



# Composition analysis of the passive film on the carbon electrode of a lithium-ion battery with an EC-based electrolyte

C.R. Yang, Y.Y. Wang<sup>\*</sup>, C.C. Wan

*Department of Chemical Engineering, National Tsing-Hua University, Hsinchu, 30043, Taiwan*

Received 17 March 1997; accepted 31 March 1997

## Abstract

This work examines the formation of a passive film on the carbon electrode of lithium-ion batteries. With a single solvent of EC (ethylene carbonate), the structure of the passive film is found to be  $(\text{CH}_2\text{OCOOLi})_2$ . In a DEC (diethyl carbonate) or DMC (dimethyl carbonate) system,  $\text{C}_2\text{H}_5\text{OCOOLi}$  and  $\text{Li}_2\text{CO}_3$  are formed on the surface of the carbon electrode. According to results from mass spectra,  $\text{CO}_2$  gas is the main product when EC is decomposed. By contrast, DEC is decomposed into CO and  $\text{C}_2\text{H}_6$ , and DMC into CO and  $\text{CH}_4$ . These findings suggest that the composition of the passive film depends on the chosen solvent. In a binary solvent system which contains EC, the passive film contains chiefly  $(\text{CH}_2\text{OCOOLi})_2$ , which is identical to a single EC solvent system. © 1998 Published by Elsevier Science S.A. All rights reserved.

*Keywords:* Lithium battery; Passive film; Organic electrolyte

## 1. Introduction

When an organic electrolyte such as  $\text{LiClO}_4/\text{PC}/\text{EC}$  (PC = propylene carbonate; EC = ethylene carbonate) is in contact with a lithium metal electrode, the lithium reacts spontaneously with the electrolyte to form a passive film [1]. Similarly, for lithium-ion batteries, a passive film is found on the surface of the carbon electrode after the charging or the discharging process. This passive film plays a critical role with regard to the discharge performance and the charge retention of lithium-ion batteries. Consequently, the structure of the passive film and its formation mechanism are the subject of increasing interest.

Alkyl carbonates such as ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC) are among the most important solvents for electrolytes of lithium-ion batteries because they are aprotic, polar, and non-volatile. It has been found [2–4] that the carbon material has good cycle life and maintains a high potential in an EC/DEC electrolyte due to the formation of a good passive film on the carbon surface. Li et al. [5] have investigated the reversibility of five different types of

carbon electrode in EC/DEC electrolyte. Chen et al. [6] revealed that the cycle efficiencies of three coke-based electrodes in EC/DMC electrolyte depended chiefly on the properties of the passive film. Zaghbi et al. [4] found that the formation of the passive film is not only due to solvent decomposition but is also affected by the nature of salt selected in the EC/DEC system. Ein-Eli et al. [7], Aurbach et al. [8,9], and Ein-Eli and Aurbach [10] published a series of studies on the passive film of lithium batteries. They claimed that both the capacity and the cycle life of the carbon electrode could be increased by adding  $\text{CO}_2$  gas or crown ether to the electrolyte and was due to the formation of a stable passive film. In-situ techniques such as impedance analysis, XRD or Raman measurements have also been used to investigate the behaviour of the passive film. For instance, Liu and Wu [11] examined the passive film in EC/DEC electrolyte by means of a.c. impedance. Takami et al. [12] also studied the kinetics and structure of the passive film via a.c. impedance and XRD.

Despite the above investigations, there has been no systematic comparative study of EC, DEC and DMC as solvents and their function in the formation of the passive film. Furthermore, the stage at which the passive film is formed during cycling is unclear. This study aims to examine the chemical nature of the passive film in various single or binary solvent systems based on EC, DEC and

<sup>\*</sup> Corresponding author.

DMC. The interaction of two solvents in a binary solvent system and the resulting effect on the passive film are also investigated.

