 Ω(50%)	45 Ω(45%)
Contact resistance	180 Ω	100 Ω(56%)	120 Ω(67%)
Charge transfer resistance	370 Ω	200 Ω(54%)	320 Ω(86%)
Discharging time	39.68 min	76.55 min (193%)	38.25 min(96%)
Capacity	66.13 μA h	127.58 μA h (193%)	63.75 μA h(96%)

value of R_{ct}. The reasons for these results are as follows. The Li ions can move two directionally, normal to both of the opposite electrodes, in the layer-built cells, so the insertion-deinsertion processes of Li ions occur at both of the two-cathode/anode interfaces of the layer-built cells simultaneously.

Fig. 3 shows the discharge curves for Cell A, B and C. These curves were measured after 10 charge/discharge cycles. The discharging times of Cell B and C were about 76.55 and 38.25 min, respectively. The reference cell's discharging time was approximately 39.68 min. Cell B shows near double the value of the reference caused by the increase of the cathode active material volume. Since, the intercalation processes at the cathode/anode interface occur more dominantly, the capacity is a little bit less than twice. In the case of Cell C, the discharging time was almost the same as that of the reference. We predicted that Cell C would show a more stable plateau region than in the reference cell because the insertion-desertion processes of Li ions occurring at the two-cathode/anode interfaces. But this was not quite so.

All measurement data are shown in Table 2. Taking the data of Cell A as reference, we show the approximate ratios of the layer-built cells to the reference cell. There are some experimental errors, which may occur due to impurities at the surfaces of electrodes, and small size differences of the electrode areas as well as non-uniform distributions of the cathode active materials in a mesh. Although, there are some experimental errors, the layer-built cells show improvement incell performance.
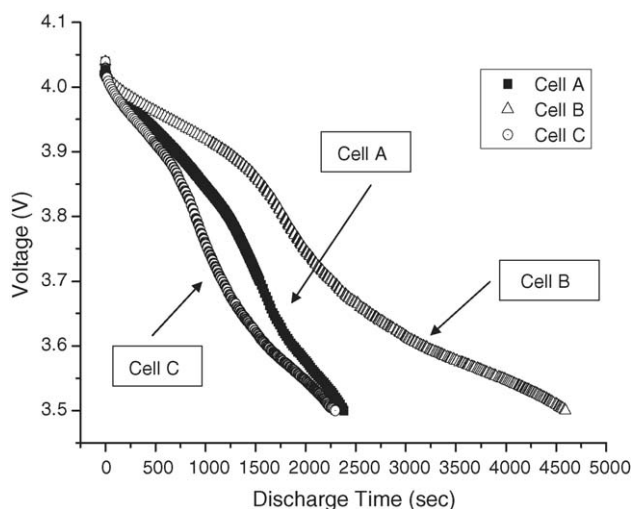
4. Conclusions

Cycling and ac impedance testing of experimental cells with screen-printed cathodes, PEO-based polymer electrolytes and the thermally evaporated Li anodes demonstrated that layer-built cells can enhance the electrochemical performance of the cells. Of the cells tested, the layer-built structure is more beneficial than the normal structure. Both of the two differently-structured layer-built cells reduced the resistive components related to the cell impedance. The two-cathode layer-built cell improved the electrolyte, contact and charge transfer resistance. The two-anode layer-built cell improved the electrolyte and contact resistance. These results are expected to enhance the electrochemical characteristics of Li secondary batteries in serial and parallel integrations. In further work, we are going to apply our Li polymer cells to serial/parallel connections and consider their electrochemical performance.

