Fabrication by using a sputtering method and charge–discharge properties of large-sized and thin-filmed lithium ion rechargeable batteries

Hiromi Nakazawa [a,*], Kimihiro Sano [a], Mamoru Baba [b]

[a] *Research and Development Center, Geomatec Co. Ltd., 3-13-7 Yaguchi, Otaku, Tokyo 146-0093, Japan*
[b] *Graduate School of Engineering, Iwate University, 4-3-5 Ueda, Morioka 020-8551, Japan*

Available online 31 May 2005

Abstract

Large-sized and thin-filmed lithium ion rechargeable batteries composed of a $Li_{2-x}Mn_2O_4$ positive electrode, a V_2O_5 negative electrode and a $Li_3PO_{4-x}N_x$ electrolyte have been developed on glass substrates by using a sputtering method, and their electrochemical characteristics were investigated. A typical cell size of the batteries was $100\,mm \times 100\,mm$ in area and about $3.1\,\mu m$ in thickness as a whole. The battery with a maximum cell size of $200\,mm \times 200\,mm$ was also successfully fabricated. These pinhole-free batteries showed a good rechargeable performance between 3.5 and 0.3 V with a typical charge–discharge capacity of about 0.9 mAh for the battery with a $100\,mm \times 100\,mm$ size and of about 5.5 mAh for the battery with a $200\,mm \times 200\,mm$ size. These batteries having almost the same characteristics have stably been fabricated with a good yield rate, and they could drive a digital watch as one of realistic portable devices more than 1 month with only one time charge.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Li-ion battery; Thin-filmed battery; Large-sized battery; $Li_{2-x}Mn_2O_4$ cathode; V_2O_5 anode

1. Introduction

Recently, much attention has been paid to the investigations of solid-state lithium ion rechargeable batteries and lithium-metal-free batteries [1–5]. 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 widespread application in many types of portable electronic devices. As one of such batteries, we have developed a thin-filmed lithium ion rechargeable battery by using a sputtering method [6]. It was composed of a thin-filmed $LiMn_2O_4$ positive electrode, a V_2O_5 negative electrode, a $Li_3PO_{4-x}N_x$, so-called LIPON electrolyte [2], and V films as a collector, and the cell size was $1\,cm^2$ in area and about $2.2\,\mu m$ in thickness. Such a thin-filmed battery showed a good rechargeable performance with a charge–discharge capacity of about $18\,\mu Ah$. The charge–discharge capacity, however, is slightly small to drive

practical electronic devices, and it is expected to increase the charge–discharge capacity. One of the effective methods to increase the capacity is to enlarge the cell size. In this study, we report the fabrication of large-sized and thin-filmed lithium ion rechargeable batteries, their charge–discharge properties, and possibilities as a realistic battery to drive practical devices.

2. Experimental

Using a dc/rf magnetron sputtering equipment, of which chamber size was $800\,mm$ in diameter and in which four targets were installed, lithium ion rechargeable batteries were fabricated on glass substrates installed in the chamber as follows. First, on a glass substrate, of which size was $100\,mm \times 100\,mm$ in area and $1.1\,mm$ in thickness, a V current collector film was deposited by a dc-magnetron sputtering method (dc method) from a V metal target with a typical dc power of $1.0\,kW$ and an Ar-gas pressure of $2.0\,mTorr$. The film thickness was $300\,nm$. Next, a thin film

* Corresponding author. Tel.: +81 3 3759 9325; fax: +81 3 3759 8789.
E-mail address: hiromi_nakazawa@geomatec.co.jp (H. Nakazawa).

of $Li_{2-x}Mn_2O_4$ as a positive electrode was deposited on it by an rf-magnetron sputtering method (rf method) from a $Li_2Mn_2O_4$ sintered target with a typical power of 1.2 kW in a mixture gas of Ar and O_2 (9:1). The gas pressure was 3.0 mTorr and the film thickness was 800 nm. Expecting the battery to enhance its charge–discharge capacity by increasing the ratio of Li atom, the $Li_2Mn_2O_4$ target was used this time for a positive electrode instead of the $LiMn_2O_4$ one. Next, a thin film of solid $Li_3PO_{4-x}N_x$ electrolyte was deposited 1000 nm by using the rf method from a Li_3PO_4 sintered target in N_2 gas. After that a V_2O_5 negative electrode was deposited 300 nm by using the rf method from a V_2O_5 sintered target in a mixture gas of Ar and O_2 (9:1). Finally, a V film was deposited again 300 nm by using the dc method, and SiN_x was deposited 400 nm on it to avoid invasion of moisture by using the rf method from a Si_3N_4 sintered target in Ar gas. These films were all deposited at room temperature without heating the glass substrate. An effective cell size was 80 mm × 80 mm in area and about 3.1 μm in thickness as a whole. The number of the substrates that could be installed into the chamber was 10 at a time, so 10 thin-filmed batteries were fabricated at once. We repeated fabrication of these batteries several times with the same condition to confirm reproducibility and to determine a yield rate. A schematic diagram of the thin-filmed battery in a cross section is shown in Fig. 1, and a photograph of the plane view is shown in Fig. 2.

