Structural evolution and capacity degradation mechanism of $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ cathode materials

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HIGHLIGHTS

- The capacity degradation of NMC 622 depends on the charge cut-off voltage.
- Surface structural transition leads to degradation at 4.5 V or below.
- Particle cracking accompanied with phase changes causes degradation at 4.8 V.
- An insulating surface film also contributes to the capacity degradation at 4.8 V.

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ABSTRACT

$LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ is a promising cathode material with a high capacity for Li-ion batteries. However, the rapid capacity degradation in the high-voltage cycles constrain their further applications. Accordingly, the performances of $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ have been systematically investigated using various microstructural characterizations as well as electrochemical analyses to explore its degradation mechanism. Our results indicate that the capacity decay of $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ strongly depends on the charge cut-off voltage. For the cell that is cycled at 4.2 or 4.5 V, the degradation mechanism is primarily due to transformation from layered to rock salt structure on the particle surface, increasing the charge transfer impedance. For the cell that is cycled at 4.8 V, another two reasons should be considered. The irreversible structural change in the bulk lattice of $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ during the high-degree delithiation process eventually disintegrates the secondary particles, resulting in the poor electrical contact between particles. Another one is that the insulating surface film which is generated on the surface of particles after cycling at 4.8 V increases the interfacial impedance of $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$. All these factors contribute to the overall capacity degradation at high voltages.

1. Introduction

High-energy density and high-power density lithium-ion batteries (LIBs) are basic necessities for extensive applications of consumer electronics and electric vehicles [1–3]. In order to meet the rapid development of the energy-demanding devices, more efforts have been made to develop electrode materials with large specific capacities at high voltages [4–6]. Compared with cathode materials of olivine- (ca. 170 mAh g^{-1}) and spinel-structured (ca. 150 mAh g^{-1}) materials, the layered cathode material of $LiNi_xMn_yCo_zO_2$ (NMC, $x + y + z = 1$) has a larger theoretical specific capacity of 280 mAh g^{-1} [7,8]. The NMC-

based materials are essentially a solid solution of $LiNiO_2$, $LiMnO_2$, and $LiCoO_2$, where nickel (Ni) provides high capacity, cobalt (Co) improves the rate capability, and manganese (Mn) increases the structural stability [9]. Ni-rich NMC compounds ($x \geq 0.5$ in $LiNi_xMn_yCo_zO_2$), such as $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC 532), $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NMC 622), and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NMC 811) are promising cathode materials, given that an extra capacity can be attained by charging the cells to a high voltage (≥ 4.5 V vs. Li/Li$^+$) [10]. However, the intrinsic thermal instability of the Ni-rich NMC materials during the delithiation process as well as their structural instability when Ni^{4+} is reduced to Ni^{2+} always decreases their capacity [11]. Many efforts have been devoted to

controlling the capacity degradation of Ni-rich compounds by modifying the preparation method [10,12,13]. A comprehensive understanding on the degradation mechanism would be fundamentally conducive to the improvement of the electrochemical performances of those Ni-rich NMC materials.

So far, several degradation mechanisms regarding the unstable structure of Ni-rich materials have been identified. Cation migration is the first reason that decreases the capacity of the Ni-rich NMC cathode. During the charging process, Li^+ is extracted from the layered structure of NMC and transitional metal (TM) ions, especially Ni^{2+} (0.069 nm) with a size close to Li^+ (0.076 nm) will migrate to the lithium layer and occupy the vacant Li^+ sites. Such a cation migration gives rise to an irreversible phase transformation of the Ni-rich NMC from a layered structure to a spinel structure or rock-salt structure, thus leading to the capacity degradation [6,14,15]. On the other hand, the migration of TM ions at the particle surface might facilitate their dissolution into the electrolyte, which has been reported for other NMC materials in the literature [8,16,17]. Formation of an undesirable surface film is the second reason that degrades cathode materials. Under high charge voltage serious oxidative decomposition of the traditional $LiPF_6$/carbonate electrolyte can generally occur [10,18]. The accumulation of side products generated from the decomposition lead to continuous growth of the surface film on the Ni-rich NMC particles, resulting in poor cycling performance and a low coulombic efficiency of the LIBs [19]. Moreover, after the full charge, Ni^{4+} in NMC is unstable and can be readily reduced to Ni^{2+}, forming an insulating NiO on the surface of NMC due to the loss of oxygen [20]. These undesirable surface films increase the impedance and deteriorate the electrochemical performance of NMC. Mechanical stress is the third reason that decreases the capacity of NMC. The solid-state diffusion and transport of Li ions induces mechanical stresses and volume changes in electrode particles during the charge and discharge process [21], which may cause particle cracking and disintegration [22]. As a result, the previously formed cathode electrolyte interphase (CEI) will be disrupted and then be rebuilt by consuming active lithium from the electrolyte. Any loss of active lithium would enhance the layered oxides degradation [23]. All the above reasons contributing to the capacity degradation of NMC usually interact and mutually aggravate, which make the studies intractable [24].

