

# Degradation Analysis of Pouch Cell Using High-Energy Cathode Material for Advanced Lithium-ion Battery

Hiroto Maeyama and Toru Sukigara  
Honda R&D Co., Ltd.

## ABSTRACT

Lithium-rich layered oxide, expressed as  $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiMO}_2$  ( $M = \text{Ni, Co, Mn, etc.}$ ), exhibits a high discharge capacity of 200 mAh/g or more and a high discharge voltage at a charge of 4.5 V or more. Some existing reports on cathode materials state that lithium-rich layered oxide is currently the most promising candidate as an active material for high-energy-density lithium-ion cells, but there are few reports on the degradation mechanism. Therefore, this study created a prototype cell using a lithium-rich layered cathode and a graphite anode, and analyzed the degradation mechanism due to charge and discharge. In order to investigate the causes of degradation, changes in the bulk structure and surface structure of the active material were analyzed using high-resolution X-ray diffraction (HRXRD), a transmission electron microscope (TEM), X-ray absorption fine structure (XAFS), and scanning electron microscope/energy dispersive X-ray spectroscopy (SEM-EDX). The results showed that dissolution of transition metals from the cathode active material is the main factor producing degradation of the full cell capacity, and that this is promoted by excessive reductive decomposition of the electrolyte due to deposition of the transition metals on the anode. In addition, voltage fade originates in the cathode active material, and is promoted by changes in the local structure resulting from oxygen release from the crystals due to charge and discharge.

**CITATION:** Maeyama, H. and Sukigara, T., "Degradation Analysis of Pouch Cell Using High-Energy Cathode Material for Advanced Lithium-ion Battery," *SAE Int. J. Alt. Power.* 4(2):2015, doi:10.4271/2015-01-1193.

## INTRODUCTION

The adoption of lithium-ion batteries (LIB) is becoming increasingly widespread, not only for consumer applications, but also for vehicles such as hybrid electric vehicles (HEV) and battery electric vehicles (BEV). Further heightening of the performance of lithium-ion batteries for vehicular use is being sought from a variety of perspectives, including energy density, input and output power density, and durability. In order to increase the energy density of lithium-ion batteries to a high level, a high-capacity active material needs to be used for the cathode. When already existing cathode active materials such as  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  and  $\text{LiFePO}_4$  are used, however, the energy density cannot readily be raised to a higher level [1][2].

There have been growing numbers of reports about how the groups of materials known as lithium-rich layered oxides display a discharge capacity of 200 mAh/g or greater when charged at 4.5 V or higher, and these are being considered promising for use as cathode active material in lithium-ion batteries for high-energy-density applications [3]. Lithium-rich layered oxides are considered to be solid solutions of  $\text{LiMO}_2$  ( $M = \text{Ni, Co, Mn, etc.}$ ) and  $\text{Li}_2\text{MnO}_3$ , and these materials

display high capacity when charged at 4.5 V (vs.  $\text{Li/Li}^+$ ) or higher [4]. Considerable research has been conducted on the charge and discharge mechanisms of these materials, on the relationship between their chemical compositions and the battery performance, and other such aspects, because of the anomalous charge and discharge behavior they display on initial charge and discharge, and because they can exist in many different chemical compositions[5] [6]. Meanwhile, in order to bring lithium-rich layered oxides to practical application, it will be important to conduct cycle testing of full-cell batteries using these materials and clarify how they degrade. The mechanisms of degradation, however, have not been made clear.

In the present research, a full-cell battery was fabricated using lithium-rich layered oxides for cathodes and graphite for anodes. The battery's charge and discharge performance were then examined and the phenomenon of degradation was investigated by cycle testing. With the focus on the surface structure and bulk structure of the active material, HRXRD, TEM, XAFS, and SEM-EDX were used to examine the mechanisms of degradation.

## EXPERIMENTAL SECTION

The coprecipitation method was used to create a precursor such that the mole ratio of the transition metal would be Ni:Co:Mn=0.13:0.13:0.54. The precursor was mixed together with lithium hydroxide and fired to synthesized lithium-rich layered oxide [7]. That oxide was surface modified with aluminum fluoride (AlF<sub>3</sub>) [8].