## 2. Experimental

A MCMB (meso-carbon micro breads) carbon electrode consisting of 10 wt.% PVDF (polyvinylidene difluoride) as binder was used as the working electrode. Metallic lithium strip was used as both the counter and the reference electrodes. The separator was made of Celgard PP (polypropylene) membrane. The working and counter electrodes were of  $2 \times 2$  cm square. The electrolyte was 1 M  $\text{LiPF}_6$  (Tomiyama) in various solvents, i.e., EC, DEC, DMC or EC/DMC (volume ratio: 1:1, 1:3 and 3:1, respectively) or EC/DEC (1:1). All solvents contained less than 10 ppm water.

The cells were maintained at  $25 \pm 0.5^\circ\text{C}$  and discharged at a constant current of  $0.25 \text{ mA cm}^{-2}$  until the cut-off voltage reached 0.05 V vs.  $\text{Li}/\text{Li}_+$ . The charge current was  $0.25 \text{ mA cm}^{-2}$  and the cut-off voltage was 1.6 V vs.  $\text{Li}/\text{Li}_+$ . The results obtained from the charging and the discharging experiments were measured by means of a charge/discharge unit with (HOKUTO DENKO HJ201B). A total of  $4 \mu\text{l}$  of gaseous products were sampled and analyzed with a HP5972 GC-MS system. Signals from argon and solvents (i.e., EC, DEC or DMC) were detected and the 'subtract' function of the HP G1034C MS Chemstation software was used to minimize the peaks of solvents and Ar ( $m/z = 40$ ). All the experiments were carried out under an argon atmosphere. After electrochemical testing, the cell was transferred to another argon-atmosphere-controlled dry box and dissected into the components. The carbon electrode was washed with DMC and dried by evaporation. The passive film on the surface of the carbon electrode was scratched with a stainless-steel knife. The powder was mixed with KBr and pelletized for composition analysis by FTIR measurements (Bomem DA3.002).

## 3. Results and discussion

Fig. 1 shows the FTIR spectrum of the passive film on the carbon electrode in contact with an electrolyte containing a single solvent, EC, and 1 M  $\text{LiPF}_6$  after the first intercalation. The EC/1 M  $\text{LiPF}_6$  electrolyte was in a liquid phase under the chosen experimental conditions. According to Aurbach et al. [13,14], the absorption peaks at 1645 ( $\nu_{\text{AS}}\text{C}=\text{O}$ ), 1400 ( $\delta\text{CH}_2$ ), 1300 ( $\nu_{\text{S}}\text{C}=\text{O}$ ), 1080 ( $\nu\text{C}-\text{O}$ ) and  $830 \text{ cm}^{-1}$  ( $\delta\text{OCOO}^-$ ) denote the existence of  $(\text{CH}_2\text{OCOOLi})_2$ . Hence, the passive film should be composed chiefly of  $(\text{CH}_2\text{OCOOLi})_2$ . This result indicates that the passive film was already formed during the first intercalation. The mass spectrum (MS) of the EC/1 M

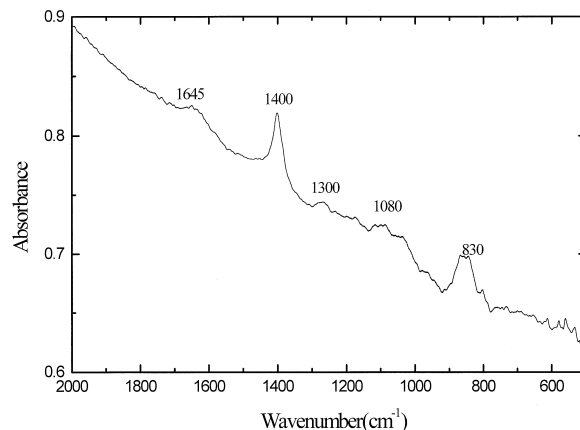


Fig. 1. FTIR spectrum of the passive film in EC/1 M  $\text{LiPF}_6$  electrolyte for the first cycle.

