Enhanced high temperature cycling performance of LiMn$_2$O$_4$/graphite cells with methylene methanedisulfonate (MMDS) as electrolyte additive and its acting mechanism

Fengju Bian$^a$, Zhongru Zhang$^{a,b}$, Yong Yang$^{a,b,c,*}$

$^a$ Engineering Research Center of Electrochemical Technology of MOE, Xiamen University, Xiamen 361100, Fujian, China; $^b$ College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, Fujian, China; $^c$ School of Energy Research, Xiamen University, Xiamen 361100, Fujian, China

[ Manuscript received November 29, 2013; revised January 14, 2014 ]

Abstract
The effects of methylene methanedisulfonate (MMDS) on the high-temperature ($\sim$50 $^{\circ}$C) cycle performance of LiMn$_2$O$_4$/graphite cells are investigated. By addition of 2 wt% MMDS into a routine electrolyte, the high-temperature cycling performance of LiMn$_2$O$_4$/graphite cells can be significantly improved. The analysis of differential capacity curves and energy-dispersive spectrometry (EDS) indicates that MMDS decomposed on both cathode and anode. The three-electrode system of pouch cell is used to reveal the capacity loss mechanism in the cells. It is shown that the capacity fading of cells without MMDS in the electrolytes is due to irreversible lithium consumption during cycling and irreversible damage of LiMn$_2$O$_4$ material, while the capacity fading of cell with 2 wt% MMDS in electrolytes mainly originated from irreversible lithium consumption during cycling.

Key words
methylene methanedisulfonate (MMDS); spinel lithium manganese oxides; electrolyte additives; reference electrode; acting mechanism

1. Introduction
In recent years, the applications for Li-ion batteries have expanded dramatically. The Li-ion battery has enabled the wireless revolution of cell phones, laptop computers, digital cameras, and ipads that have transformed global communication [1]. LiMn$_2$O$_4$ is an attracting cathode material for Li-ion battery by virtue of its low toxicity, low cost, and the high natural abundance of Mn [2]. However, the LiMn$_2$O$_4$ also suffers from irreversible capacity loss during cycling especially at high temperature [3]. This capacity loss has been attributed to several reasons: (1) the low binding energy of Mn–O bond, (2) the strong Jahn-Teller dissolution of trivalent Mn ions, (3) partial dissolution of Mn ions into liquid electrolyte and decomposition of the electrolyte [4–6]. At high temperature, LiMn$_2$O$_4$ may react also spontaneously with solution species, resulting in the formation of surface films. Hence, its electrochemical behavior could be controlled by surface films through which Li-ion transport takes place [7,8]. In recent years, many strategies have been developed to overcome this problem. Most of these researches are focused on material modification including doping with divalent metal ions [9–11], coating with metal oxides [12], reducing the particle size of LiMn$_2$O$_4$ [13,14] and other some synthesis routes. For example, Zhang et al. [15] investigated a flame-assisted spray technology to produce spinel LiMn$_2$O$_4$ powders. Jia et al. [16] reported a two-step hydrothermal process to synthesize the LiMn$_2$O$_4$/CNT nanocomposites. Recently, a little attention has also been paid to the electrolyte additives such as methylene methanedisulfonate (MMDS), which is reported to improve the capacity retention ratio of LiNi$_{0.5}$Mn$_{1.37}$Ti$_{0.13}$O$_4$/graphite cell in a cycle at a high temperature of 45 $^{\circ}$C [17]. Zuo et al. [18] also found that MMDS can significantly improve the cyclic performance of LiCoO$_2$/graphite cells.

In this work, we investigate the effects of MMDS additives on the electrochemical performance of LiMn$_2$O$_4$/graphite cells which are filled with 1 mol·L$^{-1}$ LiPF$_6$ in EC : EMC : DMC = 1 : 1 : 1 (by mass), and 2% vinylene carbonate (VC). Figure 1 shows the molecular structure of MMDS. A three-electrode system is used to monitor the

* Corresponding author. Tel: +86-592-2185753; Fax: +86-592-2185753; E-mail: yyang@xmu.edu.cn

This work was supported by the Key Project of the National Natural Science Foundation of China (Grant No. 21233004).

Copyright©2014, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. All rights reserved.
dynamic mechanism of capacity fading of LiMn$_2$O$_4$/graphite cells with and without MMDS in the electrolytes. The formation of surface film and acting mechanism of MMDS on both LiMn$_2$O$_4$ electrode and graphite electrode are studied using differential capacity curves and surface analysis techniques such as energy-dispersive spectrometry (EDS).

