



# Impacts of vinyl ethylene carbonate and vinylene carbonate on lithium manganese oxide spinel cathode at elevated temperature



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## ABSTRACT

The effects of adding vinylene carbonate (VC) and vinyl ethylene carbonate (VEC) in a 1:1:1 (weight ratio) ethylene carbonate (EC)/diethyl carbonate (DEC)/dimethyl carbonate (EMC) on the performance of LiMn<sub>2</sub>O<sub>4</sub>/Li cells at elevated temperature are studied. Linear sweep voltammetry (LSV), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) were used for the analyses. These results confirm the capability of the 1 wt.% VEC electrolyte additive to more effectively improve the cell cycling performance and stability in the (EC and DEC)-based electrolyte of LiMn<sub>2</sub>O<sub>4</sub>/Li cells.

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## 1. Introduction

Lithium manganese oxide spinel (LiMn<sub>2</sub>O<sub>4</sub>) has been proved to be the most promising cathode material for lithium-ion batteries because it is inexpensive, less toxic, and easier to prepare than alternative materials [1–3]. However, a significant weakness of LiMn<sub>2</sub>O<sub>4</sub> is that the dissolution of Mn<sup>2+</sup> at low cathode potentials and the deposition of metallic Mn by the hydrofluoric acid (HF) on the surface of the anodes are responsible for the fast capacity fading of the cells, particularly at elevated temperatures [4–6]. Many methods have been developed to solve the problem such as the: (1) partial substitution of Mn with different transition metals [2,7,8] or partial substitution of O<sup>2-</sup> anions with Cl<sup>-</sup> [9], (2) enhanced surface coatings [10–12] and (3) use of new lithium salts instead of LiPF<sub>6</sub> [13–15]. One effective method is the use of film-forming electrolyte additives which are mostly reduced on the LiMn<sub>2</sub>O<sub>4</sub> electrode surface during the first cycling process. Some film-forming additives such as Li<sub>2</sub>CO<sub>3</sub> [16], K<sub>2</sub>CO<sub>3</sub> [17] and methylene methanedisulfonate (MMDS) [18] have been successfully used to improve the electrochemical performance and modify the surface chemistry of LiMn<sub>2</sub>O<sub>4</sub> cathodes.

Vinylene carbonate (VC) is one of the most used additives in lithium-ion batteries [19–22]. It was first assumed that the most important factor of VC that improved the cycle life of lithium-ion batteries was its effect on the anode [20]. Recently, Burns et al.

[22,23] reported that VC also reduced the electrolyte oxidation at the cathode by high-precision coulometry and automated storage.

The structure of vinylene carbonate (VEC) is similar to VC, which has also the ring molecule structural and carbon double bonds. Compared with VC, the structure of VEC is deemed to be more stable because the double bond of VEC is somewhat electron rich thus not very reactive toward double bonds. VEC is an additive that has been proposed as a film-forming additive that presumably improves the cycleability of cells using graphite electrodes [24]. In situ atomic force microscope studies on Li/graphite cells seem to show that VEC creates a solid electrolyte interphase (SEI) film with a similar morphology as VC on the edge planes of highly oriented pyrolytic graphite [25]. Electrochemical mass spectroscopy indicated that VEC affects both the cathode and anode at 55 °C [26].

Petibon et al. [27,28] has studied the effects of different concentrations of VC and VEC in LiCoO<sub>2</sub>/graphite pouch cells in 1 M LiPF<sub>6</sub> ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (3:7, weight ratio) electrolyte. However, to the best of our knowledge, there is still no report in the literature to enhance the elevated temperature electrochemical performance of LiMn<sub>2</sub>O<sub>4</sub>-based lithium-ion batteries by using VC and VEC as electrolyte additives in the (DEC and EC)-based electrolytes.

Herein, the aim of this paper is to investigate the effect of VC and VEC as electrolyte additives in the electrolyte of 1 M LiPF<sub>6</sub> dissolved in ethylene carbonate (EC)/diethyl carbonate (DEC)/EMC (1:1:1, weight ratio) on the electrochemical performance of LiMn<sub>2</sub>O<sub>4</sub>/Li cells.

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## 2. Experimental

### 2.1. Preparation of electrolyte

The electrolytes of 1 M LiPF<sub>6</sub> in a 1:1:1 (weight ratio) EC/EMC/DEC (named Blank) with 1 wt.% VC, 0.5 wt.% VC + 0.5 wt.% VEC and 1 wt.% VEC additive (provided by Jiangxi Youli New Materials Co., Ltd.) were prepared in an argon-filled glove box, in which the oxygen and water content were less than 1 ppm.

