



# Lithium carbonate as an electrolyte additive for enhancing the high-temperature performance of lithium manganese oxide spinel cathode



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## ABSTRACT

The effect of lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) as an additive on the stability of the electrolyte and cycling performance of lithium manganese oxide spinel ( $\text{LiMn}_2\text{O}_4$ ) batteries at elevated temperature was studied. The addition of  $\text{Li}_2\text{CO}_3$  to the electrolyte can suppress the capacity fading of  $\text{LiMn}_2\text{O}_4$  batteries. The linear sweep voltammetry (LSV) and the cyclic voltammetry (CV) indicate that  $\text{Li}_2\text{CO}_3$  has a lower oxidation potential in the mixed solvents of ethylene carbonate (EC), diethyl carbonate (DEC) and ethyl methyl carbonate (EMC), participating in the formation process of the stable cathode electrolyte interface (CEI) film. In addition, the results of electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) demonstrate that the stable CEI film of the cells with  $\text{Li}_2\text{CO}_3$  can be formed, which can effectively reduce the dissolution of  $\text{Mn}^{2+}$  from  $\text{LiMn}_2\text{O}_4$  into the electrolyte at elevated temperature. It is concluded that the addition of  $\text{Li}_2\text{CO}_3$  to a solution of 1 M  $\text{LiPF}_6$ -EC/EMC/DEC = 1/1/1 (weight ratio) may decrease solvent decomposition and change the structure of the passivation film on the  $\text{LiMn}_2\text{O}_4$  cathode.

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## 1. Introduction

Spinel  $\text{LiMn}_2\text{O}_4$  has been demonstrated to be the most promising cathode material for lithium-ion batteries because  $\text{LiMn}_2\text{O}_4$  is inexpensive, less toxic, and easier to prepare than alternative materials [1–4]. However, a significant weakness of  $\text{LiMn}_2\text{O}_4$  is that the dissolution of  $\text{Mn}^{2+}$  ions from the cathodes and the deposition metallic of Mn on the surface of the anodes are responsible for the fast capacity fading of the cells, particularly at elevated temperatures [5–8], which is originated from the disproportionation reaction [ $2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$ ] induced by the hydrofluoric acid (HF) attacking [9,10]. Accordingly, one of the ways is taken in the investigation to change of electrolyte with low HF content instead of  $\text{LiPF}_6$ , reduced surface area of the electrode material.

Appropriate solid electrolyte interphase (SEI) films are known to stabilize the anode and enhance its cycling properties by preventing the electrolyte decomposition reactions and hence avoiding intercalation of solvent molecules [7,8,11–13].  $\text{Li}_2\text{CO}_3$  is

one of the stable components forming the SEI on graphitic anode materials in lithium-ion batteries, which can result from ethylene carbonate (EC) decomposition or other additives to the electrolyte [14–18]. The generally accepted picture of the electrochemically formed SEI is a mixture of organic materials [e.g.,  $(\text{CH}_2\text{OCO}_2\text{Li})_2$  and ROLi (R is an organic group that depends on the solvent)] in an outer layer near the SEI/electrolyte interface and inorganic materials (e.g.,  $\text{Li}_2\text{CO}_3$ , LiF and  $\text{Li}_2\text{O}$ ) in an inner layer near the SEI/electrode interface [13,19–21].

Chrétien et al. [22] showed that the influence of the salt addition for  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  (NMC) is more sensitive than that for the graphite material. Tasaki and Harris [23] found that lithium salts were present in the SEI when graphite and NMC were used as electrodes with  $\text{LiPF}_6$  1 M in EC/PC/DMC = 1/1/3 (weight ratio) as electrolyte. Wu et al. [24] suggested that Li transport through an SEI film on a cathode material could be dramatically different from Li transport through an SEI film on an anode material. Shi et al. [25] studied by the DFT calculation that an electrolyte ( $\text{LiPF}_6$ -EC/PC/DEC) containing a lithium carbonate additive was used to enable the high cycling stability of a lithium cobalt oxide ( $\text{LiCoO}_2$ ) cathode which was charged to 4.5 V for a higher capacity.

In this paper, we investigate that the addition of  $\text{Li}_2\text{CO}_3$  as a stability additive to the electrolyte can inhibit the dissolution

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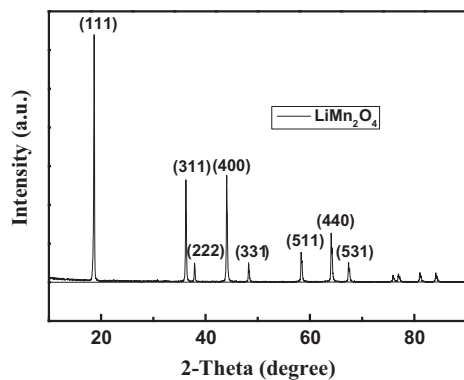


Fig. 1. XRD pattern of the fresh  $\text{LiMn}_2\text{O}_4$ .

mechanism of Mn. What is more, we find a stable SEI film of  $\text{LiMn}_2\text{O}_4$  cathode was formed and the forming-film can prevent the dissolution of  $\text{Mn}^{2+}$  from  $\text{LiMn}_2\text{O}_4$  into the electrolyte.

