Lead-free Accumulators for Renewable and Clean Energy Technologies

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Lead-free accumulators consisting of lithium aluminum manganese oxide (LAMO) and lithium titanium oxide (LTO) having spinel-framework structures are examined in 1 M $LiBF_4$ acetonitrile. Results on zero-volt storage for 2 weeks, cycle tests at 1 mA cm^{-2} in voltages of 0 to 2.9 V for 20 cycles and then at 2 mA cm^{-2} in voltages of 2.0 to 2.9 V for 100 cycles, and rate-capability tests ranging from 0.3 to 16.7 mA cm^{-2} are presented and 12 V lead-free accumulators, in which 5 cells are connected in series, are proposed for renewable and clean energy technologies.

Recent demands towards cleaner environments stimulate us to study lead-free accumulators by using a concept of lithium-ion batteries combined with lithium insertion materials. Lead-acid batteries have long, long histories since 1859, which is still one of the most important secondary batteries for automobile and stationary applications.[1,2] Twelve-volt batteries in which 6 cells are connected in series are common in applying lead-acid batteries to power sources for many applications. Maximum charge-end voltage is 14.4 V for 12 V batteries, corresponding to 2.4 V for a lead-acid battery. In designing 12 V lead-free accumulators, charge-end voltage under so-called floating condition at constant voltage was one of the most difficult problems to solve for a long time. Several lithium insertion materials for positive or negative electrodes have been reported especially during the past 15 years.[3–6] Any combination of these materials gives 2 to 5 V-class of lithium-ion batteries. Current lithium-ion batteries consisting of $LiCoO_2$ and graphite show 3.3 to 4.2 V of operating voltage, so that 12 V batteries can be made by connecting 3 cells in series. However, charge-end voltage for the cell is calculated to be 4.8 V, which is over-charged condition. When 4 cells are connected in series, charge-end voltage is 3.6 V for the cell, which is not enough voltage to charge the capacity for the current lithium-ion batteries. This impedes the developments of lead-free accumulators substituting for lead-acid batteries so far.

Materials selected are lithium aluminum manganese oxide, abbreviated to LAMO hereafter, having a spinel-framework structure and so-called zero-strain insertion material of $Li[Li_{1/3}Ti_{5/3}]O_4$ (LTO),[7] giving 2.5 V lithium-ion battery. LAMO was characterized by chemical analysis and XRD to be Li 4.41 wt %, Al 1.71 wt %, and Mn 57.2 wt % with a cubic lattice constant of 8.211 Å.[8] LTO ($a = 8.357$ Å) used was the same as reported in a previous paper.[9] To make 12 V batteries, five cells are needed to be connected in series. Consequently, charge-end voltage examined is 2.9 V for single-cell tests. Figure 1 shows charge and discharge curves of a lithium-ion cell. Electrolyte used was 1 M $LiPF_6$ ethylene carbonate (EC)/dimethyl car bonate (DMC) (3/7 by volume), which is commonly used in current lithium-ion batteries. Aluminum substrates are used as current feeders in both positive and negative electrodes. This gives a beneficial effect on gravimetric energy density. Selection of current electrolyte is done for a negative electrode based on lithium–graphite intercalation compounds of LiC_6 whose operating voltage is very close to metallic lithium electrode, so that organic or inorganic solvents reacting with lithium cannot be used. Operating voltage of the negative electrode in our lead-free accumulator is 1.55 V far from that of lithium. A limiting condition on the selection of solute and solvent is thus eliminated. Therefore, application of old, but new electrolytes to lead-free accumulators is quite possible. We do not need $LiPF_6$-based or EC-based electrolyte in considering the lead-free accumulators.