References

[1] L. Guohua, H. Ikuta, T. Uchida, M. Wakihara, J. Electrochem. Soc. 143 (1996) 178.
[2] M.H. Rossouw, A. de Kock, L.A. de Picciotto, M.M. Thackeray, W.I.F. David, R.M. Ibberson, Mater. Res. Bull. 25 (1990) 173.
[3] H. Hosoya, H. Ikuta, T. Uchida, M. Wakihara, 36th Battery Symposium Japan, Kyoto, Japan, September 1995, p. 31, Ext. Abstr.
[4] J.M. Tarascon, D. Guyomard, Electrochim. Acta 38 (1991) 1221.
[5] S. Yamaguchi, T. Uchida, M. Wakihara, J. Electrochem. Soc. 138 (1991) 687.
[6] J.M. Tarascon, E. Wang, F.K. Shokoohi, W.R. McKinnon, S. Colson, J. Electrochem. Soc. 138 (1991) 2859.
[7] M. Wakihara, T. Uchida, K. Suzuki, M. Taniguchi, Electrochim. Acta 34 (1989) 867.
[8] T. Ohzuku, M. Kitagawa, T. Hirai, J. Electrochem. Soc. 137 (1990) 769.
[9] J.M. Tarascon, E. Wang, F.K. Sholoohi, W.R. McKinnon, S. Colson, J. Electrochem. Soc. 138 (1991) 2859.
[10] Y. Xia, M. Yohsio, J. Power Sources 56 (1995) 61.
[11] D. Guyomard, J.M. Tarascon, Solid State Ionics 69 (1994) 222.
[12] J.M. Tarascon, D. Guyomard, Solid State Ionics 69 (1994) 222.
[13] D. Guyomard, J.M. Tarascon, J. Electrochem. Soc. 139 (1992) 937.
[14] M. Majima, K. Hanafusa, Y. Oka, G. Tanaka, H. Yoshida, E. Yagasaki, T. Tada, J. Power Sources 68 (1997) 448.

Fig. 3. Discharge curves measured at a constant current density of $100\ \mu A\ cm^{-2}$. The voltage range is from 4.05 to 3.5 V.

[15] M. Majima, Y. Oka, K. Miyazaki, H. Yoshida, E. Yagasaki, T. Tada, Proc. J. Electrochem. Soc. 97 (18) (1997) 362.

[16] K. Kitoh, H. Schönfelder, H. Nemoto, Proceedings of the 37th Battery Symposium in Japan vol. 95, 1996.

[17] M. Majima, T. Tada, S. Ujiie, E. Yagasaki, S. Inazawa, K. Miyazaki, J. Power Sources 81–82 (1999) 877–881.

[18] M. Majima, S. Ujiie, E. Yagasaki, K. Koyama, S. Inazawa, J. Power Sources 101 (1) (2001) 53–59.

[19] I. Uchida, X. Wang, T. Nishina, 35th Battery Symposium Nagoya, Japan, November 1994, p. 73, Ext. Abstr.

[20] M.M.E. Jacob, S.R.S. Prabaharan, S. Radhakrishna, Solid State Ionics 104 (1997) 267.

[21] Q. Li, N. Imanishi, A. Hirano, Y. Takeda, O. Yamamoto, J. Power Sources 110 (2002) 38.

[22] W.H. Meyer, Adv. Mater. 6 (1998) 10.

[23] G.B. Appetecchi, F. Alessandrini, M. Carewska, T. Caruso, P.P. Prosini, S. Scaccia, S. Passerini, J. Power Sources 97–98 (2001) 790–794.

[24] C.E. Newnham, S. Rinne, N. Scholey, J. Power Sources 54 (2) (1995) 516–518.

[25] K. Kanamura, S. Shiraishi, Z. Takehara, J. Electrochem. Soc. 141 (1994) L108.

[26] J.O. Besenhard, G. Eichinger, J. Electroanal. Chem. 68 (1976) 1.

[27] S. Tobishima, J. Yamaki, A. Yamaji, T. Okada, J. Power Sources 13 (1984) 261.

[28] S. Tobishima, T. Okada, Electrochim. Acta 30 (1985) 1715.

[29] S. Tobishima, T. Okada, J. Appl. Electrochem. 15 (1985) 317.

[30] C. Fringant, A. Tranchant, R. Messina, Electrochim. Acta 40 (1995) 513.

[31] M. Arakawa, S. Tobishima, Y. Nemoto, M. Ichimura, J. Yamaki, J. Power Sources 27 (1993) 43.

[32] M. Park, J.H. Park, H. Jung, S.K. Joo, Proceedings of the 2002 MRS Fall Meeting, Boston, U.S.A., 2002, Abstr. #EE 6.11.

[33] M. Park, H. Jung, S.K. Joo, Proceedings of the 203rd ECS Meeting, Interface, vol. 12, No. 1, Paris, France, 2003, Abstr. #190.