

Short communication

Fabrication of 5 V lithium rechargeable micro-battery

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Received 11 October 2003; received in revised form 11 December 2003; accepted 2 January 2004

Abstract

A 5 V lithium secondary cell was fabricated using $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode material with all-solid-state design. As an additional approach to improve the battery performance of the all-solid-state secondary cell, a metal oxide-retaining layer was placed between the cathode material and solid electrolyte. The cathode material has an excellent cyclability in this cell design, since it just loses 5 and 18% of its initial capacity after 100 and 500 charge–discharge cycles, respectively.

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Keywords: 5 V battery; Lithium secondary cell; Lipon; All-solid-state cell; 5 V cathode; $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$

1. Introduction

Recent developments of cathodes of lithium secondary cells have introduced 5 V cathode materials. Up to now, they have not been used for the fabrication of lithium secondary cells, and indeed technology of lithium secondary cells is still restricted to 4 V rechargeable batteries. This is due to the lack of sufficient improvement of these cathode materials to gain acceptable battery performance for the practical applications. The preliminary investigations of 5 V cathode materials [1–10] have shown that the main obstacle in use of these cathode materials is their high-voltage performance, which is accompanied by severe problems. Our recent attempts [11–13] in this context have significantly overcome this problem and have provided a new opportunity for the fabrication of 5 V lithium secondary cells. In the present communication, possibility for the fabrication of 5 V lithium secondary cells is reported. To this aim, an all-solid-state cell design was used, which reduces problems of high-voltage performance and on the other hand provides an opportunity for the fabrication of high-voltage rechargeable micro-batteries.

The most important class of 5 V cathode materials of lithium secondary cells is $\text{LiM}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (M: Ni, Co, Cr, Cu, Fe, etc). In addition to 5 V performance of this class of cathode materials, they have essential advantages as well as LiMn_2O_4 cathodes of 4 V lithium secondary batteries.

There have been numerous efforts to improve battery performance of LiMn_2O_4 as a promising alternative to current LiCoO_2 cathodes. This is due to noticeable advantages of LiMn_2O_4 in comparison with other cathode materials, such as abundance of Mn sources, non-toxicity, low-cost, etc. Thus, $\text{LiM}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinels as 5 V cathode materials are of double interest. In this class of 5 V cathode materials, $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has some advantages such as lower cost of Fe in comparison with other substituted metals. In the previous paper [11], we have extensively studied the diffusion process of Li^+ intercalation–deintercalation into/from $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel in different media. It has been demonstrated that the problems of high-voltage performance is mainly related to the direct reaction of electrolyte salt with the high-valent metals of the cathode materials at high-voltage performance. Thus, capacity fading of the cathode material can be significantly reduced by choosing appropriate electrolyte medium [11]. It is worth noting that using different substituting metals leads to different advantages of the $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel. For instance, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ provides a single plateau during the electrochemical performance due to its single redox, with relatively high-specific capacity. $\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is also known as a metal-substituted LiMn_2O_4 with a negligible capacity fading due to its crystallographic stability. However, each of them suffers from some important disadvantages such as toxicity, expensivity, etc. Overall, advantages of $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ guarantee the practical performance.

To fabricate a promising secondary cell, a more appropriate electrolyte medium viz. Lipon, which is a solid electrolyte of lithium secondary cells was used in the present

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research. Lithium phosphorous oxynitride (Lipon) is an excellent electrolyte for solid-state lithium thin-film batteries [14–16], due to their significant electrochemical stability (5.5 V stability window versus Li/Li⁺) and high ionic conductivity. Interestingly, this design provides an opportunity for the fabrication of thin-film battery (TFB), which is a promising alternative micropower source satisfying the need to derive extremely small size electronic devices of the current era (and indeed are quickly getting smaller).

