



Capacity fading behavior of Ni-rich layered cathode materials in Li-ion full cells



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ABSTRACT

We report the failure mechanism of a Ni-rich layered cathode material ($\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$) in Li-ion full cells. Laminated pouch-type full cells were cycled 300 times, after which the cells exhibited 16.3% capacity fading. After 1, 100, 200, and 300 cycles, each full cell was disassembled and the cathode was investigated via a half-cell test, X-ray diffraction (XRD), and field emission scanning electron microscopy (FE-SEM). XRD analysis showed loss of the active lithium source in the cathode, and FE-SEM observation exhibited traces of mechanical failure in the Ni-rich secondary particles. Particle strength measurements on the cathode materials by applying compressive force demonstrated that the mechanical strength of particles significantly weakened after full-cell cycling. Thus, the capacity of the Ni-rich cathode may deteriorate during full-cell cycling because of decreases in compressive particle strength. This issue should be considered in materials preparation processes.

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1. Introduction

With the rapid development of electric vehicles and large-scale energy storage systems, the demand for rechargeable batteries has grown explosively. Although research on next-generation batteries with high-energy density, such as Li-S and Li-air systems, has recently attracted attention, Li-ion batteries (LIBs) continue to dominate the market. Therefore, the development of advanced LIBs with improved energy density has been proposed to meet the increasing energy demands. To increase the energy density of current LIBs, adoption of high-capacity electrode materials is essential. Layered lithium transition-metal oxide materials are representative cathode materials for LIBs. In the early days of LIB commercialization, LiCoO_2 was mainly used because of its moderate capacity, ease of synthesis, and good cycle performance [1]. Recently, LiCoO_2 has been replaced in part with three-component layered $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ oxides ($x + y + z = 1$) because of their lower cost and relatively high capacity [1–4]. As the Ni content of a cathode material increases, its specific capacity further increases with its material cost reduction [5]. Higher Ni contents are required for increasing the specific capacity of layered transition-metal oxide cathodes, which is needed for enhancing the energy density of lithium-ion batteries to enable the aforementioned large-scale applications.

Considering its benefits, however, large amounts of Ni in the cathode material result in structural and thermal instabilities. When Li cells are

charged to voltages higher than 4 V vs. Li^+/Li , high-Ni-containing cathode materials show a transition from a hexagonal to monoclinic phase, leading to the distortion in the layered structure [6–8]. In addition, oxygen in the material becomes unstable at elevated temperatures, causing safety concerns via the exothermic thermal runaway [9–13]. To address the aforementioned issues, several strategies have been proposed and demonstrated [2,3]. Among these strategies, the surface modification by coating with materials such as metal oxide [14–16], metal phosphate [17,18], and metal fluoride [19,20] has been mainly studied. In general, a coating can prevent undesirable reactions between the active materials and the organic electrolyte, thereby improving the structural and thermal stability of the cathode material. In relevant works, the materials and electrochemical performance of the cathode are usually evaluated in half-cell tests using a Li metal counter and reference electrode. In this case, however, sufficient Li ions are provided to the cathode materials, such that the cathode degradation observed in practical full-cell conditions cannot be evaluated. Full-cell tests can provide operating conditions similar to those found in the practical use of rechargeable batteries. Some important factors that can be evaluated in full-cell tests include active material loading level, electrode density, heat produced in a large-scale cell, mechanical degradation by electrode swelling, and supply limitation of Li to the cathode by irreversible consumption in the graphite anode. From the postmortem analysis of electrodes cycled in full cells, we can observe the actual fading behavior of batteries in various applications [21–26].

In this study, we prepared pouch-type full cells by employing commercial graphite as a negative electrode (anode) material and high-Ni layered oxide ($\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$) as a positive electrode (cathode)

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material. The capacity fading of full cells with graphite anodes can be mainly attributed to the loss of active Li ions by irreversible consumption through solid electrolyte interphase (SEI) formation/repairing on the graphite surface and physical degradation of the graphite electrode induced by volume changes during Li intercalation/deintercalation reactions [27–32]. If high-Ni oxide materials are adopted in full cells, they may also suffer capacity fading and material degradation. Here, we introduce a commercial-grade high-Ni oxide without surface coating and investigate the cause of cathode material failure during full-cell cycling through postmortem analyses.

2. Experimental

Commercial-grade graphite (BTR New Energy Materials Inc.) and high-Ni layered oxide ($\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$, NCM811, GS Energy) were used as anode and cathode materials, respectively. Anodes were prepared by coating slurries containing the active materials (graphite, 96 wt%) and a binder (styrene-butadiene rubber (SBR, Zeon)/carboxymethylcellulose (CMC, Daichi), 4 wt%) dissolved in de-ionized water onto copper foil substrates. Cathodes were also prepared by coating slurries consisting of the active material (NCM811, 95 wt%), a conducting agent (Super P®, carbon black, 2 wt%) and a binder (polyvinylidene fluoride, Kureha, 3 wt%) dissolved in *n*-methyl pyrrolidinone onto aluminum foil substrates. These electrodes were pressed and dried under vacuum for 12 h at 120 °C. The electrodes were then cut into rectangular shapes (30×40 mm) and the average mass loading for anode and cathode materials was about 9.5 and 15.3 mg cm^{-2} , respectively. Pouch-type 230 mAh cells were prepared by stacking five anodes and four cathodes. First, a single-side coated anode was placed, and double-side coated cathodes and anodes were stacked sequentially. Finally, another single-side coated anode was placed to face the cathode. Polyethylene separators (Toray, 16 μm thickness) were inserted between anode and cathode to prevent physical contact and short-circuit. The total capacity of the graphite anode was designed to be 1.07 times larger than that of the Ni-rich oxide cathode to prevent Li metal deposition on the anode surface. The full cells were sealed in an aluminum-laminated polymer film box (Dai Nippon Printing) with an electrolyte composed of 1 M LiPF_6 in ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (3:7 v/v, Panax Etec) containing 2 wt% vinylene carbonate as an additive. This additive helps the formation of a stable SEI on the anode surface and facilitates observations of cathode degradation. All cell fabrication processes were performed in a dry room. After assembly, the cells were subjected to a formation cycle by charging and discharging at a constant current. In this pre-cycle, all cells were first charged in constant current (CC) mode to 4.2 V vs. Li^+/Li at a constant current of 46 mA (0.2C, 1C rate = 230 mA) and then charged in constant voltage (CV) mode until the current reached 4.6 mA. The cells were discharged to 2.75 V vs. Li^+/Li in CC mode with a constant current of 46 mA. Each cell was subsequently cycled 1, 100, 200, and 300 times within the voltage range of 2.75–4.2 V at 1C.

