

Surface degradation of mixed $\text{LiMn}_2\text{O}_4/\text{LiNiO}_2$ cathode particles and capacity fade in Li-ion batteries during accelerated calendar life test

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Spinel LiMn_2O_4 (LMO) cathode of lithium-ion battery (LIB) is inexpensive and has good safety characteristics [1], thus it seems to meet the requirements for electrical vehicle applications. However, LMO cathode is known to have severe capacity loss at elevated temperatures, thus the life performance of LMO cathode must be improved for long-term applications, such as stationary electrical energy storage. The manganese dissolution, which has strong SOC dependence, is considered to be most relevant to the capacity fade [2]. On the other hand, the capacity fade during the calendar testing seems to be related to the loss of the cyclable lithium-ions (Li^+) [3,4]. Our parameter estimation using the physical battery model described in Ref. [5] suggested that not only the loss of the cyclable Li^+ but also the degradation of the cathode is responsible for the capacity fade. In order to clarify the relation between the cathode degradation which is associated with manganese dissolution and the SOC dependence of the capacity loss, we carried out the analyses of the cathode surfaces, depositions on the anode, and electrolyte degradation and estimated the impact of cathode degradation on the capacity fade.

All the studies were done on lithium-ion cells (5 Ah) having cathodes of LiMn_2O_4 mixed with LiNiO_2 (LNO) and graphite anodes. The accelerated calendar testing was done at 55°C for 10 months with cells set at 100% and 40% SOC. The resultant capacity losses were 23% and 45%, respectively.

The estimated cyclable Li^+ losses by the parameter estimation were 17.2% and 33.4% for the 100%- and 40%-SOC cells, respectively. The decrease in the apparent volume fraction of the cathode on the 40%-SOC cell was larger than that on the 100%-SOC one.

Half cells of the faded and fresh cathodes were showed that the cathode of the 40%-SOC cell lost 12% of its original capacity. In contrast, the cathode of the 100%-SOC cell kept its original capacity during the calendar life test.

The high-angle annular dark-field (HAADF) images at the surfaces of the LMO particles showed the lowering of image contrast (see FIG), which implies the decrease in Mn density. The dark area reached a depth of 10 nm and a few nm on 40% and 100% SOC cell, respectively. The EDX analysis showed that the oxygen density decreased in the almost same regions. On the LNO particles, the contrast lowering and the decrease in oxygen density at the surface edges were also observed, but the deteriorated regions were limited to a few nm depth from the surface for both SOC.

The electron energy-loss spectrum at the surfaces of LMO particles showed that the L-edge of Mn band shifted to lower energies, which implies the decrease in Mn valence [6]. The chemically shifted region reached a depth of 20 nm and ~ 7 nm on the cathode particles of the 40%- and 100%-SOC cells, respectively. The chemical shift of Ni L-lines was also observed on LNO, but the shifted regions were limited to a few nm depth from the surface for both SOC.

The Li salt concentration in the electrolyte was found to be lower in the 40%-SOC cell than in the 100%-SOC

one, while the concentrations of Mn and Li in the deposits on the anodes were much higher in the 40%-SOC cell than in the 100%-SOC one. The SOC dependence of Li deposits on the anodes was similar to that of the cyclable Li^+ loss estimated above. The SOC dependence of Mn deposition on the anode and the HAADF images suggested that the dissolved Mn reached the anodes and the cathodes suffered from the Mn dissolution much more in the 40%-SOC cell than in the 100%-SOC one. The capacity fade of the cathode seems to be related to the surface degradation due to the oxygen and manganese deficiency of LMO particles.

The dissolutions of Ni and Mn into the electrolyte were also observed but they had smaller SOC dependence than their deposition amounts on the anodes and the amount of the deposited Ni on anodes was much smaller than that of Mn. These facts and the SOC dependence of Li deposition on anodes might imply that the deposited Mn on anodes enhances the consumption of the cyclable Li^+ .

In conclusion, the loss of cyclable Li^+ dominates the capacity fade during the accelerated calendar testing in the 100%-SOC cell, while the surface degradation of LMO particles is additionally responsible for the capacity fade on the 40%-SOC cell. The evidence of the SOC dependence of cathode degradation was observed in the HAADF images of the LMO particle surfaces. The deposited Mn on anodes which dissolved from cathodes seems to enhance the consumption of cyclable Li^+ or Li salts in the electrolytes. The degradation of LNO particles does not seem to cause much capacity fade.

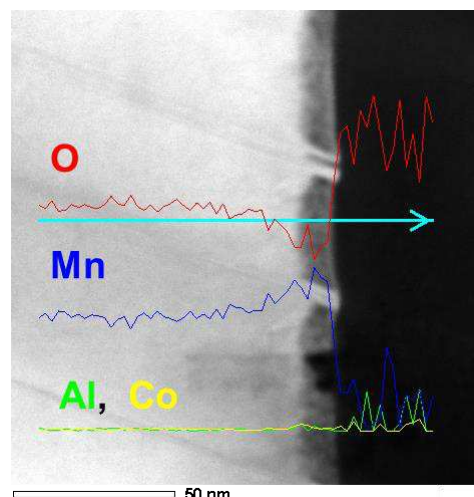


FIG: HAADF image and relative elements distribution measured by EDX at the LiMn_2O_4 particle surface after accelerated calendar testing at 55°C for 8 month with 40% SOC.

References

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