



# Study on compositions and changes of SEI film of $\text{Li}_2\text{MnO}_3$ positive material during the cycles



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## ABSTRACT

In this article, we investigated the surface series of  $\text{Li}_2\text{MnO}_3$  electrodes and the composition variation of the SEI film. XPS and FT-IR analysis indicated the compositions of a primary SEI film, containing about 20 at.% LiF, varied upon cycling including the dissolution of LiF and the accumulation of  $\text{Li}_x\text{PO}_y\text{F}_z$  and organic species, accompanied by surface corrosion. Whereas organic species showed minor change by the static corrosion. The unstable passive film caused high impedance and could not restrain the electrolyte corrosion in both dynamic and static process.

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## 1. Introduction

In recent years, rapid development of electric vehicle (EV) and hybrid electric vehicle (HEV) demands higher energy density and power density in the lithium-ion battery. Compared with traditional oxide cathode, such as layered  $\text{LiMO}_2$  species ( $M = \text{Ni}$ ,  $\text{Co}$  and  $\text{Mn}$ ) and spinel  $\text{LiMn}_2\text{O}_4$ , lithium-rich manganese-based materials (LLO) have so far demonstrated the highest capacity and  $>4.5\text{ V}$  operating voltage with low raw cost [1–4]. Monoclinic layered  $\text{Li}_2\text{MnO}_3$ , which provides over 50% capacity of the LLO cathode at above 4.5 V, plays a critical role in the lithium-rich materials [4–7]. Analyzing its electrochemical reaction is beneficial for understanding and designing the lithium-rich materials.

Plenty of the literature works concentrate on the investigations of reaction mechanisms, voltage fade and cycle performance improvement, especially by doping and surface treatment in the bulk LLO and  $\text{Li}_2\text{MnO}_3$  [8–12]. Due to high cut-off voltage and  $\text{O}_2$  release at above 4.5 V, serious electrode/electrolyte side reaction is the issue for the capacity fade, which has been rarely reported. The extracted intermediate oxygen species steadily oxidize the carbonate-based organic solvents and form passivation film on the

cathode [4,13]. Thus electrode/electrolyte interface is critical for capacity fade. Oxygen Direct contact with carbonate solvents and repeated cycling give rise to the insulating byproducts especially LiF, causing bad electrolyte/electrodes interface [13]. Li et al. have reported that the presence of a cathode surface film which compose of poly (ethylene carbonate),  $\text{Li}_2\text{CO}_3$ , and other electrolyte decomposition products. The increasing impedance of the cathode originated from thicker cathode surface film might give rise to poor capacity retention upon cycling [14]. Li et al. revealed that under the situation of long storage at  $80^\circ\text{C}$ , the degradation mechanism of cycling stability was assumed to be the accumulation of surface species like  $\text{LiF}/\text{Li}_x\text{PF}_y\text{O}_z$  initiated by the strong reactions between  $\text{LiPF}_6$  electrolyte and electrode; whereas room temperature storage hardly influenced the electrochemical performance, barely altering surface kinetics [15]. Although, there have been investigations directed at exploring the composition the compositions of the SEI film and its' effect on the electrochemical performance, the stability of passivation film and its' protection to the surface structure, especially in  $\text{Li}_2\text{MnO}_3$  cathode have not been well studied.

Herein, for the first time, we explore the dynamic and thermodynamic variation of SEI film compositions in  $\text{Li}_2\text{MnO}_3$  electrodes in order to analyze its effect on  $\text{Li}_2\text{MnO}_3$  bulk surface and capacity degradation. Ex-situ surface analysis of electrodes extracted from cells has been conducted to better understand the reactions of the electrolyte and the variation of surface species.

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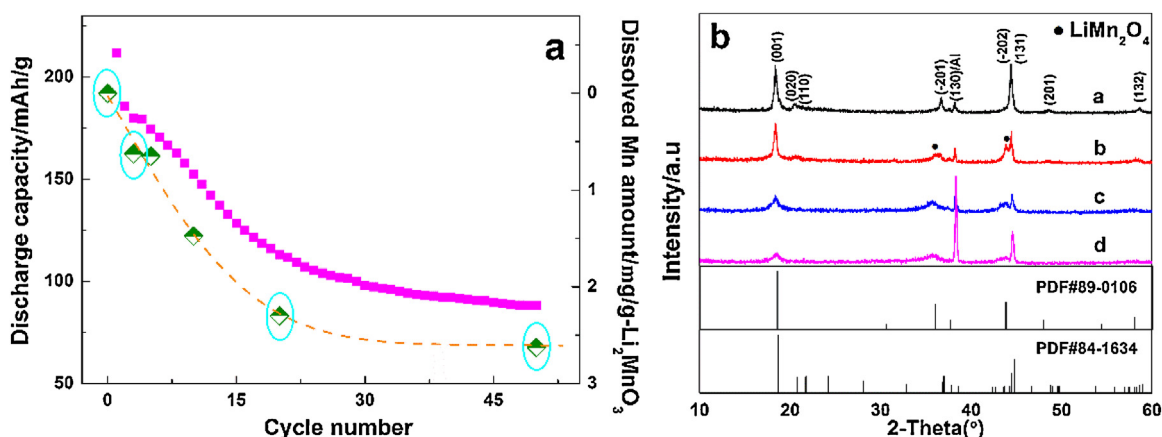


Fig. 1. The cycle performance and dissolved Mn amount in the electrolyte (a) and the XRD patterns of  $S_0$ – $S_{50}$  (b), a for  $S_0$ , b for  $S_3$ , c for  $S_{20}$  and d for  $S_{50}$ .