## 2. Experimental

### 2.1. Preparation of the cells

The electrolytes of 1 M  $\text{LiPF}_6$  in a 1:1:1 (weight ratio) EC/EMC/DEC without and with 0.2 wt.%  $\text{Li}_2\text{CO}_3$  additive were provided by Jiangxi Youli New Materials Co. Ltd. The electrolytes were prepared in an argon-filled glove box, in which the oxygen and water content were less than 1 ppm.

The spinel  $\text{LiMn}_2\text{O}_4$  was purchased from Hunan Shanshan Toda Advanced materials Co. Ltd., China. Chemical composition of major element from the commercial sample is 4.14% of Li and 58.40% of Mn by weight through ICP analysis. XRD of the commercial sample was shown in Fig. 1. The cathodes were prepared by mixing the  $\text{LiMn}_2\text{O}_4$  powder (80 wt.%), poly(vinylidene fluoride) (PVDF, 10 wt.%) and acetylene black (AB, 10 wt.%). After blended in N-methyl pyrrolidone (NMP), the mixed slurry was spread uniformly on a thin aluminum foil and dried at 120 °C in vacuum for 12 h. The electrode disks in the form of 14 mm diameter were then punched out of the coated foil sheets and weighted.  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells were fabricated with 2025-coin type cells in the argon-filled glove box using Celgard 2400 as the separator. The counter and reference electrodes were lithium foils.

### 2.2. Measurements

The water and free acid (HF) content in the electrolyte were analyzed by Karl Fischer 831 Coulometer (Metrohm) and Karl Fischer 798 GPT Titrimo (Metrohm), respectively. The water content of select electrolytes was lower than 20 ppm, and the free acid was controlled to be less than 50 ppm.

Galvanostatic charge-discharge experiments of the cells at high temperature (55 °C) was tested on Neware tester (Shenzhen, China) over the range of 4.35–3.0 V vs.  $\text{Li}/\text{Li}^+$ . The cells were cycled at 0.1 C three cycles firstly, and then turned to 0.5 C for cycling performance test.

The electrochemical window of the electrolyte was examined by linear sweep voltammetry (LSV) using an Instrumental Electrochemical Workstation (CHI604E, Chenhua, Shanghai) on a Pt working electrode with lithium as both counter and reference electrodes. The Pt electrode was made directly by sealing a Pt wire (100 mm diameter) in a glass tube. CHI604E was also used to carry out the cyclic voltammetry (CV) measurements in a three-electrode cell, with  $\text{LiMn}_2\text{O}_4$  as the working electrode and lithium foil as both counter and reference electrode at the scanning rate of  $0.1 \text{ mV s}^{-1}$ . The load of active material was  $1.29 \text{ mg cm}^{-2}$  in the working electrode.

Electrochemical impedance spectroscopy (EIS) of the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells were performed under discharged to 3.0 V status, and the initial potential was the open circuit voltage (OCV) of the cell. A sinusoidal amplitude modulation was used over the frequency range from  $10^{-2}$  Hz to  $10^5$  Hz, and the perturbation amplitude was 5 mV.

The  $\text{LiMn}_2\text{O}_4$  electrodes which were from the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells cycled at 55 °C and fresh cells were soaked in and rinsed with pure DMC to remove the residual electrolyte. Then the washed electrodes were dried in a vacuum drier at 60 °C for 6 h. The morphologies of the  $\text{LiMn}_2\text{O}_4$  electrodes were visualized by scanning electron microscopy (SEM, JEOL, JSM-5600LV) with an accelerating voltage of 20 kV. Transmission electron microscopy (TEM, Tecnai G12, 200 kV) was used to characterize the surface morphology of the  $\text{LiMn}_2\text{O}_4$  cathode. The contents of commercial  $\text{LiMn}_2\text{O}_4$  were determined by inductively coupled plasma-atomic emission spec-

trometry (ICP-AES, IRIS intrepid XSP, Thermo Electron Corporation). The phase structure of  $\text{LiMn}_2\text{O}_4$  electrodes was analyzed by X-ray diffraction (XRD, Rint-2000, Rigaku) using  $\text{Cu K}\alpha$  radiation.