2. Experimental

The synthesis procedure for the preparation of LiFe_{0.5}Mn_{1.5}O₄ spinel has been described in the literature [6,11]. Pt (150 nm)/Ti (20 nm) current collector layers were deposited on Si(100) wafer by a sputtering method. The titanium layer was used for good adhesion between the Pt current collector and silicon substrate. The cathode material LiFe_{0.5}Mn_{1.5}O₄ was deposited onto the current collector by radio frequency (rf) magnetron sputtering. A rf power of 100 W under an Ar atmosphere with 1.4 Pa pressure using a conventional rf magnetron sputtering system was employed for this purpose. The cathode film thickness was about 500 nm, and the amount of electroactive material attached to the substrate surface was about 80 μg. The solid electrolyte, Lipon, was deposited by rf magnetron sputtering of a Li₃PO₄ target in a nitrogen atmosphere [17]. The Lipon electrolyte thickness was about 1 μm, with ionic conductivity of about 2×10^{-6} S/cm. Finally, the lithium metal film was deposited over the Lipon electrolyte by conventional thermal evaporation using a small evaporator set up in an Ar-filled glove box.

Two different all-solid-state secondary cells were prepared and compared. A so-called conventional secondary cell was fabricated using simple LiFe_{0.5}Mn_{1.5}O₄ cathode, and the other using a metal oxide-coated LiFe_{0.5}Mn_{1.5}O₄ cathode. Aluminum oxide was used as a typical metal oxide as a retaining layer which avoids direct contact of the electroactive film and electrolyte solution. A thin layer of Al₂O₃ with thickness of ca. 10 nm was deposited onto the electroactive film by sputtering method. Charge–discharge tests were carried out using a battery cyclizer with C/10 rate.

3. Results and discussion

In the previous paper [11], battery performance of LiFe_{0.5}Mn_{1.5}O₄ cathode in liquid electrolytes has been extensively studied. In this direction, it is aimed to investigate the battery performance of this 5 V cathode in all-solid-state design. Fig. 1 shows a typical charge–discharge characteristic of the 5 V lithium secondary cell with an all-solid-state design described in Section 2. The curve is similar to that reported for the battery performance of LiFe_{0.5}Mn_{1.5}O₄ cathode in liquid electrolyte medium [11]. This suggests

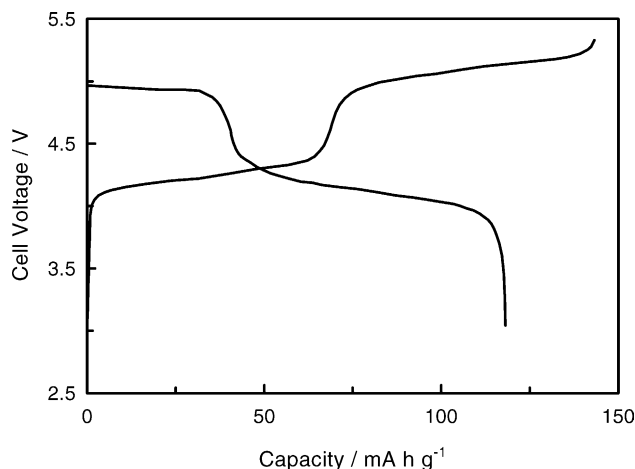


Fig. 1. Typical charge–discharge characteristic of the 5 V lithium secondary cell with all-solid-state design. Rate: C/10.

that the thin-film cathode in solid-state cell has its original electrochemical behavior. However, the main problem in the preparation of 5 V lithium secondary batteries is the appearance of significant capacity fades in the course of cycling. Thus, to fabricate a 5 V lithium secondary battery, it is needed to obtain good cyclability.

