

Analysis of surface films on lithium in various organic electrolytes

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Abstract

The surface films formed on lithium metal in ethylene carbonate (EC) + dimethyl carbonate (DMC) containing LiPF_6 , LiClO_4 and $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ electrolytes were analysed by using Auger electron spectroscopy (AES), temperature-programmed decomposition mass spectrography (TPD-MS), FT-IR, ion chromatography (IC) and atomic adsorption spectroscopy (AAS). The morphology of the film was observed by using scanning electron microscopy (SEM). The film formed in the LiPF_6 solution exhibited spherical morphology and was found to contain LiF, lithium oxide compounds (most of which seems to be inorganic), $(\text{CH}_2\text{OCO}_2\text{Li})_2$ and $\text{CH}_3\text{OCO}_2\text{Li}$. The films in LiClO_4 and $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ were dendritic and contained the lithium oxide compounds, $(\text{CH}_2\text{OCO}_2\text{Li})_2$ and $\text{CH}_3\text{OCO}_2\text{Li}$. © 1997 Elsevier Science S.A.

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1. Introduction

The reversibility of a lithium electrode in organic electrolytes is one of the key issues in obtaining rechargeable lithium batteries with high energy density. The film formation on lithium metal is strongly related to the partial consumption of lithium on charge/discharge cycles and the formation of lithium dendrites. Several analyses of surface films formed on lithium have been performed using Fourier-transform infrared (FT-IR), X-ray photospectroscopy (XPS) and other techniques [1–8]. The results have shown that surface films consist of reaction products derived from lithium, solvents, salts and impurities in the electrolytes.

We have investigated changes in the morphology and composition of surface films in ethylene carbonate–dimethyl carbonate (EC–DMC) with lithium salt (LiPF_6 , LiClO_4 , $\text{LiN}(\text{SO}_2\text{CF}_3)_2$) electrolytes. In this study, morphological observations were done by scanning electron microscopy (SEM). The analysis of surface films was achieved by FT-IR, Auger electron spectroscopy (AES), temperature-programmed decomposition mass spectroscopy (TPD-MS), ion chromatography (IC) and atomic absorption spectroscopy (AAS). TPD-MS was especially useful in identifying the organic lithium compounds. The amount of F anion and Li can be obtained by IC and AAS, respectively.

2. Experimental

The organic electrolytes used were mixtures of EC and DMC (1:1 by volume) and 1 M lithium salts such as LiPF_6 , LiClO_4 and $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ [LiTFSI]. The films for analysis were obtained in the following conditions. First, lithium was electrodeposited galvanostatically on a nickel substrate at a current density of 0.5 mA cm^{-2} and a total charge of 0.3 C cm^{-2} . Then the dissolution of lithium was carried out at same current density until the voltage reached 1.5 V versus Li/Li^+ and the electrochemically active lithium was removed. The resultant surface films on the nickel substrate after dissolution were washed with pure dimethyl carbonate (DMC) and then dried under vacuum at room temperature for 1 h.

SEM (JEOL JSM-6300F) measurements were performed on the nickel substrate after electrodeposition and dissolution of lithium. AES measurements of the films were carried out by using JEOL JAMP-7800. The depth profile of each element was obtained from AES analysis by using argon ion sputtering (2000 eV).

FT-IR (Nicolet DX 510) was measured by transmission spectroscopy. The surface films on nickel substrate were removed physically, pressed into KBr pellets in a glove box and analysed.

The gas generated from the film with varying temperature from 30 to 500 °C by 10 °C/min was analysed by TPD-MS (TPD: Ohkura ATD 700, MS: ANELVA AGS-221). The gas generated from 30 to 200 °C was trapped and analysed

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by GC-MS (GC: Hitachi G-3000, MS: ANELVA AGS 7000). The column for GC-MS measurement was poraPlotQ.

In IC (Yokogawa IC 500) and AAS (Hitachi Z 6100) analyses, the film was dissolved in water and the amount of the F anion and total Li were analysed, respectively.

Electrochemical experiments and sample preparation were conducted in a dry air glove box (dew point $-70\text{ }^{\circ}\text{C}$) at room temperature.