## 2. Experimental section

### 2.1. The synthesis of $Li_2MnO_3$ powders

The sample for studying the formation of the SEI film was synthesized by a hydrothermal method described in our previous report [16]. 3 mmol  $MnSO_4$  and 3 mmol  $(NH_4)_2S_2O_8$  were dissolved by 10 ml deionized water in Teflon liner. After the dissolution, 20 ml, 3 M LiOH solution was trickled into the solution and stirred for 30 min for the mixture. The Teflon liner was transferred to an autoclave and maintained at 180 °C for 24 h. The as-prepared powders were filtered, washed and dried at 80 °C for 24 h.

### 2.2. Electrochemical cycles

Cells with  $Li_2MnO_3$  as the cathode material were cycling for studying formation of the SEI film.  $Li_2MnO_3$  cathode was prepared by mixing the active material, super P carbon black and a polyvinylidene fluoride binder with a weight ratio of 8:1:1. The coin-type battery cell which contained a cathode, a Li metal

anode and a microporous polyethylene separator, was prepared in a nitrogen-filled glove-box. The electrochemical measurements were performed with the button type cell using the electrolyte of 1.2 M  $LiPF_6$  with ethyl methyl carbonate/ethylene carbonate (7:3 vol.%). The coin-type cells were conducted at a constant current density of 100 mA/g by Land battery test system. After cycling determined times,  $Li_2MnO_3$  electrodes were extracted from cells, washed by DMC for several times and dried in an Argon-filled glove-box. The samples were referred as  $S_0$ ,  $S_1$ ,  $S_3$ ,  $S_5$ ,  $S_{10}$ ,  $S_{20}$  and  $S_{50}$ , in which x in  $S_x$  present the cycle number and  $S_0$  the fresh electrode as well as.

For analyzing the stability of SEI formed in electrochemical cycle, the cells after the 3 cycles were stored at 25 °C for 30 days.  $Li_2MnO_3$  cathode was extracted from the cell and washed by DMC for several times in a nitrogen-filled glove-box. The obtained sample was referred as  $S_3'$ .

### 2.3. Electrochemical measurement

The electrochemical impedance of the coin-type cells after cycling in determined times was performed with electrochemical impedance spectroscopy (EIS) measurements (VMP3) in the frequency range  $10^6$ – $10^{-2}$  Hz.

### 2.4. Physical analysis

X-ray diffraction measurements were taken with a Rigaku D/max-2600PC with a Cu target  $K\alpha$  radiation ( $\lambda = 0.15406$  nm). The surface morphologies were probed by field scanning electron microscopy (S-4800) and transmission electron microscope (JEM-2100F). FT-IR spectra (Nicolet 6700) were conducted to analyze the chemical group of  $Li_2MnO_3$  samples. X-ray photoelectron spectra (ESCALAB250Xi) were used for investigation of the surface series.

### 2.5. Chemical analysis

The cycled cells were disassembled and immersed in the beakers filled with acetone. After the acetone volatilized at room temperature, the beakers were filled with nitric acid and held at 50 °C for 0.5 h. Mn amount of the obtained solution was determined by the atomic absorption spectroscopy (Shimadzu AA6880).

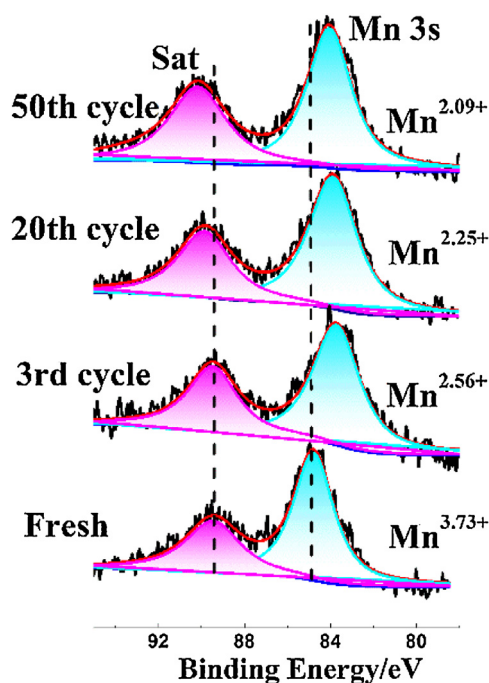


Fig. 2. Mn 3s XPS regions of the  $Li_2MnO_3$  electrodes.

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