

Degradation mechanism of alkyl carbonate solvents used in lithium-ion cells during initial charging

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Abstract

The degradation mechanism of electrolytes in the lithium-ion cell with LiCoO_2 and graphite electrodes was investigated by analyzing: (i) the composition of generated gases; (ii) thin films formed on the electrode, and (iii) the compositional change of the electrolyte during the initial charging. The solvents in this work were ethylene carbonate (EC), dimethyl carbonate (DMC), ethylmethyl carbonate (EMC) and diethyl carbonate (DEC). LiPF_6 was used as a salt. In the one- to three-component systems containing EC, carbon monoxide and ethane were detected, whereas Li_2CO_3 , RCOOLi and $(\text{CH}_2\text{OLi})_2$ were the main components of the surface film on the negative electrode. From these results, it can be assumed that the decomposition of the systems was mainly due to the reductive reaction of EC at the initial charging. Through the additional analysis of the electrolyte composition, it was confirmed that the dialkyl-2,5-dioxahexane carboxylate was produced in the electrolyte after initial charging. This suggests the occurrence of trans-esterification. © 1997 Elsevier Science S.A.

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1. Introduction

Cyclic alkyl carbonate and chain alkyl carbonate mixed solvent systems with LiPF_6 as a salt are used in the lithium-ion cells because of their electrochemical stability and highly ionic conductivity [1]. However, it has been reported that a degradation of the electrolyte with generation of gases and irreversible capacity loss occurred at initial charging [2]. Therefore, elucidation of the degradation reaction is one of the important challenges in the development of high energy density lithium-ion cells.

Numerous studies have been performed to understand the mechanism of the degradation of the electrolyte on the carbon electrode, suggesting the formation of a film on the surface of the carbon electrode at initial charging [3–6]. However, the main object of these studies was focused on the analysis of the thin film formed on the negative electrode, rather than on the composition of the electrolyte.

The purpose of this work is to clarify the degradation mechanism of alkyl carbonate solvents by analyzing the generated gases, the thin film formed on the electrode and the compositional change of the electrolyte during initial charging by means of various analytical techniques.

2. Experimental

The 400 mAh prismatic open-type cells with LiCoO_2 as the positive electrode and graphite as the negative electrode were used for the study. The solvents used in this work were ethylene carbonate (EC), dimethyl carbonate (DMC), ethylmethyl carbonate (EMC) and diethyl carbonate (DEC). Several different compositions were used; either each of the four electrolyte types in a single-component system, three types of binary system containing EC mixed separately with DMC, EMC, DEC (1:1 vol.%), or one type system composed of EC mixed with both DMC and DEC (2:2:1 vol.%). The salt used in this study was 1 M LiPF_6 .

Cells were charged to 4.2 V at a constant current of 200 mA in the paraffin oil, and the resulting generated gases were collected in glass bottles. Cells were then discharged to 2.7 V at the same current and were opened to collect the electrodes and electrolytes for analysis. Electrodes were rinsed with DMC (less than 20 ppm water) to remove the electrolyte and then dried under vacuum at 85 °C for 5 h. The collection of gases, electrolytes and electrodes was performed in a dry room and the rinsing of electrodes was carried out in an argon-atmosphere glove box.

A Yokogawa Hewlett-Packard 5890 series gas chromatography (GC) equipped with a thermal conductivity detector (TCD) was used for the composition analysis of the gener-

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ated gases. Argon was used as carrier gas. A Perkin-Elmer system 2000 Fourier-transform infrared (FT-IR) spectrometer equipped with a triglycine sulfate (TGS) detector was used to determine the chemical composition of the thin film formed on the electrode. Absorption spectra were collected using FT-IR attenuated total reflectance (FT-IR-ATR) at a resolution of 4 cm^{-1} and 50 scans in an argon-atmosphere glove box. The LC-FT-IR composite system of a Waters HPLC-510 high pressure pump equipped with ODS-2 column and a Perkin-Elmer system 2000 FT-IR spectrometer equipped with a mercury-cadmium-telluride (MCT) detector was used for the analysis of the electrolyte composition. Absorption spectra were collected using LC-FT-IR-ATR at a resolution of 8 cm^{-1} and 2 scans. A mixture of water and acetonitrile (45:55 vol.%) was used as carrier solvent.