The LiMn<sub>2</sub>O<sub>4</sub> particles (purchased from Hunan Shanshan Toda Advanced Materials Co. Ltd.) were mixed with 10 wt.% super P carbon black and 10 wt.% PVDF in NMP until homogeneous slurry was obtained. Then, the blended slurries were cast onto an aluminum current collector, followed by drying at 120 °C for 12 h. The electrode disks in the form of 14 mm diameter were then punched out of the coated foil sheets and weighted. LiMn<sub>2</sub>O<sub>4</sub>/Li cell was evaluated using CR2025-type coin cell. Coin cells are assembled in the argon-filled glove box using Celgard 2400 film as a polypropylene microporous separator. The counter and reference electrodes were lithium foils.

### 2.2. Electrochemical measurements

The water and free acid (HF) content in the electrolyte were analyzed by Karl Fischer 831 Coulometer (Metrohm) and Karl Fischer 798 GPT Titrino (Metrohm), respectively. The water content of select electrolytes was lower than 10 ppm, and the free acid was controlled to be less than 20 ppm.

The electrochemical window of the electrolyte was examined by linear sweep voltammetry (LSV) using an Instrumental Electrochemical Workstation (CHI604E, Chenhua, Shanghai). The LSV were conducted at 55 °C from the open circuit voltage (OCV) to 6.0 V vs Li/Li<sup>+</sup> by CHI604E with a three-electrode system incorporating LiMn<sub>2</sub>O<sub>4</sub> as the working electrode and Li foils as counter and reference electrodes at a scanning rate of 0.1 mV s<sup>-1</sup>.

Galvanostatic charge–discharge experiments of the cells were tested on NEW-ARE tester (Shenzhen, China) over the range of 4.35–3.0 V vs Li/Li<sup>+</sup>. The cells were cycled at 0.1 C three cycles firstly, and then turned to 0.5 C for cycling performance test both at room temperature and 55 °C.

The storage test of LiMn<sub>2</sub>O<sub>4</sub>/Li cells was carried out by the followed procedure: the assembled cells were charged cells (4.35 V) with a constant current of 0.5 C, and then the fully charged cells were put into an oven at 85 °C for 4 h. Afterward the fully charged cells were discharged to 3.0 V at room temperature.

Electrochemical impedance spectroscopy (EIS) measurements of the LiMn<sub>2</sub>O<sub>4</sub>/Li cells were performed after 100 cycles at 55 °C between 3.0 V and 4.35 V before, followed by storage at 85 °C for 4 h. The initial potential was OCV of the cell. A sinusoidal amplitude modulation was used over the frequency range from 10<sup>-2</sup> Hz to 10<sup>5</sup> Hz, and the perturbation amplitude was 5 mV.

To gain the effects of VC and VEC for the Mn dissolution, the amount of 3 mL electrolyte was putted into high density polypropylene bottles in an Argon-filled glove box, followed by adding to the 2 g spinel powder and the closing bottles were stored in thermal chambers at 60 °C for 7 days. After the storage, each vessel was opened in a glove box to sample the electrolytes, and the resulting electrolytes were analyzed with inductively coupled plasma–atomic emission spectrometry (ICP–AES, IRIS intrepid XSP, Thermo Electron Corporation). The spinel powder was dried in vacuum for 12 h at 120 °C.

To analyze the element composition and microstructure of the LiMn<sub>2</sub>O<sub>4</sub> electrodes and separators after charge–discharge cycling measurements, the cells were disassembled in an argon-filled glove box. The LiMn<sub>2</sub>O<sub>4</sub> electrodes were rinsed with pure DMC several times to remove the residual salts, and then were dried in a vacuum oven at 60 °C for 4 h. The morphological changes on both LiMn<sub>2</sub>O<sub>4</sub> electrodes and spinel powder were visualized by scanning electron microscopy (SEM, JEOL, JSM-5612LV) with an accelerating voltage of 20 kV. Transmission electron microscopy (TEM, Tecnai G12, 200 kV) was used to characterize the surface morphology of the LiMn<sub>2</sub>O<sub>4</sub> cathode. The chemical components of the LiMn<sub>2</sub>O<sub>4</sub> cathode surface were measured using X-ray photoelectron spectroscopy (XPS, K-Alpha 1063, Thermo Fisher).