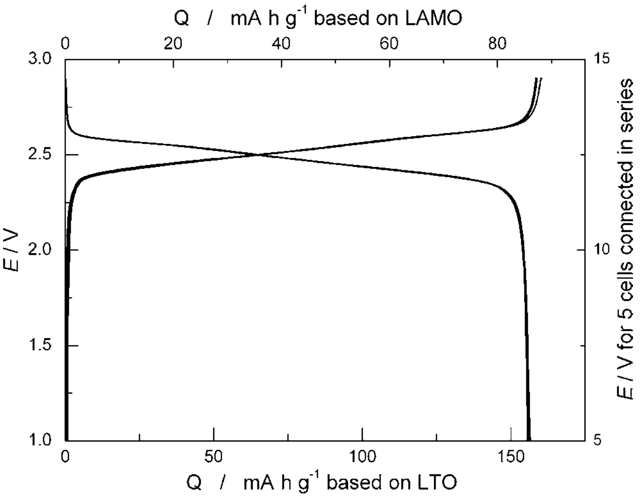

Figure 1. Charge and discharge curves of a lead-free accumulator consisting of LAMO and LTO. The cell was operated at 1 mA per 3 cm^2. Negative electrode; 88.2 mg of mix, 0.21-mm thick., and 1.42 g cm^{-3} of density. Positive electrode; 160.5 mg of mix, 0.29 mm thick and 1.85 g cm^{-3}. Electrolyte; 1 M $LiPF_6$ EC/DMC (3/7 by volume). Electrode mix consists of 88 wt % active material, 6 wt % acetylene black, and 6 wt % PVdF. The 1st to 20th cycles are shown.

Figure 2 shows the results on the twenty-cycle tests of the cell examined after two-week storage under short-circuited condition, i.e., zero volt in terminal voltage. The cell was operated in voltages of 0 to 2.9 V at 1 mA cm^{-2} at room temperature, which cannot be done for lead-acid batteries. Electrolyte used is 1 M $LiBF_4$ dissolved in acetonitrile (AN). After the twenty-cycle tests at 1 mA cm^{-2}, the cell was cycled at 2 mA cm^{-2} in voltages of 2.0 to 2.9 V for 100 cycles. Results are shown in Figure 3, which corresponds to 10 to 14.5 V of operating voltage when 5 cells are connected in series. As can be seen in Figures 2 and 3, no fatal damage can be seen for zero-volt storage, cell-cycle in voltage of 0 to 2.9 V, and continuous 100-cycle tests in voltage of 2.0 to 2.9 V even when 1 M $LiBF_4$ AN is used as an

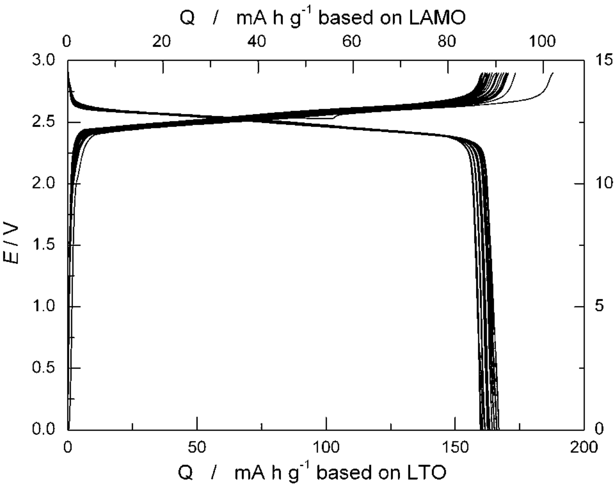

Figure 2. Charge and discharge curves of a lead-free accumulator operated at 1 mA cm^{-2} in voltage of 0 to 2.9 V after 2 week storage under short-circuited condition, i.e., zero-volt storage. Negative electrode; 62.9 mg of the mix, 0.15 mm of thick., and 1.36 g cm^{-3} of density. Positive electrode; 115.8 mg of mix, 0.22 mm of thick., and 1.78 g cm^{-3}. Electrolyte used was 1 M $LiBF_4$ acetonitrile.