3. Results and discussion

Fig. 1 shows SEM graphs after electrodeposition and then dissolution of lithium. Hemispherical lithium particles were observed in Fig. 1(a). Kanamura et al. [9] reported the hemi-

spherical formation of lithium deposited for suppression of the dendrite formation by HF as the decomposition product of the PF_6^- anion. The morphology suggests an effect of HF. In Fig. 1(b) and (c), needle-like lithium and particle-like lithium were observed. Arakawa et al. [10] proposed mechanisms of formation and isolation of these two types of lithium [10]. We observed the particle-like lithium in LiClO_4 electrolyte remained after dissolution (Figs. 1(b) and 2) but that in LiTFSI electrolyte disappeared (Figs. 1(c) and 2).

Fig. 2 shows AES depth profiles for each element in the films after dissolution of lithium. In Fig. 2(a), LiF and Li-O indicated as LiOH, Li_2O or other lithium oxide compounds were mainly observed on surface, and inside the film was Li-O the main component, and near the nickel substrate lithium metal as dead lithium increased in quantity. In the depth

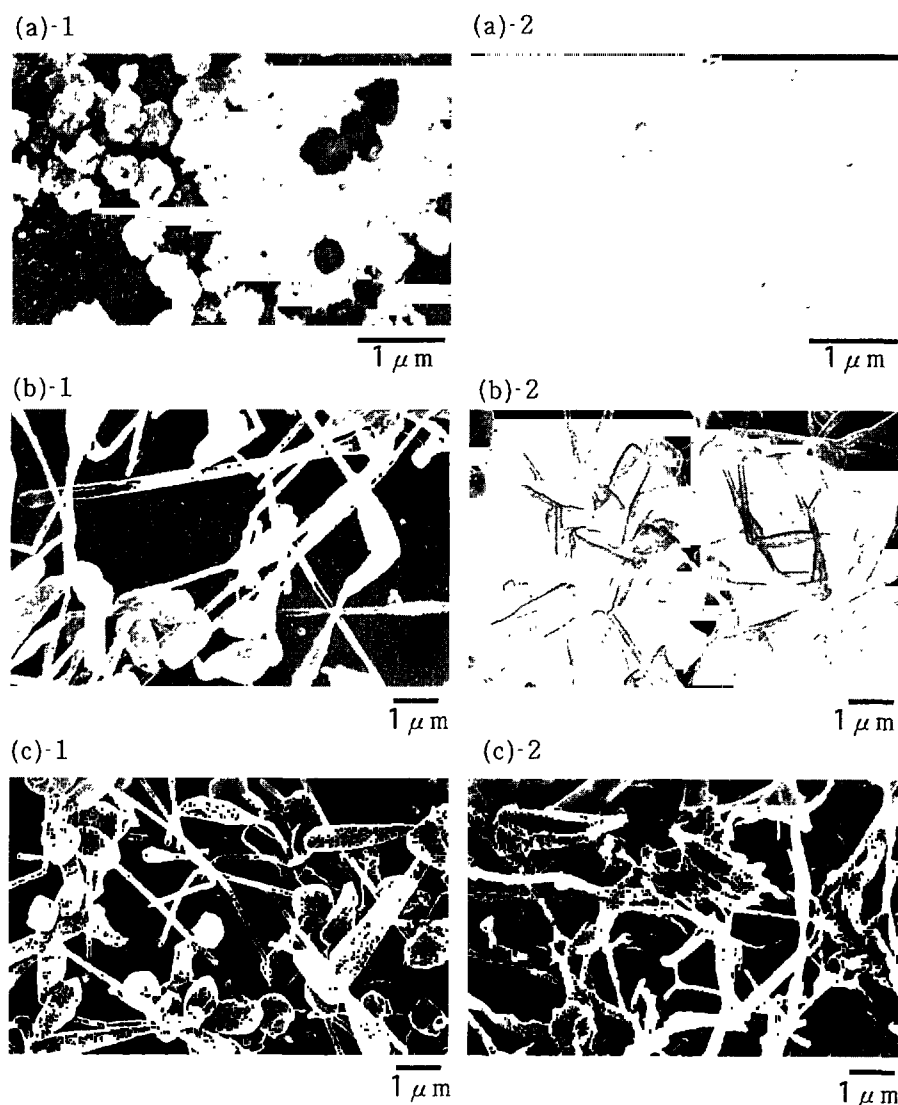


Fig. 1. SEM micrographs of the films on a nickel substrate in EC-DMC containing: (a) LiPF_6 , (b) LiClO_4 , and (c) LiTFSI (1 M) were obtained after electrodeposition and '2' after dissolution of lithium.

