



## Effect of lithium difluoro(oxalato)borate and heptamethyldisilazane with different concentrations on cycling performance of $\text{LiMn}_2\text{O}_4$

Xianwen Wu, Zhixing Wang\*, Xinhai Li, Huajun Guo, Yunhe Zhang, Wei Xiao

School of Metallurgical Science and Engineering, Central South University, Changsha, Hunan, 410083, PR China

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### ABSTRACT

Effect of lithium difluoro(oxalato)borate and heptamethyldisilazane with different concentrations as additives on cycling performance of  $\text{LiMn}_2\text{O}_4$  is studied and evaluated at 25 °C and 60 °C by cyclic voltammetry (CV) test, linear sweep voltage (LSV) test, TG-DSC analysis, conductivity, electrochemical impedance spectroscopy (EIS) and charge–discharge measurements. The results show that the addition of heptamethyldisilazane does not influence the electrochemical performance of  $\text{LiMn}_2\text{O}_4$  electrode and the conductivity of original electrolyte basically. What is more, 2 vol.% HMDS can apparently improve the cycling performance of  $\text{LiMn}_2\text{O}_4$  at room and elevated temperature, while 6 vol.% HMDS and 0.2 M LiDFOB in the electrolyte have not achieved the desired effect, and even deteriorated the cycling performance of  $\text{LiMn}_2\text{O}_4/\text{Li}$  half cells. When the concentration of the additive is 2 vol.%, the battery of  $\text{LiPF}_6$ -based electrolyte with HMDS additive shows perfect cycling performance at room temperature at 2 C rate, and the capacity fading is only 3.8 mAh  $\text{g}^{-1}$  after 200 cycles.

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### 1. Introduction

Spinel lithium manganese oxide ( $\text{LiMn}_2\text{O}_4$ ) is now popularly considered as one of the most promising cathode materials for using in large-scale lithium-ion batteries for HEV and EV applications because of its low cost, high voltage, safer performance and environmental benign nature [1]. However,  $\text{LiMn}_2\text{O}_4$  has one of the biggest problems with poor cycling performance at room temperature, resulting in the severe capacity fading, especially at elevated temperature [2–5]. The reason may be Mn dissolution, electrolyte decomposition and Jahn–Teller effect. The first two reasons can be resolved by optimizing the composition of electrolytes [6–8].

In view of electrolyte, the performance deterioration of  $\text{LiMn}_2\text{O}_4$  cathode mainly originates from acidic impurity of HF, its formation from the decomposition of  $\text{LiPF}_6$  salt in the presence of trace water is believed in accelerating the Mn dissolution and electrolyte decomposition [9–11]. So the electrolyte additives of the stability have been investigated extensively in order to suppress the capacity fading of  $\text{LiMn}_2\text{O}_4$  battery, therefore, improving the cycling performance of  $\text{LiMn}_2\text{O}_4$  in a sense [12–16].

Zuo et al. [17] reported the effects of ethanolamine on the stability of electrolyte and the cycle and calendar life of Li-ion batteries. The addition of ethanolamine could restrain the  $\text{LiPF}_6$  from hydrolysis and decomposition and also reduce the capacity loss of batteries by 50%. Yamane et al. [18] investigated the effect of addition of hexamethyldisilazane to the electrolyte solution on the storage performance and cycling performance of  $\text{Li}_{1.01}\text{Mn}_{1.99}\text{O}_4/\text{Li}$  cells, and the mechanism is that hexamethyldisilazane can remove water and neutralize acids in solutions. In addition, Li et al. [19] reported firstly the effect of heptamethyldisilazane as an additive on the stability performance of  $\text{LiMn}_2\text{O}_4$  cathode for lithium-ion battery, and the authors think heptamethyldisilazane does not dissolve in water and can be combined with acid to form the salt compound:  $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)\text{Si}(\text{CH}_3)_3 + \text{HF} \rightarrow [(\text{CH}_3)_3\text{SiNH}(\text{CH}_3)\text{Si}(\text{CH}_3)_3]^+\text{F}^-$ , but the cycling performance of  $\text{LiMn}_2\text{O}_4$  cells with this additive is not discussed in details.

