

Short communication

2,2-Dimethoxy-propane as electrolyte additive for lithium-ion batteries

Chia-Chin Chang^{a,*}, Li-Jane Her^b, Li-Chia Chen^a, Yen-Yu Lee^a,
Shyh-Jiun Liu^c, Hsien-Ju Tien^d

^a Department of Environment and Energy, National University of Tainan, Tainan 70101, Taiwan

^b E-ONE Moli Energy Corp., Southern Taiwan Science Park, Tainan County 741-47, Taiwan

^c Department of Nature Science Education, National University of Tainan, Tainan 70101, Taiwan

^d Department of Chemistry, National Cheng Kung University, Tainan 70101, Taiwan

Received 2 August 2006; received in revised form 25 September 2006; accepted 27 September 2006

Available online 13 November 2006

This article is dedicated to the late professor Tong-Ing Ho, who deceased on 14 December 2005.

Abstract

2,2-Dimethoxy-propane (DMP) was studied as an additive in 1 mol dm⁻³ LiPF₆ ethylene carbonate and diethyl carbonate (1:1, w/w) for lithium-ion battery, which was characterized by cyclic voltammetry and half cell tests. Cyclic voltammetry and half cell data show that the use of DMP as an additive to the organic solutions at very low level (*ca.* 0.005 wt%) offers the advantage of forming fully developed passive films on the graphite anode surface. The electrochemical performance of the additive-containing electrolytes in combination with LiCoO₂ cathode and graphitic anode was also tested in commercial cells 103448. The results reveal that the cyclic life test and storage performance at high temperature (*ca.* 60 °C) in electrolyte with DMP additive was better than that in an electrolyte without additive. Therefore, DMP can be considered as a desirable additive in electrolyte for lithium-ion batteries operating at high temperature, *ca.* 60 °C.

© 2006 Elsevier B.V. All rights reserved.

Keywords: 2,2-Dimethoxy-propane (DMP); Electrolyte additive; Lithium-ion battery

1. Introduction

In commercially available lithium-ion batteries, lithium ion is electrochemically intercalated into the graphite negative electrode during charging, and de-intercalated during discharging [1,2]. These reactions are basically reversible, and however, the reversibility depends greatly on the kind of electrolyte solution. Alkyl carbonates such as ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC), are among the most important solvents for electrolyte of lithium-ion batteries because they are aprotic, polar, and non-volatile. It has been found [3–6] that the carbon material has good cyclic life and maintains a high potential in EC/DEC electrolyte due to the formation of a good passive film on the carbon surface. Zaghbi et

al. [5] found that the formation of the passive film was not only due to solvent decomposition but was also affected by nature of salt in the EC/DEC system. EC/DEC mixed solvent systems are currently used in commercially available lithium-ion cells employing graphite as a negative electrode.

Nevertheless, as the above EC/DEC electrolytes have been primarily selected because of their electrochemical performance at the respective electrode electrolyte interface, some compromises regarding bulk electrolyte properties had to be made. A strategy to decouple the interface and bulk properties of the electrolyte is to use electrolyte additive that, even in small amounts, ensure the formation of the required protective interface, and thus, allow the selection of the main electrolyte component independently of its interface properties. So far, the research on such electrolyte additive mainly concentrated on the interface graphitic anode-electrolyte, where the additives participate in the formation process of the solid electrolyte interface (SEI) films [7]. Beginning with CO₂ in the early 1990s [8], electrolyte

* Corresponding author. Tel.: +886 62606123x7208; fax: +886 62602205.
E-mail address: ccchang@mail.nutn.edu.tw (C.-C. Chang).

Table 1

Charge and discharge capacity in the first cycle of graphite electrode using 1 mol dm^{-3} LiPF_6 in EC/DEC (1:1, w/w) with/without DMP addition

	Charge capacity (mAh g^{-1})	Discharge capacity (mAh g^{-1})	Initial irreversible capacity loss ratio ^a (%)
No additive	315.40	291.79	7.49
0.005 wt% DMP	335.09	313.91	6.32
0.02 wt% DMP	310.55	288.76	7.02

^a Initial irreversible capacity loss ratio (%) = (charge capacity – discharge capacity)/charge capacity \times 100.

additive such as N_2O [8], Sx^{2-} [8], SO_2 [9,10], chloroethylene carbonate [11], vinyl propylene carbonate [12], and ethylene sulfite [13] have been evaluated.