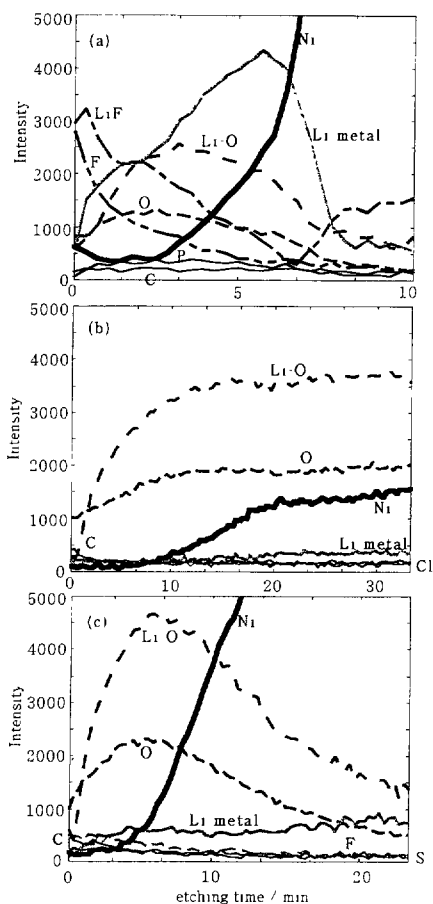


Fig. 2. AES depth profiles of various elements of the films on a nickel substrate in: (a) LiPF₆/EC + DMC; (b) LiClO₄/EC + DMC, and (c) LiTFSI/EC + DMC.

profiles of Fig. 2(b) and (c), Li-O and O elements were mainly observed and the amount of lithium metal increased gradually near the nickel substrate.

Fig. 3 shows FT-IR spectra of the film in each electrolyte. The upper line shows the surface film after dissolution and the lower line shows the remaining part after heating the film up to 200 °C by TPD. Almost identical spectra were obtained in Fig. 3(a)-(c). The peak assignments were based on Refs. [3,4]. The IR spectra of films indicate that the major component of the films is lithium alkyl carbonate (ROCO₂Li), and that LiOH and Li₂CO₃ exist in small amounts. After heating, ROCO₂Li decreased and Li₂CO₃ increased. The gas generated by heating was analysed in detail using GC-MS measurement.

The analysis of gas generated from the films with varying temperature is shown in Fig. 4(a)-(c). The major gases detected were CH₄, H₂O, CO, CH₃OH, CO₂ and ethylene oxide. N₂ gas was detected at ~160 °C in Fig. 4(c). It indicates reaction products from LiTFSI (the thermal decomposition of LiTFSI starts over 350 °C). To analyse the gas in detail, the gas generated from 30 to 200 °C was trapped and analysed by GC-MS. The spectrum is shown in Fig. 5. The

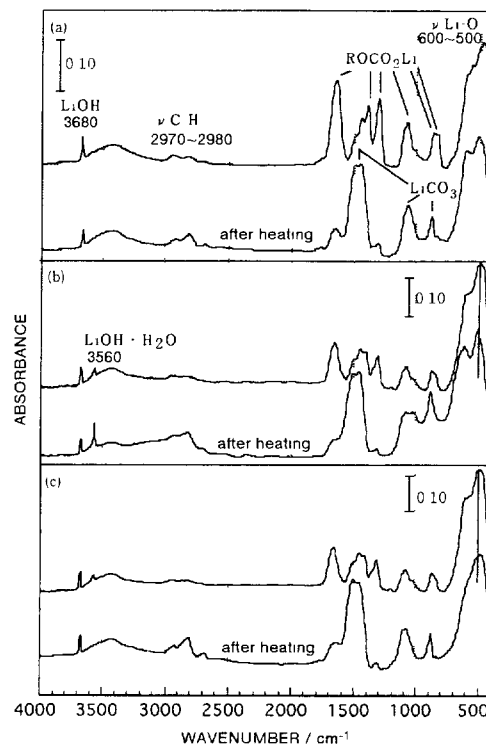


Fig. 3. FT-IR spectra obtained from films in a KBr pellet: upper line: the surface film, and lower line: the remaining after heating the film to 200 °C by TPD (a) LiPF₆/EC + DMC, (b) LiClO₄/EC + DMC, and (c) LiTFSI/EC + DMC

