

# Study on the decomposition mechanism of alkyl carbonate on lithium metal by pyrolysis-gas chromatography-mass spectroscopy

Ryo Mogi<sup>a,b</sup>, Minoru Inaba<sup>c,\*</sup>, Yasutoshi Iriyama<sup>a</sup>,  
Takeshi Abe<sup>a</sup>, Zempachi Ogumi<sup>a</sup>

<sup>a</sup>Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University,  
Sakyo-ku, Kyoto 606-8501, Japan

<sup>b</sup>Shibukawa Laboratory, Kanto Denka Kogyo Co. Ltd., 1497 Shibukawa, Gunma 377-8513, Japan

<sup>c</sup>Department of Molecular Science and Technology, Faculty of Engineering,  
Doshisha University, Kyotanabe, Kyoto 610-0321, Japan

## Abstract

The surface films formed on deposited lithium in electrolyte solutions based on ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC) were analyzed by pyrolysis-gas chromatography-mass spectroscopy (Py-GC-MS). In 1 M LiClO<sub>4</sub>/EC, the main component of the surface film was easily hydrolyzed to give ethylene glycol after exposure to air, and hence was considered to have a chemical structure of ROCH<sub>2</sub>CH<sub>2</sub>OR', of which –OR and –OR' are –OLi or –OCO<sub>2</sub>Li. Ethylene oxide, acetaldehyde, and 1,4-dioxane were detected in decomposition products, and they were considered to have been formed by pyrolysis of ROCH<sub>2</sub>CH<sub>2</sub>OR' in the pyrolyzer. The presence of ethanol in decomposition products confirmed that ring cleavage at the CH<sub>2</sub>–O bonds of EC occurs by one electron reduction. In addition, the presence of methanol implied the cleavage of the C–C bond of EC upon reduction. From the surface films formed in 1 M LiClO<sub>4</sub>/DEC and /DMC, ethanol and methanol, respectively, were detected, which suggested that corresponding lithium alkoxides and/or lithium alkyl carbonates were the main components. In 1 M LiClO<sub>4</sub>/EC + DEC (1:1), EC dominantly decomposed to form the surface film. The surface film formed in 1 M LiPF<sub>6</sub>/EC + DEC (1:1) contained a much smaller amount of organic compounds.

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**Keywords:** Alkyl carbonate; Decomposition mechanism; Lithium metal; Pyrolysis-gas chromatography-mass spectroscopy

## 1. Introduction

Lithium metal has a high energy density, and is expected to be used as a negative electrode in rechargeable lithium batteries [1]. However, lithium metal negative electrode shows a low cycling efficiency, which is mainly caused by unfavorable morphology of deposited lithium, called dendrites [1–3]. It is widely recognized that a protective surface film, called the solid electrolyte interface (SEI) [4], is formed on lithium surface by reductive decomposition of electrolyte solution, and that this surface film greatly affects the morphology of deposited lithium.

The compositions of the surface films formed on lithium in non-aqueous electrolyte solutions have been extensively investigated with a variety of analytical tools, e.g. Fourier transform-infrared spectroscopy (FT-IR) [5–12], X-ray

photoelectron spectroscopy (XPS) [5,9,11,13–18], electrochemical quartz crystal microbalance (EQCM) [15,19–21], pyrolysis-gas chromatography-mass spectroscopy (Py-GC-MS) [10,22], etc. The results in these studies have shown that the surface film on lithium consists of decomposition products of solvent molecules, lithium salts, contaminants such as H<sub>2</sub>O, CO<sub>2</sub> and O<sub>2</sub>, and additives such as HF.

In the present study, the Py-GC-MS technique was applied to the surface films formed on lithium in electrolyte solutions based on ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC). The mechanisms for reductive decomposition of these alkyl carbonates on lithium metal were discussed.

## 2. Experimental

The electrolyte solutions used in the present study were 1 mol dm<sup>−3</sup> (M) lithium perchlorate (LiClO<sub>4</sub>) dissolved in

\* Corresponding author. Tel.: +81-774-65-6591; fax: +81-774-65-6803.  
E-mail address: [minaba@mail.doshisha.ac.jp](mailto:minaba@mail.doshisha.ac.jp) (M. Inaba).