## 3. Results and discussion

### 3.1. LSV of Pt electrode and $\text{LiMn}_2\text{O}_4$ electrode in different electrolytes

Figs. 2 and 3 show LSV curves of Pt electrode and  $\text{LiMn}_2\text{O}_4$  electrode using 1 M  $\text{LiPF}_6$  in EC/DEC/EMC (1:1:1, weight ratio) without and with  $\text{Li}_2\text{CO}_3$ . It can be observed from Fig. 2 that the reference electrolyte without  $\text{Li}_2\text{CO}_3$  is decomposed at 5.5 V, while the electrolyte with 0.2 wt.%  $\text{Li}_2\text{CO}_3$  is oxidized at 5.1 V. As expected,  $\text{Li}_2\text{CO}_3$  has lower oxidation potential than those of solvents, which indicates the  $\text{Li}_2\text{CO}_3$  is likely to be decomposed on  $\text{LiMn}_2\text{O}_4$  cathode prior to the solvents, and may result in the suppression of the electrolyte oxidized decomposition. Fig. 3(a) indicates that there are two oxidation peaks in linear sweep curve which can be attributed to the two-step process of lithium-ion extraction from  $\text{LiMn}_2\text{O}_4$  cathode. For the electrolyte sample with  $\text{Li}_2\text{CO}_3$ , no new oxidation peak appears in Fig. 3 except for a little oxidation peak at 3.1 V and the oxidation current increases.  $\text{Li}_2\text{CO}_3$  is oxidized at 3.1 V to form a stable CEI film on the surface of  $\text{LiMn}_2\text{O}_4$  cathode electrode during the voltage range of 3.0–4.6 V (vs.  $\text{Li}/\text{Li}^+$ ). The results mean that  $\text{Li}_2\text{CO}_3$  does influence the electrochemical performance of  $\text{LiMn}_2\text{O}_4$  electrode. Meanwhile, the electrolyte with  $\text{Li}_2\text{CO}_3$  has the broad electrochemical stability windows (3.0–4.6 V vs.  $\text{Li}/\text{Li}^+$ ).

### 3.2. CV of $\text{LiMn}_2\text{O}_4$ electrode in the different electrolytes

In order to further investigate the effect of  $\text{Li}_2\text{CO}_3$  on the  $\text{LiMn}_2\text{O}_4$  cathode, the CV of  $\text{LiMn}_2\text{O}_4$  cathode was measured. First cycle CV, second cycle CV and third cycle CV are shown in Fig. 4(a)–(c), respectively. As seen in Fig. 4(a), there are three oxidation peaks at 3.1 V, 4.1 V and 4.2 V, meanwhile three reduction peaks at 3.85 V, 3.9 V and 4.1 V can be observed. The oxidation peaks and the reduction peaks are related to  $\text{Li}^+$  extraction and insertion, respectively. For the electrolyte with  $\text{Li}_2\text{CO}_3$ , the current of the oxidation peak at 3.1 V is lower than that of without  $\text{Li}_2\text{CO}_3$  and corresponds to excessive intercalated-Li leading to irreversible phase transition. It may be explained  $\text{Li}_2\text{CO}_3$  can suppress the HF. So the oxidation peaks and the current reduction peaks of the containing- $\text{Li}_2\text{CO}_3$  electrolyte are higher than those of without  $\text{Li}_2\text{CO}_3$ . We separated that the oxidation potential of  $\text{Li}_2\text{CO}_3$  on  $\text{LiMn}_2\text{O}_4$  cathode is almost equal to the  $\text{Li}^+$  extraction potential, the two peaks are nearly overlapped, and thus enhance the intensity of current peak at 4.1 V and 4.2 V. During the reverse sweeping from

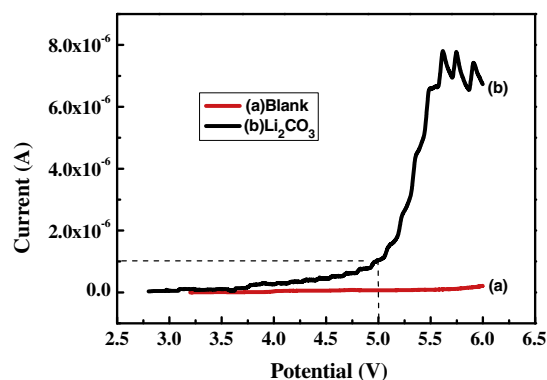


Fig. 2. LSV of Pt electrode using 1 M  $\text{LiPF}_6$ -EC/EMC/DEC = 1/1/1 (weight ratio) without (a) and with (b) 0.2 wt.%  $\text{Li}_2\text{CO}_3$  as electrolytes, scan rate  $0.1 \text{ mV s}^{-1}$ .

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