In this paper, we introduce DMP as electrolyte additive for liquid organic electrolyte based lithium-ion cells. DMP has been suggested as H_2O removal agent for chemical reaction system [14]. Here, we show the DMP as film forming additive allows the successful use of graphite anode and LiCoO_2 cathode in liquid 1 mol dm^{-3} LiPF_6 EC/DEC (1:1, w/w) electrolyte, as 103448 size battery.

2. Experimental

DMP (Merck, >97%), lithium hexafluorophosphate (LiPF_6 , Kanto Denka Koyo Co. Ltd., battery grade), ethylene carbonate (EC, Ferro Corp., battery grade) and diethyl carbonate (DEC, Ferro Corp., battery grade) were stored under an argon atmosphere and used without further purification. Lithium foil was obtained from FMC Inc. Polyvinylidene fluoride (PVdF, Kuraha Inc.) was used as a binder for both cathodes and anodes. Copper and aluminum from Nippon foil Inc. were used as current collectors for the anodes and cathodes, respectively. LiCoO_2 and graphite obtained from Nippon Chemical Inc. (grade C-10N) and China Steel Chemical Corp. (grade MGP) were used as active materials for the anodes and cathodes, respectively. 103448 cells were made from E-ONE Moli Energy Corp. The size of 103448 cell is wide 34 mm, high 48 mm, and thick *ca.* 10.5 mm. Electrodes were wound with polyethylene separator (0.025 mm thick). The approximate cell capacity was 1800 mAh. The cells were filled with 1 mol dm^{-3} LiPF_6 in EC/DEC (1:1, w/w) with/without DMP and were hermetically sealed. The electrolyte contained less than 10 ppm of water and less than 80 ppm of hydrofluoric acid. The cells were assembly in a dry room (1% relative humidity (RH)).

Electrolyte preparation and three-electrode cell assembly were carried out under a dry argon atmosphere in a glove box. O_2 and H_2O content in the atmosphere of the glove box was usually at the ppm level. Cyclic voltammetry (CV) was carried out in polypropylene cells with three electrodes. Graphitic carbon electrodes were served as the working electrode and lithium metal foil was applied for counter and reference electrodes. Autolab model PGSTAT 30 was used to measure CV.

Electrochemical measurements were conducted galvanostatically using a Starbuck battery testing system. Each 103448 cell was initially subjected to a formation cycle in which the charge rate with 0.2 C constant current followed by 4.2 V constant voltage charging, keep in 25°C over 24 h, then 1.0 C constant current discharging with the termination voltage of 3.0 V, rest 10 min,

0.2 C constant current discharging with the termination voltage of 3.0 V.

3. Results and discussion

3.1. Half cell performance test

In order to compare the charge/discharge effect of 2,2-dimethoxy-propane (DMP), the variation of initial (formation cycle) charge and discharge capacities measured at 0.1 C rate are summarized in Table 1. An examination of Table 1, it can be observed that the half cell with 0.005 wt% DMP addition has the lowest irreversible capacity. It is well known that there is a difference between the charge and discharge capacities, termed as irreversible capacity, during the formation cycle. This irreversible capacity is caused by the formation of solid electrolyte interface (SEI) film on the graphite electrode surface. In this half cell investigation, there is no difference between graphite electrodes, and therefore, the performance of discharge capacity involves the different SEI film caused by DMP addition. Based on this opinion, it can be assumed that DMP electrolyte additive involves the formation of SEI film. According to the above data, it indicates that 0.005 wt% DMP addition in this work exhibits constructive efficiency of half cell discharge for Li-ion battery.