Recently, a novel lithium salt, lithium difluoro(oxalato)borate (LiDFOB) [20,21], has drawn intensive attention as a potential lithium salt in place of  $\text{LiPF}_6$  since 2006. Fu et al. [22] discussed the LiDFOB-based electrolyte from the standpoint of the properties that inhibit Mn dissolution and film formation on the surface  $\text{LiMn}_2\text{O}_4$  electrode, and the results show that the LiDFOB-based electrolyte has good electrochemical stability and compatibility with  $\text{LiMn}_2\text{O}_4$  cathode, improving the cycle performance of  $\text{LiMn}_2\text{O}_4/\text{Li}$ .

\* Corresponding author. Tel.: +86 731 88836633; fax: +86 731 88836633.  
 E-mail address: [691210084@qq.com](mailto:691210084@qq.com) (Z. Wang).

In order to improve the cycling performance of  $\text{LiMn}_2\text{O}_4$  at room and elevated temperature, the effect of heptamethyldisilazane and lithium difluoro(oxalato)borate as additives on cycling performance of  $\text{LiMn}_2\text{O}_4$  was studied and evaluated at 25 °C and 60 °C in this paper.

## 2. Experimental

### 2.1. Preparation of the cells

Battery-grade  $\text{LiPF}_6$ ,  $\text{LiDFOB}$ , EC, DMC, EMC were bought from Guangzhou Tinci Materials Technology Co., Ltd. The spinel  $\text{LiMn}_2\text{O}_4$  was from Hunan Shanshan Toda Advanced materials Co., Ltd. The electrolyte was prepared by dissolving 1 M  $\text{LiPF}_6$  in a blend solvent of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl(methyl) carbonate (EMC) (EC:DMC:EMC = 1:1:1 in volume), which was abbreviated 1#, and then one drop of distilled water was added to 1#, at last 0.2 M  $\text{LiDFOB}$  (in electrolyte) or heptamethyldisilazane (HMDS for short in this paper) with different concentrations as additives was added to the 1# electrolyte. All the electrolytes were prepared in a dry Ar-filled glove box.

The working cathode was composed of 80 wt.%  $\text{LiMn}_2\text{O}_4$  powders, 10 wt.% acetylene black as conducting agent, and 10 wt.% poly(vinylidene fluoride) as binder. After being blended in N-methyl pyrrolidinone, the mixed slurry was spread uniformly on a thin aluminum foil and dried in vacuum for 12 h at 120 °C. The counter and reference electrodes were lithium foils. Electrodes were punched in the form of 14 mm diameter disks, and the typical positive electrode loading was about 1.42 mg  $\text{cm}^{-2}$ . The  $\text{LiMn}_2\text{O}_4/\text{Li}$  half cells were assembled as CR2032 type coin cells in a dry Ar-filled glove box using a polypropylene micro-porous film as the separator.

### 2.2. Measurements

Karl-Fisher 831 Coulometer (Metrohm) and Karl-Fisher 798 MPT Titrino (Metrohm) were used to determine water and free acid (HF) contents, respectively. When one drop of distilled water was added to 1#, water content was 55 ppm and free acid (HF) content was 28 ppm in the electrolyte.

Charge-discharge tests at room temperature (25 °C) and high temperature (60 °C) were carried out by Land BT-10 Tester (Wuhan, China) with the utilization of  $\text{LiMn}_2\text{O}_4/\text{Li}$  half cells, and the temperature was controlled by oven. The initial charge-discharge test was carried by CC-CV mode, firstly cycled with a constant current of 0.1 C to 4.35 V, followed by a constant voltage of 4.35 V until the current decreased to 0.01 C, then discharged at 0.1 C current rate to 3.3 V, and then the test cells were cycled between 3.3 V and 4.35 V at different rates.

A CH Instrumental Electrochemical Workstation (CHI660A) with a three-electrode system incorporating  $\text{LiMn}_2\text{O}_4$  as the working electrode and Li foils as counter and reference electrodes was used for cyclic voltammetry (CV) and linear sweep voltammetry (LSV) at the scanning rate of 0.1  $\text{mV s}^{-1}$ . Electrochemical impedance spectroscopy (EIS) measurements were performed using  $\text{LiMn}_2\text{O}_4/\text{Li}$  cell with discharged state, and the initial potential was the open circuit voltage (OCV) of the cell. The working frequency was from  $10^{-2}$  Hz to  $10^5$  Hz, and the perturbation amplitude was 5 mV.

Thermal gravimetric/differential scanning calorimeter (TG/DSC) of the electrolytes was performed on a SDT Q600 TG-DSC instrument (America). The electrolytes were heated at 5 °C  $\text{min}^{-1}$  from 20 to 200 °C in a  $\text{N}_2$  atmosphere, and the flow rate of  $\text{N}_2$  was 200  $\text{mL min}^{-1}$ .

