



Short communication

An advanced electrolyte for improving surface characteristics of LiMn_2O_4 electrodeGuo Yongxing^{a,*}, Yin Zhenguo^b, Tao Zhiyong^b, Li Xinhai^a, Wang Zhixing^a^a School of Metallurgical Science and Engineering, Central South University, Changsha 410083, China^b Shenzhen Herwin Technology Co. Ltd., Shenzhen 518104, China

ARTICLE INFO

Article history:

Received 22 December 2007

Received in revised form 19 February 2008

Accepted 10 March 2008

Available online 20 March 2008

Keywords:

Lithium manganese oxides

Storage performance

Elevated temperature

LiBOB

ABSTRACT

To apply widely the cathode material lithium manganese oxide (LiMn_2O_4) with spinel structure, temperature characteristics of LiMn_2O_4 electrode were studied to decrease the expansion extent by applying different additives in the electrolytes. Different addition contents of 1,3-propane sultone (1,3-PS) and propylene carbonate (PC) in the electrolytes were studied. The results showed PC and 1,3-PS could decrease the thickness variation of cells stored at elevated temperature.

Lithium bis(oxalate) borate (LiBOB) additive was investigated to improve the storage characteristics at elevated temperature and cycling performance (25 °C) of the cell with LiMn_2O_4 cathode. The results showed that LiBOB improved remarkably the storage characteristics and cycling performance of the cells. And an advanced electrolyte was developed.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

In view of cheapness, safety and environmental benignancy, lithium manganese oxide (LiMn_2O_4) with spinel structure has been considered as a promising cathode material for Li-ion power batteries [1]. However, LiMn_2O_4 has a defect of structural instability at high temperature and Mn dissolves into the electrolyte due to hydrofluoric acid (HF) produced by the reaction of LiPF_6 and H_2O in the electrolyte. Also, some large cell groups are applying widely now, which are easy to produce a mass of heat when used, and LiPF_6 and solvents decompose easily to produce gas at elevated temperature and cells may swell seriously.

Some additives were used to improve the solid electrolyte interface (SEI) film forming. Prominent additive examples include CO_2 , N_2O , SO_2 , chloroethylene carbonate, fluoroethylene carbonate, vinylpropylene carbonate, vinylene carbonate, catechol carbonates, 12-crown-4, ethylene sulfite [2–10]. Korepp et al. [11] studied 2-cyanofuran (2CF) as an additive for propylene carbonate (PC)-based electrolytes. And 2CF shows good SEI-forming behavior on graphite and suppresses solvent co-intercalation. Chen et al. [12] investigated the electrotype containing butylene sulfite (BS) which can effectively prevent the co-intercalation of PC with solvation lithium ion into graphite.

In this work, 1,3-propane sultone (1,3-PS) was included into the electrolyte to suppress PC co-intercalation into graphite. And various amounts of 1,3-PS and PC as co-solvent added into the electrolyte (1 M LiPF_6 , EC:EMC:DEC) were investigated to improve the storage performance of cells at elevated temperature.

Lithium bis(oxalate) borate (LiBOB) was investigated to suppress Mn from dissolving into the electrolyte. And the performance of advanced electrolyte was studied to prevent cells from swelling when stored at 85 °C for 4 h.

2. Experimental

The tested full cell was LiMn_2O_4 Li-ion cell of type 457090 with nominal capacity of 1800mAh packed with Al-laminated film. Cathode electrode was prepared by combining, by mass, 92% LiMn_2O_4 , 2% conductive carbon and 6% polyvinylidene fluoride (PVDF, from Kuraha Chemical). Anode electrode was prepared by mixing 95% graphite, 2% sodium carboxymethyl cellulose (CMC-Na), 3% styrene-butadiene rubber (SBR). UP3085 (0.025 mm, from UBE Co. Ltd., Japan) was used as separator. The electrodes were preserved after coating and then assembled into cells in the dry room.

Ethylene carbonate (EC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC), PC, 1,3-PS, lithium hexafluorophosphate (LiPF_6 , from Guotai Huarong, China) and LiBOB (from Chemetall, Germany) were all battery grade reagents. HF or H_2O content is lower than 20 ppm. LiPF_6 was dissolved into solvents to get electrolyte in an Ar-filled glove box.

* Corresponding author. Tel.: +86 731 8836633; fax: +86 731 8836633.
E-mail address: 13510505511@139.com (G. Yongxing).

The cells were charged at constant current (CC) of 1 C rate to 4.2 V, followed by a constant voltage (CV) of 4.2 V until the current decreased to 0.02 C at room temperature. For storage performance test at high temperature, the full charged cells were stored at 85 °C for 4 h in a SWY-1 constant temperature oven (Song Ling Co. Ltd., China). And the maximum thickness of cell after storage (no rupture) is measured by a vernier caliper at 85 °C in the constant temperature oven. The swell value of cell is calculated by the following formula:

$$\text{Swell value (\%)} = \frac{(T - T_0)}{T_0} \times 100$$

T_0 is the initial thickness of the cell and T is the thickness of the cell after storage.

