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Reliability of Lithium-ion Cells using Lithium Iron Phosphate as Cathode Material

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Olivine lithium iron phosphate ($LiFePO_4$) is very prospective positive electrode material from the points of environment and cost. Compared with other iron based positive electrode materials, it is very attractive because of the properties such as high potential (3.4V) and high density (3.6g/cc).

A big problem of $LiFePO_4$ as positive electrode material is low electronic conductivity. Various methods, however, have overcome this problem in recent years. The methods are (i) nano-powder [1], (ii) nano-composite with carbon [2], (iii) metal additive [3], and (iv) partial substitution of metal element for Li [4]. Despite the low electronic conductivity, one of excellent advantages is that $LiFePO_4$ is much safer than usual positive electrode materials.

Though the improvement of electronic conductivity and safety were extensively studied by many researchers, the reliability of $LiFePO_4$ as positive electrode material for lithium-ion battery has not well reported yet. Therefore, cell performances on cycle life and storage have been examined in this presentation.

$LiFePO_4$ was synthesized by a solid-state method from Li_2CO_3, $FeC_2O_4 \cdot 2H_2O$ and $NH_4H_2PO_4$. All the procedure was done under Ar atmosphere. The stoichiometric amounts of starting materials were mixed and thoroughly grounded. The mixture was pre-calcined at 300℃ for 12h and then ground again. The intermediate was calcined at 600℃ for 24h. The crystal structure of powder was characterized with X-ray diffraction method. The powder had the crystalline phase of olivine structure.

The electrochemical behavior of positive electrode was examined by using a flat-type cell. Slurry, containing the active material, acetylene black as a conductive support, 1-poly (vinyliden fluoride) binder and N-methylpyrrolydine-2-on was coated on Al foil. The positive electrode was prepared by drying and pressing the slurry. Graphite was used as negative electrode material and a porous polypropylene film was used as separator. Solution of 1M-$LiPF_6$ ethylene carbonate (EC) / ethyl methyl carbonate (EMC) was used as an electrolyte.

Storage test was carried out. Figure 1 shows voltage profiles for the cell of $LiFePO_4$/Graphite and that of $LiMn_2O_4$/Graphite before and after storage at 85 degrees C for 24h. The voltages before the storage test were 4V for $LiFePO_4$ cell and 4.3V for a comparative $LiMn_2O_4$ cell, respectively. The cell employing $LiFePO_4$ gave a good cell performance after 85 degrees C storage as compared with that employing $LiMn_2O_4$.

The amount of deposited metal (Fe or Mn) on the anode after 85 degrees C storage was measured by ICP method. Each anode was dissolved into an aqueous acid solution for the ICP analysis. Figure 2 shows the amount of deposited metal on the negative electrode after 85 degrees C storage. The amount of Fe in the cell of $LiFePO_4$/Graphite was much less than that of Mn in the cell of $LiMn_2O_4$/Graphite. Therefore, the dissolution of Fe from the charged $LiFePO_4$ electrode was not easy at 85 degrees C in comparison with the $LiMn_2O_4$ electrode. In addition, the storage performance and cycle performance under various conditions were examined. From these results, we will discuss the reliability of the Li-ion battery using $LiFePO_4$ as positive electrode material.

References:

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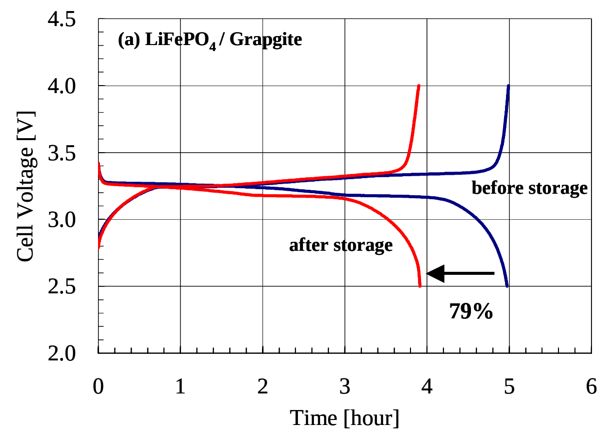

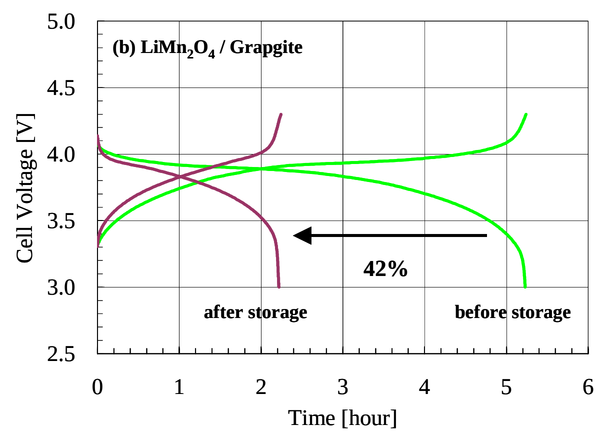

Fig. 1 Voltage Profiles for the cell of (a) $LiFePO_4$ / Graphite and (b) $LiMn_2O_4$/Graphite before/after storage at 85℃ for 24hours at 0.2C-Rate in room temperature

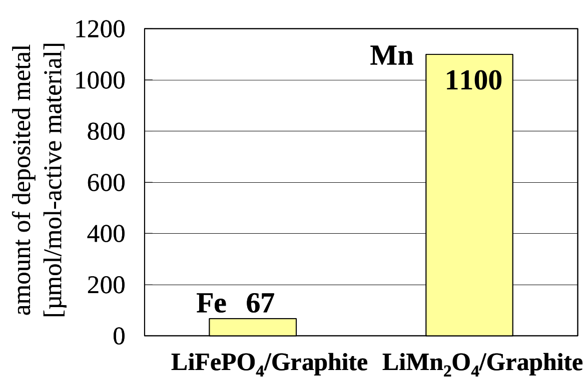

Fig. 2 The amount of deposited metal (Fe or Mn) on anode electrode after 85 degrees C/24 hours storage.