The conductivity was measured by the AC impedance method in the frequencies range  $10^{-2}$  Hz to  $10^5$  Hz, using a conductivity

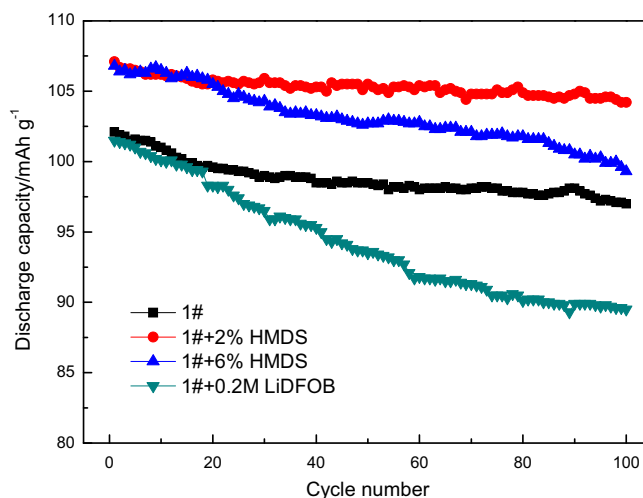


Fig. 1. Cycling performance of  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells at 25 °C, which was recorded at a constant rate 1 C and cutoff voltage was from 3.3 to 4.35 V.

cell (cell constant = 0.98). The cell was calibrated with 0.1 M KCl solution. A high-low temperature test-chamber (GDH-2005C) was used to provide a constant temperature environment for test. The estimated error of experimental conductivity was  $\pm 1\%$ .

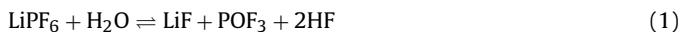
## 3. Results and discussion

### 3.1. Cycling performance of $\text{LiMn}_2\text{O}_4/\text{Li}$ cell

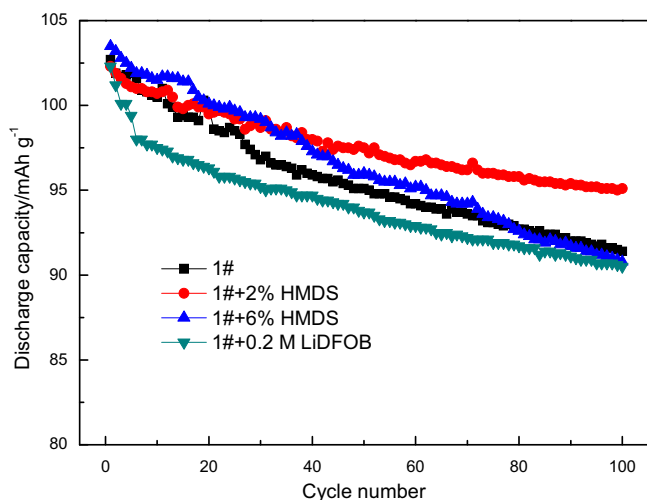
Fig. 1 shows the cycling performance of  $\text{LiMn}_2\text{O}_4/\text{Li}$  cell at 25 °C using 1# without and with  $\text{LiDFOB}$  or HMDS of different concentrations.

It can be observed from Fig. 1, when the 0.2 M  $\text{LiDFOB}$  was added in the 1# electrolyte, the cycling performance of  $\text{LiMn}_2\text{O}_4/\text{Li}$  cell deteriorated at once, it initially delivered 101.5  $\text{mAh g}^{-1}$  and retained 89.5  $\text{mAh g}^{-1}$  after 100 cycles. The fact that the capacity fading was so fast was contradicted with Ref. [22]. However, we found that the conductivity of the electrolyte (8.5  $\text{ms cm}^{-1}$ ) was worse than that (9.12  $\text{ms cm}^{-1}$ ) of the 1# electrolyte. This showed that although the  $\text{BOB}^-$  in  $\text{LiDFOB}$  and  $\text{Mn}^{2+}$  combined together to form an insoluble film on the cathode surface [22], the addition of  $\text{LiDFOB}$  to original electrolyte decreased the conductivity.