$\text{LiPF}_6$  electrolyte system is shown in Fig. 2. Obviously, a strong intensity is found at  $m/z = 44$ ; this indicates the formation of a significant amount of  $\text{CO}_2$ . In addition, the signal that represents  $\text{CO}_2$  increases in intensity during the discharging process (a gas sample was taken every 2 h). The intensities at  $m/z =$  (i) 28, (ii) 12, 28 and 27; (iii) 26, 30, 29, (iv) 28, 16, 15 and 14, indicate the existence of CO,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CH}_4$ , respectively. The amounts of these compounds are smaller than that of  $\text{CO}_2$ , however, and are therefore only minor products of EC reduction. Aurbach et al. [13] studied the passive film in an EC/DEC system, they proposed that  $(\text{CH}_2\text{OCOOLi})_2$  was first formed on the electrode by reduction and subsequently reacted with water molecules in the electrolyte to produce  $\text{CO}_2$ . Water molecules existed in the electrolyte as a trace impurity. It appears that the gas products after intercalation are also consistent with their reaction mechanism.

Fig. 3 presents the FTIR spectrum of the passive film in a DEC/ $\text{LiPF}_6$  electrolyte when lithium ions are intercalated into the carbon electrode in the first intercalation. Although the data in Figs. 1 and 3 are similar, an additional absorption peak of  $\nu_{\text{S}}\text{CH}_3$  at  $2870 \text{ cm}^{-1}$  is found in the DEC/ $\text{LiPF}_6$  system. According to the results of Aurbach et al. [15], the major component of the passive film should be  $\text{C}_2\text{H}_5\text{OCOOLi}$  rather than  $(\text{CH}_2\text{OCOOLi})_2$ . From the GC-MS results shown in Fig. 4, large amounts of CO,  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  gases are found in the DEC system

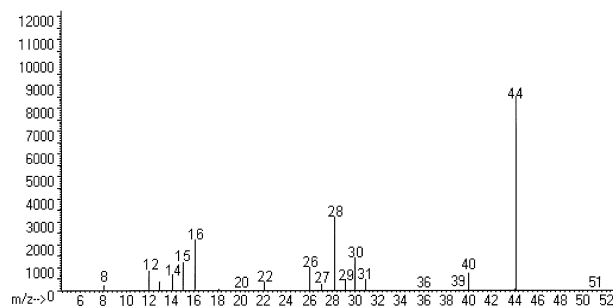


Fig. 2. MS spectrum for EC/1 M  $\text{LiPF}_6$  electrolyte.

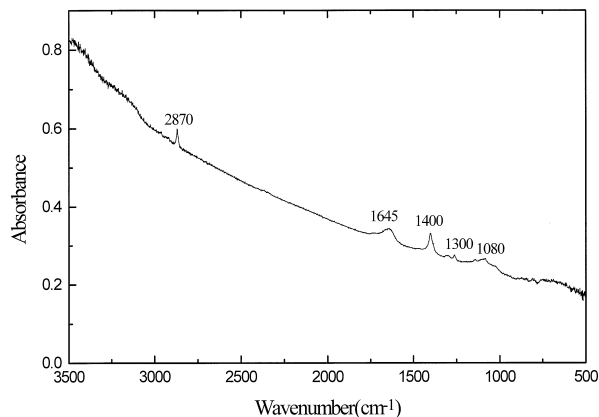


Fig. 3. FTIR spectrum of passive film in DEC/1 M LiPF<sub>6</sub> electrolyte for the first cycle.

but CO<sub>2</sub> is unexpectedly absent. Given the acyclic structure of DEC, DEC may be broken to release a C<sub>2</sub>H<sub>5</sub>O structure and CO. On the other hand, C<sub>2</sub>H<sub>5</sub>O can form alcohol and dissolve in the electrolyte. Hence, only CO is found in the mass spectrum. From the intensities of the gaseous products in the spectrum, it is concluded that significant reduction of solvent can occur when lithium ions are intercalated into carbon in a DEC system. This reaction then induces gas generation. Aurbach et al. [14] also claimed that DEC is less electrochemically stable than EC. This conclusion is substantiated by the results of the gas analysis conducted here.