3. Results and discussion

Table 1 shows the composition of generated gases at initial charging. In a single-component system of EC or mixed solvents containing EC, the release of CO and C_2H_4 was mainly detected. In a single-component system of DMC and EMC, the release of CO and CH_4 gases was mainly detected. Because of a good agreement observed in the composition of generated gases between single component of EC and mixed solvents containing EC, it was suggested that a decomposition of EC occurred mainly at initial charging. In a single-component system of DEC, a continuous gas generation, containing high ratio of H_2 , was observed. As consequence, the cell could not be charged. This result suggests that a peculiar decomposition reaction occurred.

FT-IR-ATR analysis of the electrodes after the initial charging process, revealed that no absorption bands were observed on the positive electrode, whereas, several compounds were detected on the negative electrode. From this result, it was confirmed that at initial charging a reaction between the negative electrode and the electrolyte occurred.

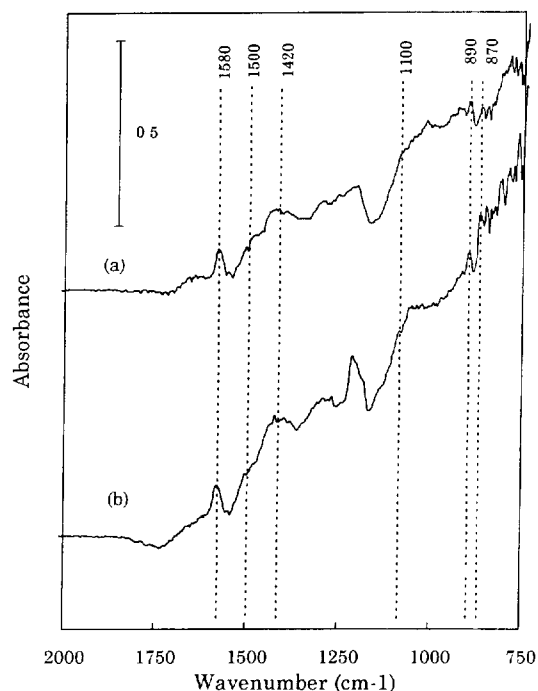


Fig. 1. FT-IR-ATR spectra of the negative electrodes after initial charging: (a) in 1 M LiPF_6/EC , and (b) in 1 M $\text{LiPF}_6/\text{EC} + \text{DMC}$ (1:1).

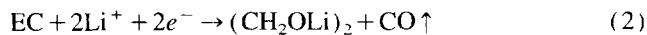
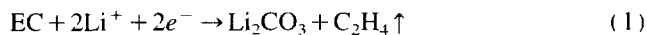
Fig. 1 shows the FT-IR-ATR spectra of the negative electrode after the initial charging in 1 M LiPF_6/EC (Fig. 1(a)) and 1 M $\text{LiPF}_6/\text{EC} + \text{DMC}$ (Fig. 1(b)). In both cases, bands corresponding to Li_2CO_3 ($\nu = 1420, 870\text{ cm}^{-1}$), RCOOLi ($\nu = 1580\text{ cm}^{-1}$) and $(\text{CH}_2\text{OLi})_2$ ($\nu = 1500, 1100, 890\text{ cm}^{-1}$) were observed. This result suggests that these materials formed a surface film on the carbon negative electrode. Similar results were also observed when other mixed containing-EC solvents were used. Therefore, it could be assumed that the decomposition of EC occurred mainly in the mixed solvents containing EC.

