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Multi-layered Li-ion rechargeable batteries for a high-voltage and high-current solid-state power source

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

[a]*Faculty of Engineering, Iwate University, 4-3-5 Ueda, Morioka 020-8551, Japan*
[b]*Laboratoire L12C-Electrochimie, Universite Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France*

Abstract

The first experiments of multi-layered Li-ion rechargeable batteries were carried out for developing a high-voltage and high-current solid-state power source. The thin-filmed battery, so-called twin-type one which is composed of two unit cells externally connected in parallel and in series could easily realize twice the total capacity and twice the total voltage of 6.5 V compared with those of its unit cell, respectively, although the battery is twice the operating area of the unit cell in this case. The other thin-filmed battery, so-called stacked-type one which is internally connected only in series could be well operated at least up to the high voltage of 5.5 V without any increase in its operating area. Experimental results obtained here suggest that the stacked-type battery composed of several thin-filmed cells can easily supply a high voltage more than 10 V for many types of portable electronic devices.

Keywords: Solid-state battery; Li-ion battery; Multi-layered battery; $LiMn_2O_4$ cathode

1. Introduction

Recently, considerable attention has been paid to the investigations of solid-state lithium rechargeable batteries [1–5]. If such a rocking-chair type of battery is constructed with only thin films for two electrodes and electrolyte, it will be very compact, light and highly reliable, and therefore find widespread application in many types of portable electronic devices. Because such a thin-film battery being only 2–3 μm in thickness has an outstanding capability to be made in the form of several unit cells being layered or stacked for the purpose of increasing its discharge capacity and battery voltage. In this study, we reported the first experimental attempt of multi-layered Li-ion rechargeable batteries for a high-voltage and high-current solid-state power source, using thin-filmed $LiMn_2O_4$ and V_2O_5 electrodes.

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 [2] was deposited (1000 nm in thickness) on it using the same sputtering method in nitrogen gas [3,4]. After that, a V_2O_5 film as a negative electrode and a vanadium film as a current collector were deposited with a typical thickness 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. In the first case, two cells were prepared at the same deposition run of rf-sputtering, in order for each cell to have characteristics as similar as possible for evaluation of parallel and series operation under external connection. Then, a typical operational area of the cell was 1 cm^2. In the second case of a stacked-type battery, the areas of the first and second component cells were typically 4.0 and 0.7 cm^2, respectively. Charge and discharge measurements of the cells were performed basically with the same current density of 2 $\mu A/cm^2$, using a laboratory-made system composed of a source-meter (Keithley 2400) and a personal computer, because a usual commercially available battery evaluation system does not have a current resolution smaller than 10 μA.

3. Results and discussion

Fig. 1 shows two types of batteries, that is, (a) a twin-type battery in which two cells are simultaneously prepared with

* 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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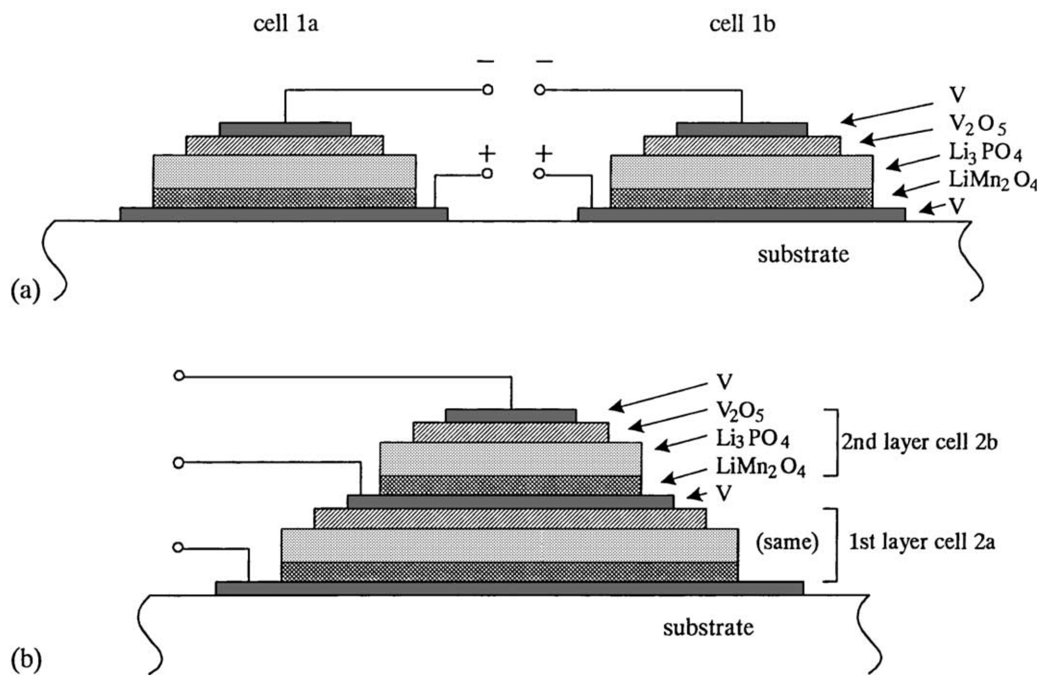