However, the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cell with HMDS added into the 1# electrolyte as additive had different cycling performance from the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cell above. As shown in Fig. 1, the initial discharge capacity of battery with 6 vol.% HMDS in the electrolyte was a little higher than that without HMDS in the electrolyte. Although the discharge capacity only decreased by 8  $\text{mAh g}^{-1}$  after 100 cycles, the capacity retention of 92.98% was worse than the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cell without any additive in the electrolyte of which the capacity retention was 95.00%. However, the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cell with 2 vol.% HMDS in the 1# electrolyte showed better cycling performance, it delivered 107.1  $\text{mAh g}^{-1}$  initially and the capacity retention 97.29% after 100 cycles was much higher than the battery with 1# electrolyte. This can be explained as follows:



The additive of silane as the electrolyte stabilizer such as HMDS can be combined with HF to form the salt compound and the equilibrium shifts towards right until there is no water in the system of electrolyte [15,19]. So a little excessive additive can increase the initial coulomb efficiency, the initial discharge capacity, and even the cycling performance of the battery. At the same



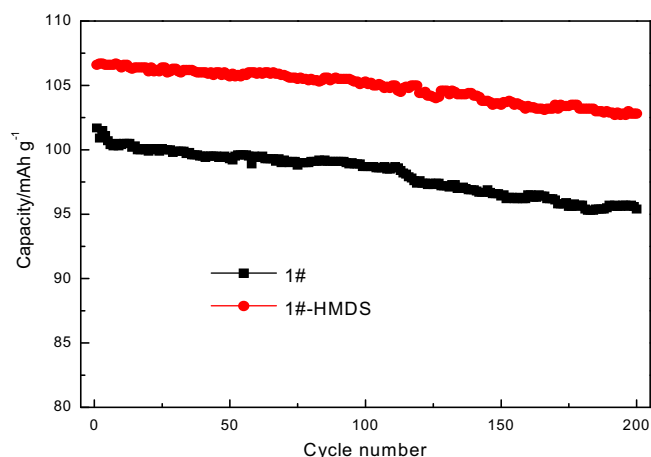
**Fig. 2.** Cycling performance of  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells at  $60^\circ\text{C}$ , which was recorded at a constant rate 1 C and cutoff voltage was from 3.3 to 4.35 V.

time, the nitrogen core with its lone-pair electrons of excessive  $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2\text{Si}(\text{CH}_3)_3$  (HMDS) can complex  $\text{PF}_5$  to reduce the reactivity and acidity of  $\text{PF}_5$  and as a result suppress the dissolution of the cathode materials [23]. In fact, 2 vol.% HMDS is more enough to remove water. However, when the additive added into the electrolyte, not only the conductivity decreased, but also the more a large amount of the additive was the worse the conductivity of electrolyte was. In this paper, the conductivity of the electrolyte with HMDS addition was worse than that 1# electrolyte ( $9.12 \text{ ms cm}^{-1}$ ), the conductivity of the electrolyte with 2 vol.% HMDS ( $8.93 \text{ ms cm}^{-1}$ ) was better than that ( $8.59 \text{ ms cm}^{-1}$ ) with 6 vol.% HMDS. Therefore, the initial discharge capacity of the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cell with 1# electrolyte containing HMDS was better than that without HMDS, while the cycling performance with 6 vol.% HMDS was not better than that with 2 vol.% HMDS. So the phenomenon which appeared above was the combined effect of conductivity decreasing and HF reducing in the 1# electrolyte with HMDS.

Fig. 2 shows the cycling performance of  $\text{LiMn}_2\text{O}_4/\text{Li}$  cell at  $60^\circ\text{C}$  using 1# without and with LiDFOB or HMDS of different concentrations. It can be observed from Fig. 2, when the 0.2 M LiDFOB was added in the 1# electrolyte, the discharge capacity of  $\text{LiMn}_2\text{O}_4/\text{Li}$  cell initially delivered  $102.3 \text{ mAh g}^{-1}$  and retained  $90.5 \text{ mAh g}^{-1}$  after 100 cycles, a little more smaller compared with the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cell without additive in the electrolyte, whose first and last discharge capacity were  $102.7 \text{ mAh g}^{-1}$  and  $91.4 \text{ mAh g}^{-1}$ , respectively. However, after initial 12 cycles, the capacity retention of the former was 95.1%, far more smaller than that of the latter 97.5%. The result can also be explained from the conductivity decreasing of the 1# electrolyte with 0.2 M LiDFOB. While the capacity fading was also serious for  $\text{LiMn}_2\text{O}_4/\text{Li}$  cell without additive in the electrolyte at elevated temperature due to the decomposition of  $\text{LiPF}_6$ , producing the same result at last.