Aurbach et al. [5] reported that EC undergoes a reductive reaction to form lithium alkyl carbonate and C_2H_4 on lithium

Table 1
Comparison of generated gases at initial charging (vol %) (1 M LiPF_6)

Composition	Electrolyte component system							
	EC	DMC	EMC	DEC	EC + DMC	EC + EMC	EC + DEC	EC + DMC + DEC
H_2	1.1	9.1	1.9	35.2	3.3	2.9	2.8	2.6
N_2	32.6	27.9	58.2	20.1	24.4	32.3	32.0	34.4
O_2	8.7	4.6	9.7	3.5	5.8	5.9	6.5	7.0
CO	37.5	50.4	28.7	20.2	48.4	42.8	45.1	44.9
CO_2	0.3			0.1	0.2	0.2	0.1	0.1
CH_4		8.0	1.5	0.7	0.7	0.2	0.1	0.6
C_2H_4	19.3			0.6	17.0	15.6	13.1	10.3
C_2H_6	0.2			19.6	0.2			
C_3H_8	0.2							
C_4H_{10}	0.1							

metal. However, this mechanism cannot explain the results obtained. Another mechanism is then proposed to explain our GC and FT-IR data in the decomposition reaction of mixed solvents containing EC:



However, the generation of RCOOLi on the negative electrode cannot be explained by Eqs. (1) and (2). Matsumura et al. [6] reported that during the initial charging, propylene carbonate (PC) undergoes a reductive reaction to form unstable radical anions ($\text{CH}_2\text{C}_2\text{H}_4\text{OCO}_2^-$), then, RCOOH is formed. If RCOOH can be formed from EC with the same mechanism, the generation of RCOOLi can be explained by the direct reaction between RCOOH and lithium.

Fig. 2 shows the FT-IR-ATR spectra of the negative electrode after initial charging in 1 M LiPF₆/DMC (Fig. 2(a)) and 1 M LiPF₆/DEC (Fig. 2(b)). In the 1 M LiPF₆/DMC, bands corresponding to ROLi ($\nu = 1050 \text{ cm}^{-1}$) and Li₂CO₃ were observed. Similar result was also obtained when 1 M LiPF₆/EMC was used. Aurbach et al. [4] reported that DMC undergoes a reductive reaction to form lithium alkyl carbonate and C₂H₆ on lithium metal. However, our results cannot be explained by this mechanism. Therefore, a decomposition mechanism of DMC is proposed and shown in Eqs. (3) and (4). It is assumed that the Eq. (3) occurred mainly in the decomposition of EMC:

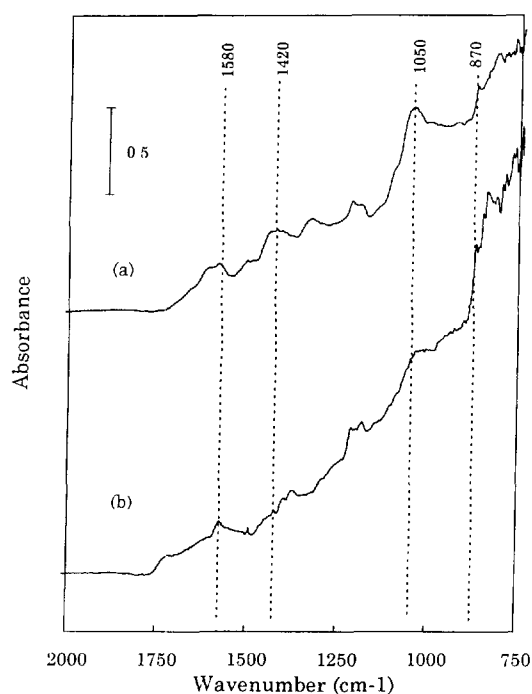


Fig. 2. FT-IR-ATR spectra of the negative electrodes after initial charging: (a) in 1 M LiPF₆/DMC, and (b) in 1 M LiPF₆/EC + DEC (1:1).

In 1 M LiPF₆/DEC, the band corresponding to ROLi decreases, while that of Li₂CO₃ was not observed. The reason why Li₂CO₃ was not observed is probably because of the occurrence of the peculiar progressive decomposition reaction in the single-component system of DEC.