Fig. 5 shows the FTIR spectrum of the passive film that is formed when lithium ions are initially intercalated into a carbon electrode in contact with a DMC/LiPF<sub>6</sub> electrolyte. The data differ strongly from those of Figs. 1 and 3. For instance, the peaks at 2870, 1645, 1400, 1300, and 830 cm<sup>-1</sup> in Figs. 1 and 3 are all missing in Fig. 5. New peaks at 1500, 1433 and 866 cm<sup>-1</sup> appear in Fig. 5. Several researchers [10,16,17] have pointed out that absorption peaks for Li<sub>2</sub>CO<sub>3</sub> appear at 1500–1490, 1440–1430 and 880–860 cm<sup>-1</sup>. Obviously, the main component of the passive film formed on the surface of the carbon electrode is Li<sub>2</sub>CO<sub>3</sub> in this system. The mass spectra for the DMC/LiPF<sub>6</sub> system is shown in Fig. 6. It shows that the main gaseous product is CH<sub>4</sub> and that there is also a small amount of CO. A possible explanation for the formation of

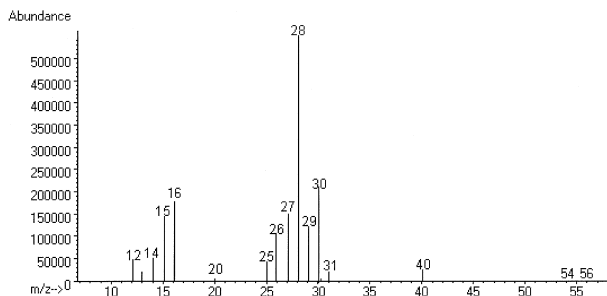


Fig. 4. MS spectrum for DEC/1 M LiPF<sub>6</sub> electrolyte.

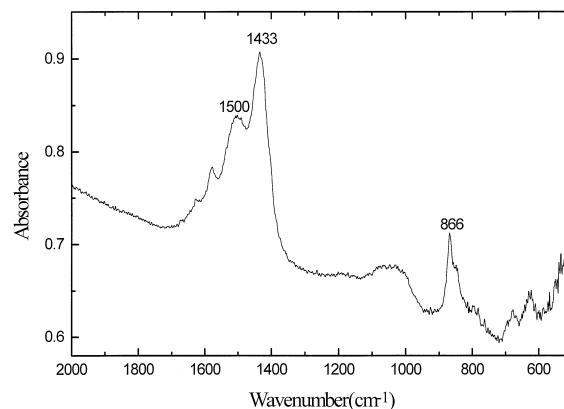


Fig. 5. FTIR spectrum of passive film in DMC/1 M LiPF<sub>6</sub> electrolyte for the first cycle.

Li<sub>2</sub>CO<sub>3</sub> in the DMC system is that CO<sub>3</sub><sup>2-</sup> could be formed as the DMC is reduced on the carbon electrode. Furthermore, CO<sub>3</sub><sup>2-</sup> reacts with Li<sup>+</sup> to form Li<sub>2</sub>CO<sub>3</sub>.

The effect of solvent on the cycle life of lithium-ion batteries is illustrated in Fig. 7. Obviously, single solvents perform poorly in this study. Although EC can generate a (CH<sub>2</sub>OCOOLi)<sub>2</sub> passive film, it exhibits a poor conductivity of around 10<sup>-4</sup> to 10<sup>-5</sup> S cm<sup>-1</sup>. Therefore, the internal resistance is very large for a system with EC as a single solvent. Consequently, the cycling behaviour is very poor. Both DEC and DMC are unstable electrochemically and both would generate large amounts of gas during charging or discharging. Furthermore, although the passive film is stable for the DMC system [9], too much Li<sub>2</sub>CO<sub>3</sub> impedes the intercalation and de-intercalation of lithium ions inside the carbon structure. Consequently, the capacity decreases rapidly with cycling [17]. Moreover, the boiling point of DMC is very low (viz., 89°C). Hence, EC, DEC or DMC is unsuitable as a single solvent to prepare electrolyte for lithium-ion batteries.