Cycling performance of the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cell with different concentrations of HMDS at elevated temperature was also evaluated. After 100 cycles, the capacity retention was about 87.7% and 93.0% for 6 vol.% and 2 vol.% HMDS in the electrolyte, respectively, and the latter showed better cycling performance. This can be explained similar to the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cell at room temperature above. In the following discussion section, the batteries with and without 2 vol.% HMDS in the electrolyte were investigated only, to be convenient for discussion, so 1#-HMDS was referred to as the electrolyte.

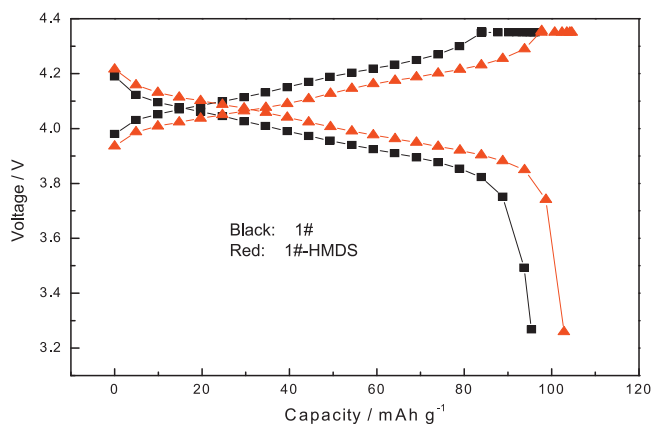
Figs. 3 and 4 show the cycling performance of  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells at  $25^\circ\text{C}$  with 1# and 1#-HMDS electrolyte at 2 C rate. It can be seen



**Fig. 3.** Cycling performance of  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells at  $25^\circ\text{C}$  with 1# and 1#-HMDS electrolyte, which was recorded at a constant rate 2 C and cutoff voltage was from 3.3 to 4.35 V.

from Fig. 3, the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells with 1#-HMDS electrolyte whose capacity fading was only  $3.8 \text{ mAh g}^{-1}$  after 200 cycles showed perfect cycling performance compared with the battery with 1# electrolyte, and the discharge capacity of the former  $102.8 \text{ mAh g}^{-1}$  was higher than that of the latter  $95.4 \text{ mAh g}^{-1}$  after 200 cycles. At the same time, from Fig. 4 it can be seen clearly that the charge plateau of the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cell with 1# electrolyte increased and the discharge plateau decreased compared with the battery with 1#-HMDS electrolyte, indicating that the polarization of the former was more serious than the latter.

Fig. 5 shows the rate performance of  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells at  $25^\circ\text{C}$  using 1#-HMDS electrolyte at different current density. It can be seen from Fig. 5, the capacity of charge and discharge at different rates was all the same basically, and the discharge capacity was all about  $107.0 \text{ mAh g}^{-1}$ . The coulomb efficiency of the 0.1 C rate was 88.58%, and was up to 97% at other different rates. There were two main reasons influencing the rate performance of  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells, they were the active substances and electrolyte, so Fig. 5 shows that the active substances and electrolyte did not affect the conductivity of  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells basically at these low rates. The conductivity test also shows that the addition of HMDS to the 1#-based electrolyte did not seriously affect the conductivity of original electrolyte, whose conductivity was  $9.12 \text{ ms cm}^{-1}$ , just a little bigger than that ( $8.93 \text{ ms cm}^{-1}$ ) of the 1#-HMDS electrolyte.



**Fig. 4.** The charge–discharge curves of  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells with different electrolytes after 200 cycles, which was recorded at a constant rate 2 C and cutoff voltage was from 3.3 to 4.35 V.

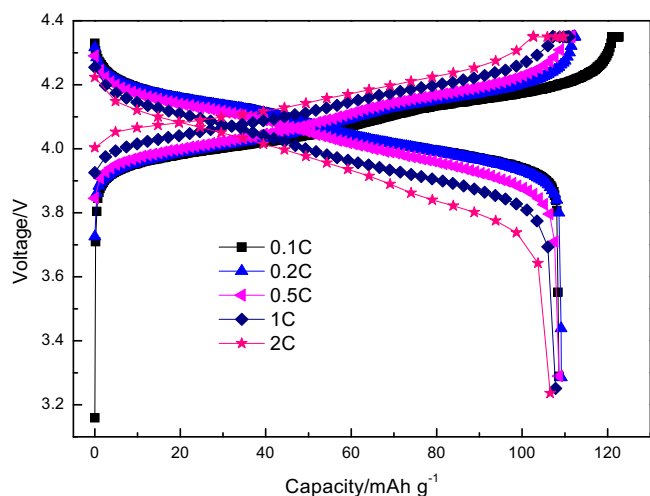


Fig. 5. Rate performance of  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells with 1-HMDS-based electrolyte at  $25^\circ\text{C}$ , cutoff voltage was from 3.3 to 4.35 V.