EC, DEC, DMC, and a 1:1 (by volume) mixture of EC and DEC (EC + DEC), and 1 M lithium hexafluorophosphate ( $\text{LiPF}_6$ ) dissolved in EC + DEC. All these solutions were purchased from Kishida Reagents Chemicals. The water content of each solution was less than 30 ppm, which was measured with a Karl–Fischer moisture titrator. The working electrode was a nickel plate, and the counter and reference electrodes were lithium foil.

Lithium deposition and dissolution was carried out on the nickel electrode at  $0.5 \text{ mA cm}^{-2}$  in a three-electrode cell made of polytetrafluoroethylene. Lithium was deposited by  $0.3 \text{ C cm}^{-2}$  and dissolved to 1.5 V versus  $\text{Li}^+/\text{Li}$ . After the fifth dissolution, the cell was disassembled, and the nickel electrode was dried under vacuum at room temperature to remove the solvent. The sample was set at the sample holder in a pyrolyzer (GP-1028, Yanaco). All the treatments so far were carried out in an argon-filled glove box (MDB-1B, Miwa) with a dew point lower than  $-70^\circ\text{C}$ . The pyrolyzer was sealed and then transported to a GC-MS apparatus. After the heating zone located at a lower part of the pyrolyzer was heated to  $300^\circ\text{C}$ , the sample was dropped to the heating zone. Gaseous products formed by pyrolysis were analyzed with a gas chromatograph (HP6890, Hewlett-Packard) equipped with a capillary column (PoraPLOT Q, Hewlett-Packard), and further identified with a mass spectrometer (JMS-600W, JEOL). The ionization for MS was carried out by electron impact (EI) with a voltage and a current for acceleration of 70 eV and  $100 \mu\text{A}$ , respectively.

### 3. Results and discussion

#### 3.1. Ethylene carbonate

Panel (a) in Fig. 1 shows a gas chromatogram of thermal decomposition products of the residual surface film formed on Ni in 1 M  $\text{LiClO}_4/\text{EC}$ . The chemical structures of the decomposition products were identified by MS, and are specified in Fig. 1(a). Methanol, ethanol, acetaldehyde, ethylene oxide, ethylene glycol, and 1,4-dioxane were detected in addition to residual EC. Only EC was detected when a nickel plate was just soaked in the solution; hence, the compounds except for EC shown in Fig. 1(a) are attributed to the decomposition products of the surface film formed on the lithium metal during the deposition and dissolution cycles. Panel (b) in Fig. 1 shows a gas chromatogram after the sample was exposed to air for 3 min. The peak of ethylene glycol became larger, whereas the other peaks disappeared or were greatly suppressed. It is therefore reasonable to consider that the main component of the surface film is easily hydrolyzed to ethylene glycol. The most probable chemical structure for the main component is thus  $\text{ROCH}_2\text{CH}_2\text{OR}'$ , of which  $-\text{OR}$  and  $-\text{OR}'$  groups can be  $-\text{OLi}$ ,  $-\text{OCO}_2\text{Li}$ ,  $-\text{O-alkyl}$ , etc. that are stable against strongly reductive lithium metal. One of the candidates is  $(\text{CH}_2\text{OLi})_2$ , which is formed by two-electron reduction of EC, followed by CO elimination (Eq. (1)).

