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Pyrolysis/gas chromatography/mass spectroscopy analysis of the surface film formed on graphite negative electrode

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Abstract

The chemical constituents of the protective surface film formed on graphite negative electrode in ethylene carbonate (EC)-based electrolyte solutions were analyzed by pyrolysis/gas chromatography/mass spectroscopy (Pyro/GC/MS). Oligomers that consist of oxyethylene units, such as ethylene glycol, di(ethylene glycol), and tri(ethylene glycol) methyl ester, were detected. These oligomers were formed by reductive decomposition of EC, and their presence suggested that the surface film contained polymer-like substances that have repeated oxyethylene units. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Graphite; Surface film; Pyrolysis/gas chromatography/mass spectroscopy; Polymer

1. Introduction

Carbonaceous materials have been extensively studied for use as negative electrodes in lithium-ion batteries. Their charge (lithium intercalation) and discharge (deintercalation) reactions take place at extremely negative potentials close to Li/Li^+ (-3.045 V versus NHE), and hence non-aqueous solutions are used in place of aqueous solutions. Even nonaqueous solvents cannot be thermodynamically stable at such negative potentials. It is widely believed that a kind of protective film, called solid electrolyte interface (SEI), is formed on carbon negative electrodes in the initial stage of charging [1]. The presence of SEI prevents further solvent decomposition and improves the safety and cycle-ability of lithium-ion cells. The chemical constituents of SEI formed on carbon negative electrodes have been studied so far using Fourier transform infrared spectroscopy (FTIR) [2–6] and X-ray photoelectron spectroscopy (XPS) [4–6], and the presence of organic compounds, such as lithium alkyl carbonates and lithium alkoxides, and inorganic compounds, such as LiF , Li_2CO_3 , etc., in SEI has been reported.

Mass spectroscopy (MS) is a useful tool for detection and precise identification of small amounts of organic compounds, and has been used to analyze gaseous products formed by decomposition of solvents on carbon negative electrodes [7–10]. The techniques used in these studies

include temperature programmed decomposition mass spectroscopy (TPD-MS) [9] and differential electrochemical mass spectroscopy (DEMS) [10]. Most of these studies aimed at detecting gaseous or volatile reduction products; however, recent studies using scanning electron microscopy (SEM) have revealed the presence of polymer-like substances on carbon negative electrodes [11,12]. Although the knowledge of the gaseous and volatile products is useful in considering the mechanism for solvent decomposition, it does not give direct evidence for the chemical constituents of the SEI layer. In the present study, pyrolysis/gas chromatography/mass spectroscopy (Pyro/GC/MS) [13] was used to obtain direct evidence for decomposed products of relatively high-molecular weights formed on graphite negative electrode.

2. Experimental

Natural graphite flakes of 1–2 mm in particle size, which were produced in China, were used as test samples. The graphite flakes (30 mg) were wrapped with nickel mesh and pressed moderately to obtain good electrical contacts between flakes, and used as test electrodes. The test electrodes did not contain any binders. A conventional three-electrode cell was used for electrochemical pretreatments. The solutions were 1 M LiClO_4 dissolved in ethylene carbonate (EC) (Kishida Chemicals) and a 1:1 (by volume) mixture of EC and diethyl carbonate (DEC) (Kishida Chemicals). The water contents of the solutions were less than 30 ppm. The

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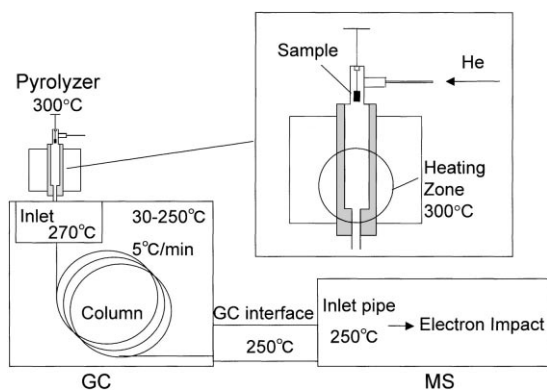