For cathode electrodes, the active material, acetylene black, and polyvinylidene fluoride (PVdF) binder were mixed 90:5:5 in N-Methyl-2-Pyrrolidone (NMP) to form slurry, which was then coated onto an Al foil. For anode electrodes, the active material (artificial graphite, D50=20 μm) and PVdF binder were mixed 95:5 in NMP to form slurry, which was then coated onto a Cu foil. Both the cathode and anode were subjected to hot-air drying to evaporate the NMP and the electrodes were then press-formed, after which they were vacuum dried to make them into electrodes. 1 M LiPF<sub>6</sub> in fluoroethylene carbonate (FEC), ethylene carbonate (EC), and ethyl methyl carbonate (EMC) with the volume ratio of 1:2:7 was used as the electrolyte. The single-layer pouch cell was fabricated in an argon-filled glove box with a dew point of −100°C or lower.

The charge and discharge tests were carried out in constant current, constant voltage (CCCV-CC) mode within a charge and discharge range of 4.5–2.0 V and at 25°C. The first and second charge and discharge were conducted at rates of C/20 and C/10, respectively. After that each cells were cycled at different rates of C/3, C/2, and 1C. This cycle test was conducted for 200 cycles.

Inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer, and ELAN DRC II) were used for quantitative analysis of the chemical composition of the synthesized cathode active material and the transition metal deposited on the graphite anode. The cathode active material was subjected to thermal decomposition with nitric acid and hydrofluoric acid, and the solution recovered with dilute nitric acid was used as the sample for measurement. The quantity of transition metal deposited on the anode was determined by separating the powder from the electrode, using ultrasound extraction (45 kHz for 5 min) with dilute nitric acid, and using the solution filtered through a membrane filter (pore diameter 0.2 μm) as the measurement sample. SEM-EDX (Carl Zeiss, Ultra55) was used for observation of the surface shape. Analysis of the crystal structure was carried out using HRXRD and TEM (JEOL, JEM-2100F). The HRXRD was conducted with the BL15XU at SPring-8 [9]. The measurement sample was packed into a glass capillary tube (diameter 0.1 mm) in an argon-filled glove box and the tube sealed with resin. X-ray wavelength of 0.65297 Å was used. The X-ray diffraction pattern obtained was analyzed by the Rietveld method using RIETAN-FP to refine the crystal structure [10]. TEM observation was carried out with an accelerating voltage of 200 kV. XAFS analysis was used to analyze local structure. XAFS measurement was carried out with the BL-3 in the Ritsumeikan University SR Center. The measurement sample used was molded into pellets (diameter 10 mm) with boron

nitride in an argon-filled glove box, then vacuum packed in water-resistant polymer film. XAFS spectra were collected in transmission mode using a Si monochromator.

## RESULTS AND DISCUSSION

### Full-Cell Battery Performance

As shown in Table 1, the results from quantitative analysis of the synthesized active material, performed by ICP-MS, show that its chemical composition was as prepared, and confirm that the material can be described as Li(Li<sub>0.2</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>Mn<sub>0.54</sub>)O<sub>2</sub>. Figure 1 shows the results from Rietveld analysis of HRXRD using the chemical composition obtained through quantitative analysis.

Table 1. Chemical composition ratio of synthesized active material.

| Li / Metal | Mn / Metal | Ni / Metal | Co / Metal |
|------------|------------|------------|------------|
| 1.53 mol%  | 0.672 mol% | 0.164 mol% | 0.164 mol% |

This synthesized active material was found to have distinctive superlattice diffraction, and the broadened peak profile of the superlattice diffraction suggested the existence of stacking faults. When this superlattice diffraction is excluded, the observed Bragg diffraction allows for indexing with space group *R*-3m, and fitting was therefore carried out with space group *R*-3m. The analysis results did not show any crystal impurities, confirming that the synthesized lithium-rich layered oxides are single phase.

