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Short communication

Effect of heptamethyldisilazane as an additive on the stability performance of $LiMn_2O_4$ cathode for lithium-ion battery

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ABSTRACT

The effect of heptamethyldisilazane as additive on the stability of the electrolyte and cycling performance of $LiMn_2O_4$ batteries was studied by linear sweep voltammetry, charge–discharge of battery, stability measurement and high temperature test. The results show that the addition of heptamethyldisilazane to the electrolyte can suppress the contents of HF in the electrolyte and the cycling performance of $LiMn_2O_4$ batteries can be improved. After storage at 60 °C for 7 days, the stability of batteries using electrolyte with heptamethyldisilazane can be improved, however the stability of batteries using the electrolyte with heptamethyldisilazane can be weakened after storage at 85 °C for 4 h.

1. Introduction

Lithium-ion batteries, which are made of lithium transition metal oxides as a cathode and carbonaceous materials as an anode, have been widely used in portable electronics and are under intensive research for application in hybrid electric vehicle (HEV) and electric vehicle (EV) because of their relatively high energy density and power density [1,2].

Spinel $LiMn_2O_4$ is a promising cathode material for rechargeable lithium-ion batteries because of its high voltage, low cost, and safety. However $LiMn_2O_4$ cathode has problems with capacity fading and poor cycling at elevated temperature [3–5]. The reasons for capacity fading are the following: manganese dissolution, Jahn–Teller effect, and electrolyte discomposing. The erosion to $LiMn_2O_4$ of the electrolyte is the important reason for capacity fading and poor cycling performance [6–9]. HF formation from the decomposition of $LiPF_6$ salt in the presence of trace water is believed in accelerating the Mn dissolution [10–12]. The addition of the stability additives to the electrolyte can suppress the capacity fading of $LiMn_2O_4$ batteries and the cycling performance of lithium-ion battery with $LiMn_2O_4$ as the cathode can be improved [13–19].

Yamane et al. [20] reported the effect of hexamethyldisilazane as an additive on the storage performance of the electrolyte and cycling performance of lithium-ion batteries with $Li_{1.01}Mn_{1.99}O_4$ as the cathode. Hexamethyldisilazane ($(CH_3)_3SiNHSi(CH_3)_3$) is used as an organic liquid desiccant and it can remove water and neutralize acids in solutions as follows: $(CH_3)_3SiNHSi(CH_3)_3 + H_2O \rightarrow (CH_3)_3SiOSi(CH_3)_3 + NH_3$. The authors used the cell assembled with Li metal/electrolyte/$Li_{1.01}Mn_{1.99}O_4$ cathode for the storage test at the fully discharged state at 80 °C for 6 h, 36 h, etc. The preserved ratios of discharge capacity of cell are 98.44% and 73.64%, respectively. They studied the substances causing the capacity fading and the mechanism of the capacity fading of $Li_{1.01}Mn_{1.99}O_4$ cathode material.

In this paper, the effect of heptamethyldisilazane ($(CH_3)_3SiN(CH_3)Si(CH_3)_3$) which does not dissolve in water and can be combined with acid to form the salt compound as an additive on the stability performance of $LiMn_2O_4$ cathode for lithium-ion battery has been investigated.

2. Experimental

2.1. Electrolyte preparation

Ethylene carbonate (EC), propylene carbonate (PC) and ethyl (methyl) carbonate (EMC), were purified by distilling and with molecular sieve till the purity was higher than 99.95%, which was

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determined with GC-14C (SHIMADZU). $LiPF_6$ was supplied by Japan Stella Chemical (Osaka). The electrolyte solutions were prepared by dissolving 1 mol L^{-1} $LiPF_6$ in the mixture solvents in a dry glove box (H_2O, O_2 < 1 ppm) filled with high purity argon.