**Figure 1.** The molecule structure of methylene methanesulfonate (MMDS)

### 2. Experimental

#### 2.1. Preparation of electrolytes and pouch cells

Solvents and lithium hexa-fluorophosphate (LiPF$_6$) were obtained from Zhangjiagang Guotai Huarong New Chemical Materials Co., Ltd. (China), and solvents were further dried over molecular sieves. VC (99.96%) and MMDS (98.6%) were purchased from Fujian Chuangxin Science and Develops Co., Ltd. (China). The base electrolyte composition was 1 mol·L$^{-1}$ LiPF$_6$ in EC : EMC : DMC = 1 : 1 : 1 (by mass) and 2% VC. The cathode electrodes contained 93.0 wt% LiMn$_2$O$_4$ (Wujie Science and Technology Co., Ltd.), 4.0 wt% conductive carbon, and 3.0 wt% polyvinylidene fluoride (PVDF). The anode electrodes were prepared by combining 95 wt% graphite (BTR Battery Materials Co. Ltd.), 3.0 wt% LA-132, and 2.0 wt% conductive carbon. Both electrodes were dried at 85 °C for 24 h under vacuum condition prior to the assembling operation. The design capacity of pouch cell was 650 mAh. The electrolyte filling was done in an argon-filled glove box (MIKROUNA, super(1220/750)). After electrolyte filling, the cells were stored in a 50 °C temperature controlled box, and cycled at a constant current of 0.5 C charging rate, followed by a constant potential of 4.2 V until the current reached C/20, then a constant current of 0.5 C discharging rate to 3.0 V.

The chemical compositions of the surface layer on the LiMn$_2$O$_4$ and graphite were analyzed by energy-dispersive spectrometry (EDS). After first charge and discharge at room temperature at 0.2 C rate, the LiMn$_2$O$_4$ and graphite were carefully separated from the half coin cells and rinsed with a dimethyl carbonate (DMC) solvent to remove the residual electrolyte, and dried in the argon-filled glove box. Differential capacity curves were plotted from first cycle data [19].

In order to study the in situ reactions occurring at the surface of working electrode, a reference electrode (RE) with a constant interfacial potential is needed [20]. The configuration and its test method of three-electrode pouch cell are shown in Figure 2. The RE consists of lithium foil and a 115-μm-diameter copper wire. Lithium was pressed on the top of copper wire in the argon-filled glove box, putted into a small separator bag, and then placed among electrodes of pouch cells. The electrochemical processes taking place in the negative and positive electrodes of pouch cells were investigated using a reference electrode. The potential change of negative and positive electrodes can be recorded in situ by an auxiliary channel of the equipment (Neware CT-3008W) while the charge-discharge process carried between positive and negative electrode.

**Figure 2.** The configuration and test method of three-electrode pouch cell

The charge-discharge performances were tested using a computer-controlled battery charger test (Neware CT-3008W). The cells were stored in a 50 °C temperature controlled box, and cycled at a constant current of 0.5 C charging rate, followed by a constant potential of 4.2 V until the current reached C/20, then a constant current of 0.5 C discharging rate to 3.0 V.

The chemical compositions of the surface layer on the LiMn$_2$O$_4$ and graphite were analyzed by energy-dispersive spectrometry (EDS). After first charge and discharge at room temperature at 0.2 C rate, the LiMn$_2$O$_4$ and graphite were carefully separated from the half coin cells and rinsed with a dimethyl carbonate (DMC) solvent to remove the residual electrolyte, and dried in the argon-filled glove box. Differential capacity curves were plotted from first cycle data [19].
3. Results and discussion

3.1. Electrochemical performance of the cells and EDS analysis

The charge/discharge profiles and $dQ/dV$ vs. voltage curves with and without addition of MMDS at the first cycle are shown in Figure 3. Figure 3(a) shows the charge/discharge curves of $\text{LiMn}_2\text{O}_4$/Li coin cell for charging (delithiation) to 4.2 V and discharging (lithiation) to 3 V. As Figure 3(b) shows, the peak voltages of $A'$ and $B'$ are observed to be higher than those of $A$ and $B$ during charging, and the peak voltages of $C'$ and $D'$ are observed to be lower than those of $C$ and $D$ during discharging. The corresponding plateau of charge and discharge in the voltage profile can be seen in Figure 3(a), indicating that the $\text{LiMn}_2\text{O}_4$ polarization at first cycle with 2 wt% MMDS in electrolyte is slightly higher than that of the electrode without MMDS in electrolyte. Figure 3(c) shows the charge/discharge curves of graphite/Li coin cell for charging (lithiation) to 0.005 V and discharging (delithiation) to 2.5 V. During the charge, a small peak is observed at 1.1 V (Figure 3d). This peak is due to the reduction of MMDS at graphite anode. Meanwhile, a higher polarization of graphite anode can be also observed at Figure 3(c) and Figure 3(d).