Fig. 1. Schematic diagram of the Pyro/GC/MS system. The inset is an expanded view of the pyrolyzer.

reference and counter electrodes were lithium metal (Honjyo Metal). The test electrodes were charged to 0 V and discharged to 3 V at constant currents. The currents were chosen so that a change of $\Delta x = 1$ in Li_xC_6 (372 mAh g^{-1}) takes 24 h. After one cycle of charge and discharge, the cell was disassembled. The test electrodes were washed twice with 1,2-dimethoxyethane (DME) (Battery grade, Mitsubishi Chemicals) and dried under vacuum at room temperature for 10 min to remove low-molecular weight compounds. These electrochemical pretreatments were carried out in an argon glove box (MDB-1B, Miwa) with a dew point lower than -60°C .

A schematic diagram for the apparatus for Pyro/GC/MS used in the present study is shown in Fig. 1. The sample after the electrochemical pretreatment was suspended from the upper part of a pyrolyzer (GP-1028, Yanaco), which was carried out in the glove box. The pyrolyzer was sealed, and set to the GC/MS apparatus. After the heating zone at the lower part of the pyrolyzer was heated to 300°C , the sample was dropped in the heating zone. Vaporized gas was introduced to a gas chromatograph (HP6890, Hewlett Packard) equipped with a capillary column (HP-5, Hewlett Packard). The carrier gas was helium at a flow rate of $2 \text{ cm}^3 \text{ min}^{-1}$. The column was heated from 30 to 250°C at a constant rate of 5°C min^{-1} . The gas from the outlet of GC was continuously analyzed with a mass spectrometer (JMS-600W, JEOL). The ionization of the gas was carried out by electron impact. The ionization voltage and current were set at 70 V and $100 \mu\text{A}$, respectively. Mass spectra obtained were analyzed with a help of a mass spectral search program (Version 1.5) developed by the National Institute of Standards and Technology (NIST), USA. All the organic compounds specified in the present study were identified at matching factors greater than 80% on the program.

3. Results and discussion

Fig. 2 shows a gas chromatogram of thermally decomposed products of SEI formed in 1 M LiClO_4/EC . Organic

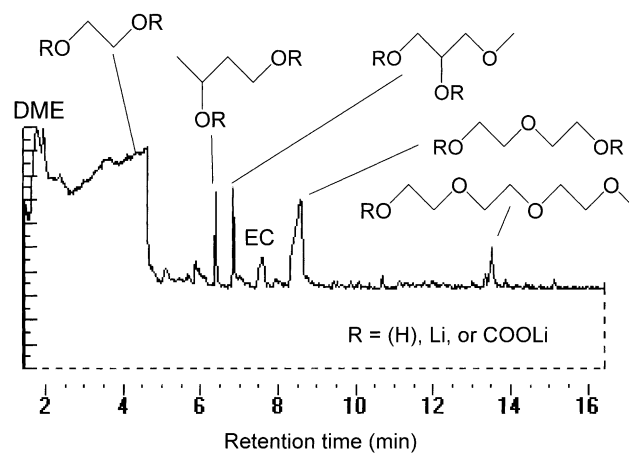


Fig. 2. Gas chromatogram of thermally decomposed products of SEI on natural graphite flakes after charged and discharged in 1 M LiClO_4/EC .

compounds identified by MS are specified in Fig. 2. A peak assigned to EC appeared at a retention time of 7 min 30 s. The molecular-ion peak was observed at $m/z = 88$ in the mass spectrum, and the fragmentation pattern was in agreement with that of EC. In a similar manner, the peak at around 2 min was assigned to DME that had been used as washing solvent.