Water and free acid contents in the electrolyte were controlled below 20 ppm. Karl-Fisher 831 Coulometer (Metrohm) was used to determine the water content of the electrolyte. About 0.3–0.5 g sample was added to the Karl-Fisher titration cup. The methanol traps the water which is titrated to an end point with Karl-Fisher reagents to determine the water content of the electrolyte. Karl-Fisher 798 MPT Titrino (Metrohm) was used to determine the free acid content of the electrolyte by acid–base neutralization reaction principle. About 3–4 g sample was immited into the reaction tank of acidity equipment. The free acid is titrated to an end point with potassium hydroxide solution to determine the HF content of the electrolyte.

2.2. Battery performances

Battery performances were determined with utilization of 053048-size batteries with nomimal capacity of 550 mAh using a programmable computer-controlled battery charge (BS-8305H-L2, Guangzhou, China). The cathode and anode were made of lithium manganese oxide ($LiMn_2O_4$) and graphite, respectively. The temperature was controlled with a WD4003 oven (Chongqing Yinhe experimental equipment Co. Ltd., China). The batteries were charged at constant current of 1 C rate to 4.2 V, followed by a constant voltage of 4.2 V until the current decreased to C/30 at room temperature. For room temperature performance determination, the charged batteries were discharged at 1 C rate to 2.75 V. For high temperature performance determination, the charged batteries were stored at 60 °C for 7 days and at 85 °C for 4 h, respectively then discharged at 1 C rate to 2.75 V.

2.3. Linear sweep voltammetry (LSV)

A three-electrode cell was used for LSV, with $LiMn_2O_4$ and graphite as the working electrode, respectively and Li foils as counter and reference electrodes. The graphite electrodes were prepared as follows: carbonaceous mesophase sphere (CMS) was mixed with 8% (by weight) polyvinylidene fluoride (PVDF), and the mixture was rolled onto copper foil, pressed and dried. The $LiMn_2O_4$ electrodes were prepared as follows: the mixture of $LiMn_2O_4$ powder, carbon black and PVDF with a mass ratio of 85:10:5 was rolled onto aluminum foil, pressed and dried. Electrochemical measurements were carried out on Autolab (PGSTAT30, ECO Echemie B.V. Company).

2.4. Stability performance

One drop of distilled water was added to the two electrolytes without and with 0.1 wt.% heptamethyldisilazane, respectively. After the two electrolytes were stored at room temperature for a week, the contents of H_2O and free acid (HF) in the electrolyte were determined.

3. Results and discussion

3.1. LSVs of graphite electrode and $LiMn_2O_4$ electrode in the electrolytes without and with heptamethyldisilazane

Figs. 1 and 2 show LSVs of graphite electrode and $LiMn_2O_4$ electrode using 1 mol L^{-1} $LiPF_6$/EC:EMC:PC = 3:6:1 without and with 0.1 wt.% heptamethyldisilazane as electrolytes, scan rate 0.1 mVs^{-1}.

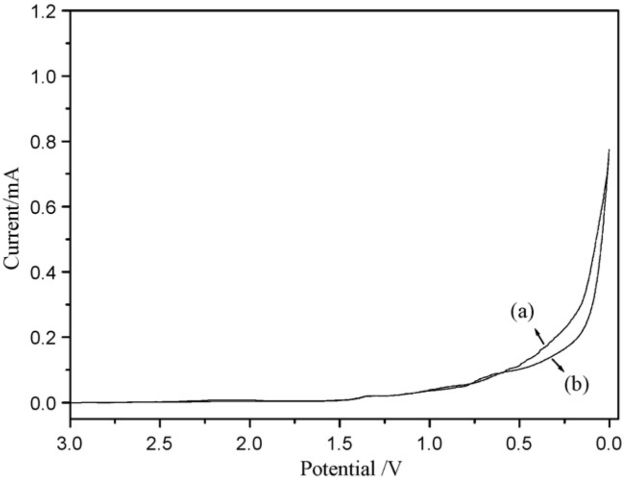


Fig. 1. LSVs of graphite electrode using 1 mol L^{-1} $LiPF_6$/EC:EMC:PC = 3:6:1 without (a) and with (b) 0.1 wt.% heptamethyldisilazane as electrolytes, scan rate 0.1 mVs^{-1}.

