An Approach to 12-V Lead-free Batteries: High Temperature 3600-cycle Examinations on a 2.5-V LTO/LAMO Battery

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(Received September 25, 2009; CL-090865; E-mail: ohzuku@a-chem.eng.osaka-cu.ac.jp)

A 2.5-V battery consisting of lithium titanium oxide (LTO) and lithium aluminum manganese oxide (LAMO) having spinel-framework structures was examined from 1 to 3 V at 55 °C. After several trials on capacity retention at high temperatures, we have succeeded to show that the rechargeable capacity is retained at greater than 80% even after 3600 cycles at 55 °C by applying cellulose nonwoven cloth as a separator, satisfying requirement for 12-V automobile applications.

In previous papers,[1,2] we proposed 12-V lead-free batteries consisting of lithium insertion materials. The first generation of 12-V lead-free batteries consists of the zero-strain lithium insertion material of $Li[Li_{1/3}Ti_{5/3}]O_4$ (LTO) and $Li[Li_{0.1}Al_{0.1}Mn_{1.8}]O_4$ (LAMO). The single cell shows 2.5-V operating voltage, meaning 12-V batteries[3] can be made connecting 5 cells in series. A characteristic feature of the first generation of 12-V batteries is high-rate capability for both charge and discharge, so that the batteries can be used as power sources for hybrid electric vehicles (HEV) or plug-in HEV. Capacity fading is negligibly small when the cells are cycled at or below room temperature.[4] However, capacity fading is observed at high temperatures. Chemically inactive polymers, such as polypropylene or polyethylene, are usually used as a separator in lithium batteries. The capacities of the 2.5-V batteries faded at high temperatures when such separators were used. To improve the capacity retention, we have examined several separators made of different 8 polymer fibers. Among them, cellulose showed the profound effect on capacity retention of the 2.5-V batteries at 55 °C.

Figure 1 shows the charge and discharge curves of the LTO/LAMO cell operated at 0.50 mA cm^{-2} at 25 °C. LAMO and LTO are the same as those described previously.[2] To prepare the electrodes, a black viscous slurry consisting of 88 wt % LAMO or LTO, 6 wt % acetylene black, and 6 wt % poly(vinylidene fluoride) dissolved in *N*-methyl-2-pyrrolidone (NMP) was cast onto aluminum foil. NMP was evaporated at room temperature in air and then under vacuum at 60 °C for 30 min, and finally the electrodes were dried under vacuum at 150 °C for 14 h. After drying, the electrodes were punched out into a 16.0 mm diameter (2.0 cm^2) disk. The cell with three-electrode configuration used in this study is the same as described previously[5] except the positive-electrode material. The electrolyte is 1 M $LiPF_6$ dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC) (3/7 by volume) (Kishida Chemical Co., Ltd., Japan). The separator is two sheets of cellulose nonwoven cloth (TF44-25, Nippon Kodoshi Co., Ltd., Japan). Cellulose consists of numerously linked glucose, each of which has three hydroxy groups unless they are substituted for other groups. Therefore, cellulose is hydrophilic and chemically reactive. To apply cellulose to nonaqueous batteries, special care has been done to remove adsorbed water on cellulose. The separator was dried under vacuum at

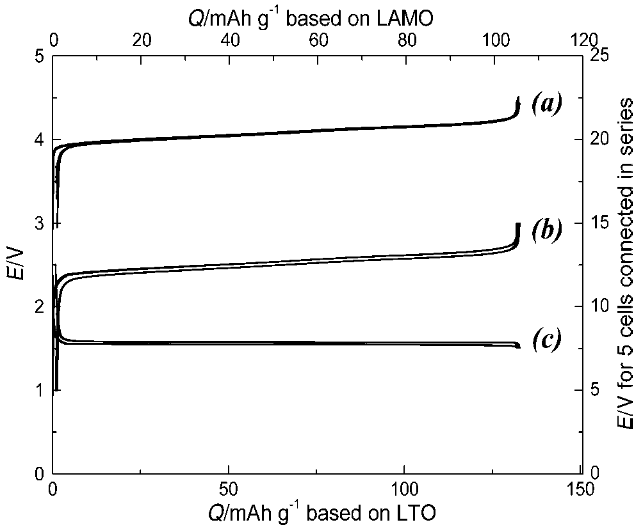

Figure 1. Charge and discharge curves of the LTO/LAMO cell operated at 0.50 mA cm^{-2} at 25 °C. The voltages of (a) LAMO-positive and (c) LTO-negative electrodes are monitored with respect to an auxiliary lithium electrode in addition to (b) the terminal voltage of the LTO/LAMO cell. The right vertical axis is the voltage expected when five LTO/LAMO cells are connected in series. The initial 6 cycles of freshly fabricated cell are shown in this figure.