Fig. 1. Schematic drawings of two types of multi-layered thin-film batteries: (a) a twin-type battery (#1) and (b) a stacked-type battery (#2).

the same sputter-deposition run and are externally connected in parallel or series, and (b) a stacked-type battery which has an internal series connection between two cells just as a pyramid in this case. Fig. 2 shows typical charge–discharge curves of cell 1a and cell 1b in the twin-type battery #1 which were measured separately with a current density of 2 μA/cm^2. Although there is a slight difference in each profile of charge and discharge curves, these so-called twin cells had a nearly equal capacity of about 10 μAh/cm^2 between 3.5 and 0.3 V. An inset in Fig. 2 shows the cyclic behavior in charge (△) and discharge (●) processes for cell 1a.

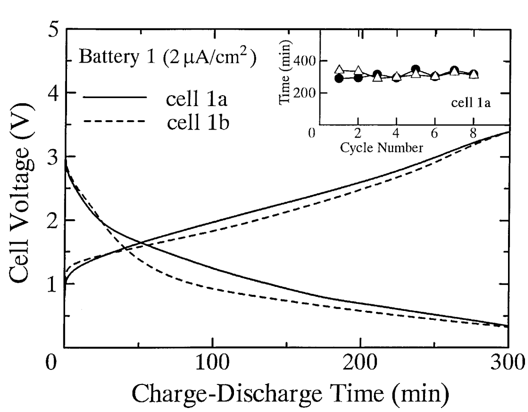

Fig. 2. Typical charge–discharge curves of two cells which compose the twin-type battery operating between 3.5 and 0.3 V, showing only a slight difference between them. Each cell is made of the $LiMn_2O_4$/Lipon/V_2O_5 multi-layers. See the text for the inset.

Next, two separate cells described above were connected in parallel or in series each other. Fig. 3a shows the parallel operation of such a battery connected in parallel, together with the curve of the single cell 1a for comparison. Then, the battery had the same charge–discharge time of about 300 min between 3.5 and 0.3 V under a current flow of 4 μA, which was twice of the current used for the single cell 1a. In Fig. 3a, the charge–discharge curves are plotted for a unit of capacity (μAh) to give an easy comparison. An inset there shows the cyclic behavior in charge (△) and discharge (●) processes for parallel connection. As a result, it was experimentally shown that the total or effective capacity of this battery was roughly doubled as expected. On the other hand, Fig. 3b shows another operation of the battery under a series connection. In this case, the charge–discharge curve was measured between 6.5 and 1.0 V under a current flow of 2 μA. Although an exact comparison of capacity cannot be done between the battery connected in series and the single cell 1a, a roughly equal capacity may be estimated from extrapolation to 7.0–0.6 V of its characteristics. An inset in Fig. 3b shows the cyclic behavior in charge (△) and discharge (●) processes under connection in series. At any rate, the battery connected in series operated well up to the high cell voltage of 6.5 V. Here, it should be noted that increasing and decreasing rates of voltage for both charging and discharging processes are reasonably twice of those of the single cell, as can be seen for instance from a comparison of the slopes of the two corresponding curves at about 100 min. This means that when the scale of the vertical axis in the charge–discharge curve is divided by two, then the resultant curves coincide with the curves of the single