Fig. 3 shows the liquid chromatograms of 1 M LiPF₆/EMC before and after initial charging. The amount of EMC solvent decreases, while new peaks corresponding to the formation of DMC and DEC appear. In the case both DMC and DEC were used, EMC was also produced after initial charging while the amount of initial solvents DMC and DEC decreases. Therefore, it is concluded that the chain alkyl carbonates were in equilibrium by the trans-esterification shown in Eq. (5)



Figs. 4–6 show the liquid chromatograms of the electrolytes of three types of binary system containing EC before and after initial charging. In the binary systems of EC + DMC (Fig. 4) and EC + DEC (Fig. 5), the A1 and A3 compounds were observed, respectively, after initial charging. The production of A1 and A3 is caused by the trans-esterification of

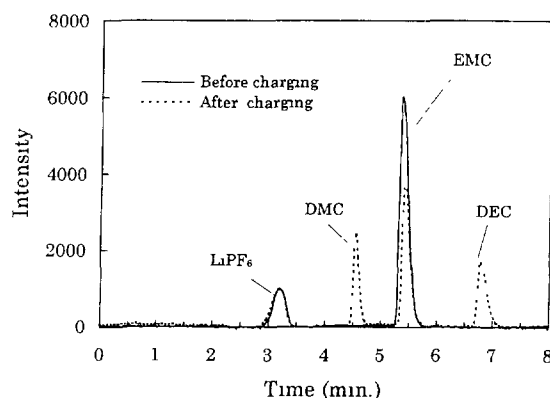


Fig. 3. Liquid chromatograms of 1 M LiPF₆/EMC before and after initial charging.

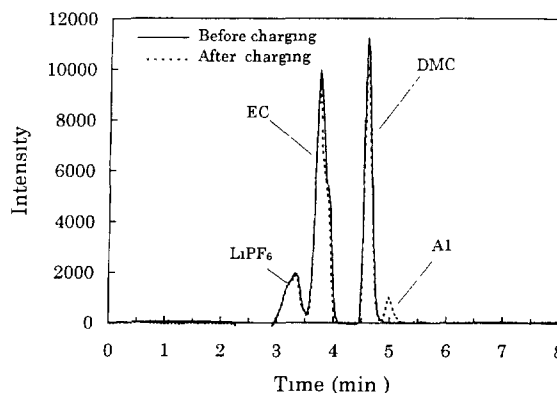


Fig. 4. Liquid chromatograms of 1 M LiPF₆/EC + DMC (1:1) before and after initial charging.

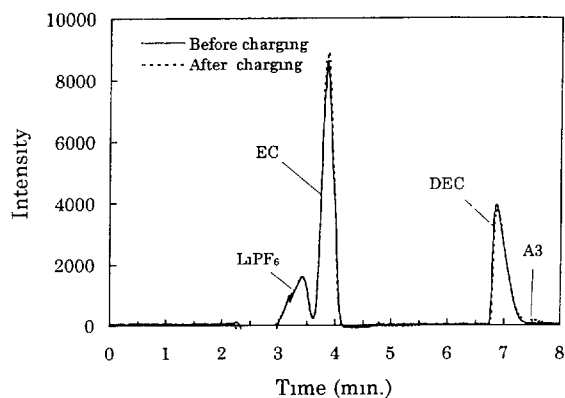


Fig. 5. Liquid chromatograms of 1 M LiPF₆/EC + DEC (1:1) before and after initial charging.

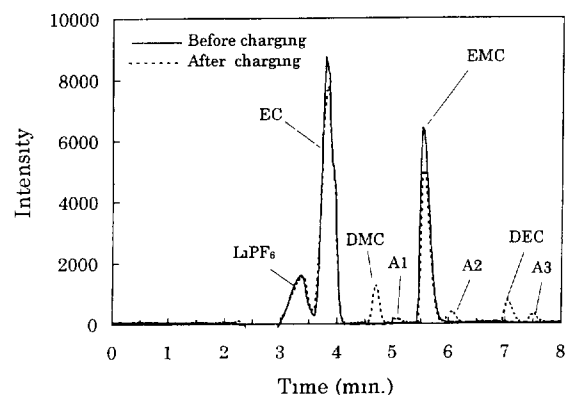


Fig. 6. Liquid chromatograms of 1 M LiPF₆/EC + EMC (1:1) before and after initial charging.