3.2. Electrochemical test

According to the above half cell results, it is assumed that DMP electrolyte additive involves the formation of SEI film. In order to confirm this assumption, cyclic voltammetry is employed for this purpose. Fig. 1 shows the cyclic voltammograms of graphite electrode in 1 mol dm^{-3} LiPF_6 -EC/DEC (1:1,

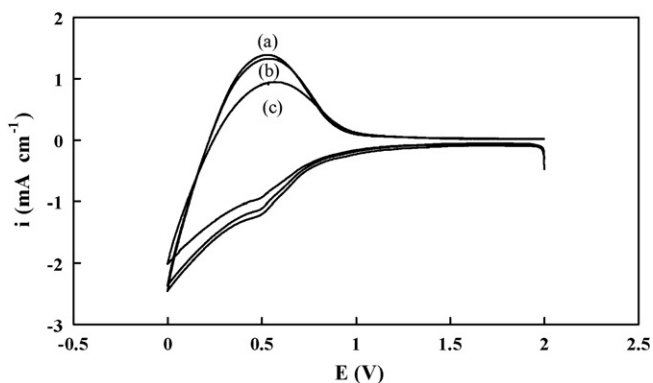


Fig. 1. Cyclic voltammograms of graphite electrode using 1 mol dm^{-3} LiPF_6 in EC/DEC (1:1, w/w) as electrolyte (a) without additive, (b) with 0.005 wt% DMP, and (c) with 0.02 wt% DMP. The scan rate was 1 mV s^{-1} .

w/w) with different DMP addition. For all plots in Fig. 1, there is an obvious oxidation peak, which is interpreted as the deintercalation of lithium from the graphite layer into the electrolyte, at about 0.5 V. The relative maximum reduction current, which is contributed by the intercalation of Li^+ into the graphite layer, is at 0 V. Besides, it can be observed another reduction peak at 0.5 V. It is caused by the formation of SEI film. Note that the plot with no DMP addition has the highest reduction peak current of SEI film formation. The reduction peak current is decreased with DMP addition, which indicates the decrease of graphite–electrolyte reaction for SEI film formation.

The less graphite involves the SEI film formation, the more active site of graphite layer can be used for lithium storage. However, an examination of Fig. 1, it can be found that the oxidation peak current becomes lower after DMP addition. It can be interpreted that the SEI film becomes more thin and dense, and therefore, it is difficult for the transfer of lithium.

3.3. Full cell investigation

Subsequently, the full cell test is employed in order to confirm the better performance after DMP electrolyte additive addition. The cell formation is an important step for SEI film formation, and Table 2 shows the formation data in this study. The interior resistance (ACR) after cell formation becomes lower than that (ACR1) before formation because of the SEI film formation. The similar thickness of the both cell indicates that there is no extortionate gas formed due to the addition of DMP. Interestingly, the discharge capacity becomes higher after the addition of DMP. It indicates that less graphite loss on the formation of SEI film and more Li^+ can be stored in the graphite layer.

Fig. 2 shows the results of cycling number test at different temperature for comparison the contribution of DMP additive. Note that, with the increasing cycling numbers at 23 °C, the discharge capacity of the cell with DMP becomes worse than that without DMP addition. However, at 45 °C, there is no distinct difference in the performance of cycling number whether DMP is added or not. Surprisingly, the cell with DMP addition exhibits better discharge capacity after 60 cycling test at 60 °C. This differential behavior is caused by the SEI film modified with DMP electrolyte additive.

Since the cell shows better performance with DMP electrolyte additive addition at high temperature, the cells with/without DMP addition are stored at 60 °C for 1 week for comparison. The results of high temperature storage are shown in Table 3. The discharge capacity of the first cycle (0.2 C) shows no difference whether DMP is added or not. However, the cell with DMP addition maintains higher discharge capacity (0.2 C Ret.) than that without DMP addition after 1-week storage at high temperature. One reason of the above phenomenon represents the destruction of SEI film at high temperature. The other is the increase graphite–electrolyte interface reaction. In order to confirm the contribution of DMP electrolyte additive, the cells after high temperature storage are re-charged/discharged. As we can see in Table 3, the cell with DMP addition still shows higher discharge capacity (0.2 C Rec.). Based on this evidence, it can indicate that the SEI film with DMP modification is stable and