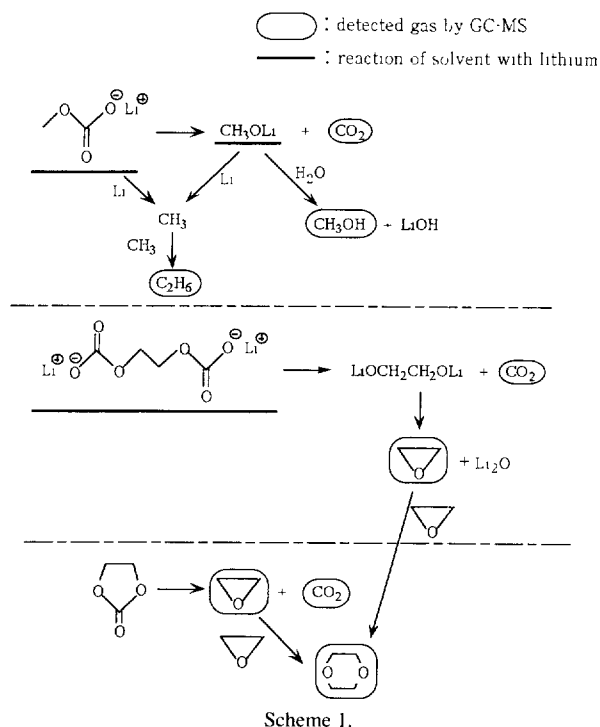


Table 1

Summary of the results obtained from surface films in LiX/EC + DMC electrolytes (LiX: LiPF₆, LiClO₄ and LiTFSI)

	Morphology by SEM	Chemical composition			
		by AES	by FT-IR	by TPD-MS	by IC and AAS
LiPF ₆ /EC-DMC	Collapsed Hemispherical	Li-F C, O, Li-O metallic Li	ROCO ₂ Li Li ₂ CO ₃ LiOH	H ₂ O (CH ₂ OCO ₂ Li) ₂ CH ₃ OCO ₂ Li	LiF/total Li mole or ratio 1/3
LiClO ₄ /EC-DMC	Dendritic	C, O Li-O metallic Li	ROCO ₂ Li Li ₂ CO ₃ LiOH	H ₂ O (CH ₂ OCO ₂ Li) ₂ CH ₃ OCO ₂ Li	
LiTFSI/EC-DMC	Dendritic	C, O Li-O metallic Li	ROCO ₂ Li Li ₂ CO ₃ LiOH	H ₂ O (CH ₂ OCO ₂ Li) ₂ CH ₃ OCO ₂ Li	no F anion detected