As we can see from Fig. 1(a), during the cathodic potential sweeping, a reduction reaction happens, resulting in the formation of SEI film on graphite electrode. As the potential becomes more negative, the reduction current increases, which corresponds to the increasing of quantity of lithium ions inserted into graphite. Fig. 1(b) shows the addition of heptamethyldisilazane to the electrolyte, no new reduction peak appears and only the reduction current decreases. Heptamethyldisilazane is not reduced on the surface of graphite anode electrode during the voltage range of 0–3.0 V (vs. Li/Li^+). Fig. 2(a) indicates that there are two oxidation peaks in linear sweep curve which should be attributed to the two-step process of lithium-ion extraction from $LiMn_2O_4$ cathode. The addition of heptamethyldisilazane to the electrolyte, no new oxidation peak appears in Fig. 2(b) and only the oxidation current decreases. Heptamethyldisilazane is not oxidized on the surface of $LiMn_2O_4$ cathode electrode during the voltage range of 3.0–4.9 V (vs. Li/Li^+). The results mean that heptamethyldisilazane does not influence the electrochemical performance of graphite electrode and $LiMn_2O_4$ electrode. The electrolyte with heptamethyldisilazane has the broad electrochemical stability windows (0–4.9 V vs. Li/Li^+).

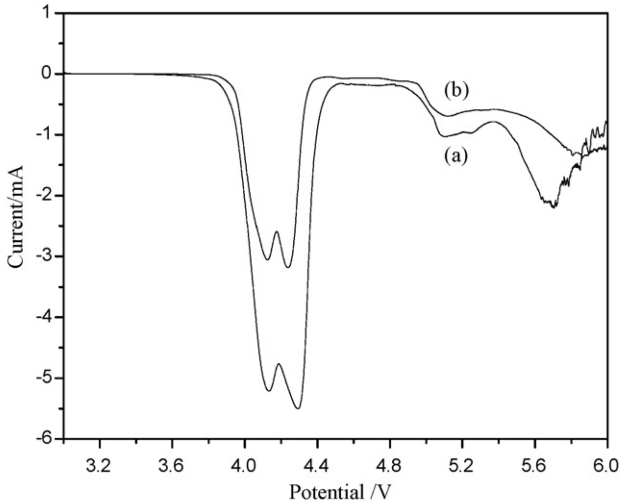


Fig. 2. LSVs of $LiMn_2O_4$ electrode using 1 mol L^{-1} $LiPF_6$/EC:EMC:PC = 3:6:1 without (a) and with (b) 0.1 wt.% heptamethyldisilazane as electrolytes, scan rate 0.1 mVs^{-1}.

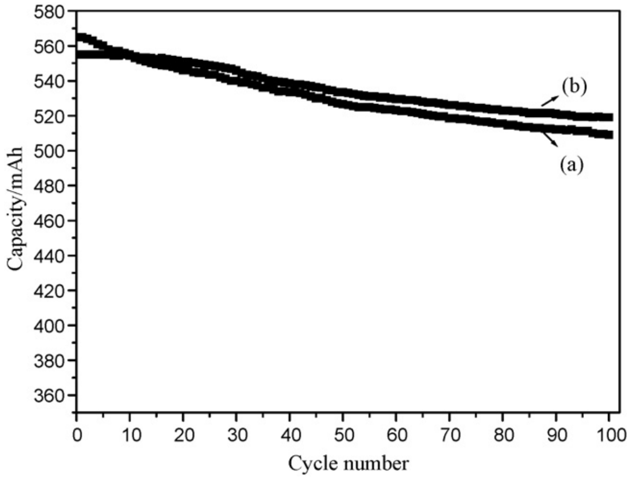


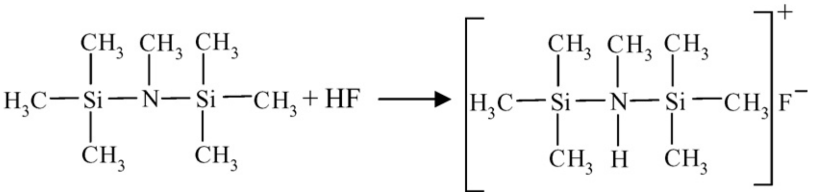
Fig. 3. Cycling performance of the batteries using 1 mol L^{-1} $LiPF_6$/EC:EMC:PC = 3:6:1 without (a) and with (b) 0.1 wt.% heptamethyldisilazane as electrolytes at room temperature.

