



X-ray and thermal analysis of high-capacity iron- and nickel-containing lithium-rich layered-oxide cathode treated by carbothermal reduction

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ABSTRACT

A high-capacity iron- and nickel-substituted Li_2MnO_3 cathode [i.e., $\text{Li}_{1.26}\text{Fe}_{0.11}\text{Ni}_{0.11}\text{Mn}_{0.52}\text{O}_2$ (LFNM)] treated by carbothermal reduction was analyzed, and the results clarified that it has both high capacity and high safety levels. X-ray analysis of a reduced LFNM (R-LFNM) cathode clarified the following. Migration of transition metals in the lattice as a result of the carbothermal reduction stabilizes the layered lattice structure, which prevents lattice shrinkage during charging and enhances charge compensation. As a result, more lithium ions can return to the cathode during discharging; namely, the irreversible capacity of the cathode decreases. Thermal stability of the R-LFNM cathode was evaluated by differential scanning calorimetry (DSC), and the results show that the total heat evolved from the R-LFNM cathode remains at a lower level compared with that of other cobalt- and nickel-containing Li_2MnO_3 cathodes. An analysis of the lattice structure reveals that low exothermic heat from the charged R-LFNM cathode results from the distinctive property of its crystal lattice changing from layered to thermally stable spinel during charging.

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1. Introduction

The demand for high-capacity, compact, and lightweight (i.e., high-energy-density) batteries has grown rapidly because cutting-edge technologies (such as electric vehicles, robots, drones, and mobile terminal devices) need a lot of power. Lithium (Li)-ion batteries meet that power demand and have already been used for various applications [1,2]. However, Li-ion batteries have an inherent tendency to set off “thermal runaway” at high temperatures, and as the energy density of the battery cells becomes higher, it becomes more difficult to overcome that safety issue [3]. Accordingly, developing “safe” Li-ion battery cells with higher energy density is an urgent task.

Li-rich layered oxide [4–8] is one of the promising cathode materials for next-generation high-capacity Li-ion batteries. The

capacity of a Li-rich material that contains the transition metals nickel (Ni), cobalt (Co), and manganese (Mn) (NCM-Li-rich) exceeds 280 mAhg^{-1} , which is 1.5–2-times higher than the capacities of the cathodes of commonly used Li-ion batteries. The thermal stability of the cathode materials plays a crucial role in the safety of high-capacity Li-ion battery cells because the crystal structures of layered-oxide materials change and generate a lot of heat and oxygen at high temperatures [4,8–12].

We have studied and developed iron (Fe)-containing (Co-free) Li-rich layered-oxide cathode materials [13–26] because we anticipate their potential for higher safety and lower cost compared with NCM-Li-rich cathode materials. As we reported previously [27], we applied a so-called “LFNM” cathode material ($x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$; $M = \text{Fe}$ and Ni) to an 8-Ah-class battery cell, which achieved energy density of 270 Whg^{-1} and passed the safety tests (heating and overcharge tests). That result validated the potential of LFNM for both high capacity and high safety. We have also improved the cycle performance of a cell with LFNM cathodes

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[16,27] and clarified the deterioration mechanism [28]. The drawback of LFNM is that its capacity (up to about 250 mAhg^{-1} after a few initial charge-discharge cycles [29–38]) is less than that of state-of-the-art NCM-Li-rich materials. Generally, the total amount of heat evolved from the charged cathode at elevated temperatures increases as its capacity increases. When the heat evolved from a cathode material is evaluated and its thermal stability is compared with that of other material, it becomes clear that the capacities of the materials should be the same. Therefore, it is necessary to further improve capacity so that the thermal stability of an LFNM cathode becomes comparable with that of an NCM-Li-rich cathode. One way to improve the performance of cathode materials is to apply a process called “carbothermal reduction”. Tabuchi et al. [14,39] applied a carbothermal reduction process using sucrose to Ti- and/or Fe-substituted Li-rich cathodes, and improved their capacities and rate-capabilities. By X-ray analysis, they verified that the lattice parameters and transition metal occupancy increased, and the valence of Mn ions was reduced after the carbothermal reduction.

In this work, we analyzed an LFNM and a reduced version of LFNM (R-LFNM) cathodes treated by carbothermal reduction, and we clarified the mechanism that increases capacity and the reason for low heat evolution from them by using X-ray diffraction (XRD), hard X-ray photoemission spectroscopy (HAXPES), and differential scanning calorimetry (DSC).