The results obtained from repetitive charging–discharging of the 5 V lithium secondary cell are presented in Fig. 2. It is obvious that the cyclability of the all-solid-state lithium secondary cell using Lipon electrolyte is significantly higher than that of previously reported using conventional LiPF₆ electrolyte salt and even stable electrolyte salt of LiBF₄ [11]. The 5 V lithium secondary cell fabricated exhibits only about 10% capacity fade after 100 charge–discharge cycles. The results obtained from cyclability investigation of the all-solid-state cell with Al₂O₃-retaining layer are also reported in Fig. 2 for comparison. The latter secondary

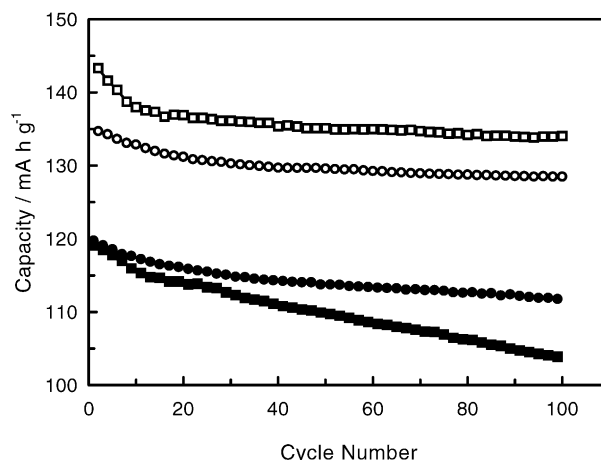


Fig. 2. Cyclability data for: the conventional 5 V lithium secondary cell using a conventional LiFe_{0.5}Mn_{1.5}O₄ cathode ((□) charge and (■) discharge); and using a Al₂O₃-coated LiFe_{0.5}Mn_{1.5}O₄ cathode ((○) charge and (●) discharge). The charge–discharge profiles were recorded as in Fig. 1.

cell exhibits an excellent battery performance, since it loses only 5% of its initial capacity after 100 cycles during 5 V performance.

The values corresponding to the charge capacity are also reported in Fig. 2. Since the capacity fading is stronger in the course of discharge in comparison with charging, the gap between the charge and discharge capacity increases upon cycling. In fact, charge capacity decreases due to weaker Li diffusion resulting in more incomplete insertion. Since a lesser amount of Li is inserted, a lesser capacity is expected during discharging. Thus, the discharge capacity decreases as well as the charge capacity, plus an additional capacity fading (in addition to the mentioned capacity fading due to lesser amount of Li in $\text{Li}_x\text{Mn}_2\text{O}_4$) due to other side reactions mainly electrolyte decomposition. This failure is only appropriate for the discharging process, since electrolyte decomposition occurs at high-voltage performance of discharging, which is very strong for 5 V cathodes. The main advantage of the all-solid-state cell is to reduce electrolyte decomposition due to the absence of liquid electrolyte. Therefore, it is expected to achieve a lesser gap between the charge and discharge capacity. This behavior can be observed by comparison of the results reported in Fig. 2, and corresponding gaps appeared in two different cells.

For the conventional all-solid-state cell, this gap decreases during the initial cycles up to 10th to reach a minimum, and then increases. The gradual increase of the gap is expected since the discharge capacity fading is stronger at high cycle numbers, but the initial decrease of the gap is extraordinary. The latter behavior can be attributed to the modification of surface structure appearing during the initial cycles. Note that all-solid-state design does not guarantee a perfect contact of the rigid electroactive material with the solid electrolyte. However, this behavior is not observed for the battery performance of the $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode in liquid electrolyte, since the electrolyte fills empty pores of the cathode material and makes a perfect contact at the electroactive film–electrolyte solution interface. Interestingly, it is observable in Fig. 2 that this failure also disappears for the all-solid-state cell with Al_2O_3 -retaining layer, since the metal oxide is less rigid in comparison with the electroactive material and also avoids subsequent changes in the surface structure upon cycling. This is another advantage of this metal oxide-retaining layer.