Figure 3. The first charge/discharge profiles and $dQ/dV$ curves of half coin cell (25 °C, 0.2 C). (a) $\text{LiMn}_2\text{O}_4$/Li half cell, (b) $dQ/dV$ for a $\text{LiMn}_2\text{O}_4$/Li half cell, (c) graphite/Li half cell (illustration: profiles between 0 V to 2 V), (d) $dQ/dV$ for a graphite/Li half cell (illustration: profiles between 0 V to 2.75 V)

Figure 4 shows EDS analysis profiles of the above electrode materials. The EDS data shows clearly the appearance of the element S on both cathode surface (Figure 4b) and anode surface (Figure 4d) after one cycle in the electrolyte with 2% MMDS. The element S can only be observed from MMDS-added system. It can be inferred that MMDS decomposed on both cathode and anode.

Figure 5 shows a comparison of capacity grading data of pouch cells. As a result of an increasing polarization of cells with 2% MMDS in the electrolyte, the initial specific capacity of the cell decreased. However, the resistances of the cells have no significant difference. Compared with Figure 3, it is concluded that the cell polarization caused by decomposition of MMDS is electrochemical polarization rather than ohmic polarization. The initial coulombic efficiency of cells is lower with 2% MMDS in the electrolyte, indicating that the lower efficiency is caused by the lithium consumption during SEI forming process.

Based on Figures 3–5, it is supposed that MMDS participates in the formation process of the SEI film on both $\text{LiMn}_2\text{O}_4$ cathode and graphite anode surface, which results in an increasing polarization and a descending initial specific capacity.
3.2. High temperature cycling performance of the cells

The effects of MMDS additive on the cycling performance of LiMn$_2$O$_4$/graphite pouch cells at 50 °C are shown in Figure 6. It can be seen that the capacity retention of the cell is much higher in the electrolyte with 2% MMDS than that of the cell without addition of MMDS. As presented in Figure 7(a), the capacity retention of the cell at the 450th cycle is 62% without MMDS, while it is 85% with addition of 2% MMDS. The resistance at the 450th cycle also increases 72% without MMDS, and it only increases 12% with 2% MMDS in the electrolyte (Figure 7b). It is obvious that the addition of MMDS into electrolyte remarkably improves the cycling stability of LiMn$_2$O$_4$/graphite cell at 50 °C.
Figure 7. Comparison of the 1st cycle and the 450th cycle of specific capacity (a) and resistance (b) of the LiMn$_2$O$_4$/graphite cell without MMDS and with 2% MMDS in the electrolyte.

Figure 8. The first charge/discharge curves of three-electrode LiMn$_2$O$_4$/graphite pouch cell at 50 °C with 0.5 C. (a) Charging profiles of full cells, (b) charging profiles of the LiMn$_2$O$_4$ vs. Li reference electrode, (c) discharging profiles of full cells, (d) discharging profiles of the LiMn$_2$O$_4$ vs. Li reference electrode.

3.3. Electrochemical analysis with three-electrode system

3.3.1. The first cycle capacity loss

Figure 8 is the first charge/discharge curves of three-electrode LiMn$_2$O$_4$/graphite pouch cell at 50 °C with 0.5 C. As shown in Figure 5, the first cycle capacity of pouch cells is lower with 2% MMDS than that without MMDS in the electrolyte. Figure 8(a) shows a higher cell polarization during charging process with 2% MMDS, and the charging time at the constant voltage region is much longer. Figure 8(b) shows the results of in situ potential measurement of LiMn$_2$O$_4$ vs. Li and graphite vs. Li of charging. It can be seen that, using 2% MMDS in the electrolyte, the graphite potential is lower and the LiMn$_2$O$_4$ potential is higher. Higher electrode polarization leads the cell voltage reaching 4.2 V (cut-off voltage).
earlier while charging. Thus the constant current charging time is shorter and the constant voltage charging time is longer. Figure 8(c) shows the discharge curve at the first cycle, and Figure 8(d) shows the results of in situ potential measurement of \( \text{LiMn}_2\text{O}_4 \) vs. Li and graphite vs. Li during discharging process. It can be seen from Figure 8(d) that, at the end of discharge, the \( \text{LiMn}_2\text{O}_4 \) potential goes down to less than 3.4 V, and the graphite potential goes up to higher than 0.3 V. Thus it can be inferred that the \( \text{LiMn}_2\text{O}_4 \) is fully lithiated, and the graphite is fully delithiated of both two different electrolyte cells. At the end of charge (Figure 8b), the \( \text{LiMn}_2\text{O}_4 \) potential is 4.33 V without MMDS, and the \( \text{LiMn}_2\text{O}_4 \) potential is 4.29 V with 2% MMDS in the electrolyte, which means that the \( \text{LiMn}_2\text{O}_4 \) electrodes with 2% MMDS in electrolyte is not fully delithiated. As analyzed of Figure 8, due to the decomposition of MMDS on both \( \text{LiMn}_2\text{O}_4 \) and graphite, the polarizations of both electrodes become higher, which results in the decrease of constant current charging time and the increase of constant voltage charging time. Then the charge process stops earlier for the cell voltage first reaching cut-off voltage. Meanwhile, there still has part of active lithium stored in \( \text{LiMn}_2\text{O}_4 \) cathode at the end of charging, so the charge capacity decreased, which leads to a decreased discharge capacity thereafter.