3.2. Electrolyte stability performance analysis

In order to identify the effect of heptamethyldisilazane on the stability performance of the electrolyte, we conducted the storage experiment adding some water to the electrolyte solution at room temperature.

Table 1 gives the results of the contents of H_2O and HF in 1 mol L^{-1} $LiPF_6$/EC:EMC:PC = 3:6:1 without and with 0.1 wt.% heptamethyldisilazane, after the two electrolytes were stored at room temperature for a week.

As shown in Table 1, after the electrolyte without heptamethyldisilazane was stored at room temperature for a week, $LiPF_6$ salts react with H_2O to produce much free acid (HF). Whereas in the electrolyte with 0.1 wt.% heptamethyldisilazane, heptamethyldisilazane can be combined with HF to form the salt compound as follows:



$$\mathrm{H_3C{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}\overset{CH_3}{N}{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}CH_3 + HF \longrightarrow \left[H_3C{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}\overset{CH_3}{\underset{H}{N}}{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}CH_3\right]^{+} F^{-}}$$

The contents of HF in the electrolyte can be restrained, resulting in the improving of stability performance of the electrolyte.

3.3. Cycling performance analysis

Fig. 3 shows the cycling performance of the batteries using 1 mol L^{-1} $LiPF_6$/EC:EMC:PC = 3:6:1 without and with 0.1 wt.% heptamethyldisilazane as electrolytes at room temperature. The contents of H_2O and HF in the two electrolytes were controlled at 9.2 ppm and 9.7 ppm.

As shown in Fig. 3, after 100 cycles, the preserved ratios of discharge capacity of batteries using 1 mol L^{-1} $LiPF_6$/EC:EMC:PC = 3:6:1 without and with 0.1 wt.% heptamethyldisilazane as electrolytes are 90.1% and 93.5%, respectively. For addition of heptamethyldisilazane, the initial discharge capacity just only can be reduced by about 1.77%, but the cycling performance can be significantly improved.

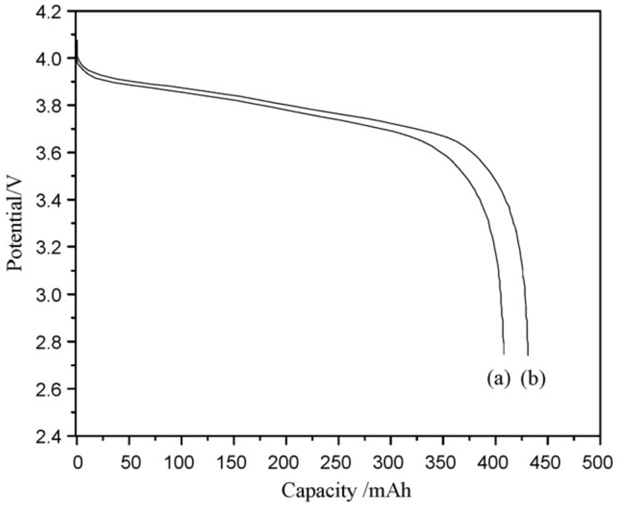


Fig. 4. Discharge curves of batteries using 1 mol L^{-1} $LiPF_6$/EC:EMC:PC = 3:6:1 without (a) and with (b) 0.1 wt.% heptamethyldisilazane as electrolytes after storage at the fully charged state at 60 °C for 7 days.

In the electrolyte with $LiPF_6$ as lithium salt, $LiPF_6$ can react with trace water to produce free acid (HF), and then HF can react with $LiMn_2O_4$, the reaction is as follows: $2LiMn_2O_4 + 4H^+ \rightarrow 2Li^+ + 3\lambda\text{-}MnO_2 + Mn^{2+} + 2H_2O$. Mn dissolution not only reduces the amount of $LiMn_2O_4$, but also brings on the transformation of $LiMn_2O_4$ crystal lattice. Heptamethyldisilazane can be combined with HF to form the salt compound and the contents of HF in the electrolyte can be suppressed, resulting in the improving of cycling performance of $LiMn_2O_4$ batteries.