In addition, the aforementioned reasons are very sensitive to the composition of the electrode material and strongly depend on the cycling and storage conditions of the batteries [25]. Therefore, each LIB system shows its unique fatigue features which is too complex to be comprehensively predicted by any model, and thus needs to be investigated separately [26]. For instance, the degradation mechanism involved in the NMC532 material has been systematically studied and found to be different from that of the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NMC111) material [8,20,26], indicating that the degradation mechanisms of NMC may vary with different contents of Ni, Co and Mn. In the Ni-rich NMC materials, NMC622 is a promising material which possesses not only the high capacity, close to that of NMC811, but also the good thermal stability comparable to NMC532. However, compared with other commercialized NMC materials, investigations on the degradation mechanism of NMC622 are relatively rare [11,15]. Particularly, the origin of the accelerated degradation of cycle performance and a change of the critical fade mechanism with the cut-off voltage still need to be further investigated.

In this work, the degradation mechanism of NMC 622 after a long time cycling is systematically investigated by analyzing structural changes of NMC 622 at different cut-off voltages. Various micro-structural analyses such as SEM、TEM、STEM and EELS are applied to elucidate the structural changes on the surface of the cathode material. XRD、TG-DSC and electrochemical techniques are used to evaluate changes in the bulk sample, which are related to the evolution of Ni^{2+}/Ni^{3+}/Ni^{4+}. It is expected that a solid understanding on the degradation mechanisms can be definitely shed light on the performance improvement for the NMC622 material.

2. Experimental

2.1. Material and electrode preparation

Spherical, micron-sized $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622) active material without any surface modification was obtained from Umicore and stored in an argon-filled glove box before use. The cathode was prepared by 92.8 wt% NMC622, 3.2 wt% carbon-black (Denka Black) and 4 wt% polyvinylidene fluoride binder (PVDF, Aldrich) binder. All the powders were mixed in N-methyl-2-pyrrolidone (NMP, 99.5%, Aldrich) using a homogenizer at 3000 rpm (Polytron PT 10–35) to form a uniform slurry. The slurry was then cast onto a Al-foil with a doctor-blade to form the cathode. After that, the cathode was dried in an antechamber to a glovebox under vacuum at 130 °C for 12 h. The loading density of the active material in cathode is about 5 mg/cm². Porosity of the electrode is about 40%.

2.2. Characterization

The structure of the NMC622 samples were examined by powder X-ray diffraction (XRD; Bruker, Germany) using Cu Kα radiation (λ = 0.154 nm) at a scanning speed of 1° min⁻¹ in the 2θ range of 10–70°. The thermal analysis for the charged cathode at different depth of charge was carried out using a TG-SDT by Q600 instruments (USA) from room temperature to 600 °C with a heating rate of 5 °C/min. The particle morphology and element distribution of the cathode material were analyzed by scanning electron microscopy (SEM; Philips XL30ESEM) and energy dispersive spectroscopy (EDS). High resolution HRTEM/STEM imaging analyses and electron energy loss spectroscopy (EELS) were carried out using a probe Cs corrected JEM-2100 F at 200 kV. EELS spectra were obtained from the outermost surface region (2 nm) with an acquisition time of 2 s. The energy resolution in EELS was about 0.9 eV, which was sufficient to investigate the fine edge structures of the O K-edge and the TM (Ni, Mn, and Co) L-edges.

2.3. Electrochemical performance characterization

The electrochemical tests were performed using 2325 coin-type cells, which were composed of NMC622 cathode, lithium metal anode, Celgard 2400 separator, and standard electrolyte of 1 M $LiPF_6$ dissolved in ethylene carbonate (EC) and diethyl carbonate (DEC) solvent (1:2 mass ratio, Daikin Industries, America). Galvanostatic charge-discharge cycling tests for LIBs using the NMC622 cathode were conducted on a Maccor (series 4000) multichannel battery test system in different voltage ranges of 2.8–4.2 V, 2.8–4.5 V, and 2.8–4.8 V. The LIBs receive the nomination according to the depth of charge during cycling, which 4.2 V-cell, 4.5 V-cell, and 4.8 V-cell represents the LIB to be cycled under the cut-off charge voltage of 4.2 V, 4.5 V and 4.8 V, respectively. The current for all the cells on charge and discharge was set at 0.1C. (1C = 160 mA g⁻¹). After the cycling test, the cells were transferred back into the glovebox and disassembled for the ex-situ analyses. The cathodes were washed with DMC solvent for several times to remove the residual electrolyte thoroughly, and then dried under vacuum.

Cyclic voltammetry (CV) tests were carried out on a Bio-Logic SA electrochemical workstation within a potential range of 2.8–4.9 V. Electrochemical impedance spectroscopy measurements were carried out using a Bio-Logic VMP3 electrochemical workstation. After all the test cells were discharged to 3.73 V and maintained at this voltage for 2 h, the impedance of the three cells were collected in the frequency range of 200 kHz to 0.01 mHz.