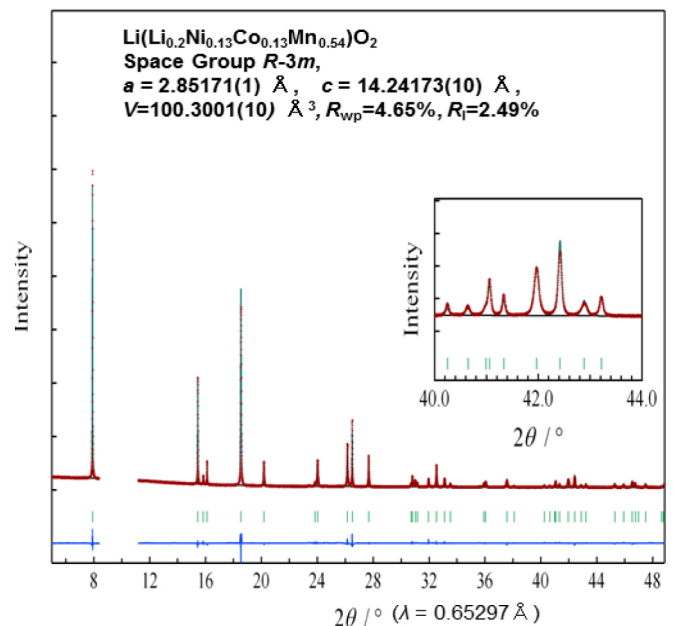


Figure 1. Results of synchrotron X-ray Rietveld analysis of synthesized active material.

Figure 2 shows first and second full-cell charge and discharge curves using the synthesized active material.

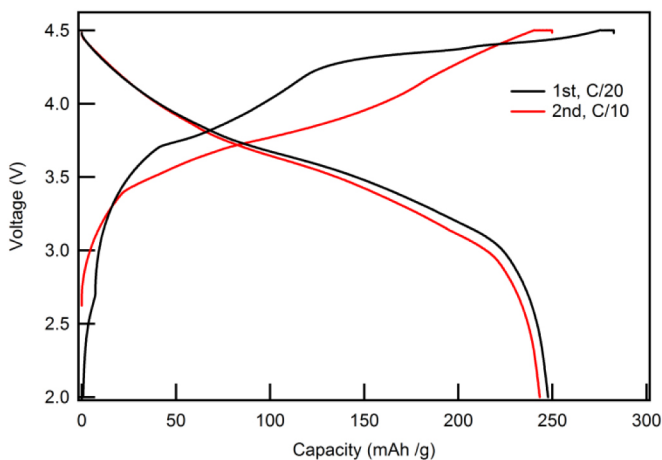


Figure 2. Charge and discharge curves for full cell using lithium-rich layered active material and graphite active material.

The initial discharge capacity showed a high capacity of about 250 mAh / g as well as a high discharge voltage. Distinctive initial charge plateaus were observed at two stages in these materials. This distinctive initial charge behavior closely resembles the characteristics of  $\text{Li}_2\text{MnO}_3$ , and it is related to the way in which lithium and oxygen are released from crystal lattice at the same time [11].

Figure 3 shows the results for cycle performance. Measurements of cycle performance were carried out over 200 cycles in the three patterns of C/3 charge and C/2 discharge, C/3 charge and 1C discharge, and 1C charge and 1C discharge. This shows the discharge capacity retention, with the discharge capacity obtained on initial discharge in each cell taken as 100%. The cycle performances differ with the charge and discharge rate, and the greatest degradation was seen in cells subjected to charge and discharge at the 1C rate.

