Degradation mechanism of LiMn$_2$O$_4$ cathode at high charge cut-off voltages

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Abstract: Degradation mechanism of LiMn$_2$O$_4$ cathode at high cut-off voltage of 4.8V has been investigated. Electrochemical tests of the cathode show that the rapid capacity loss due to the oxidation of electrolyte and the generation of oxygen species under high voltage operation leads to the increase of electrode resistance. In addition, a thick layer is found on the cathode surface from scanning electron microscope. The thickness of the layer increases with the increment of charge potentials.

1. Introduction

To meet the increasing demand from small electronics products to transportation means, the application of the rechargeable lithium ion batteries (LIBs) has become an overwhelming trend in the power battery technology and market [1]. LiMn$_2$O$_4$, which has already applied in commercial markets, is regarded as one of the most promising materials to take the place of the tradition cathode material of LIBS. However, this material suffers from poor capacity retention and serious capacity degradation, which is especially aggravated at elevated temperatures [2].

Besides, there are still many other factors contributing to the capacity fade such as upper cutoff voltage (UCV), different states of charge (SOC) and C-rates operation [3-4]. Modern LIBS are often desired to operate at wide electrochemical windows initially by charging to higher voltage for higher capacity. However, this operation will post grand challenges in the field of materials research, as issues with faster decrease of capacity, the expense of electrolyte stability resulting in the decomposition reaction of electrolyte.

Here, we investigate the degradation mechanisms of LiMn$_2$O$_4$ at a charge cut-off voltage of 4.8 V. Besides, the interfacial changes after the high voltage operations are studied through the analysis of surface morphology.

2. Experiment

The standard LiMn$_2$O$_4$ slurry was prepared by mixing 80 wt.% LiMn$_2$O$_4$ powder, 10 wt.% acetylene black, and 10 wt.% polyvinylidene difluoride (PVDF) binder in N-methyl pyrrolidone (NMP) solvent. The as-prepared slurry was then pasted on a Al foil. The coin cells were assembled in an Ar-filled glovebox with Li foil as the counter electrodes. A Celgard 2400 separator and 1 M LiPF$_6$ electrolyte...
solutions in ethylene carbonate (EC) and ethyl-methyl carbonate (EMC, 1:1 in volume) were used to fabricate the cells. After assembly, the electrochemical cells were stored at room temperature for a period of time to ensure the infiltration of the electrodes and separators with the electrolyte solution completely.

Cycling tests were conducted galvanostatically on a battery test system (LAND CT-2001A instrument, Wuhan, China) at C/2 in the range of 3.5-4.3 V and 3.5-4.8 V at room temperature. Three formation cycles were performed at 0.1 C in order to form intact interface films. Electrochemical impedance spectroscopy measurements were carried out on the electrochemical workstation with the frequency from 0.01 Hz to 100 kHz.

After testing, the cycle-aged cells were disassembled in an Ar glove box and the obtained LiMn$_2$O$_4$ electrodes were then rinsed with dimethyl carbonate (DMC) thoroughly. SEM measurement with high resolution was utilized to observe the morphology of the positive electrode material.

3. Results and discussion

![Figure 1](image1.png)

**Figure 1** Voltage profiles of LiMn$_2$O$_4$ after three cycles.

The trend of charge-discharge process of LiMn$_2$O$_4$ at 4.3 V and 4.8 V are shown in Figure 1. The as-prepared samples exhibit the discharge capacities of 107.1 mAh/g and 113.2 mAh/g, respectively. Obviously, the capacity of the samples increase with the increasing charge potentials due to more available Li$^+$ extracted from cathode material. Spinel electrodes represent two obvious platforms at 3.9-4.1 V which can be attributed to the redox reaction of Mn ions caused by the migration of Li-ions [5]. It should be noted that an additional small platform at around 4.6 V in blue circle can be observed when cells charging to 4.8 V. This may be due to the presence of manganese in the tetrahedral sites [6].

Figure 2 shows the cycling stability of cells at two cut-off voltages after 60 cycles. Obviously, the capacity of cell cycled at 4.8 V is higher than that of at 4.3 V in the initial cycles and keep a high discharge capacity in the subsequent charge-discharge process. This may be ascribed to the driving-force come from high voltage operation. However, the cell shows a serious fluctuation of capacity as well as the poor capacity retention of 55.8 % at 4.8 V compared with that of 77.3 % at 4.3 V. This may be attributed to the decomposition of electrolyte and oxygen loss from crystal surface to balance the charge [7] during each charging process to 4.8 V.

![Figure 2](image2.png)

**Figure 2** Cycling performance at 0.2 C in the voltage ranges of 3.5-4.3 V and 3.5-4.8 V.
The initial impedance in charge state of two voltage configurations are presented in Figure 3. The Nyquist Plot trends are similar which all consisted of the semicircles in the high and medium frequency and a low-frequency tail. The first semicircle reflects the migration of Li$^+$ through the CEI film, while the medium-frequency semicircle is $R_{ct}$ which is related to the charge-transfer resistance at the electrode /electrolyte interface, and the low-frequency tail represents the Li$^+$ diffusion process in the solid phase of the electrode, which indicates Warburg impedance in the equivalent circuit diagram. While constant phase element CPE is used to instead of the double-layer capacitance (Cdl) to consider the surface roughness of the particle. Generally, this graph depicts the large impedance value of 4.8 V whether $R_{CEI}$ or $R_{ct}$.

The high-resolution SEM images of LiMn$_2$O$_4$ electrodes harvested from cycled cells are shown in Figure 4. Figure 4a shows the pristine spinel structure of LiMn$_2$O$_4$ with clean surface. However, when cell is charged to 4.3 V, the surface is covered by thick layer and the shapes of particles become blurry. More seriously, when cell is cycled at 4.8 V (shown as Figure 4c), the thickness of surface layer grow rapidly with more oxidation products originated from interface reaction depositing on the particle surface [8]. In addition, the generation of oxide makes the layer loose and porous, which hinder the transportation of Li$^+$ and increase the electrode impedance resulting in a poor electrochemical performance of LiMn$_2$O$_4$ cathodes.

4. Conclusions
In this paper, we investigate the surface degradation mechanism of LiMn$_2$O$_4$ on the high-voltage cycling. The primary reason behind the rapid capacity fade at high voltage is the growth of surface layer in the cathode /electrolyte interphase. When cell was charged to high voltage, the decomposition of electrolyte will be accelerated with more byproducts depositing on the particles surface which eventually leads to an increased impedance and more barriers for Li$^+$ diffusion. Therefore, LiMn$_2$O$_4$ significantly exhibits faster capacity degradation during cycling at a cut-off of 4.8 V.

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Corrigendum: Degradation mechanism of LiMn$_2$O$_4$ cathode at high charge cut-off voltages

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Page 2: Figure:

![Figure 1 Voltage profiles of LiMn$_2$O$_4$ after three cycles.](image)

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