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

A three-electrode system incorporating  $\text{LiMn}_2\text{O}_4$  as the working electrode and Li foils as counter and reference electrodes was used for cyclic voltammetry measurement, and all the electrodes subject to cyclic voltammetry (CV) measurements were the same in electrode area and thickness and thus contain the same amount of active materials. Fig. 6 shows the cyclic voltammograms of  $\text{LiMn}_2\text{O}_4$  electrode. It can be seen from the Fig. 6(a) and (b), there are two pairs of peak reflecting the typical oxidation processes of  $\text{LiMn}_2\text{O}_4$  in about 4.08 and 4.19 V (vs.  $\text{Li}/\text{Li}^+$ ) and reduction processes in the 3.97 and 4.11 V, respectively, which involves phase transitions. In fact, there exist no other peaks except that lithium ions extracted from and inserted into the spinel lithium manganese oxide lattice via a two-step process. What is more, the peak intensity of 1#-HMDS-based electrolyte half-cell is bigger than that of 1# electrolyte half-cell, and the peak shape is sharper at the same time. The results suggest that when the HMDS added into the 1#-based electrolyte, the HMDS does not oxidize on the surface of  $\text{LiMn}_2\text{O}_4$  cathode electrode during the voltage range 3.3–4.35 V (vs.  $\text{Li}/\text{Li}^+$ ), and the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells with 1#-HMDS-based electrolyte have

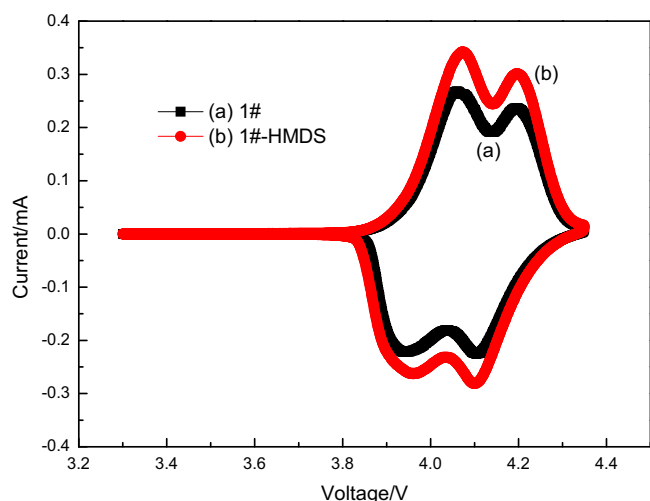


Fig. 6. CVs of  $\text{LiMn}_2\text{O}_4$  electrode in the electrolyte of 1# and 1#-HMDS between 3.3 V and 4.35 V at a scan rate  $0.1\text{ mV s}^{-1}$ .

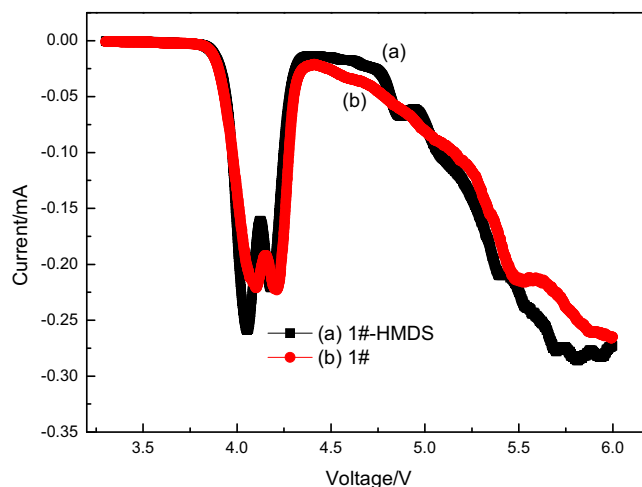


Fig. 7. LSVs of  $\text{LiMn}_2\text{O}_4$  electrode in the electrolyte of 1# and 1#-HMDS at a scan rate  $0.1\text{ mV s}^{-1}$ .

good reversible characteristic as well, showing perfect cycling performance.