Figs. 8 and 9 show the FTIR spectra of the passive films formed after the first intercalation in binary solvent systems containing EC/DEC (vol. 1:1)/LiPF<sub>6</sub> and EC/DMC (vol. 1:1)/LiPF<sub>6</sub>, respectively. The data in Fig. 8 indicate that the passive film contains mainly (CH<sub>2</sub>OCOOLi)<sub>2</sub> instead of C<sub>2</sub>H<sub>5</sub>OCOOLi. Interestingly, CO<sub>2</sub> could be detected by mass spectroscopy. By contrast, CO<sub>2</sub>

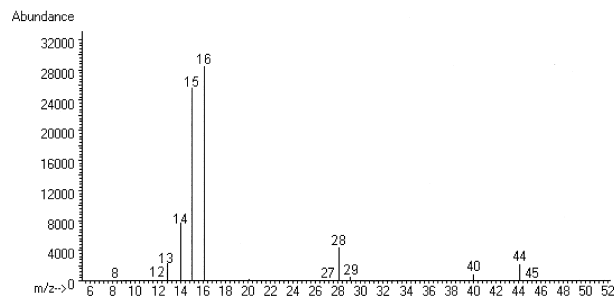


Fig. 6. MS spectrum for DMC/1 M LiPF<sub>6</sub> electrolyte.

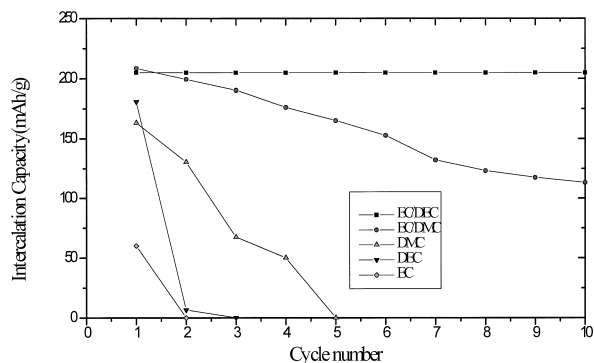


Fig. 7. Capacity vs. cycle life for EC/DEC, EC/DMC, DMC, DEC and EC electrolyte systems.

could not be found in a single DEC solvent system. According to Fig. 9, the passive film contains only  $(\text{CH}_2\text{OCOOLi})_2$  with a EC/DMC system, and  $\text{Li}_2\text{CO}_3$  is not present. This is remarkable since, for a single DMC solvent system,  $\text{Li}_2\text{CO}_3$  should be the main constituent of passive film. The volume ratio of EC:DMC was varied from 1:1 to 1:3 and 3:1, but still the formation of  $\text{Li}_2\text{CO}_3$  was not observed. Although why  $\text{Li}_2\text{CO}_3$  disappears in this binary solvent system is still unclear, at least it is clear that the missing of  $\text{Li}_2\text{CO}_3$  is not due to the shortage of DMC in the EC/DMC system. The above results imply that the passive film is formed chiefly due to the decomposition of EC in the EC/DEC and EC/DMC binary solvent systems. Presumably, EC is more easily reduced on the carbon surface than the other solvent. It is thought that the cyclic structure of EC could more closely contact the surface of the carbon electrode than the acyclic structure of either DEC or DMC. Besides, the polarity and dipole moments of EC are greater than those of either DEC or DMC. The EC molecules, preferentially being reduced on the surface of the carbon electrode to form a passive film, may impede the decomposition of DEC or DMC on the surface. Hence, the formation of the passive film becomes totally controlled by the EC solvent.

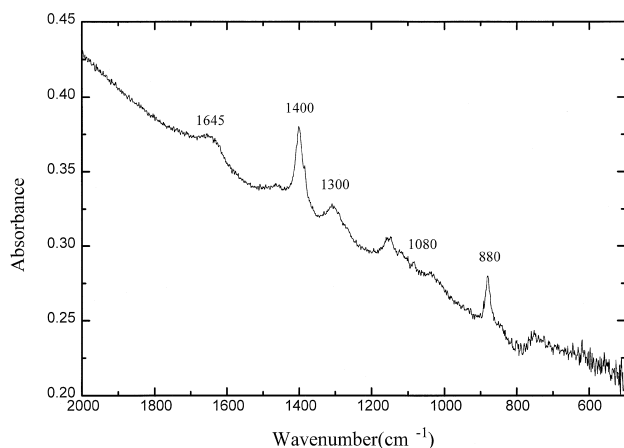


Fig. 8. FTIR spectrum of passive film in EC/DEC/1 M  $\text{LiPF}_6$  electrolyte for the first cycle.