150 °C overnight and transferred to an argon-filled glove box as quickly as possible. The positive LAMO-electrode mix weighted 47.6 mg and was 138 µm thickness while the negative LTO-electrode mix weighted 37.9 mg and was 144 µm. The capacity loaded on the positive electrode is 4.40 mAh calculated from the observed rechargeable capacity of 105 mAh g^{-1} in Li/LAMO cells and the capacity loaded on the negative electrode is 5.50 mAh calculated from the observed rechargeable capacity of 165 mAh g^{-1} in Li/LTO cells, so that the cell capacity is limited by the positive-electrode capacity. The initial 6 cycles are shown in Figure 1. Irreversible capacity is negligibly small in this case, and the cell capacity is limited by the positive-electrode capacity as is expected. After the initial 6 cycles at 25 °C at a rate of 0.50 mA cm^{-2}, the cell was heated to 55 °C and operated at 4.19 mA cm^{-2} in voltages ranging from 1 to 3 V. The current corresponds to 200 mA g^{-1} based on LAMO weight and 251 mA g^{-1} based on LTO, so that it takes about 1 h per cycle.

Figure 2 shows the selected charge and discharge curves of the LTO/LAMO cell operated at 4.19 mA cm^{-2} at 55 °C. As can clearly be seen in Figure 2, the LTO/LAMO cell shows excellent cycleability for more than 3600 cycles. Rechargeable capacity at the 3600th cycle is observed to be ca. 80 mAh g^{-1} based on LAMO weight. Increase in polarization for both the positive and negative electrodes is hardly observed during the

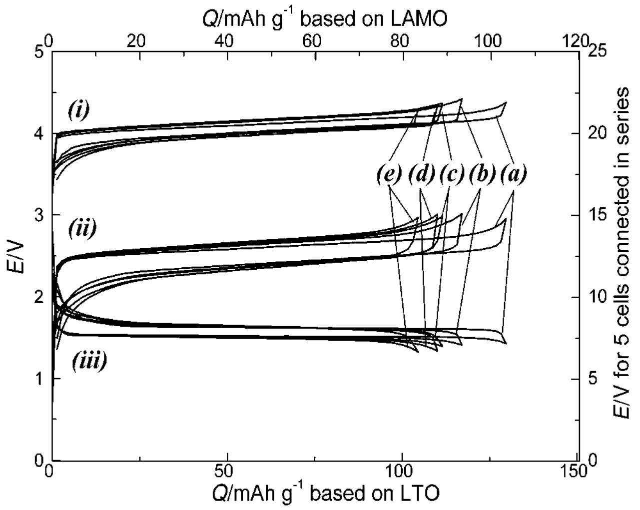

Figure 2. Charge and discharge curves observed at (a) 1st, (b) 1000th, (c) 2000th, (d) 3000th, and (e) 3600th cycles for the LTO/LAMO cell operated at 4.19 mA cm^{-2} in voltages ranging from 1 to 3 V at 55 °C. An auxiliary lithium electrode is placed around the electrodes, and the voltages of (i) LAMO-positive and (iii) LTO-negative electrodes are monitored with respect to an auxiliary lithium electrode in addition to (ii) the terminal voltage of the LTO/LAMO cell.