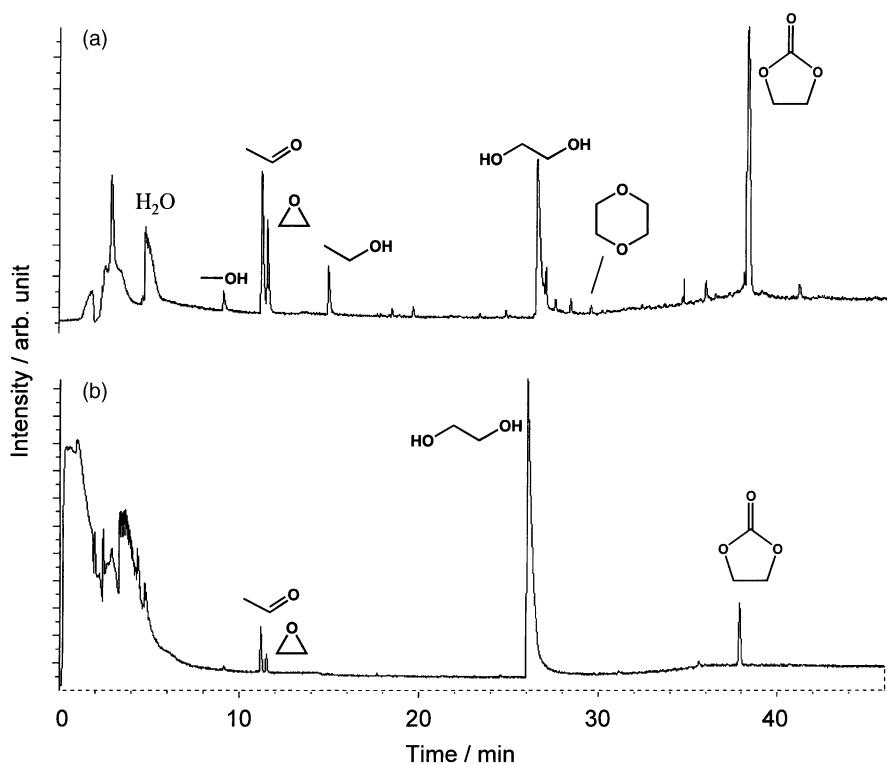
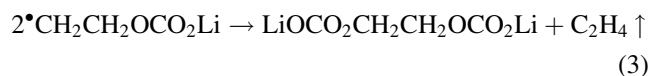
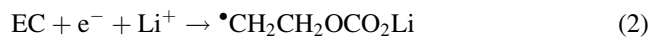


Fig. 1. Gas chromatograms of thermal decomposition products of the residual surface film formed on Ni after five cycles of Li deposition and dissolution in 1 M  $\text{LiClO}_4/\text{EC}$ . The samples were pyrolyzed at  $300^\circ\text{C}$  (a) without and (b) with exposure to air for 3 min.

Another candidate is  $\text{LiOCO}_2\text{CH}_2\text{CH}_2\text{OCO}_2\text{Li}$  ( $-\text{OR}$  and  $-\text{OR}'$  are  $-\text{OCO}_2\text{Li}$ ), which Aurbach et al. [5,6] have proposed as the main component of the surface film. They suggested that  $\text{LiOCO}_2\text{CH}_2\text{CH}_2\text{OCO}_2\text{Li}$  would be formed via the following reactions:

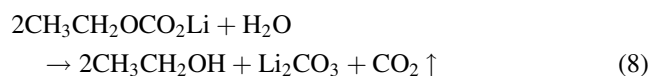


In this reaction scheme, EC is reduced by one electron, and the EC ring is opened by cleavage of the  $\text{CH}_2-\text{O}$  bond to form a Li salt of the resulting radical anion (Eq. (2)).

Of the compounds detected in Fig. 1(a), ethylene oxide, 1,4-dioxane, and acetaldehyde seem to have the same origin. The reactions for the formation of these three compounds can be described in the following Scheme 1.

As shown in Eq. (4),  $-\text{O}^-$  is first formed by elimination of  $\text{R}^+$  in the pyrolyzer, and it attacks  $-\text{CH}_2-$  and ring closure occurs with elimination of  $-\text{OR}'$  to form ethylene oxide. If the ring closure reaction occurs between two molecules, 1,4-dioxane will be formed as in Eq. (5). Acetaldehyde may be formed through the mechanism shown in Eq. (6), in which a hydride shift is involved. This mechanism is similar to the pinacol rearrangement [23] under acidic conditions.

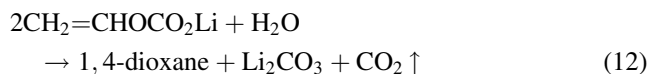
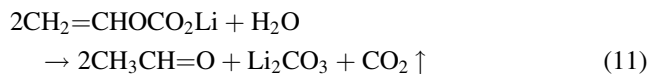
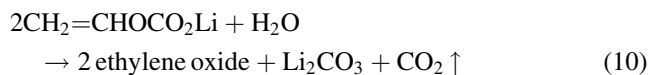
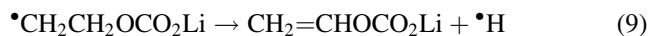
Ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) in Fig. 1(a) may be formed from  $\bullet\text{CH}_2\text{CH}_2\text{OCO}_2\text{Li}$  in Eq. (2) according to the following reactions:



Most of  $\bullet\text{CH}_2\text{CH}_2\text{OCO}_2\text{Li}$  transforms to the lithium alkyl carbonate,  $\text{LiOCO}_2\text{CH}_2\text{CH}_2\text{OCO}_2\text{Li}$ , as mentioned earlier (Eq. (3)). If a radical termination reaction takes place with  $\bullet\text{H}$  that is provided from an unavoidable  $\text{H}_2\text{O}$  contaminant or another EC molecule, part of  $\bullet\text{CH}_2\text{CH}_2\text{OCO}_2\text{Li}$  will be changed to ethyl lithium carbonate as in Eq. (7). The ethyl lithium carbonate precipitates on Li as a surface film com-

ponent, which may explain the formation of ethanol by hydrolysis with a trace amount of  $\text{H}_2\text{O}$  (Eq. (8)).

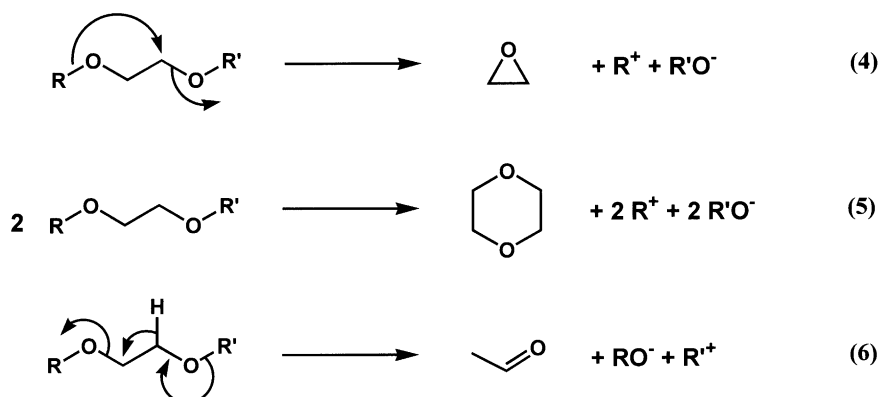
Another possible radical termination reaction is elimination of  $\bullet\text{H}$  from  $\bullet\text{CH}_2\text{CH}_2\text{OCO}_2\text{Li}$  to form lithium vinyl carbonate (Eq. (9)). It may be hydrolyzed to form ethylene oxide (Eq. (10)), acetaldehyde (Eq. (11)), or 1,4-dioxane (Eq. (12)).



We proposed earlier that ethylene oxide, acetaldehyde, and 1,4-dioxane are formed by the pyrolysis of  $\text{ROCH}_2\text{CH}_2\text{OR}'$  described in Eqs. (4)–(6), respectively. The route in Eqs. (9)–(12) can also give the same products. Several other possible routes to form these compounds can be considered, but it is difficult to specify them at present.

Methanol was also detected in Fig. 1(a). It is difficult to understand the mechanism for methanol formation in this system, but it implies that the  $\text{CH}_2-\text{CH}_2$  bond cleavage occurs in the reductive decomposition of EC.

The total scheme that took place on the lithium electrode in 1 M  $\text{LiClO}_4/\text{EC}$  and in the pyrolyzer is summarized in Fig. 2. The chemical structure of the main component in the surface film can be represented as  $\text{ROCH}_2\text{CH}_2\text{OR}'$ , which should be hydrolyzed to form ethylene glycol or pyrolyzed to form ethylene oxide, acetaldehyde, and 1,4-dioxane in the pyrolyzer. Several routes are plausible to produce compounds that have a structure of  $\text{ROCH}_2\text{CH}_2\text{OR}'$  as shown in Fig. 2. In route a, EC is reduced by two electrons to form  $\text{ROCH}_2\text{CH}_2\text{OR}'$  ( $-\text{OR} = -\text{OR}' = -\text{OLi}$ ) accompanied by elimination of carbon monoxide (CO). The EC ring is cleaved by one-electron reduction to form a lithium salt



Scheme 1.