A three-electrode system was also used for linear sweep voltammetry measurement. Fig. 7 displays the LSVs of  $\text{LiMn}_2\text{O}_4$  electrode using 1# and 1#-HMDS electrolyte, respectively. As we can see from Fig. 7(a), during the anodic potential sweeping, there are two obvious anodic peaks on the voltammogram, which should be associated with the two-step process of lithium-ion extraction from  $\text{LiMn}_2\text{O}_4$  cathode, and then with the potential increasing there is only smaller current until the potential reaches up to 4.77 V. However, with the addition of HMDS to the electrolyte, there is no new oxidation peak in Fig. 7(b), and this means HMDS is not oxidized as well on the surface of  $\text{LiMn}_2\text{O}_4$  cathode electrode between 3.3 V and 4.77 V (vs.  $\text{Li}/\text{Li}^+$ ). In addition, the oxidation current between 4.4 V and 4.77 V because of the decomposition of electrolyte is smaller than that of the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells with 1#-based electrolyte, this shows that when HMDS added into the 1#-based electrolyte, the stability of electrolyte has been enhanced. This can be explained as follows, for one thing, HMDS reacts with HF which can accelerate the Mn dissolution and the decomposition of electrolyte. For another, the salt generated due to the reaction between HMDS and HF could not decompose easily at room temperature, at the same time, the nitrogen core with its lone-pair electrons of excessive HMDS can form a 1:1 weak complex with  $\text{PF}_5$  which is a typical Lewis acid, weakening the activity of  $\text{PF}_5$  and inhibiting the decomposition of solvent caused by  $\text{PF}_5$  [23]. These can be explained further from TG-DSC curve below. So from the results indicated in Figs. 6 and 7 we can see that HMDS does not influence the electrochemical performance of  $\text{LiMn}_2\text{O}_4$  cathode electrode.

### 3.3. Electrolyte stability performance analysis

We investigated the stability of 1# and 1#-HMDS by TG-DSC measurements. The results are shown in Fig. 8. It can be seen apparently from the TG curves that the weight loss of the electrolyte mixtures is very seriously as soon as the measurement begins, indicating bad thermal stability of the liquid electrolyte because of decomposition. However, with the addition of HMDS to 1# electrolyte, the stability of the electrolyte has increased a lot. There is only 9.5% weight loss of the 1#-HMDS-based electrolyte compared with 18% of the 1# electrolyte at  $80^\circ\text{C}$ , 22% weight loss compared with 34.5% of the 1# electrolyte with the temperature increasing up to  $100^\circ\text{C}$ . Subsequently, we can draw a conclusion that the stability of 1#-HMDS-based electrolyte is better than that of 1# electrolyte, and it can be proved as well from the DSC curves that the top value

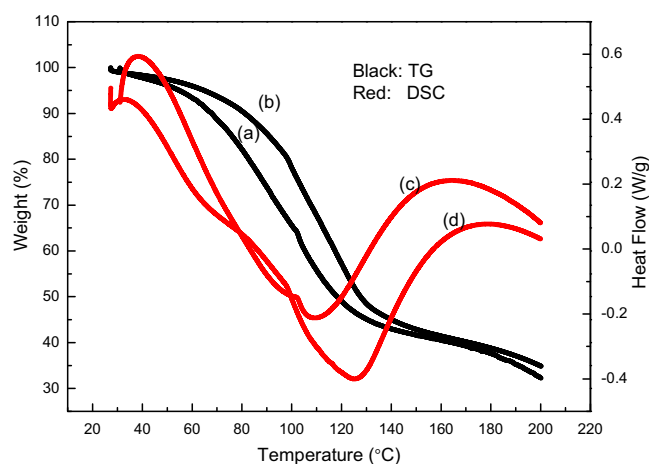


Fig. 8. TG-DSC curves of 1# (a and c) and 1#-HMDS (b and d) at a rate of  $5^{\circ}\text{C min}^{-1}$ .

of endothermic peak of 1#-HMDS-based electrolyte is much higher than that of 1# electrolyte.