The discharge performance was tested at low temperature in an ITH-150 constant temperature and humidity chamber (Giant Force Instrument Co. Ltd., China). First, the 0.2 C discharge capacity of cells were tested at room temperature, then the full charged cells were discharged to get the 0.2 C discharge capacity at –20 °C after the batteries were stored for 12 h in the chamber.

3. Results and discussion

Because of trace of acid (HF) in the electrolyte, Mn of LiMn_2O_4 can be dissolved into the electrolyte, and the electrolyte can be decomposed to produce gas so that the cells will swell seriously, especially, SEI film can be destroyed and the decomposed reactions will react intensively and produce more gas at elevated temperature. So some measures should be taken to prevent the SEI film from destroying and decrease Mn dissolution into the electrolyte.

3.1. 1,3-PS and PC evaluation for effecting storage performance

It has been known that EC is an essential component to form a stable SEI film. The roles of EMC and DEC are to dilute viscosity, enhance wettability, and participate in SEI formation. So a EC/EMC/DEC (1:1:1 wt%) tertiary solvent mixture was chosen to formulate a Li-ion electrolyte which was compatible with LiMn_2O_4 cathode. And various contents of 1,3-PS and PC were added into the solvent mixture. Then LiPF_6 was dissolved into solvent mixture to form the electrolyte of 1 M concentration.

Table 1 presented swell value of cells with different contents of 1,3-PS as 5% PC was fixed.

It could be seen that the cell swelled 28.70% when the electrolyte was without 1,3-PS as 5% PC was fixed. While 3% 1,3-PS was added into the electrolyte keeping other conditions invariable, the cell swelled only 12.40%.

Therefore, 1,3-PS is helpful to suppress swelling of cells at high temperature, which is mainly because 1,3-PS contains sulfur atoms and its decomposed voltage is lower than that of the solvents and contributes to form an excellent SEI film. The SEI film is more stable in the electrolyte. So the SEI film is difficult to decompose and the reaction between the electrodes and electrolyte is prevented, so gas production decreases and cells will swell less.

Table 1
The swell value of cells with different contents of 1,3-PS

Solvent	1,3-PS (wt%)	PC (wt%)	Swell value (%)
EC:EMC:DEC (1:1:1 wt)	0	0	35.11
	0	5	28.70
	1	5	19.83
	2	5	17.64
	3	5	12.40
	4	5	14.73
	5	5	15.97

Table 2
The swell value of cells with different contents of PC

Solvent	1,3-PS (wt%)	PC (wt%)	Swell value (%)
EC:EMC:DEC (1:1:1 wt)	3	0	31.41
	3	2	27.88
	3	4	26.34
	3	5	12.40
	3	6	22.52
	3	8	25.54
	3	10	34.92

Table 2 presented swelling value of cells with different contents of PC as 3% 1,3-PS was fixed.

The results showed PC was a good solvent that could be used to improve the storage performance of cells at high temperature. As 5% PC was added into the electrolyte while 3% 1,3-PS was fixed, the cell swelled 12.40% which was least, but it swelled 31.41% without PC and swelled more if PC was added excessively. PC has a high boiling point and viscosity, and it can lower the swelling of cells as a co-solvent in the electrolyte.

All of these results showed that 1,3-PS and PC could remarkably decrease swelling extents of thickness when cells were stored at high temperature. And conjunct function of both components was better than that of any single solvent. 3% 1,3-PS and 5% PC were contained into the electrolyte, the variation of thickness was the least.

3.2. Effect of LiBOB on storage performance

LiBOB, a fluorine-free salt, has some unique properties that reduce Mn dissolution into the electrolyte and co-operate in SEI film formation and stabilize SEI film [13].

Optimizing ratio of LiBOB to LiPF_6 was obtained to improve the performance of LiMn_2O_4 cells at elevated temperature environments especially. The experimental results were displayed in Table 3 as 5% PC was fixed.

From the experimental results, we found cells would swell less with increase of LiBOB contents in the electrolyte. When LiBOB concentration was 0.10 M, the cell swelled 10.51%, but without LiBOB, the cell swelled 28.70%. If 3% 1,3-PS was added when LiBOB concentration was 0.10 M as 5% PC was fixed, the cell would swell 4.22% slightly.

The results showed LiBOB was an effective lithium salt to suppress LiMn_2O_4 Li-ion cells from swelling when stored at 85 °C for 4 h. And 1,3-PS and LiBOB co-worked much more excellently.