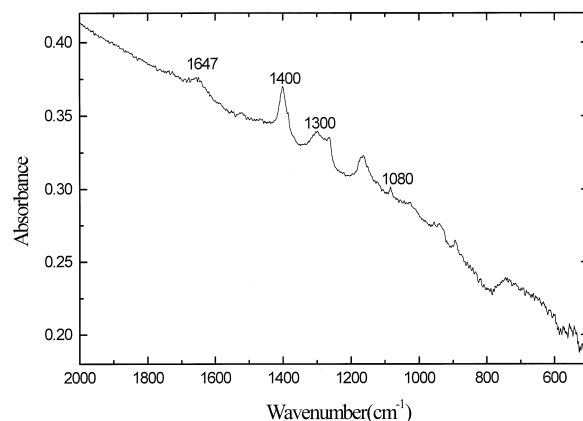


Fig. 9. FTIR spectrum of passive film in EC/DMC/1 M  $\text{LiPF}_6$  electrolyte for the first cycle.

The passive film may change its composition during repeated cycling. Yet very little published information mentions the effect of cycling on the passive film. The FTIR spectrum of an EC/DEC/ $\text{LiPF}_6$  electrolyte after 10 charge–discharge cycles is shown in Fig. 10. A comparison with the data of Fig. 8 indicates that the basic chemical structure does not change from the first to the tenth cycle. The major constituents remain  $(\text{CH}_2\text{OCOOLi})_2$  and  $\text{Li}_2\text{CO}_3$  although the absorption peaks seem more distinct, indicating that the passive film is more complete and thicker as cycling increases. Similarly, Fig. 11 is the FTIR spectrum of the passive film in an EC/DMC/ $\text{LiPF}_6$  system at the 10th cycle. Although  $(\text{CH}_2\text{OCOOLi})_2$  and  $\text{Li}_2\text{CO}_3$  are found in both Figs. 9 and 11, additional peaks appear at 1482, 1197, 1157, 775 and 726  $\text{cm}^{-1}$  in Fig. 11. Apparently, the structure of the passive film becomes more complex as additional cycles are applied to an EC/DMC system. The peak at 775  $\text{cm}^{-1}$  demonstrates the existence of LiF. This LiF is not detected in the first cycle, as shown in Fig. 9. Hence, the formation of LiF is induced by repeated cycling in the EC/DMC system. Therefore, based

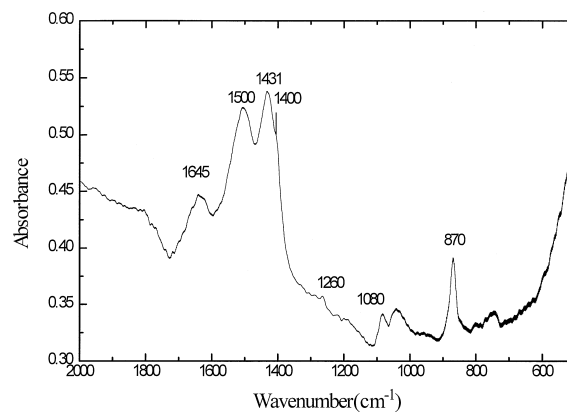


Fig. 10. FTIR spectrum of passive film for EC/DEC/1 M  $\text{LiPF}_6$  electrolyte after 10th cycle.

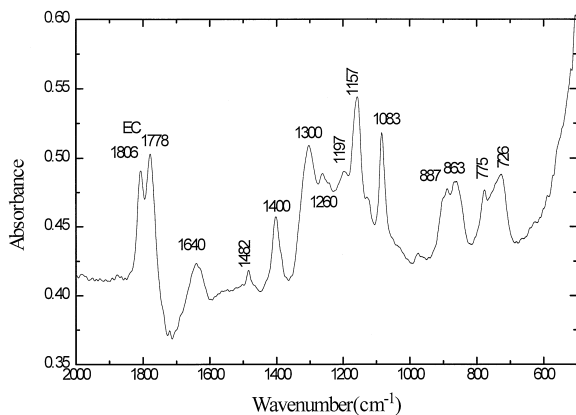


Fig. 11. FTIR spectrum of passive film for EC/DMC/1 M LiPF<sub>6</sub> electrolyte after 10th cycle.

on the cycling results and the stability of the passive film, it appears that EC/DEC performs better than EC/DMC as a binary solvent for lithium-ion batteries.