For cathode analysis, the pouch-type full cells were dismantled in the fully discharged state in an Ar-filled glovebox. The electrodes were washed in pure EMC solution (Panax Etec) and dried under vacuum to eliminate the effect of surface impurities. To evaluate the specific capacity of the cycled cathode, coin-type half-cell tests (CR2032) were galvanostatically conducted in fresh electrolyte using lithium metal foil (Honjyo Chemical) as the counter/reference electrode. The cycled electrodes were cut into a 12 mm-diameter disc for the coin-cell tests. For in-situ X-ray diffraction (XRD) analysis, a special laboratory-made pouch cell consisting of an anode and a cathode was used and XRD patterns were obtained at each potential step after the first, 100th, 200th, and 300th cycle. XRD measurements were carried out on the electrode using a PANalytical Empyrean XRD system with $\text{Cu-K}\alpha$ radiation (40 kV, 30 mA). The lattice parameters were obtained by Rietveld refinement using HighScore Plus software. Inductively coupled plasma mass

spectrometry (ICP-MS, Bruker Aurora M90) was used to quantify the ratio of transition metal elements (i.e., Ni, Co, Mn) in the cathode material after cycling. Instrumental errors for the composition are typically below 1%. The morphology and microstructure of the electrodes were examined by using a field emission scanning electron microscope (FE-SEM, JEOL JSM-7000F). For cross-sectional SEM observation, the electrodes were cut using a cross-section polisher (CP, JEOL SM-09010). After washing in pure EMC solution in an Ar-filled glovebox, the cycled electrodes were protected from air using a tightly sealed polyvinyl bag during transfer to the polisher and SEM chamber. To evaluate particle strength, the compression strength of the particle was measured by a micro-compression tester (Shimadzu MCT-W500). For in-situ internal pressure monitoring, cells consisting of an electrode charged to 4.3 V vs. Li^+/Li and fresh electrolyte (10 μL) were heated up to 95 °C for 3 h and then stored at a constant temperature for an additional 9 h in an oven. The internal pressure of the cell was then recorded by a pressure sensor (GE).

3. Results and discussion

Fig. 1a shows the voltage profiles of the pouch full cells measured at a rate of 0.2 C. The full cells were first cycled 1, 100, 200, and 300 times at 1 C, respectively and the profiles were then obtained at the very next cycle at 0.2 C. It was confirmed that the cell capacity at the first cycle was about 230 mA. The profiles obtained are typical of graphite/NCM811 full cells, and the average voltage for discharge was about 3.6 V [33]. As the cycle number increased, a slight increase in polarization, which could be attributed to an increase in internal resistance, was observed. The cycling performance of the full cell at 1 C shows gradual capacity fading (Fig. 1b). After 100, 200, and 300 cycles, the capacity retention ratios were about 89.9%, 86.1%, and 83.7%, respectively. In the early stages of cycling, capacity fading occurred first rapidly and then more gradually. Capacity fading in full cells with graphite anodes can be mainly ascribed to the loss of active Li ions in the graphite electrode. As cycling is performed, Li ions are irreversibly consumed on the graphite surface by SEI formation and repair, and the physical degradation of graphite occurs by volume changes through Li intercalation and deintercalation processes [27–32]. Although deterioration of the graphite electrodes largely affects full cells, the cathode also exhibits degradations in terms of both material and capacity. In particular, layered oxides with high Ni contents require further investigation when they are employed in full cells [21,22,34,35].

Fig. 1c shows the voltage profiles of NCM811 electrodes tested with a Li metal counter/reference electrode in the half cells. The half cells were galvanostatically tested at 0.2 C after disassembly of the full cells that had been cycled 1, 100, 200, and 300 times. Similar to the full cell profiles, the shapes obtained in the figure are typical of high-Ni layered oxide electrodes, and increased polarization was observed with increasing cycle numbers. The specific discharge capacities of the cathodes measured in half-cells after full-cell cycling are displayed in Fig. 1d. After the first cycle, the electrode exhibited a discharge capacity of 208.4 mAh g^{-1} , and the capacity retention ratios of electrodes cycled 100, 200, and 300 times in full cells were about 96.8%, 94.8%, and 93.0%, respectively. The capacity retention ratios of the cathode were higher than those of the full cells; however, the Ni-rich cathodes also showed considerable capacity fading even at half-cell test conditions, where the fresh Li counter electrode provides sufficient Li ions. Thus, to examine the cause of cathode degradation, several analytical methods were applied.

In-situ XRD measurement was performed to achieve detailed investigations on the structural changes of the cathode materials during cycling. Fig. 2a shows the in-situ XRD patterns obtained from the laboratory-made cells after 1, 100, 200, and 300 full-cell cycles. The crystal structure of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ is indexed to a hexagonal α - NaFeO_2 type structure, with a space group $R\bar{3}m$. This material has several

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