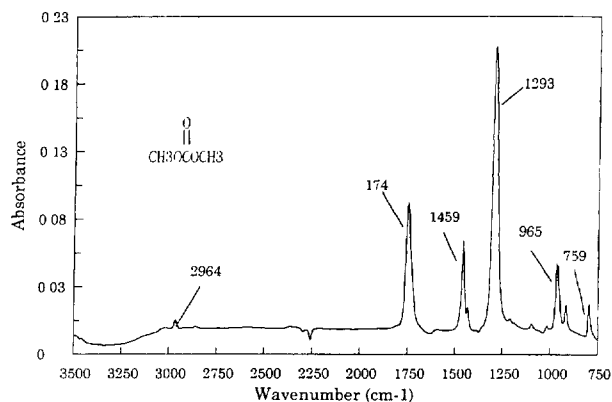


Fig. 7 FT-IR-ATR spectrum of dimethyl carbonate.

EC + DMC and EC + DEC, respectively. When using the binary system of EC + EMC (Fig. 6), DMC and DEC were produced according to the Eq. (5). The production of A2 is caused by the trans-esterification of the initial solvent EC + EMC. Whereas, the formation of A1 and A3 is due to

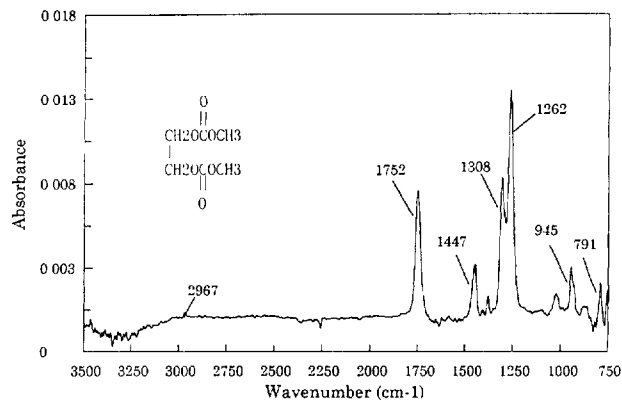


Fig. 8. FT-IR-ATR spectrum of the A1 compound (dimethyl-2,5-dioxahexane carboxylate).

the trans-esterification of the initial EC and the produced DMC and DEC, respectively.

Figs. 7 and 8 show the FT-IR-ATR spectra of DMC and the compound A1, respectively. Since both figures are almost similar, one could deduce that the molecular structure of A1 is similar to that of DMC. Furthermore, A2 and A3 were found to have similar molecular structure compared with EMC and DEC, respectively, because they present similar absorption spectra. By comparing the above results with standard substances specially prepared, it was confirmed that A1, A2 and A3 compounds are dimethyl-2,5-dioxahexane carboxylate (DMDOHC), ethylmethyl-2,5-dioxahexane carboxylate (EMDOHC) and diethyl-2,5-dioxahexane carboxylate (DEDOHC), respectively. Further experiments have confirmed that EC and DMC could be produced from DMDOHC indicating the trans-esterification equilibrium between (EC + chain alkyl carbonate) and dialkyl-2,5-dioxahexane carboxylate as shown in Eqs. (6)–(8):



The trans-esterification shown in Eqs. (5)–(8) took place only when the cell is initially charged. The trans-esterification was activated by lithium alkoxide (ROLi), rather than by Li₂CO₃, LiOH or RCOOLi. By taking into account the additional data from FT-IR, the trans-esterification shown in Eqs. (5)–(8) could be also activated by (CH₂OLi)₂ formed on the negative electrodes by a reductive reaction of the electrolytes during initial charging.

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