#### 4. Conclusions

It is concluded that with a single EC solvent, the passive film is mainly (CH<sub>2</sub>OCOOLi)<sub>2</sub> and the gaseous product after cycling is CO<sub>2</sub>. If the solvent is DEC, however, the passive film structure is composed of C<sub>2</sub>H<sub>5</sub>OCOOLi and the gaseous product becomes CO and C<sub>2</sub>H<sub>6</sub>. With a DMC solvent system, the passive film is Li<sub>2</sub>CO<sub>3</sub> and it also produces CO and CH<sub>4</sub>.

Only EC is decomposed in a binary solvent consisting of EC/DEC or EC/DMC. DEC or DMC is not decomposed in the presence of EC. Hence, the function of DEC and DMC in a binary solvent system is probably mainly to improve solubility and conductivity rather than to participate in the formation of the passive film. Moreover, these solvents do not contribute significantly to the formation mechanism of the passive film.

#### Acknowledgements

The research was supported by the material research laboratory of ITRI (Taiwan) and the National Science Council (Project No. NSC85-2214-E007-022).

#### References

- [1] Z.X. Shu, R.S. Mcmillan, J.J. Murray, *J. Electrochem. Soc.* 140 (1993) 922.
- [2] K. Tatsumi, K. Zaghbi, H. Abe, S. Higuchi, T. Ohsaki, Y. Sanada, *J. Power Sources* 54 (1995) 425.
- [3] H. Abe, K. Zaghbi, K. Tatsumi, S. Higuchi, *J. Power Sources* 54 (1995) 236.
- [4] K. Zaghbi, K. Tatsumi, H. Abe, T. Ohsaki, Y. Sawada, S. Higuchi, *J. Power Sources* 54 (1995) 435.
- [5] G. Li, R. Xue, L. Chen, Y. Huang, *J. Power Sources* 54 (1995) 271.
- [6] J.M. Chen, C.Y. Yao, C.H. Cheng, W.M. Hung, T.H. Kao, *J. Power Sources* 54 (1995) 494.
- [7] Y. Ein-Eli, B. Markovsky, D. Aurbach, Y. Carmeli, *Electrochim. Acta* 39 (1994) 2559.
- [8] D. Aurbach, Y. Ein-Eli, O. Chusid, Y. Carmeli, M. Babai, H. Yamin, *J. Electrochem. Soc.* 141 (1994) 603.
- [9] D. Aurbach, Y. Ein Eli, B. Markovsky, A. Zaban, S. Luski, Y. Carmeli, H. Yamin, *J. Electrochem. Soc.* 142 (1995) 2882.
- [10] Y. Ein-Eli, D. Aurbach, *J. Power Sources* 54 (1995) 281.
- [11] P. Liu, H. Wu, *J. Power Sources* 56 (1995) 81.
- [12] N. Takami, A. Satoh, M. Hara, T. Ohsaki, *J. Electrochem. Soc.* 142 (1995) 371.
- [13] D. Aurbach, Y. Gofer, M. Ben-Zion, P. Aped, *J. Electroanal. Chem.* 339 (1992) 451.
- [14] D. Aurbach, A. Zaban, A. Schechter, Y. Ein-Eli, E. Zinigrad, B. Markovsky, *J. Electrochem. Soc.* 142 (1995) 2873.
- [15] D. Aurbach, M.L. Daroux, P. Faguy, E.B. Yeager, *J. Electrochem. Soc.* 134 (1987) 1611.
- [16] R. Fong, U. von Sacken, J.R. Dahn, *J. Electrochem. Soc.* 137 (1990) 2009.
- [17] Y. Masumura, S. Wang, J. Monduri, *J. Electrochem. Soc.* 142 (1995) 2914.