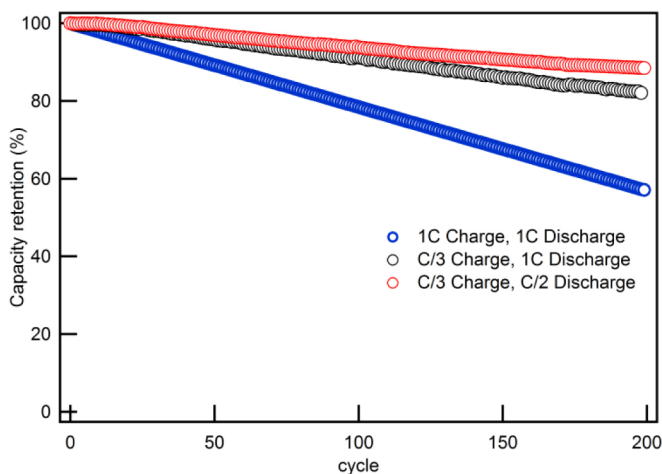


Figure 3. Discharge capacity retention at each C rate.

Figure 4 shows the average discharge voltage retention for each cell, which occurs with cycles. The average discharge voltage showed a decrease across the board, independent of charge and discharge rates.

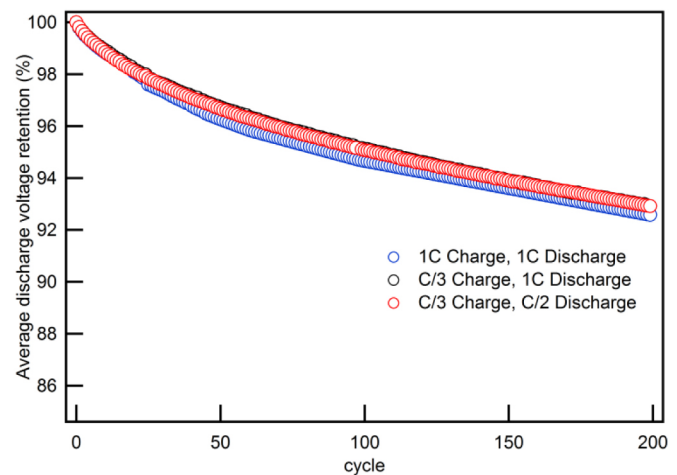


Figure 4. Average discharge voltage retention for each cell.

Figure 5 shows the dQ/dV curves for the cell that was cycle tested with C/3 charge and C/2 discharge, which had the highest capacity retention. Carrying out cycle testing caused a lowering of high voltage peaks, which had been observed in the area of 3.6 V in initial charge and discharge, and peaks observed in the area of 2.8 V also showed a shift to the lower potential side.

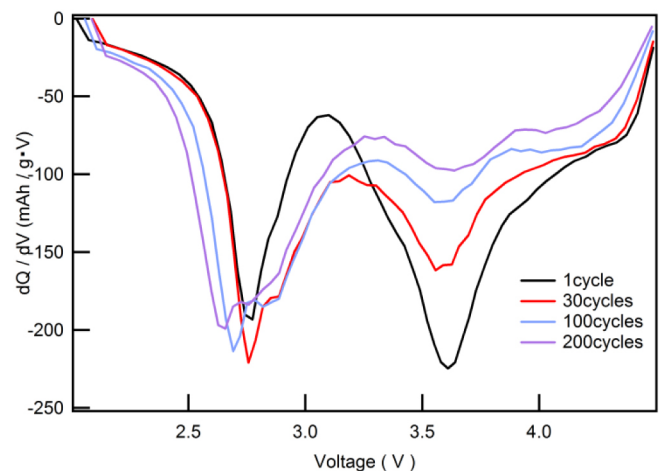


Figure 5. dQ/dV curves for cell in cycle testing with C/3 charge and C/2 discharge.

In the full cell with lithium-rich layered oxides used for the cathode, carrying out cycles not only led to capacity degradation, but also to a conspicuous lowering of discharge voltage. Since not just capacity degradation but also discharge voltage fade causes a lowering of energy density, the drop in voltage is a major issue for the use of this material. In order to analyze the capacity degradation and discharge voltage fade, a cell subjected to 200 cycles of C/3 charge and C/2 discharge was disassembled inside an argon-filled glove box, the cathode and anode were extracted, and half-cells were made with them using lithium for the respective counter electrodes. A charge and discharge rate of C/20 was implemented. Almost no change was observed in the capacity and charge and discharge curves for the anode before and after degradation.