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Fabrication and electrochemical characteristics of all-solid-state lithium-ion rechargeable batteries composed of $LiMn_2O_4$ positive and V_2O_5 negative electrodes

M. Baba[a,*], N. Kumagai[a], N. Fujita[a], K. Ohta[a], K. Nishidate[a], S. Komaba[a], H. Groult[b], D. Devilliers[b], B. Kaplan[b]

[a] *Faculty of Engineering, Iwate University, 4-3-5 Ueda, Morioka 020-8551, Japan*

[b] *LaboratoireLI2C-Electrochimie, Universite Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France*

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Abstract

A new type of all-solid-state lithium-ion rechargeable batteries composed of $LiMn_2O_4$ positive and V_2O_5 negative electrodes were developed and their electrochemical characteristics were investigated for the first time. Both amorphous thin-filmed electrodes as well as a lithium phosphorus oxynitride electrolyte (Lipon) were deposited on a substrate by using a rf-magnetron sputtering method. The present rocking-chair type battery showed good charge and discharge characteristics with a typical charge and discharge capacities of about 18 μAh/cm^2 between 3.5 and 0.3 V. This battery revealed a remarkable forming process which means that the charge and discharge capacities dramatically increase with the cycle number in its early stages. The battery also showed a good charge–discharge operation in vacuum which is one of the advantageous properties expected for the solid-state devices.

Keywords: Solid-state battery; Li-ion battery; $LiMn_2O_4$ cathode; V_2O_5 anode

1. Introduction

Recently, considerable attention has been paid to the investigations of lithium-metal-free batteries [1] and solid-state lithium rechargeable batteries [2–4]. If such a rocking-chair type of battery is constructed with only a thin-filmed type of electrode and electrolyte, it will be very compact, light and highly reliable, and therefore find wide-spread application in many types of portable electronic devices. Because such a thin-filmed battery system has an outstanding capability to be made in the form of several unit cells being layered or stacked for increasing its discharge capacity. Manganese based oxides are one of the most promising candidates as a cathode material because of their high theoretical energy density, low cost and low toxicity [5]. In this study, we reported the electrochemical characteristics of all-solid-state lithium-ion rechargeable batteries composed of thin-filmed $LiMn_2O_4$ and V_2O_5 electrodes for the first time.

2. Experimental

A thin film of $LiMn_2O_4$ was prepared on a stainless steel substrate or the like by a rf-magnetron sputtering method with a typical rf power of 100 W and an Ar-gas pressure of 10 mTorr. Then, the film thickness was about 800 nm. Next, a thin film of solid electrolyte $Li_3PO_{4-x}N_x$, so-called Lipon [3] was deposited 1000 nm in thickness on it using the same sputtering method in nitrogen gas [4]. After that, a V_2O_5 negative electrode and a vanadium as a current collector were deposited with thicknesses of 250 and 200 nm by the sputtering method in a mixture gas (9:1) of Ar and O_2 and pure Ar gas, respectively. These films were all in an amorphous state. Thus, an all-solid-state lithium-ion battery was fabricated by only the rf-magnetron sputtering method throughout the cell preparation. A typical cell size was 1 cm^2 in area and about 2.2 μm in thickness as a whole.

3. Results and discussion

The charge–discharge performance of the sputter-deposited $LiMn_2O_4$ film as a cathode active material has been

* Corresponding author. Tel.: +81-19-621-6387; fax: +81-19-621-6387.
E-mail address: baba@dragon.elc.iwate-u.ac.jp (M. Baba).

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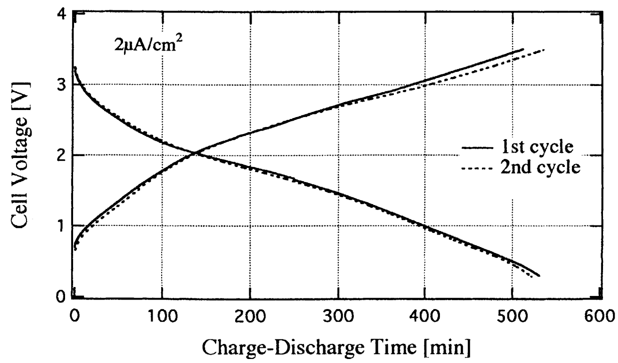

Fig. 1. Typical steady-state charge–discharge characteristics of the $LiMn_2O_4$/Lipon/V_2O_5 rechargeable battery, showing two successive charging and discharging curves after the forming process.

obtained for Li-metal anode in electrolyte solution of $LiClO_4$-propylene carbonate [6]. The charge–discharge performance of the sputter-deposited $LiMn_2O_4$ and V_2O_5 films as cathode active materials was evaluated by using a Li-metal anode in electrolyte solution of $LiClO_4$–propylene carbonate [1,6]. In case of the V_2O_5 film, the $Li_xV_2O_5$/electrode operated also as an anode in the rocking-chair type battery with the cell structure of V_2O_5/Lipon/$Li_xV_2O_5$ [4]. Based on the respective electrochemical behaviors of these oxide electrodes, Fig. 1 shows a typical charge–discharge characteristics of the thin-filmed $LiMn_2O_4$/Lipon/V_2O_5 rechargeable battery at a current density of 2 μA/cm^2 between 3.5 and 0.3 V, where only two successive cycles in the steady-state were displayed. In this case, the discharge capacity was about 18 μAh/cm^2, corresponding to a capacity per unit cathode volume of about 22 mAh/cm^3. In addition, the ratio between charge and discharge capacities was nearly one. This means that any retention which is often seen in solid-state batteries does not occur in the present solid-state cell.