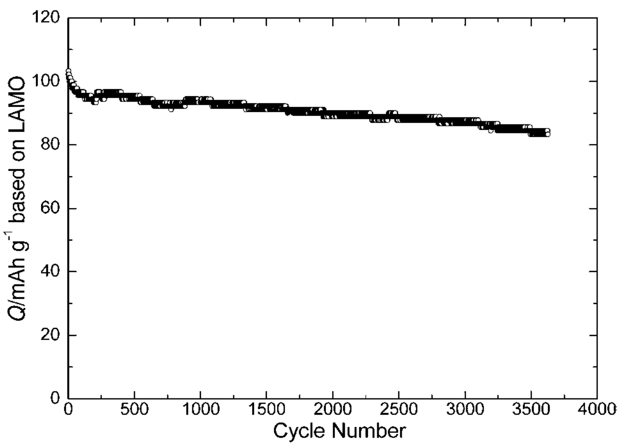

Figure 3. Charge and discharge capacities as a function of cycle number for the LTO/LAMO cell operated at 4.19 mA cm^{-2} in voltages of 1 to 3 V at 55 °C. Open and closed circles indicate the charge and discharge capacities, respectively.

3600 cycles at 55 °C. Figure 3 shows the charge and discharge capacities of the LTO/LAMO cell as a function of cycle number. The cell was continuously cycled for 3627 cycles or 3283 h. In other words, the 2.5-V LTO/LAMO cell can be operated at 55 °C for more than 4 months with continuous deep charge and discharge, which cannot be done with 12-V lead-acid batteries. The rechargeable capacities drop during the initial 200 cycles and almost linearly decrease up to 3627 cycles. The capacity more than 80% with respect to the initial capacity is retained even after 3627 cycles. This indicates that the current efficiency influenced the capacity retention is 99.994% for a charge–discharge cycle at 55 °C although the ampere–hour efficiency[3] is lower than that value.

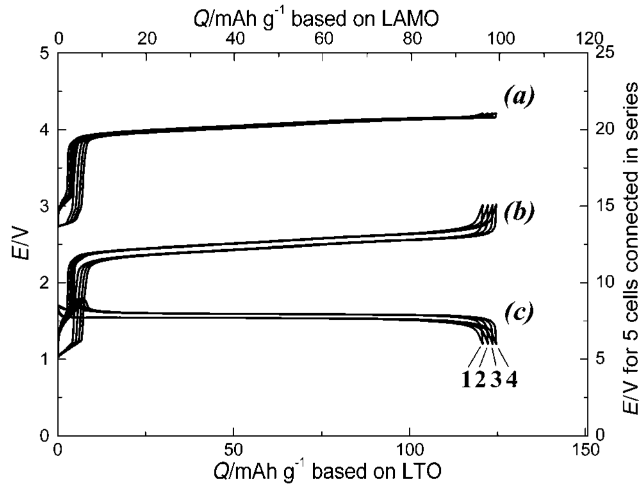

Figure 4. Charge and discharge curves of the LTO/LAMO cell operated at 0.50 mA cm^{-2} at 25 °C after 3627 cycles at 55 °C. The voltages of (a) LAMO-positive and (c) LTO-negative electrodes are monitored with respect to an auxiliary lithium electrode in addition to (b) the terminal voltage of the LTO/LAMO cell. The cycle numbers are indicated at the bottom of the figure since the cell is examined at 25 °C.

In order to examine the change in voltage profiles after the high-temperature cycling compared to those shown in Figure 1, the cell was discharged to 1 V, cooled from 55 to 25 °C under the open-circuited condition, and operated in voltages ranging from 1 to 3 V at 0.50 mA cm^{-2}. The results are shown in Figure 4. The rechargeable capacities increase cycle by cycle because of the change in current density together with temperature from 4.19 mA cm^{-2} at 55 °C to 0.50 mA cm^{-2} at 25 °C. As can be seen in Figure 4, the charge capacity of the cell is limited by the LTO-negative electrode in contrast to the initial cycles in Figure 1, and the reaction at ca. 3 V is seen for the LAMO-positive electrode. By comparing Figure 4 to Figure 1, it is evident that the capacity fading is due to the imbalance in the state of charges between the LAMO-positive and the LTO-negative electrodes, not the deterioration or destruction of lithium insertion materials of both LTO and LAMO.

In this paper, we have shown that the 2.5-V LTO/LAMO cell can be operated at 55 °C for more than 3600 cycles. The underlying chemistry behind this is complicated. To understand the chemistry, cooperative research among polymer science, organic chemistry, and electrochemistry is necessary. Such an approach is now in progress in our research group.

References and Notes

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Published on the web (Advance View) November 21, 2009; doi:10.1246/cl.2009.1202