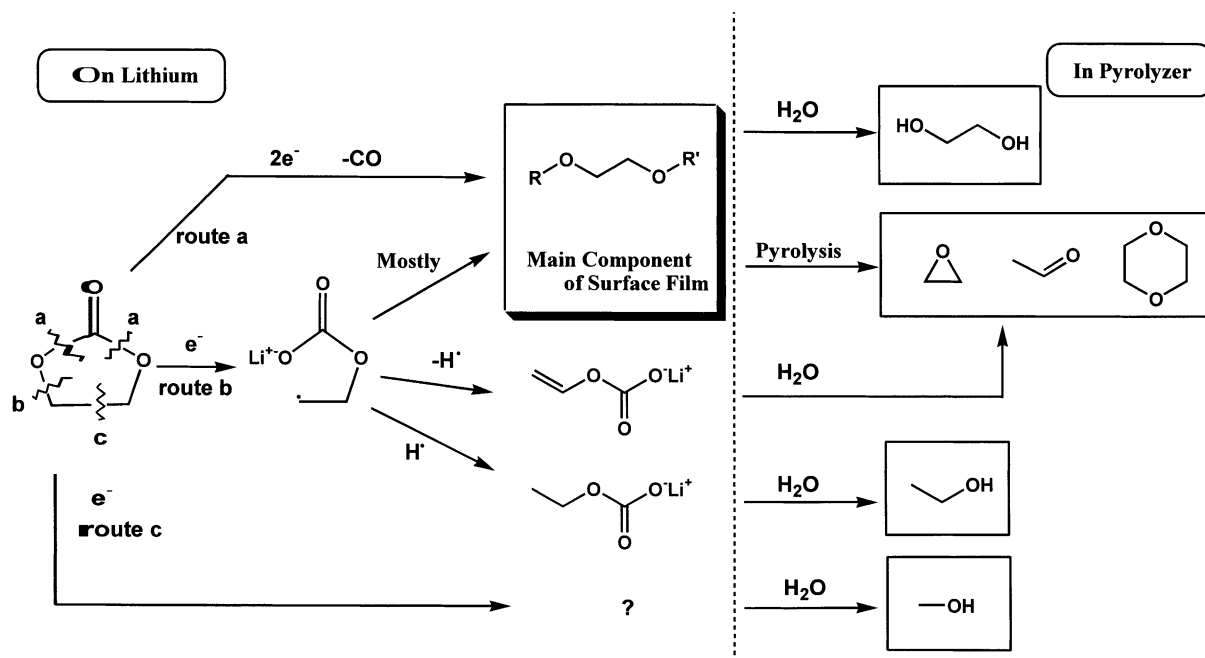


Fig. 2. General scheme for the reactions on lithium metal in 1 M LiClO<sub>4</sub>/EC and in the pyrolyzer heated at 300 °C.

of the radical anion,  $\bullet\text{CH}_2\text{CH}_2\text{OCO}_2\text{Li}$ , in route b. Two radical anions,  $\bullet\text{CH}_2\text{CH}_2\text{OCO}_2\text{Li}$ , react each other to form  $\text{ROCH}_2\text{CH}_2\text{OR}'$  ( $-\text{OR} = -\text{OR}' = -\text{OCO}_2\text{Li}$ ) with elimination of  $\text{C}_2\text{H}_4$ .  $\bullet\text{CH}_2\text{CH}_2\text{OCO}_2\text{Li}$  is partially terminated by trapping  $\bullet\text{H}$ , and the resulting lithium ethyl carbonate is hydrolyzed to form ethanol in the pyrolyzer. When termination of  $\bullet\text{CH}_2\text{CH}_2\text{OCO}_2\text{Li}$  occurs with  $\bullet\text{H}$  elimination, lithium vinyl carbonate is formed, and it is hydrolyzed to form ethylene oxide, acetaldehyde, and 1,4-dioxane in the pyrolyzer. In route c, another ring opening by the cleavage of the C–C bond gives an unidentified product that transforms to methanol with a trace amount of water in the pyrolyzer.