To investigate that the capacity fading appeared for the $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is mainly due to the high-voltage performance of the cathode, it is needed to inspect the capacity fading in the course of conventional 4 V performance (Fig. 3). It is obvious that the capacity fading appearing in the course of 4 V performance is negligible. This suggests that the common Mn dissolution of LiMn_2O_4 is not responsible for strong capacity fading of $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 5 V cathode, since it is known that substituting transition metal into LiMn_2O_4 spinel can reduce Mn dissolution. Indeed, it was the main reason for investigation of metal-substituted LiMn_2O_4 : to reduce capacity fading of LiMn_2O_4 cathodes

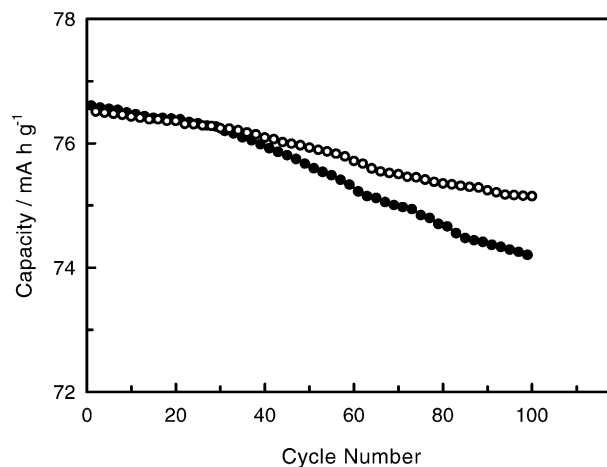


Fig. 3. Cyclability data for 4 V performance of: (●) the conventional all-solid-state secondary cell and (○) the all-solid-state secondary cell using Al_2O_3 -retaining layer. The charge–discharge cycles were recorded in potential window of 3.0–4.4 with $C/10$ rate.

at elevated temperature, which is due to Mn dissolution. Interestingly, it is observable that surface coating of the $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ also improves its 4 V performance, because avoiding the direct contact of the cathode with electrolyte has an effect to reduce possible Mn dissolution (though it is significantly less in metal-substituted LiMn_2O_4). This is due to the metal oxide-retaining layer which avoids surface structural changes of the cathode material.

Although, this is an acceptable cyclability for this new class of lithium secondary cells (i.e. 5 V rechargeable batteries), further improvements in cyclability of such 5 V lithium secondary cell is required for practical applications and commercialization, since higher numbers of charge–discharge cycles is desired for applied purposes. As stated above, the main reason for capacity fading of 5 V cathode materials due to high-voltage performance is related to the direct reaction of electrolyte and cathode material at the cathode–electrolyte interface. This has a great importance for LiMn_2O_4 and similar compounds, e.g. $\text{LiM}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as they have very complex surfaces [18], which are subject of significant surface changes upon cycling [19]. Thus, it is possible to reduce such capacity fades by avoiding such direct contact or even incorporation of metal oxide into the electroactive film (to cover the individual particle surfaces) [20]. It has been reported [11] that as well as LiMn_2O_4 cathodes, surface coating of 5 V cathode materials is an efficient approach to reduce capacity fading. Thus, surface coating the electroactive film with a retaining layer is useful to gain battery performance in the course of more cycling. Further investigations in this context showed that this cell can be successfully used for 500 charge–discharge cycles with only 18% capacity fades (not shown). This is an acceptable cyclability for this new class of lithium secondary batteries, though, it is just preliminary investigations in this direction and future researches will surely provide significantly better cyclability and performance.

4. Conclusion

The results reported here obviously showed that by favor of recent achievements and according to the approach proposed for improvement of the battery performance of 5 V cathode materials it is possible to construct 5 V lithium rechargeable batteries. From applied point of view, these rechargeable batteries have most of advantages of conventional 4 V lithium batteries. The typical 5 V lithium secondary cell reported here is comparable with its similar LiMn_2O_4 cathode-based 4 V lithium battery. However, this is just the beginning and certainly better 5 V lithium rechargeable batteries will be fabricated for commercialization in the light of future investigations. However, birth of this new class of lithium rechargeable batteries will be an important achievement in electrochemical energy conversion.

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