First, LiBOB is a kind of fluorine-free salt which does not produce HF to suppress Mn dissolution into the electrolyte. Second, thermal stability of LiBOB can suppress decomposition of the electrolyte from producing gas at elevated temperature.

To summarize all the experimental results, 1,3-PS, PC and LiBOB are all effective to suppress cells from swelling when stored at 85 °C for 4 h. On one hand, 1,3-PS and LiBOB are positive to form more stable SEI film on graphite, and LiBOB changes surface characteristics of LiMn_2O_4 electrode to suppress Mn dissolution into the electrolyte. On the other hand, PC can form more stable co-solvent

Table 3
The swell value of cells with different contents of LiBOB

Solvent	LiPF_6 (M)	LiBOB (M)	PC (wt%)	1,3-PS (wt%)	Swell value (%)
EC:EMC:DEC (1:1:1 wt)	1	0	5	0	28.70
	0.95	0.02	5	0	26.72
	0.98	0.05	5	0	25.70
	0.90	0.10	5	0	10.51
	0.90	0.10	5	3	4.22

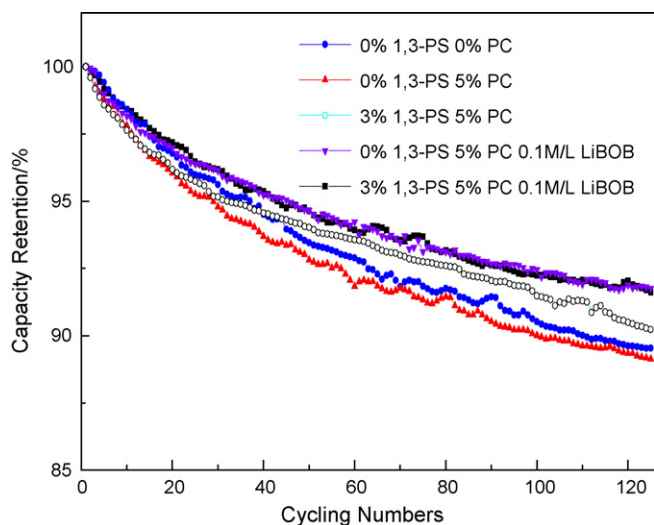


Fig. 1. Cycling performance of electrolyte with different additives at room temperature (charge: CC/CV 1800 mA, 4.2 V, end current: 36 mA; discharge: CC 1800 mA, end voltage: 3.0 V).

mixture with EC/EMC/DEC tertiary solvent to decrease swelling extents of cells at elevated temperature.

Accordingly, we mixed an advanced electrolyte which was composed of EC:EMC:DEC (1:1:1 wt) including 3% 1,3-PS and 5% PC, and the salt concentration was 0.90 M LiPF_6 and 0.10 M LiBOB.

3.3. Cycling performance at room temperature

The cycling performance of advanced electrolyte at room temperature was compared with other electrolytes of different composition.

Fig. 1 showed the cycling curves of cells using electrolytes (EC:EMC:DEC, 1:1:1 wt%) with different additives. It was found that the cycling performance of electrolyte solely containing 5% PC was the worst, and the performance of electrolyte without any additives was also bad. The cycling performances of electrolytes with 0.10 M LiBOB and 0.90 M LiPF_6 were outstanding. However, while without LiBOB, the performance of electrolyte with 3% 1,3-PS was better than that without 1,3-PS. Thereby, 1,3-PS has a function that can improve the cycling performance because of its SEI-forming advantage. And LiBOB was the most effective additive that was able to remarkably enhance the cycling performance.

Also, we investigated the cycling performance of advanced electrolyte at 60 °C, the results showed in Fig. 2. We found the capacity still kept 86.5% after 100 cycles even at 60 °C, and more than 80% after 160 cycles. However, the cycling performance of the cell using normal electrolyte (EC:EMC:DEC, 1:1:1 wt and 1 M LiPF_6) is very poor, the capacity faded rapidly and capacity retention was lowered to 80% after 60 cycles only. The advanced electrolyte showed very excellent performance to suppress capacity fading of the LiMn_2O_4 cell at high temperature.

3.4. Discharge performance of advanced electrolyte at low temperature

Fig. 3 compared the discharge curve of batteries at room temperature with that at -20 °C, the capacity remained 86.1% at room temperature. The results indicated that the advanced electrolyte was able to work very well at low temperature.