### 3.2. Linear carbonates

In linear carbonate solutions such as 1 M LiClO<sub>4</sub>/DMC and 1 M LiClO<sub>4</sub>/DEC, the coulombic efficiencies of lithium

deposition and dissolution were very low (5–15%). Fig. 3 shows a chromatogram of thermal decomposition products of the residual surface film formed on Ni in 1 M LiClO<sub>4</sub>/DEC. As shown in Fig. 3, ethanol was the main product. Because only a negligible amount of ethanol was detected when fresh 1 M LiClO<sub>4</sub>/DEC was analyzed by Py-GC-MS, the ethanol detected in Fig. 3 was not a pyrolyzed product of DEC, but was derived from the precipitates. Consequently, the most probable chemical structure of the component of the precipitates is  $\text{CH}_3\text{CH}_2\text{OR}$ , of which  $-\text{OR}$  is  $-\text{OLi}$  or  $-\text{OCO}_2\text{Li}$ , and it can be formed from DEC according to the following reactions:

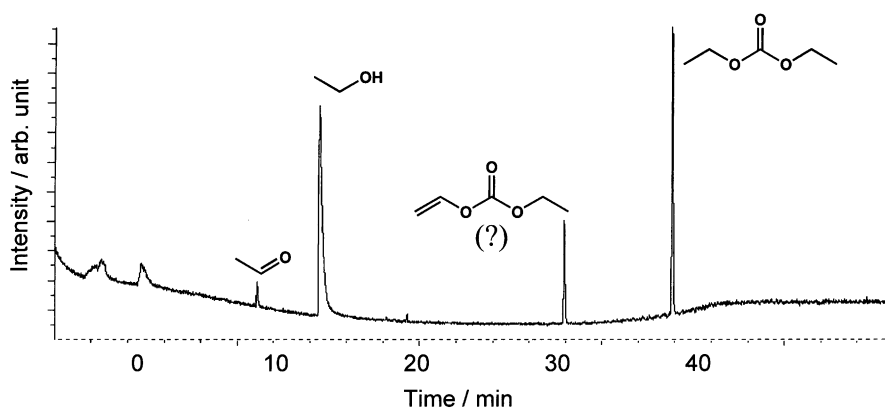
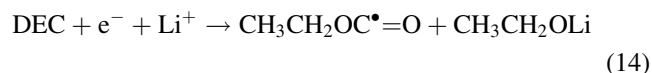
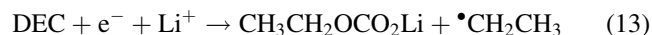


Fig. 3. Gas chromatogram of thermal decomposition products of the residual surface film formed on Ni after five cycles of Li deposition and dissolution in 1 M LiClO<sub>4</sub>/DEC. The sample was pyrolyzed at 300 °C.

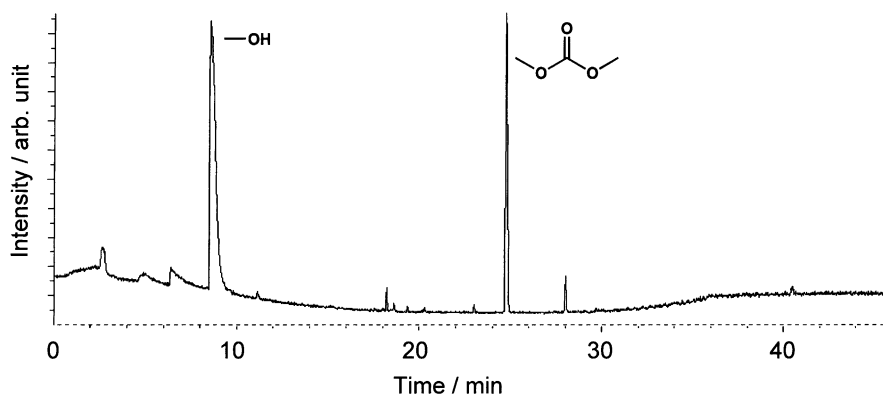
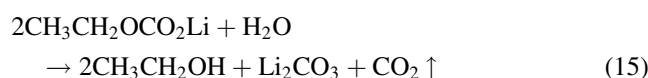


Fig. 4. Gas chromatogram of thermal decomposition products of the residual surface film formed on Ni after five cycles of Li deposition and dissolution in 1 M LiClO<sub>4</sub>/DMC. The sample was pyrolyzed at 300 °C.



These compounds do not seem to work effectively as protective surface films as was indicated by the low coulombic efficiencies, though the reason is not clear.