Table 2
Formation data of full cells (as 103448) using $1 \text{ mol dm}^{-3} \text{ LiPF}_6$ in EC/DEC (1:1, w/w) with/without 0.005 wt% DMP addition

	Cell interior resistance (before formation) ACR-1 (m Ω)	Charge capacity (Ch) (mAh)	Cell thickness F1-T (mm)	1.0 C discharge capacity 1C-D (mAh)	0.2 C discharge capacity 0.2C-D (mAh)	Initial irreversible capacity loss ratio ^a (%)	Cell interior resistance (after formation) ACR (m Ω)
No additive							
Average	50.3	2064	10.40	1681	135	12.0	44.4
S.D.	0.8	12.5	0.03	9.0	8.4	0.3	0.3
0.005 wt% DMP							
Average	51.2	2070	10.39	1694	125	12.1	44.8
S.D.	0.8	8.3	0.04	13.9	12.1	0.3	0.2

^a Initial irreversible capacity loss ratio = $(\text{Ch} - 1\text{C-D} - 0.2\text{C-D}) / (\text{Ch} \times 100)$.

Table 3
Data of full cell (as 103448) storage test results using LiPF_6 in EC/DEC (1:1, w/w) at 60 °C with/without 0.005 wt% DMP addition

Cell code	0.2 C (mAh)	0.2 C Ret. (mAh)	0.2 C Rec. (mAh)	C100 (mAh)
No additive	1770	1542	1679	1303
	100%	87.12%	94.86%	73.62%
0.005 wt% DMP	1769	1567	1709	1375
	100%	88.59%	96.65%	77.73%

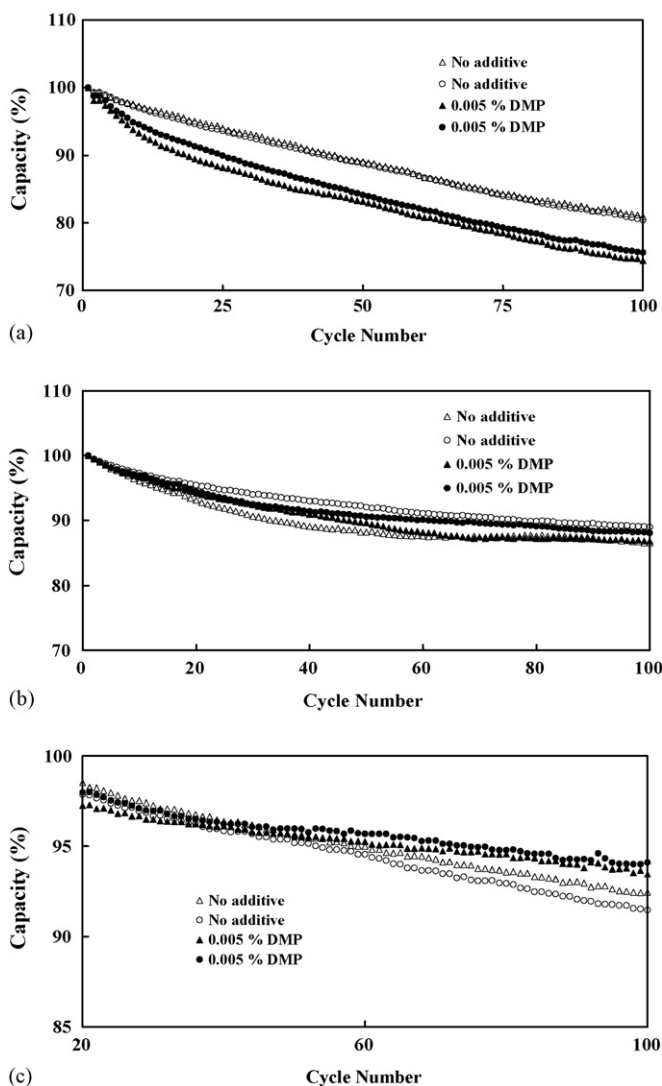


Fig. 2. Cycle life performance of full cells (as 103448) using $1 \text{ mol dm}^{-3} \text{ LiPF}_6$ in EC/DEC (1:1, w/w) as electrolyte with/without DMP addition at (a) 23 °C, (b) 45 °C, and (c) 60 °C.

protect graphite from the reaction with electrolyte at high temperature. The cell is subsequently studied the cycling number test at 60 °C. After 100 cycling number test, the cell with DMP addition still shows better performance for discharge capacity (C100) than that without DMP.