In addition to those batteries with a 100 mm × 100 mm size, we have fabricated a wider battery on a glass substrate, of which size was 200 mm × 200 mm in area and 3.1 μm in thickness, by the same fabricating conditions. The effective cell size was 170 mm × 170 mm in area and only one sample was fabricated at a time, because it is too large for the 200 mm × 200 mm glass substrate to be installed into the chamber more than two pieces.

The crystal structures of those films were investigated by XRD measurement. No XRD peaks, however, were observed for any of the films. Therefore, it was confirmed that these films were all in an amorphous state. Here, the deposition
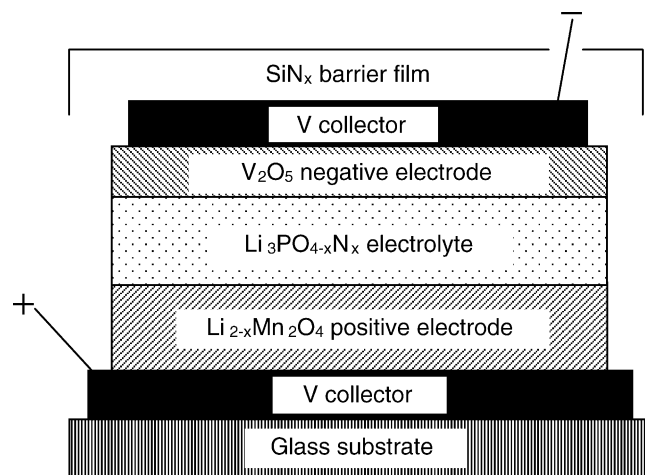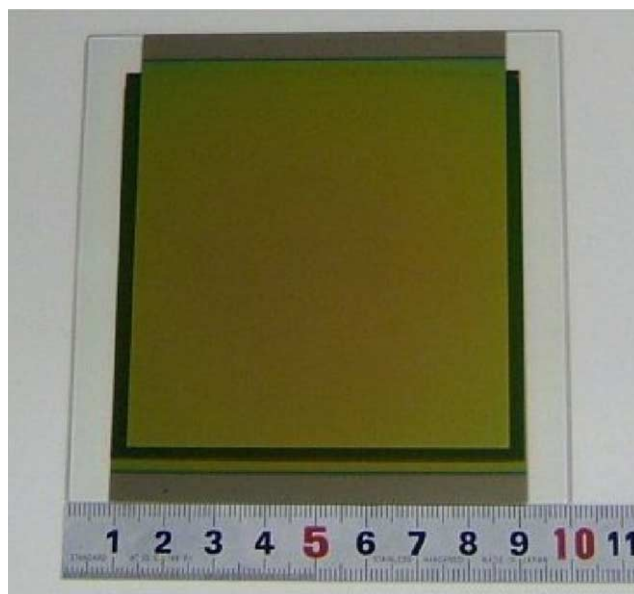

Fig. 2. A photograph of the thin-filmed battery with a 100 mm × 100 mm size in a plane view.

of each film has been executed by using a sintered target of which the atomic composition ratio was indicated with the subscripts of each compound described above. Then, the atomic composition ratio of each film would be thought to nearly agree with that of the sintered target, but such a ratio is not correctly investigated yet, because the precise determination of atomic ratios in case of amorphous films, especially for a Li atom, are considerably difficult.

Charge–discharge properties of these batteries were measured with a current of 0.4 mA between 3.5 and 0.3 V for the batteries with a 100 mm × 100 mm size and with a current of 1.0 mA between 3.5 and 0.3 V for the battery with a 200 mm × 200 mm size by using a charge–discharge measuring instrument.

