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# Anodic oxidation of propylene carbonate and ethylene carbonate on graphite electrodes

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## Abstract

Electrochemical oxidation of electrolytes becomes a more serious problem in high voltage lithium cells. In this paper, the reaction mechanisms of propylene carbonate (PC) and ethylene carbonate (EC) are investigated by using in situ mass spectrometry and gas chromatography–mass spectrometry. When PC is oxidized, it decomposes into carbon dioxide and propylene oxide, which in turn react to form other by-products, such as propanal and 2-ethyl-4-methyl-1,3-dioxolane. Carbon dioxide is generated during EC oxidation.

**Keywords:** Propylene carbonate; Ethylene carbonate; Graphite electrodes; Anodic oxidation

## 1. Introduction

Lithium rechargeable cells with charge voltages exceeding 4.0 V are becoming more common. In these cells, ethers are seldom used as the electrolyte solvent although they are normally used in lithium cells that use lithium metal as the anode [1]. This is because the electrochemical oxidation of the electrolyte is a more serious problem in these high voltage lithium cells, and ethers are less stable for electrochemical oxidation [2]. Therefore, the proposed electrolyte systems for high voltage lithium cells consist of esters such as propylene carbonate (PC), diethyl carbonate (DEC), ethylene carbonate (EC) and dimethyl carbonate (DMC) [3,4].

Both EC and PC are well-known solvents with relatively high oxidation potentials. However, EC and PC oxidation has to be considered if these solvents are used in high voltage lithium cells, as their oxidation potentials are around 5.0 V, which is close to the maximum charge voltage of the cells. Cell voltage can easily reach their oxidation potential if the cells are overcharged. It is therefore important to investigate the electrochemical reactions of electrolytes due to overcharging in order to understand cell performance and safety.

Electrochemical oxidation of PC has been investigated by using in situ mass spectrometry [5,6] and in situ

Fourier-transform infrared spectroscopy (FT-IR) [6,7]. However, the electrochemical oxidation mechanism of PC is still unclear. This study investigates the anodic oxidation of PC and EC by using in situ mass spectrometry and gas chromatography–mass spectrometry and discusses their reaction mechanisms.

## 2. Experimental

### 2.1. Electrolyte preparation

LiClO<sub>4</sub> (Tomiyama Pure Chemical), LiBF<sub>4</sub> (Tomiyama Pure Chemical), LiAsF<sub>6</sub> (Agri Chemical Inc.) and LiPF<sub>6</sub> (Hashimoto Chemical Industry Inc.) were used as-received. These salts were dissolved into purified PC and EC (Tomiyama Pure Chemical). Traces of water in the electrolytes were reduced with activated alumina (Woelm, neutral, super I) column. The remaining water content was less than 20 ppm.

### 2.2. Test cell preparation

The test cells used for the experiments are shown in Fig. 1. The working electrodes were 13 mm diameter disks and consisted of graphite powder combined with polytetrafluoroethylene. Lithium metal was used as the counter electrode (13 mm diameter) and reference electrode.

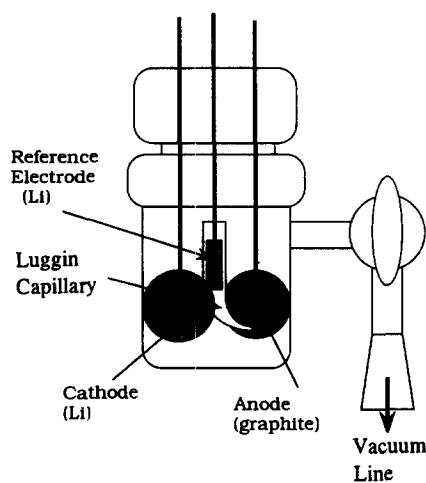


Fig. 1. Schematic drawing of the cell used for oxidation products measurements.

### 2.3. Analysis of reaction products

The test cells were connected to a vacuum line and evacuated. The volume of gas species which evolved from the cell during galvanostatic and potentiostatic oxidation was measured by an oil manometer in the vacuum line. The contents of the gas were analysed by using the double-focusing mass spectrometer of a DX-3000 gas chromatography–mass spectrometer (GC–MS) (JEOL) and the MSQ-150 quadrupole mass spectrometer (ULVAC) connected to the vacuum line. Other species produced during anodic oxidation in the electrolyte were analysed with the gas chromatography–mass spectrometer. A packed glass column (3 m, PEG 20M) was used. The carrier gas was helium with a 30 ml/min flow rate. The injection room temperature was 150 °C and the oven temperature was 30 °C.

## 3. Results and discussion

### 3.1. Anodic oxidation propylene carbonate

Fig. 2 shows the voltage profile and gas volume generated by galvanostatic oxidation at 3.77 mA/cm<sup>2</sup> in the cells using 1 M LiClO<sub>4</sub>. The cell voltage began to rise immediately up to about 4.5 V. It then rose gradually, showing some inflections until about 7.5 V, at which point galvanostatic oxidation could not continue because the lithium ion had been depleted by its deposition at the cathode. The inflections suggest the intercalation of ClO<sub>4</sub><sup>-</sup> ion into the graphite. Gas generation was observed on the anode (graphite electrode) from about 4.5 V. Slight gas evolution was also observed from the cathode (lithium electrode).