3.3.2. Cyclic capacity fading

Figure 9 shows the charge/discharge curves of \( \text{LiMn}_2\text{O}_4 \)/graphite cell at 1st cycle and 450th cycle in the electrolyte without MMDS at 50 °C with 0.5 C. Figure 9(a and c) shows the comparison of the charging/discharging curves of the full cells at the first cycle and after 450th cycle. As Figure 9(b) shows, at the end of 450th charge, the graphite potential is around 0.14 V and the \( \text{LiMn}_2\text{O}_4 \) potential is around 4.33 V, which means that the graphite is not fully lithiated and the \( \text{LiMn}_2\text{O}_4 \) is fully delithiated. It can be inferred that part of lithium has been exhausted during cycling. This is one reason for cycle capacity fading without MMDS in the electrolyte. As shown in Figure 9(d), at the end of 450th discharge, the graphite potential is around 0.15 V and the \( \text{LiMn}_2\text{O}_4 \) potential has been under 3.2 V, which means that the graphite is not fully delithiated and the \( \text{LiMn}_2\text{O}_4 \) is also fully lithiated. It can be inferred that at the end of discharge, there is still part of reversible lithium stored in graphite while \( \text{LiMn}_2\text{O}_4 \) can not accept more, indicating that some irreversible damage has
happened to the LiMn$_2$O$_4$ material and resulted in the faster capacity fading. Therefore, the reasons of cycle capacity fading of LiMn$_2$O$_4$/graphite cell should include two major parts: (1) lithium consumption during cycling; (2) some irreversible damage happened to the LiMn$_2$O$_4$ material.

Figure 10 shows the charge/discharge curves of LiMn$_2$O$_4$/graphite cell at 1st cycle and 450th cycle in the electrolyte with 2% MMDS at 50 °C with 0.5 C. Figure 10(a) shows the comparison of charging curve at the 1st cycle and 450th cycle, and Figure 10(c) shows the comparison of discharging curve at the 1st cycle and 450th cycle. As seen in Figure 10(b), at the end of 450th charge, the graphite potential is around 0.14 V and the LiMn$_2$O$_4$ potential is around 4.34 V, which means that the graphite is not fully lithiated and the LiMn$_2$O$_4$ is fully delithiated. As Figure 10(d) shows, at the end of 450th discharge, the graphite potential is above 0.3 V and the LiMn$_2$O$_4$ potential is under 3.2 V, which means that the graphite is fully delithiated and the LiMn$_2$O$_4$ is also fully lithiated. Therefore it can be inferred that the capacity fading in the cells is due to lithium consumption during cycling rather than the material damage.

Based on analysis of Figure 9 and Figure 10, by adding 2 wt% MMDS into the electrolyte, LiMn$_2$O$_4$ cells can be cycled well at 50 °C. It is believed that suitable state of charge/discharge could affect greatly the cycling performance of LiMn$_2$O$_4$/graphite cell.

4. Conclusions

MMDS is evaluated as a new electrolyte additive for the LiMn$_2$O$_4$/graphite cell cycled at high-temperature (~50 °C). It shows that the addition of 2 wt% MMDS in the electrolyte can significantly improve the cyclic performance of LiMn$_2$O$_4$/graphite cell. MMDS is supposed to participate in the formation process of the SEI film on both the LiMn$_2$O$_4$ cathode and the graphite anode, which results in an increasing polarization and a descending initial specific capacity. However, the reduced first cycle capacity is reversible, and the small amount of lithium is still actively stored in positive electrode. The capacity fading of cells without MMDS in electrolyte is due to lithium consumption during cycling and irreversible damage of LiMn$_2$O$_4$ material, while the capacity fading of cell with 2 wt% MMDS in electrolyte mainly results from lithium consumption during cycling. By adding 2 wt% MMDS into the electrolyte, LiMn$_2$O$_4$ can be thought as “partially-protection” during 50 °C cycling process.
Acknowledgements

This project is supported by the Key Project of the National Natural Science Foundation of China (Grant No. 21233004). The authors are also grateful for Fujian Chuangxin Science and Develops Co. Ltd. for proving MMDS samples and financial support.

References