Conventional, the SEI film will be destructed with the increasing temperature. However, according to the full cell capacity test, the capacity of the cell with DMP addition exhibits better performance. This may be caused by the addition of DMP

that makes the thin SEI film on graphite surface and reduce graphite–electrolyte interface reaction. The properties of SEI films were different with various temperatures. In room temperature range (20–45 °C), the SEI film may be too sluggish and dense to help the transfer of Li/Li^+ into graphite layer. In high temperature range (*ca.* 60 °C), the SEI film may become flexible and increase the transfer rate of Li/Li^+ into graphite layer, and also can protect graphite surface from electrolyte reaction.

4. Conclusion

In this work, half cell, full cell and cyclic voltammetry are employed to investigate the contribution of DMP as an additive in electrolyte for lithium-ion battery. The cell with 0.005 wt% DMP addition shows higher discharge capacity than others from the half cell results. According to the cyclic voltammograms, it is found that DMP electrolyte additive involves the formation of SEI film and decreases the graphite–electrolyte interface reaction in the first cycle. Besides, the SEI film with DMP modification may become thin and dense. The transfer of Li/Li^+ is inhibited by this modified SEI film at room temperature range. However, this flexible not only maintains stable but also protect graphite surface from electrolyte reaction at high temperature range. Therefore, the electrolyte with 0.005 wt% DMP additive in lithium-ion battery shows better cycle life and storage performances at high temperature range (*ca.* 60 °C).

Acknowledgements

We are grateful to E-ONE Moli Energy Corp. supported this research work. Financial support of this work by the National Science Council of the Republic of China under contract NSC 95-2221-E024-017.

References

- [1] M. Winter, P. Novak, A. Monnier, J. Electrochem. Soc. 145 (1998) 428.
- [2] T. Nakajima, J. Fluorine Chem. 105 (2000) 229.
- [3] K. Tatsumi, K. Zaghbi, H. Abe, S. Higuchi, T. Ohsaki, Y. Sanade, J. Power Sources 54 (1995) 425.
- [4] H. Abe, K. Zaghbi, K. Tatsumi, S. Higuchi, J. Power Sources 54 (1995) 236.
- [5] K. Zaghbi, K. Tatsumi, H. Abe, T. Ohsaki, Y. Sawada, S. Higuchi, J. Power Sources 54 (1995) 435.
- [6] G. Li, R. Xue, L. Chen, Y. Huang, J. Power Sources 54 (1995) 271.
- [7] E. Peled, D. Golodnitsky, G. Adriel, J. Electrochem. Soc. 144 (1997) 823.
- [8] J.O. Besenhard, M.W. Wagner, M. Winter, A.D. Jannakoudakis, P.D. Jannakoudakis, E. Theodoridou, J. Power Sources 43–44 (1993) 413.

- [9] J.D. Besenhand, M. Winter, J. Yang, W. Biberacher, J. Power Sources 54 (1995) 228.
- [10] Y. Ein-Eli, S.R. Thomas, V.R. Koch, J. Electrochem. Soc. 142 (1997) 1159.
- [11] Z.X. Shu, R.S. McMillan, J.J. Murray, J. Electrochem. Soc. 142 (1995) L161.
- [12] K. Abe, H. Yoshitake, T. Kitakura, T. Hattori, H. Wang, M. Yoshio, Electrochim. Acta 49 (2004) 4613.
- [13] G.H. Wrodnigg, J.O. Besenhard, M. Winter, J. Electrochem. Soc. 146 (1999) 470.
- [14] K. Tomishige, K. Kunimori, Appl. Catal. A: Gen. 237 (2002) 103.