2. Experiment

2.1. Sample preparation

The LFNM used was $\text{Li}_{1.26}\text{Fe}_{0.11}\text{Ni}_{0.11}\text{Mn}_{0.52}\text{O}_2$ ($0.15\text{LiFeO}_2 \cdot 0.15\text{LiNiO}_2 \cdot 0.7\text{Li}_2\text{MnO}_3$) synthesized by the co-precipitation-calcination method [27] by Tanaka Chemical Corporation. The obtained LFNM was reduced by carbothermal reduction. Instead of using sucrose for the reduction process, as described in Ref. [14], polyethylene glycol (PEG) was used in this experiment. The mixture of an aqueous solution of PEG and the powder of LFNM were dried and calcined at the temperature of 350°C in N_2 gas flow ambient for three hours. Using the reduced LFNM (R-LFNM) powder as a cathode active material, aluminum-laminated film-packed cells were assembled. Each cell was composed of a cathode, an anode, and a porous polyolefin separator containing an electrolyte. The cathode was composed of the active material, a conductive additive (Ketjen black), and polyvinylidene-difluoride (PVDF) binder at a weight ratio of 92:4:4. Lithium was used for the anode. A 1-M-concentration of LiPF_6 in a mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) (EC/DEC volume ratio of 3:7) was used for the electrolyte. For comparison references, cells with NCM111 cathode ($\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$) and NCM-Li-rich cathode ($\text{Li}_{1.26}\text{Ni}_{0.15}\text{Co}_{0.07}\text{Mn}_{0.52}\text{O}_2$: $0.2\text{LiNiO}_2 \cdot 0.1\text{LiCoO}_2 \cdot 0.7\text{Li}_2\text{MnO}_3$) were also assembled using exactly the same assembly scheme as the LFNM cells. The capacities of NCM111 and NCM-Li-rich cathodes are about 200 and 300 mAhg^{-1} , respectively. Using these high-capacity cathodes for references, the trend curve of their capacity versus evolved heat was investigated and compared with that of LFNM (and R-LFNM) cathode.

2.2. Cell evaluation

Among the assembled cells, the Li-rich cathode cells (LFNM, R-LFNM, and NCM-Li-rich cells) needed to be activated. Accordingly, they were activated by a four-step treatment consisting of constant-current (CC) and constant-voltage (CV) charge-discharge (Chg-Dis) cycles as listed in Table 1.

Table 1
4-step activation treatment of Li-rich cathode cell.

Step	Chg/Dis	CC/CV, current/voltage value, upper/lower limit
1st	Chg	CC 60 mAhg^{-1} to 4.8 V
	Dis	CC 60 mAhg^{-1} to 2.0 V
2nd	Chg	CC 30 mAhg^{-1} to 4.8 V
	Dis	CC 30 mAhg^{-1} to 2.0 V
3rd	Chg	CC 15 mAhg^{-1} to 4.8 V with (CV 4.8 V to 3.75 mAhg^{-1})
	Dis	CC 15 mAhg^{-1} to 2.0 V
4th	Chg	CC 7.5 mAhg^{-1} to 4.8 V with (CV 4.8 V to 1.875 mAhg^{-1})
	Dis	CC 7.5 mAhg^{-1} to 2.0 V

To create charged cathode samples, the activated cells were re-charged under the same condition as the fourth charging step of the activation treatment. To create highly delithiated cathodes for the thermal analysis, the activated cells were fully charged to a certain evaluation voltage (V_{full}) under the charging condition that CC (7.5 mAhg^{-1}) charges to V_{full} with CV charged to the current limit of 0.75 mAhg^{-1} . After that the cells were disassembled in inert gas ambient, the charged and discharged cathodes were retrieved.

2.3. Analysis

For the thermal analysis, the heat from the cathode materials was measured using DSC measurement equipment (Netzsch DSC3100SA). The retrieved cathodes were washed by DEC and dried in a vacuum oven, and a few milligrams of material scratched from the cathode was put in a hermetic high-pressure stainless-steel vessel with argon gas, and the evolved heat was measured at elevated temperatures using a temperature scan rate of $10^\circ\text{C}/\text{min}$. To evaluate the reaction between the charged cathode and electrolyte as many others reported [10,40–45], not only dry samples (charged cathode materials only) but also wet samples were made by adding $3 \mu\text{l}$ of electrolyte (1-M LiPF_6 EC/DEC(3/7)) to the vessel. Because gas leakage from the vessel during the DSC measurement degrades measurement quality, we measured the weight of the sample before and after each measurement and confirmed that the loss of the material weight was less than a few percent.

To clarify the mechanism by which capacity is increased by carbothermal reduction and the difference in evolved heat, the crystal structure and transition-metal-ion valence were analyzed by XRD and HAXPES, respectively. Pristine powder and the retrieved cathodes from the charged (and discharged) cells were measured by XRD (Panalytical X'Pert Pro). The obtained XRD profiles were analyzed with the Rietveld method using RIETAN-FP [46] software. The HAXPES spectra of the LFNM and R-LFNM cathodes in charged, discharged, and as-prepared states were obtained using the 7.95-keV hard X-ray beam at the BL46XU beam line of the synchrotron radiation facility SPring-8 in Hyogo, Japan. All the processes for handling the samples (i.e., retrieving cathodes from cells, transferring them to the HAXPES beam line, and setting them in the measurement chamber) were done in an inert-gas atmosphere.

3. Results

3.1. Charge and discharge properties

The charge-discharge curves of the cells with the R-LFNM (after reduction) and LFNM (before reduction) cathodes are shown in Fig. 1.

Here, the charge-discharge cycles were conducted in accordance with the activation treatment described in Table 1. The fourth-discharge capacities of the LFNM and R-LFNM cells were 234 and

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