3.4. Battery stability performance analysis

Figs. 4 and 5 show the discharge curves of $LiMn_2O_4$ batteries using 1 mol L^{-1} $LiPF_6$/EC:EMC:PC = 3:6:1 without and with 0.1 wt.% heptamethyldisilazane as electrolytes after storage at the fully charged state at 60 °C for 7 days and at 85 °C for 4 h, respectively.

As shown in Fig. 4, after storage at 60 °C for 7 days, the preserved ratios of discharge capacity of batteries using 1 mol L^{-1} $LiPF_6$/EC:EMC:PC = 3:6:1 without and with 0.1 wt.% heptamethyldisilazane as electrolytes are 74.18% and 78.36%, respectively. The addition of heptamethyldisilazane to the electrolyte, the stability performance of batteries at 60 °C can be improved, because heptamethyldisilazane can be combined with HF to form the stable salt compound.

As shown in Fig. 5, after storage at 85 °C for 4 h, the preserved ratios of discharge capacity of batteries using 1 mol L^{-1} $LiPF_6$/EC:EMC:PC = 3:6:1 without and with 0.1 wt.% heptamethyldisilazane as electrolytes are 85.64% and 75.64%, respectively. Adding heptamethyldisilazane to the electrolyte, the reasons for the stability performance of batteries decreasing at 85 °C are the decomposing of the salt compound which can be formed by combining heptamethyldisilazane and HF and other factors.

Table 1
Contents of H_2O and HF in two electrolytes before and after storage at room temperature for a week

	Electrolyte without heptamethyldisilazane		Electrolyte with 0.1 wt.% heptamethyldisilazane	
	H_2O (ppm)	HF (ppm)	H_2O (ppm)	HF (ppm)
Before storage	132.7	9.8	132.7	9.8
After storage	3.0	266.8	3.1	50.5

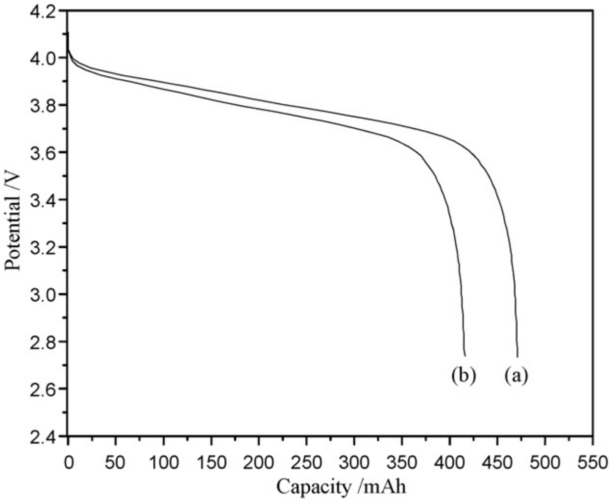


Fig. 5. Discharge curves of batteries using 1 mol L^{-1} $LiPF_6$/EC:EMC:PC = 3:6:1 without (a) and with (b) 0.1 wt.% heptamethyldisilazane as electrolytes after storage at the fully charged state at 85 °C for 4 h.

4. Conclusions

Heptamethyldisilazane is not reduced on the surface of graphite anode electrode and oxidized on the surface of $LiMn_2O_4$ cathode electrode and the electrolyte with heptamethyldisilazane has the broad electrochemical stability windows (0–4.9 V vs. Li/Li^+). The addition of heptamethyldisilazane to the electrolyte, the stability performance of the electrolyte and the cycling performance of $LiMn_2O_4$ batteries can be improved, because of heptamethyldisilazane being combined with HF to form the stable salt compound. Adding heptamethyldisilazane to the electrolyte, the stability performance of batteries can be improved after storage at 60 °C for 7 days and be weakened after storage at 85 °C for 4 h.

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