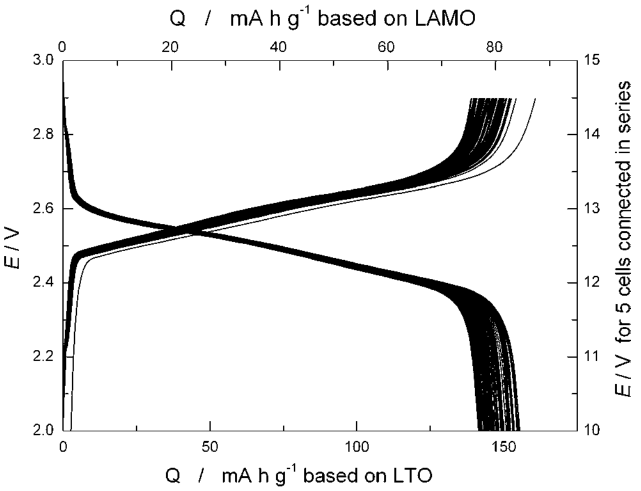

Figure 3. Charge and discharge curves of a lead-free accumulator operated at 2 mA cm^{-2} in voltage of 2.0 to 2.9 V. After 20 cycle tests in Figure 2, discharge-end voltage and current are respectively adjusted to be 2.0 V and 2 mA cm^{-2}.

electrolyte. Figure 4 shows the results of rate-capability tests on the lead-free accumulator. Rate-capability is fairly good when AN-based electrolyte is used. In addition to such a merit in determining electrolyte, we do not need precious membrane. Specially designed porous membranes have been used in current lithium-ion batteries in order to prevent possible thermal runaway initiated by shortage between positive and negative electrodes due to dendrite growth of lithium on LiC_6 during charge. In the lead-free accumulator with $Li[Li_{1/3}Ti_{5/3}]O_4$-negative electrode, such a situation that lithium metal is deposited on the negative electrode cannot be expected. Non-woven cloth or other materials may be enough to separate the positive and negative electrodes. In other words, there are several options in determining lithium salt, solvent, and separator for the lead-free accumulators under considerations.

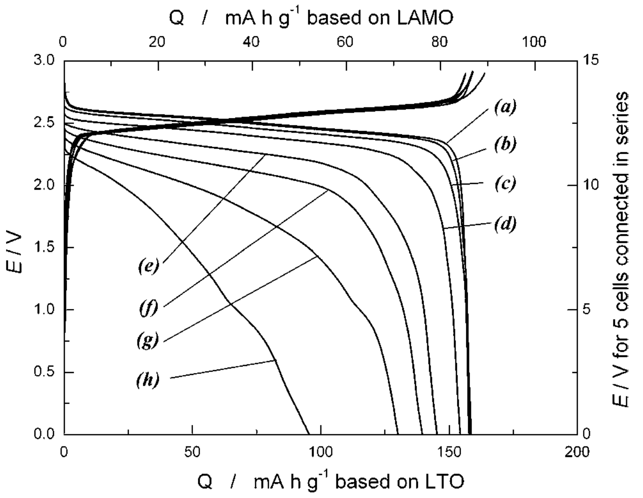

Figure 4. Rate-capability tests on a lead-free accumulator consisting of LAMO and LTO. Negative electrode; 89.4 mg of mix, 0.207 mm of thick., and 1.44 g cm^{-3} of density. Positive electrode; 162.0 mg of mix, 0.287 mm of thick., and 1.88 g cm^{-3}. The cell was charged to 2.9 V at a rate of 0.7 mA cm^{-2} and discharged at (a) 0.3, (b) 0.7, (c) 1.7, (d) 3.3, (e) 6.7, (f) 10.0, (g) 13.3, and (h) 16.7 mA cm^{-2}.

As were briefly described above, 12 V lead-free accumulators based on green elements of titanium and manganese can be designed and applied to power sources for renewable and clean energy technologies, such as solar and wind power generation systems, in addition to automobile and stationary applications. Optimization of electrolyte together with positive-electrode materials is still under way in our laboratory.

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