Another peak appeared at 28 min in Fig. 3, and we tentatively assigned this peak to ethyl vinyl carbonate on the basis of its fragments ( $m/e = 90$  ( $\text{CH}_3\text{CH}_2\text{OCO}_2\text{H}^{\bullet+}$ , 16.9%), 60 ( $\text{CO}_3^{\bullet+}$ , 14.2%), 45 ( $\text{HOCO}_2^{\bullet+}$  or  $\text{CH}_3\text{CH}_2\text{O}^{\bullet+}$ , 100.0%), and 29 ( $\text{HOC}^{\bullet+}$  or  $\text{CH}_3\text{CH}_2^{\bullet+}$ , 9.9%)). Yoshida

et al. [24] reported the generation of a large amount of hydrogen during the first charging process on a graphite negative electrode in 1 M LiPF<sub>6</sub>/DEC. Hence the formation of ethyl vinyl carbonate is reasonable, considering the following H<sub>2</sub> elimination from DEC:



However, the detailed mechanism for the formation of ethyl vinyl carbonate is not clear at present.

The result for 1 M LiClO<sub>4</sub>/DMC is shown in Fig. 4, and methanol was detected as the main product. Methanol is formed by a mechanism similar to that of the ethanol

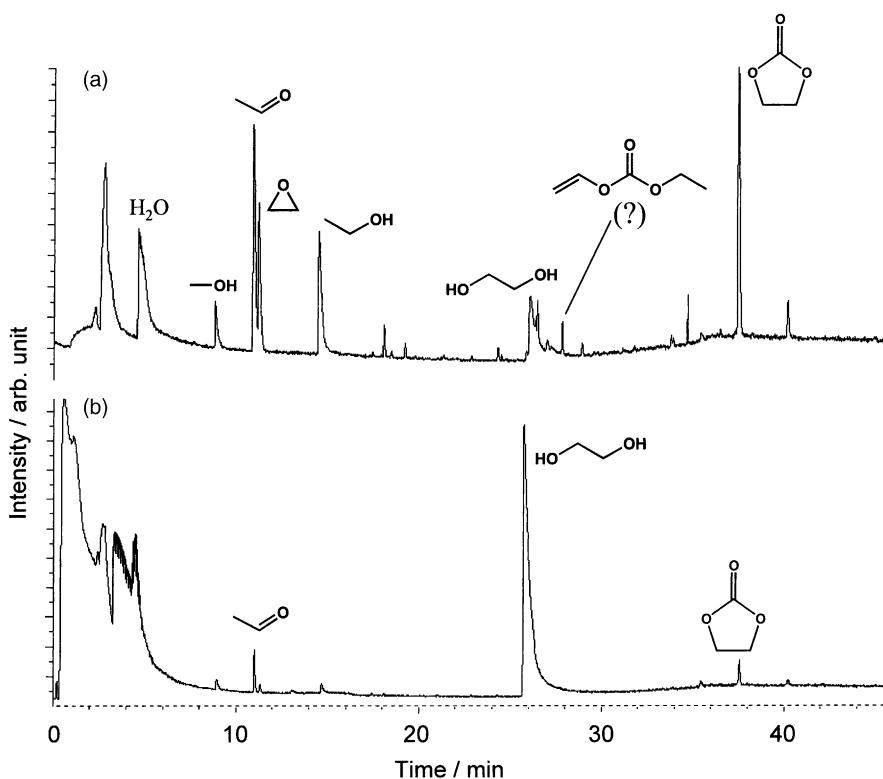


Fig. 5. Gas chromatograms of thermal decomposition products of the residual surface film formed on Ni after five cycles of Li deposition and dissolution in 1 M LiClO<sub>4</sub>/EC + DEC. The samples were pyrolyzed at 300 °C (a) without and (b) with exposure to air for 3 min.