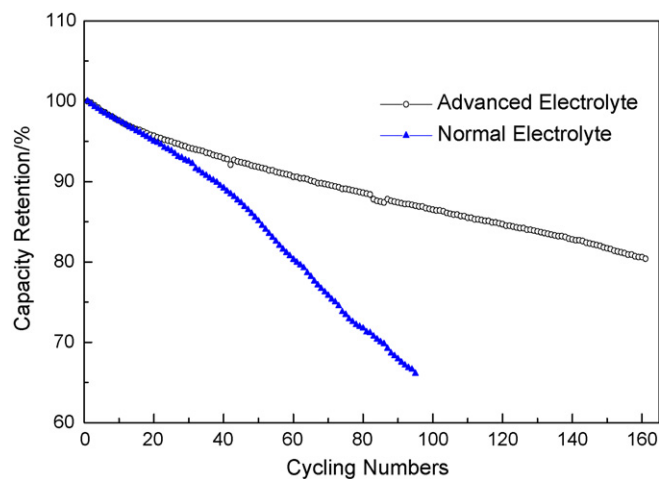


Fig. 2. Cycling performance of electrolytes at 60 °C (charge: CC/CV 1800 mA, 4.2 V, end current: 36 mA; discharge: CC 1800 mA, end voltage: 3.0 V).

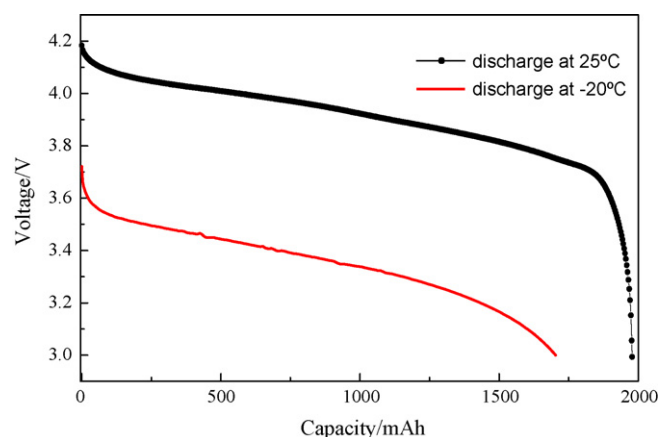


Fig. 3. Discharge curves at room temperature and at -20 °C (charge: CC/CV 1800 mA, 4.2 V, end current: 36 mA; discharge: CC 1800 mA, end voltage: 3.0 V).

4. Conclusion

In this work, 1,3-PS was used as a SEI-forming additive and suppresses PC from co-intercalating into graphite. The results showed PC was able to form an excellent co-solvent with EC/EMC/DEC, and it was helpful to avoid cells from swelling that 3% 1,3-PS and 5% PC were contained in the electrolyte.

An appropriate concentration of LiBOB is 0.10 M and LiPF_6 is 0.90 M in the advanced electrolyte.

The advanced electrolyte which was composed of EC/EMC/DEC/PC including 1,3-PS and mixed salts of LiBOB and LiPF_6 blended could evidently decrease swelling extent of the cells when stored at elevated temperature. Also, the cycling performance is very excellent, especially at high temperature. At the same time, it has a good discharge performance at low temperature.

Acknowledgements

The project was sponsored by National Basic Research Program of China (973 Program, 2007CB613607). The authors would like to appreciate the support of Central South University in Changsha and Herwin Technology Co. Ltd. in Shenzhen in China.

References

- [1] A. Ritchie, W. Howard, J. Power Sources 162 (2006) 809–812.
- [2] G.H. Wrodnigg, J.O. Besenhard, M. Winter, J. Electrochem. Soc. 146 (1999) 470.
- [3] Y. Ein-Eli, S.R. Thomas, V.R. Koch, J. Electrochem. Soc. 144 (1997) 1159.
- [4] A. Naji, J. Ghanbaja, D. Billaud, Electrochim. Acta 45 (2000) 1893.
- [5] R. McMillan, H. Selegre, Z.X. Shu, W. Wang, J. Power Sources 81/82 (1999) 20.
- [6] M. Inaba, Y. Kawatate, A. Funabiki, S.-K. Jeong, T. Abe, Z. Ogumi, Electrochemistry 67 (1999) 1153.
- [7] H. Nakamura, H. Komatsu, M. Yoshio, J. Power Sources 62 (1996) 219.
- [8] S.-K. Jeong, M. Inaba, R. Mogi, Y. Iriyama, T. Abe, Z. Ogumi, Langmuir 17 (2001) 8281.
- [9] C. Wang, H. Nakamura, H. Komatsu, H. Noguchi, M. Yoshio, H. Yoshitake, Electrochemistry 66 (1998) 286.
- [10] C. Wang, H. Nakamura, H. Komatsu, M. Yoshio, H. Yoshitake, J. Power Sources 74 (1998) 142.
- [11] C. Korepp, H.J. Santner, T. Fujii, M. Ue, J.O. Besenhard, K.-C. Moller, M. Winter, J. Power Sources 158 (2006) 578–582.
- [12] R.J. Chen, F. Wu, L. Li, Y.B. Guan, X.P. Qiu, J. Power Sources 172 (2007) 95–403.
- [13] K. Amine, J. Liu, S. Kang, et al., J. Power Sources 129 (2004) 14.