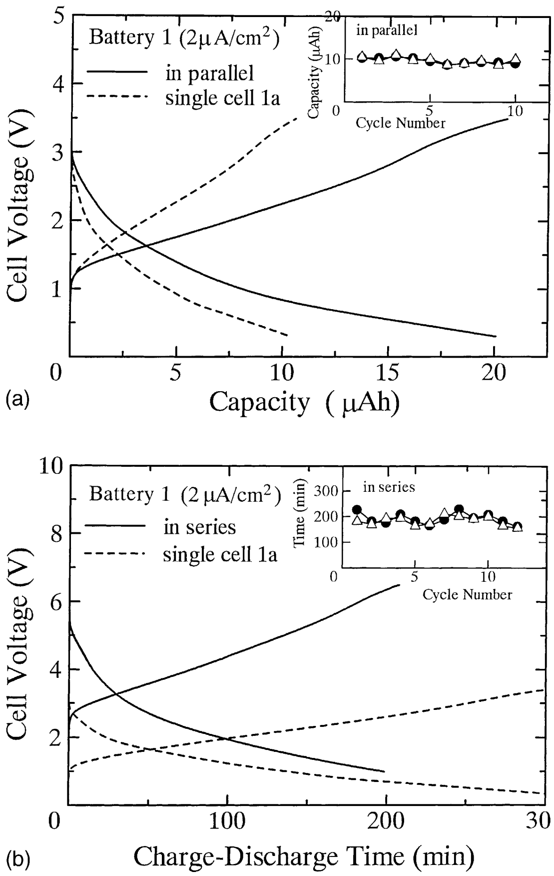

Fig. 3. Charge–discharge curves of the twin-type battery: (a) connected in parallel and (b) connected in series externally between two component cells, respectively. See the text for the insets.

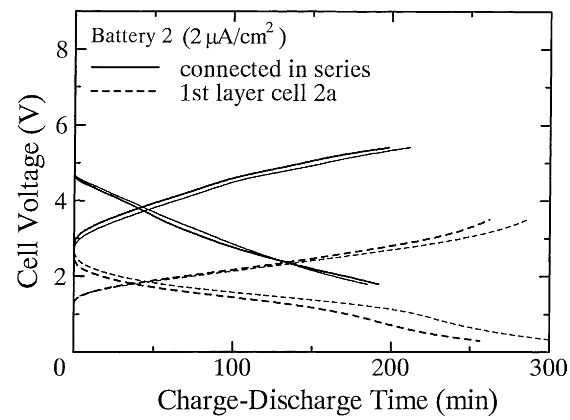

Fig. 4. A charge–discharge curve of the stacked-type battery internally connected in series which is compared with a composite cell.

cell. After all, it is concluded that the batteries externally connected in parallel and in series between two unit cells can realize twice the capacity and twice the cell voltage of its unit cell, respectively, although the battery is twice the operating area of the unit cell in the case of twin-type battery. This type of battery can be extended to three-cell and four-cell batteries and so on with ease to meet the necessity of its large capacity (that is, high current) or high voltage.

The battery #1 described above was designed to increase the operating area in exchange for getting the advantages of high-current and high-voltage operations. Here, in order to give a solution to avoid any increase in the operating area of the battery, we prepared another type of battery #2, that is, the stacked-type one described in Fig. 1b. Such a pyramidal battery was constructed by using several masks with a different size in order to prevent a short-circuit accident between two layers over every other layers. The effective operation areas of first- and second-layer cells were 4 and 0.7 cm^2, respectively. Fig. 4 shows the charge and discharge curves each in the first two cyclic times for the battery internally connected in series with a current of 1.4 μA (a current density of 2 $\mu A/cm^2$ for the second-layer cell) between 5.5 and 1.8 V, together with the curve of the first-layer cell for comparison. This time, it was directly confirmed that the stacked-type battery without substantial increase in area operates to a high voltage of 5.4 V and perhaps up to a higher voltage around 6–7 V. As can be seen in this case, increasing and decreasing rates of voltage for both charging and discharging processes are roughly equal to those of the first-layer cell. This behavior is semi-quantitatively understood as follows. Taking the ratio ($0.7/4.0 = 0.18$) of the second-cell area to the first one into consideration, a measurement current of 1.4 μA may contribute little to the change in charging and discharging voltages of the first-layer cell.

4. Conclusions

The first experiments of multi-layered Li-ion rechargeable batteries were carried out. The thin-film battery, so-called twin-type one which is composed of two unit cells externally connected in parallel and in series could easily realize twice the total capacity and twice the total voltage of 6.5 V compared with those of its unit cell, respectively. The other thin-film battery, so-called stacked-type one which is internally connected only in series could be well operated at least up to the high voltage of 5.5 V without any increase in its operating area. A new layered-type battery is now in preparation, where two unit cells have the same size of the operating area by using an appropriate isolating layer between them.

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