3. Results and discussion

The charge–discharge characteristics of the thin-filmed battery with a 100 mm × 100 mm size on the first five cycles are shown in Fig. 3. At the first charge cycle, the charge voltage starts from a negative voltage and the capacity reaches about 2.4 mAh which exceeds largely the following discharge capacity of about 1.1 mAh. After the second cycle, the discharge capacity agrees with the charge one. Though irreversible Li ions corresponding to the capacity of 1.3 mAh (=2.4 − 1.1 mAh) exist at the first charge–discharge cycle, it is considered that the reversible charge–discharge processes succeed after the first cycle. Fig. 4 shows the charge–discharge characteristics until the 90th cycle. Any cycles except the first cycle show almost the same charge–discharge profile and the reversible charge–discharge performance, and the charge capacity agrees with the discharge one of

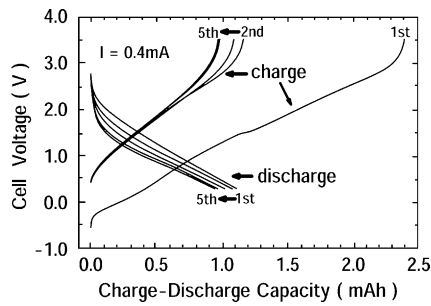Fig. 1. A schematic diagram of the thin-filmed battery in a cross-section.

Fig. 3. Charge–discharge characteristics of the thin-filmed battery with a 100 mm × 100 mm size on the first five cycles.
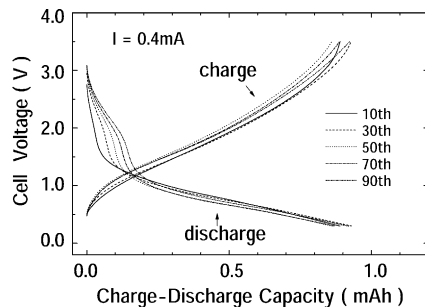

Fig. 4. Charge–discharge characteristics of the thin-filmed battery with a 100 mm × 100 mm size until the 90th cycle.

about 0.9 mAh. In comparison with ordinary non-solid type Li batteries, the present thin-filmed battery is not changed in quality in spite of a deep discharge down to 0.3 V, although the voltage decreases rapidly a little at a discharge process.

Fig. 5 shows a cycle performance of the thin-filmed battery on the discharge capacity until about the 100th cycle. During the first 10 cycles, the capacity shows a gradual decrease. After that, however, it retains almost a constant capacity of 0.9 mAh with a small scatter and the discharge capacity is 50 times larger than that of about 18 μAh of the cell with a 1 cm^2 size that we have fabricated before [6]. The cycle performance on the charge capacity also showed almost the same one on the discharge capacity. Corresponding to the full capacity of the cell, the capacity per unit area is estimated to be about 14 μAh cm^{-2}, and this value is a little smaller than that of 18 μAh cm^{-2}. The capacity per unit positive electrode volume is estimated to be about 180 mAh cm^{-3}.
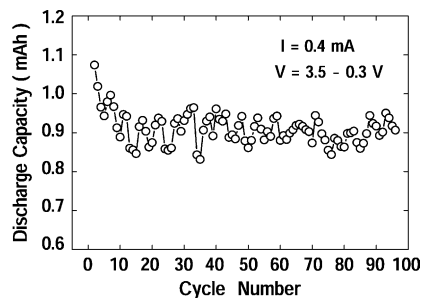

Fig. 5. Cycle performance of the thin-filmed battery with a 100 mm × 100 mm size on the discharge capacity until about the 100th cycle.
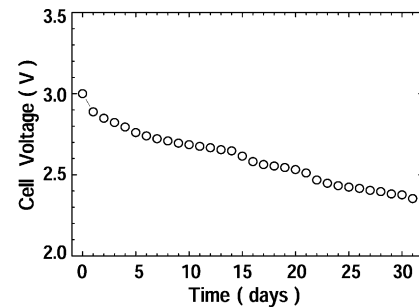

Fig. 6. Self-discharge characteristics of the thin-filmed battery with a 100 mm × 100 mm size during about 30 days.

Charge–discharge properties were measured for other thin-filmed batteries with a 100 mm × 100 mm size, and it was confirmed that 9 batteries among 10 batteries which were fabricated at the same time showed almost the same charge–discharge characteristics as shown above. Also, we repeated the fabrication of the thin-filmed batteries with a 100 mm × 100 mm size for three times by the same condition and every time we confirmed that about 9 batteries among 10 batteries showed roughly the same charge–discharge properties as shown above.

A self-discharge characteristic was investigated by measuring the voltage of the battery everyday after charging it upon 3.5 V at a current of 0.4 mA. Fig. 6 shows the self-discharge characteristic of this thin-filmed battery. At first the voltage is 3.0 V and decreases gradually day by day. But the rate of its decrease is gentle and even after 30 days the battery maintains a voltage of 2.4 V.