A considerable percentage of virgin cells of the present rechargeable battery revealed a so-called forming behavior increasing the charge–discharge capacity with increasing the cycle number. Fig. 2(a) and (b) show several charge–discharge curves of such a remarkable cell in the range from 10th to 30th cycle and charge–discharge capacity versus cycle number, respectively. A dramatic increase in capacity can be seen especially in the early stage of the charge–discharge performance until the 20th cycle. This suggests that the amount of mobile Li ions increases by repeating the cycles. We called this phenomenon a forming or aging process in the battery operation, which may originate from the decrease of the cell voltage in charge and the increase of the cell voltage in discharge increasing cycle number, suggesting a decrease of the cell resistance probably correlated to a gradual decrease of the interface resistances. Passing through such a forming process, the cell kept a steady-state charge–discharge performance with a high capacity and any degradation was not observed at least until several tenth of charge–discharge cycle.

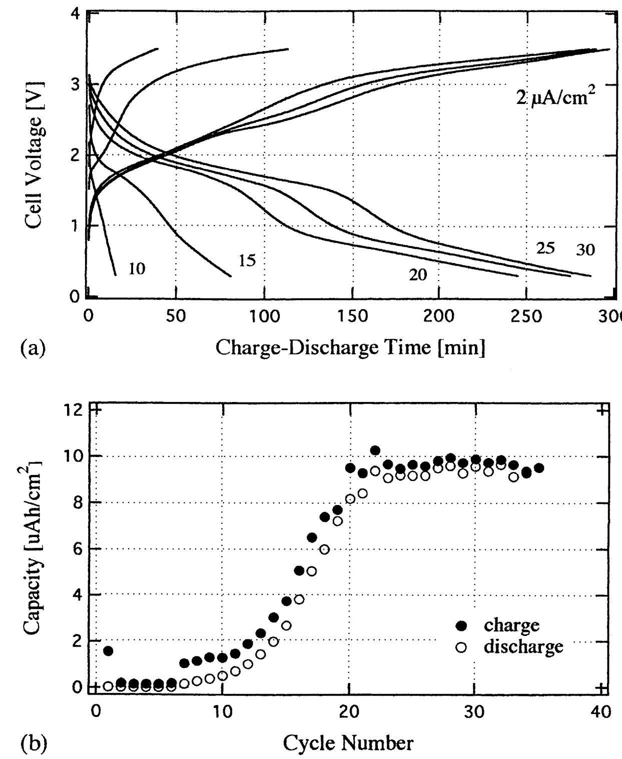

Fig. 2. A typical forming process seen early in the charge–discharge cycles of the $LiMn_2O_4$/Lipon/V_2O_5 rechargeable battery: (a) shows several charge–discharge curves until the initial thirtieth cycle, and (b) shows the cyclic performance of charge and discharge capacities between 3.5 and 0.5 V.

As one of the advantageous properties which are expected for the solid-state devices, a battery operation in vacuum was investigated. Fig. 3 shows the charge–discharge characteristics of the thin-filmed $LiMn_2O_4$/Lipon/V_2O_5 rechargeable battery set in a chamber which allows atmosphere evacuation. No difference is seen between two discharging processes each in air and in vacuum, nor any influence can be seen just after air-introduction or re-evacuation on a charging curve. Such a good rechargeable performance of the battery comes clearly from no use of any liquid or polymer

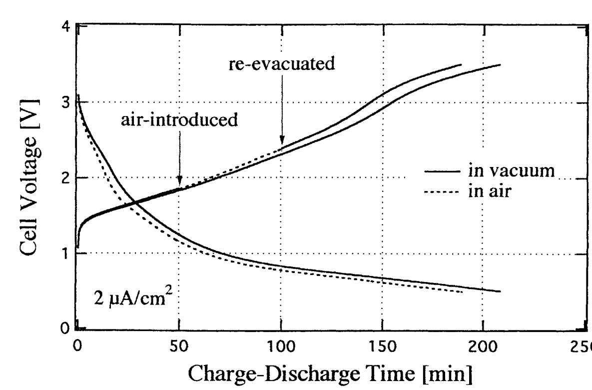

Fig. 3. Charge–discharge characteristics of the thin-filmed $LiMn_2O_4$/Lipon/V_2O_5 battery operated alternately in vacuum and in air.

material in its composition. This indicates that the present battery endures the use in space or somewhere else.

In summary, we have accomplished the lithium-ion rechargeable battery in which all of the electrodes and the electrolyte were simply made of metal oxides and produced only by a dry process with the rf-sputtering method. As a result, a very light and compact dry cell with a good reliability and reproducibility was realized in a completely solid-state and thin-filmed configuration.

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References

[1] N. Kumagai, H. Kitamoto, M. Baba, S. Durand-Vidal, D. Devilliers, H. Groult, J. Appl. Electrochem. 28 (1998) 41.
[2] S.D. Jones, J.R. Akridge, Solid State Ion. 5356 (1992) 628.
[3] J.B. Bates, N.J. Dudney, G.R. Gruzalski, R.A. Zuhr, A. Choudhury, C.F. Luck, J. Power Sources 4344 (1993) 103.
[4] M. Baba, N. Kumagai, H. Kobayashi, O. Nakano, K. Nishidate, Electrochem. Solid-State Lett. 2 (1999) 320.
[5] J.M. Tarascon, D. Guyomard, Electrochem. Acta 38 (1993) 1221.
[6] S. Komaba, N. Kumagai, M. Baba, F. Miura, N. Fujita, H. Groutt, D. Devilliers, B. Kaplan, J. Appl. Electrochem 30 (2000) 1179.