After the DME peak, a large broad peak appeared up to 5 min. Although the molecular-ion peak was missing, the fragmentation pattern agreed with that of ethylene glycol. Alcohols usually do not give their molecular-ion peaks in their mass spectra; hence, we assigned this peak tentatively to ethylene glycol. In similar manners, other peaks at 6.5, 7, 8.5, and 13.5 min were identified with 1,3-butanediol, 3-methoxy-1,2-propanediol, di(ethylene glycol) (3-oxa-1,5-pentandiol), and tri(ethylene glycol) methyl ester (3,6,9-trioxa-1-decanol), respectively. Here these peaks were tentatively assigned to alcohols, but may be assigned to lithium alkoxides or lithium alkyl carbonates because hydrolyzed products of alkoxides and thermally decomposed products of alkyl carbonates would have given fragmentation patterns similar to those of the corresponding alcohols. Alcohols cannot be stable under strongly reductive atmosphere on fully lithiated graphite. Hence, it is reasonable to think that lithium alkoxides or lithium alkyl carbonates, rather than alcohols, were present in the SEI layer as suggested by Aurbach et al. [2]. The use of chemical ionization, instead of electron impact, can give the molecular-ion peaks of alcohols, which will allow us more precise identification of the products.

Another possibility is that the observed alcohols were formed by thermal decomposition of longer-chain polymers. We analyzed poly(ethylene glycol) dimethyl ether ($M_n = 250$) by Pyro/GC/MS, but only a single peak assigned to the ether was observed on the gas chromatogram. This is due to the relatively low pyrolysis temperature (300°C) employed in the present study. Hence, the observed alcohols were not

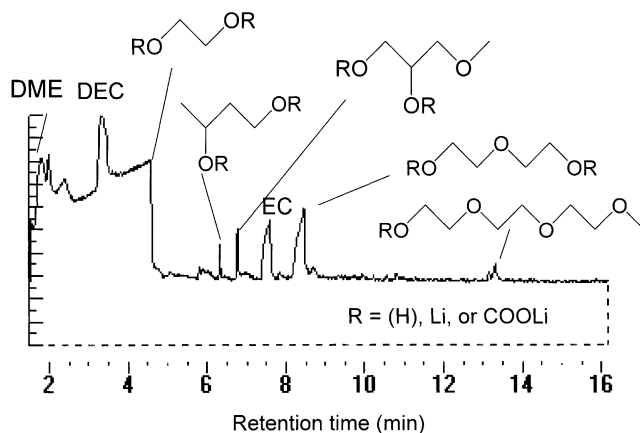


Fig. 3. Gas chromatogram of thermally decomposed products of SEI on natural graphite flakes after charged and discharged in 1 M LiClO₄/EC + DEC.

thermally decomposed fragments of polymers in the SEI layer.

It should be noted that ethylene glycol, di(ethylene glycol), and tri(ethylene glycol) methyl ester are oligomers that consist of oxyethylene units. It is considered that these oligomers were formed by reductive decomposition of EC. Furthermore, the presence of these oligomers suggests that the SEI layer contained polymer-like substances with repeated oxyethylene units, similar to poly(ethylene oxide) (PEO), although direct evidence for the presence of such polymers was not obtained by Pyro/GC/MS as mentioned above. The presence of such PEO-like polymers in SEI is reasonable because the SEI layer should have lithium-ion conductivity.

Fig. 3 shows the result for SEI formed in 1 M LiClO₄ dissolved in a mixed solvent, EC + DEC. The chromatogram was very similar to that in Fig. 2 except a peak assigned to DEC was observed at 3 min 30 s. Each peak was identified with the same compound as that in Fig. 2. The relative intensities of the peaks were also very similar. This result indicates that the SEI layer consisted mainly of the decomposed products of EC. The decomposed products of DEC may be soluble to the solution.

4. Conclusions

The results obtained in this study showed that Pyro/GC/MS is a powerful tool for direct detection of the chemical constituents of the SEI layer formed on graphite negative electrode. Oligomers with oxyethylene units, such as ethylene glycol, di(ethylene glycol), and tri(ethylene glycol) methyl ester, which are decomposition products of EC, were detected, and their presence suggested that the SEI layer contained polymer-like substances that have repeated oxyethylene units.

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