### 3.4. Impedance analysis

Fig. 9 presents the impedance spectra of the  $\text{LiMn}_2\text{O}_4$  half-cells containing two different electrolytes before and after cycling at room temperature. As shown in Fig. 9, the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells with 1# electrolyte before and after cycling consist of two parts, a semicircle at high frequency, a semicircle at medium frequency and a sloping line at the low frequency, and they represent the resistance ( $R_f$ ) and capacitance ( $C_f$ ) of the interface film, the charge-transfer resistance ( $R_{ct}$ ) and double layer capacitance ( $C_{dl}$ ) and the Warburg impedance. However, the radius of the two semicircles of the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells with 1# electrolyte after cycling becomes bigger than that before cycling, this shows that the resistance of the  $R_f$  and  $R_{ct}$  increases quickly after cycling, predicating the surface film becomes thicker as well, which is also associated with  $\text{MnO}_2$  deposited on the surface of  $\text{LiMn}_2\text{O}_4$  electrode due to Mn dissolution [11].

At the same time, it can be seen from Fig. 9 that the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells with 1#-HMDS-based electrolyte before and after cycling consist of only one semicircle and a sloping line and the radius of the semicircle is smaller than the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells with 1# electrolyte at the same condition, which is apparently different from the 1# electrolyte half-cells. The parameters of impedance spectra of the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells with 1#-HMDS-based electrolyte in Fig. 9 were

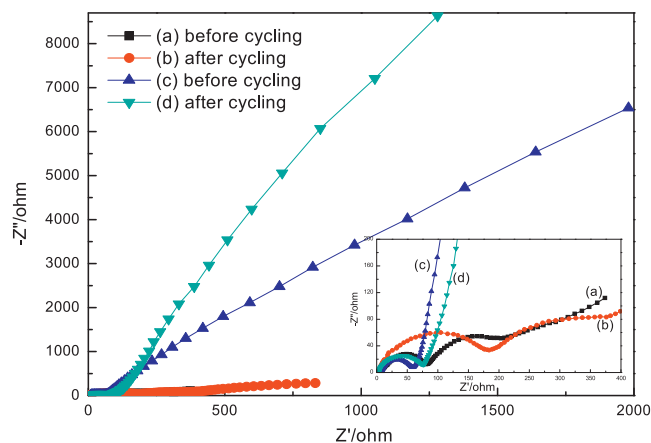


Fig. 9. EIS of the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells with 1# and 1#-HMDS electrolyte before (a and c) and after (b and d) cycling.

**Table 1**  
Impedance parameters of equivalent circuit of  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells with 1#-HMDS.

$\text{LiMn}_2\text{O}_4$ state	$R_s$ ( $\Omega$ ) (error %)	$R_{ct}$ ( $\Omega$ ) (error %)
Before cycling	8.261 (1.6579%)	52.99 (0.98448%)
After cycling	3.483 (2.8206%)	61.39 (1.63%)

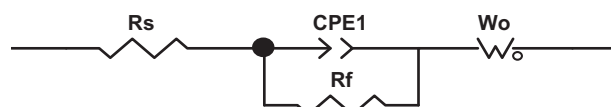


Fig. 10. Equivalent circuit of  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells with 1#-HMDS before and after cycling.

simulated by Zview 2.0. The parameter results are listed in Table 1. The fitting results indicate that the surface film resistance ( $R_f$ ) of the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells with 1#-HMDS after cycling is increased a little (in general,  $R_f$  always exists in lithium-ion battery.). As we know, the formation of the SEI film will result in the decrease of the initial charge-discharge capacity, because of HF consuming some lithium salts. However, with the addition of the HMDS to 1# electrolyte, the HF can be removed basically from the beginning, and thus reduced the  $R_f$  resistance of the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells, increasing the initial discharge capacity and cycling performance the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells (Fig. 10).

## 4. Conclusions

The addition of 0.2M LiDFOB to 1# electrolyte can deteriorate the performance of  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells, this is mainly because LiDFOB can influence the conductivity of the original electrolyte. The HMDS of different concentrations in 1# electrolyte has different effect on the cycling performance of  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells at room temperature and elevated temperature at different rates. When the concentration of the additive is 2 vol.%, the battery of 1#-HMDS-based electrolyte shows perfect cycling performance at room temperature at 2C rate, and the capacity fading was only  $3.8\text{mAh g}^{-1}$  after 200 cycles. The results of cyclic voltammetry (CV) test, linear sweep voltage (LSV) test, TG-DSC analysis, conductivity, electrochemical impedance spectroscopy (EIS) and charge-discharge measurements show that the addition of 2 vol.% HMDS to the 1# electrolyte can not affect the conductivity of the original electrolyte basically, and can increase the stability of the electrolyte, reduce the surface film resistance of the batteries, improving the cycling performance of  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells.

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