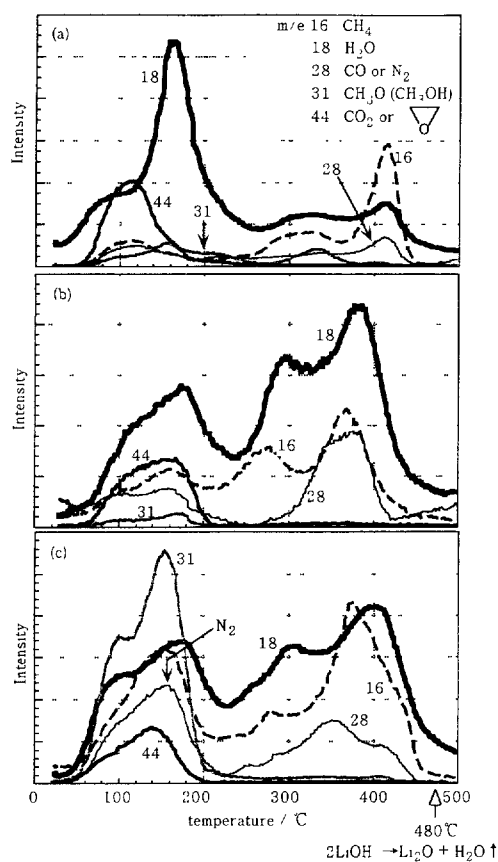


Fig. 4. TPD-MS spectra of gas generated from surface films with varying temperature. The films were obtained in (a) LiPF₆/EC + DMC, (b) LiClO₄/EC + DMC, and (c) LiTFSI/EC + DMC.

same gas components were detected in Fig. 5(a)–(c) showing no correlation to the solute types. This indicates that the detected gasses were generated from the reaction products of lithium and the solvent (EC or DMC). The H₂O detected was most likely adsorbed on the surface film during sample preparation because the amount of H₂O was larger than that expected from the content of the electrolyte. The reaction scheme determined by heat decomposition is shown in the

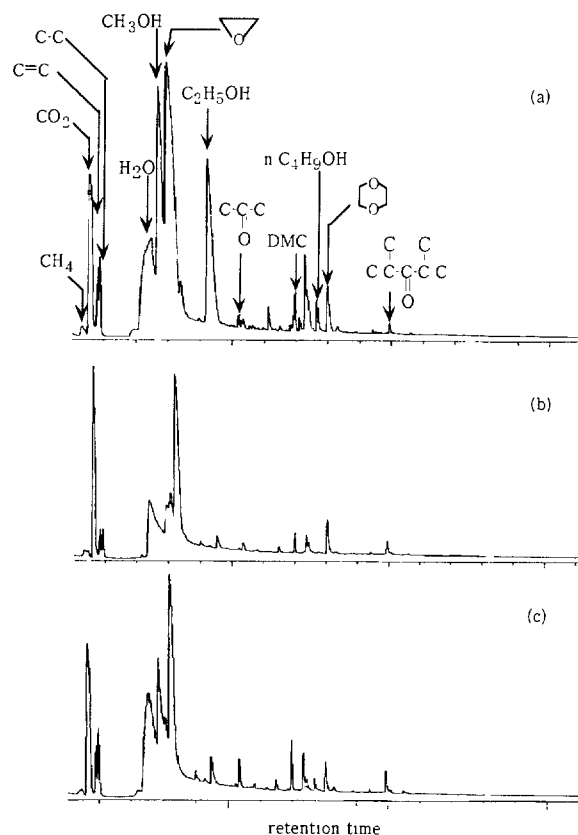


Fig. 5. GC-MS spectra of gases trapped by heating the films from 30 to 200 °C: (a) LiPF₆/EC + DMC; (b) LiClO₄/EC + DMC, and (c) LiTFSI/EC + DMC.

reaction Scheme 1. Since CO₂, ethylene oxide and CH₃OH were detected in large quantities, (CH₂OCO₂Li)₂ and CH₃OCO₂Li produced from the reaction of EC and DMC with lithium existed mainly as organic lithium compounds in the surface films. However, it is possible that ethylene oxide generated from the decomposition of EC was adsorbed on the surface film. Further study will be needed.

Results of the chemical composition and morphology of the surface films are summarized in Table 1. For the $\text{LiPF}_6/\text{EC-DMC}$ system, the amount of LiF was determined to be one third of the total lithium in the film after dissolution of lithium by using IC and AAS measurements.

4. Conclusions

A comparative study of morphology and chemical composition of surface films which are dependent on the type of solute, were made in this paper. The film formed in the LiPF_6 electrolyte contained LiF in large quantities and the morphology electrodeposited was spherical. The LiF accounted for one third of the total lithium, including lithium compounds and dead lithium. The morphology of the lithium oxide compounds was mainly dendritic in the LiClO_4 and LiTFSI electrolytes. $(\text{CH}_2\text{OCO}_2\text{Li})_2$ and $\text{CH}_3\text{OCO}_2\text{Li}$ were detected as the main organic lithium compounds in the three types of electrolyte.

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