## 3. Results and discussion

### 3.1. LSV of LiMn<sub>2</sub>O<sub>4</sub> electrode in different electrolytes

Fig. 1 shows LSV curves of LiMn<sub>2</sub>O<sub>4</sub> electrode. It can be seen from Fig. 1 that two oxidation peaks were found about 4.08 V and 4.20 V using three different electrolytes on the cathode at 55 °C, which should be associated with the two-step process of lithium-ion extraction from LiMn<sub>2</sub>O<sub>4</sub> cathode [29]:

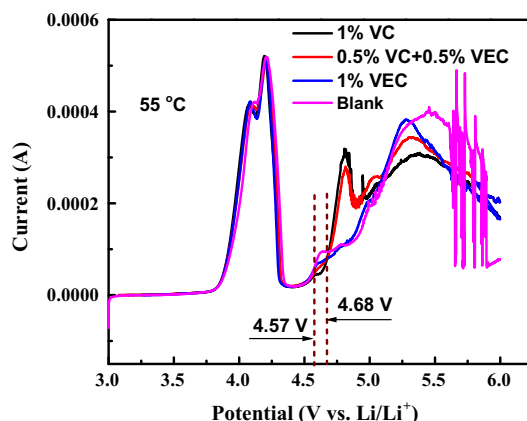
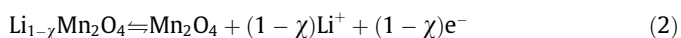
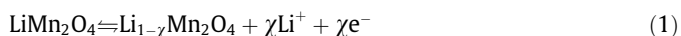


Fig. 1. LSV of LiMn<sub>2</sub>O<sub>4</sub> electrode using the Blank electrolyte, 1 wt.% VC, 1 wt.% VEC and 0.5 wt.% VC + 0.5 wt.% VEC additive electrolyte, scan rate 0.1 mV s<sup>-1</sup>.

The following peak between 4.57 V and 4.68 V vs Li/Li<sup>+</sup> is believed to be solvent oxidation on the LiMn<sub>2</sub>O<sub>4</sub> cathode and subsequent formation of a passive film on the cathode interface [30]. It is obvious that the passive film on the cathode interface with Blank electrolyte is thicker than that on the cathode interface with additive. The last peaks of the cells using 1 wt.% VC, 0.5 wt.% VC + 0.5 wt.% VEC and 1 wt.% VEC are respectively about 4.80, 4.83 and 5.2 V vs Li/Li<sup>+</sup>, which show that the passive film is broken. This is followed by a dramatic decomposition of the solvents. These results indicate that the 1 wt.% VEC-containing electrolyte has a quite wide electrochemical window.

### 3.2. Cycling performances and rate performances of LiMn<sub>2</sub>O<sub>4</sub>/Li cells

Fig. 2 shows cycle performances of the LiMn<sub>2</sub>O<sub>4</sub>/Li cells with different electrolytes. It can be observed from Fig. 2a that the cells with different additives exhibit different cycling characteristics when the charge cut-off voltage is 4.35 V at room temperature. The cyclability of the LiMn<sub>2</sub>O<sub>4</sub>/Li cell containing 1 wt.% VEC is better than those of others. The discharge capacities of the cells using the electrolytes with Blank, 1 wt.% VC, 1 wt.% VEC and 0.5 wt.% VC + 0.5 wt.% VEC at the 100th are 91.7, 94.3, 99.3 and 95.9 mA h g<sup>-1</sup>, respectively. The corresponding capacity retentions are 80.4%, 82.4%, 87.6% and 84.6%, respectively.

Meanwhile, the cycling characteristics of cells with different additives at 55 °C are shown in Fig. 2b. It is obvious that the discharge capacity of the VEC-containing cell shows good cycling stability. In addition, the difference among of cells at elevated temperature is more apparent than that at room temperature. After 100 cycles, the capacity of LiMn<sub>2</sub>O<sub>4</sub>/Li cell with 1 wt.% VEC is 93.8 mA h g<sup>-1</sup> and the capacity fading is 17.1 mA h g<sup>-1</sup>. Corresponding to cells with other electrolytes, the capacity of LiMn<sub>2</sub>O<sub>4</sub>/Li cells are 78.5 (Blank), 88.6 (1 wt.% VC) and 91.8 mA h g<sup>-1</sup> (0.5 wt.% VC + 0.5 wt.% VEC), respectively. The cell with VEC electrolyte shows superior cycling performance compared with the other cells. It was reported [31] that energy level of LUMO of VEC (−1.555 eV) was lower than VC (−1.121 eV), EC (−0.389 eV) and DEC (0.007 eV). That is to say, VEC will be reduced prior to VC, EC and DEC during the first lithium ion insertion process. It is clearly indicated that VEC molecules can easily accept electrons and bear a higher reaction activity. So when VEC is added into the electrolyte, the further reaction between the solvent and lithium-ions can be prevented.

From Fig. 2c, it can be seen that the coulombic efficiency of the cell with 1 wt.% VEC is higher than those of others. The initial coulombic efficiency with 1 wt.% VEC is 98.2%, corresponding to Blank,

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