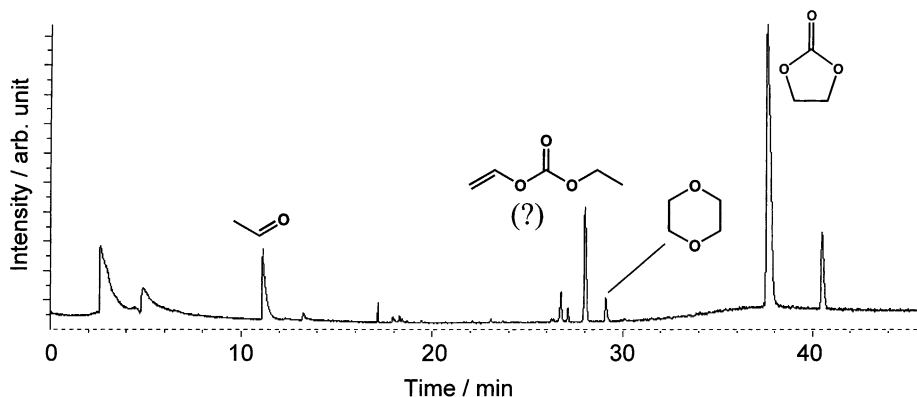


Fig. 6. Gas chromatogram of thermal decomposition products of the residual surface film formed on Ni after five cycles of Li deposition and dissolution in 1 M  $\text{LiPF}_6/\text{EC} + \text{DEC}$ . The sample was pyrolyzed at 300 °C.

formation from DEC mentioned above, and the main component of the precipitates can be described as  $\text{CH}_3\text{OR}$ , of which  $-\text{OR}$  is  $-\text{OLi}$  or  $-\text{OCO}_2\text{Li}$ . In the case of DMC, hydrogen elimination similar to Eq. (17) does not occur, because the reaction should form an unstable radical species.

### 3.3. Mixed solvent systems

Panels (a) and (b) in Fig. 5 show chromatograms for the residual surface film formed on Ni in 1 M  $\text{LiClO}_4/\text{EC} + \text{DEC}$ . The results were very similar to those obtained for 1 M  $\text{LiClO}_4/\text{EC}$  shown in Fig. 1. Methanol, acetaldehyde, ethylene oxide, ethanol, and ethylene glycol were detected as major products. The amount of ethylene glycol increased significantly after the sample was exposed to air as shown in Fig. 5(b). These results indicate that the surface film consisted mainly of the reductive decomposition products of EC, rather than those of DEC. In Fig. 5(a), a small peak was detected at 28 min, and this peak can be attributed to ethyl vinyl carbonate as discussed in the previous section. Hence the film probably contained a small amount of the decomposition products of DEC.

A chromatogram for the residual surface film formed in 1 M  $\text{LiPF}_6/\text{EC} + \text{DEC}$  is shown in Fig. 6. Acetaldehyde, ethanol, ethyl vinyl carbonate, 1,4-dioxane, and EC were detected; however, their intensities were much weaker than those in Fig. 5(a). It should be noted that ethylene glycol was not detected even after exposure to air (not shown). Many researchers have investigated the compositions of surface films formed on lithium metal in electrolyte solutions containing  $\text{LiPF}_6$  by a variety of methods [7,10,12,17–19,21]. These studies generally revealed that the surface film mainly consists of inorganic compounds such as  $\text{LiF}$ ,  $\text{Li}_2\text{O}$  and  $\text{Li}_x\text{PO}_y\text{F}_z$ . Therefore, it can be concluded that decomposition of the solvent molecules is greatly suppressed in electrolyte solutions containing  $\text{LiPF}_6$ , or the organic decomposition products react with HF contaminant to form inorganic compounds such as  $\text{LiF}$  and  $\text{Li}_x\text{PO}_y\text{F}_z$  upon storage.

## 4. Conclusions

Py-GC-MS is a powerful tool for investigating the chemical composition of the surface film formed on lithium metal. In 1 M  $\text{LiClO}_4/\text{EC}$ , the main component of the surface film was found to be hydrolyzed to give ethylene glycol, and thereby it was considered to have a chemical structure of  $\text{ROCH}_2\text{CH}_2\text{OR}'$ , of which  $-\text{OR}$  and  $-\text{OR}'$  are  $-\text{OLi}$  or  $-\text{OCO}_2\text{Li}$ . The presence of ethanol in decomposition products confirmed that the ring cleavage at the  $\text{CH}_2-\text{O}$  bonds of EC occurs by one electron reduction. Linear carbonates, such as DEC and DMC, reductively decomposed to give lithium alkoxides and/or lithium alkyl carbonates, though these species do not work effectively as protective films on lithium. In a mixed solvent electrolyte of 1 M  $\text{LiClO}_4/\text{EC} + \text{DEC}$ , decomposition of EC occurred dominantly and  $\text{ROCH}_2\text{CH}_2\text{OR}'$  was the main product in the surface film. The surface film formed in 1 M  $\text{LiPF}_6/\text{EC} + \text{DEC}$  (1:1) contained a much smaller amount of organic compounds.

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