The present large-sized and thin-filmed battery with those characteristics of the charge–discharge and of the self-discharge is possible to drive a realistic portable device. To confirm this, we tried to drive a digital watch by this large-sized and thin-filmed battery. After being charged upon 2.0 V at a current of 0.4 mA only one time, the battery could drive the digital watch more than 1 month.

Fig. 7 shows the charge–discharge characteristics of the thin-filmed battery with a 200 mm × 200 mm size until the 100th cycle. At any cycle, the discharge capacity almost agrees with the charge one. Although the charge and discharge capacities gradually decrease, the profiles of the
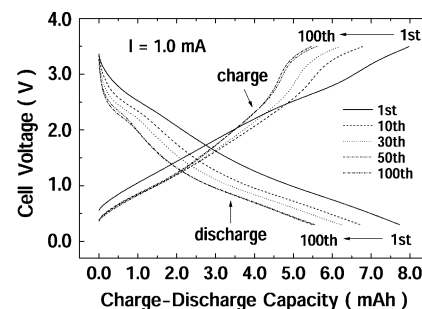

Fig. 7. Charge–discharge characteristics of the thin-filmed battery with a 200 mm × 200 mm size until the 100th cycle.
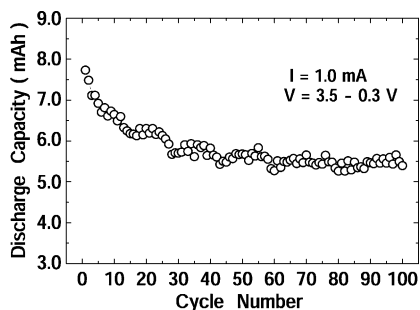
Fig. 8. Cycle performance of the thin-filmed battery with a 200 mm × 200 mm size on the discharge capacity until the 100th cycle.

charge and discharge characteristics are almost the same in any cycles except the first cycle and those profiles resemble to that of the battery with a 100 mm × 100 mm size shown above. Most importantly, such a good performance indicates that any short-cut accident between two electrodes does not occur through a local defect like a pinhole.

Fig. 8 shows a cycle performance of the thin-filmed battery with a 200 mm × 200 mm size until the 100th cycle. At the first cycle, the discharge capacity shows a maximum value of about 8 mAh, and gradually decreases as the cycle progresses. But it maintains a discharge capacity of 5.5 mAh even after the 100th cycle. The capacity per unit area corresponding to the full capacity of the cell is estimated to be about 19 μAh cm^{-2}, and this value is a little larger than that of 14 μAh cm^{-2} of the cell with a 100 mm × 100 mm size. Also, the capacity per unit positive electrode volume is estimated to be about 240 mAh cm^{-3}, which is larger than that of 180 mAh cm^{-3} of the cell with a 100 mm × 100 mm size. This reason is now being analyzed.

In summary, we have accomplished large-sized and thin-filmed lithium ion rechargeable batteries of which the typical cell size was 100 mm × 100 mm in area and about 3.1 μm

in thickness as a whole, and of which the maximum size was 200 mm × 200 mm in area. These batteries showed good charge and discharge characteristics between 3.5 and 0.3 V with a typical charge–discharge capacity of about 0.9 mAh for the battery with a 100 mm × 100 mm size and of about 5.5 mAh for the battery with a 200 mm × 200 mm size. These batteries with almost the same characteristics has been fabricated stably with a good yield rate, and they could drive a digital watch as a realistic portable device more than 1 month with only one time charge.

Acknowledgments

References

[1] S.D. Jones, J.R. Akridge, Solid State Ionics 53–56 (1992) 628.
[2] J.B. Bates, N.J. Dudney, G.R. Gruzalski, R.A. Zuhr, A. Choudhury, C.F. Luck, J. Power Sources 43–44 (1993) 103.
[3] N. Kumagai, Y. Tateshita, Y. Takatsuka, M. Baba, T. Ikeda, K. Tanno, J. Power Sources 54 (1995) 175.
[4] N. Kumagai, H. Kitamoto, M. Baba, S. Durand-Vidal, D. Devilliers, H. Groult, J. Appl. Electrochem. 28 (1998) 41.
[5] M. Baba, N. Kumagai, H. Kobayashi, O. Nakano, K. Nishidate, Electrochem. Solid-State Lett. 2 (1999) 320.
[6] M. Baba, N. Kumagai, N. Fujita, K. Ohta, K. Nishidate, S. Komaba, H. Groult, D. Devilliers, B. Kaplan, J. Power Sources 97–98 (2001) 798.