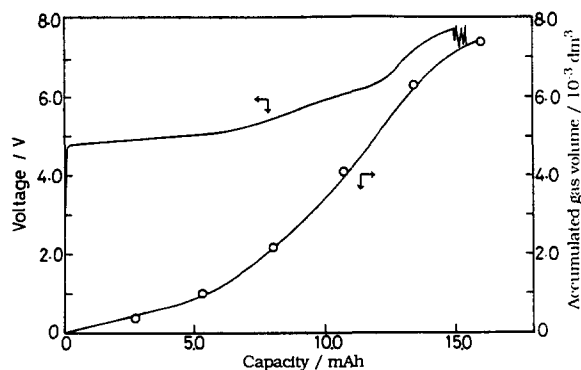


Fig. 2. Potential curve and gas volume due to anodic oxidation of electrolyte (1 M LiClO<sub>4</sub>-PC).

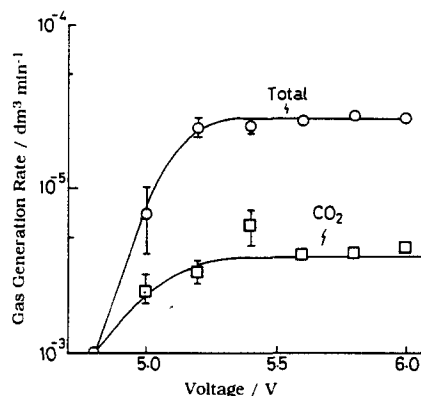


Fig. 3. Gas generation rate vs. voltage.

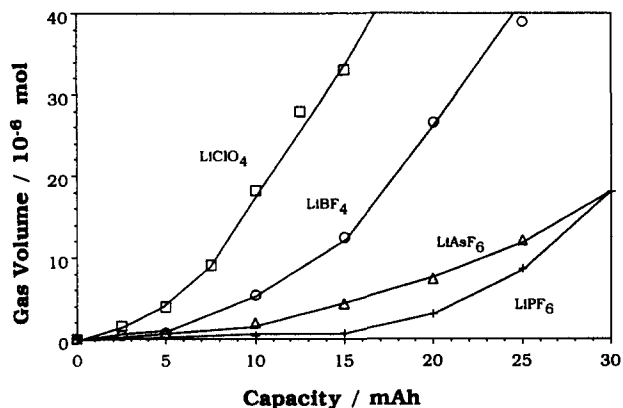


Fig. 4. Gas volume dependence on electrolyte salts. Electrolyte salts were dissolved in PC to make 1 M solution.

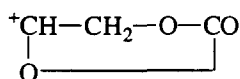
Fig. 3 shows the gas generation rate dependence on voltage as measured during potentiostatic oxidation of the electrolyte. The generation rate was almost constant above 5.2 V.

Gas generation by PC anodic oxidation was affected by the kind of the electrolyte salt used. Fig. 4 shows the difference in gas volume among 1 M LiClO<sub>4</sub>-PC, 1 M LiBF<sub>4</sub>-PC, 1 M LiAsF<sub>6</sub>-PC and 1 M LiPF<sub>6</sub>-PC electrolytes during galvanostatic oxidation. PC oxidation resulting in gas generation was enhanced in the LiClO<sub>4</sub>/PC. The order of gas volume generated was LiPF<sub>6</sub> < LiAsF<sub>6</sub> < LiBF<sub>4</sub> < LiClO<sub>4</sub>. There are two possible explanations for gas-generation dependence on

the kind of salt. One is PC oxidation due to the catalytic effect of anion-intercalated graphite compounds. The other is PC oxidation due to the radical reaction as reported in  $\text{LiAsF}_6$ -dioxolane [8]. It has also been reported that perchlorate ion is reduced to perchlorate radical [9].

To investigate whether PC decomposition is proceeded by radical reaction, 2,2'-azobisisobutyro-nitrile (AIBN), which is the initiator in free radical reaction, reacted with PC at 45 °C for one day. The PC solution was analysed with a GC-MS. Only tetramethyl pyrazine was observed as reaction product. This compound must have been produced by dimerization of the AIBN radicals. Consequently, PC may be oxidized by the catalytic effect of anion-intercalated graphite compounds.

Fig. 5 shows the mass spectrum of gas which was generated by galvanostatic oxidation of 1 M  $\text{LiClO}_4$ -PC and was directly introduced into the double-focusing mass spectrometer of the GC-MS. The mass spectrum was obtained by subtracting the background mass spectrum (volatile PC and traces of air) from the mass spectrum of the gas by using the data analysis computer system of the GC-MS. Eggert [5] reported the  $\text{CO}_2$  ( $m/e=44$ ) and  $\text{ClO}_2$  ( $m/e=67$  and  $69$ ) generation by anodic oxidation of  $\text{LiClO}_4$ -PC. The authors identified  $\text{CO}_2$ , however,  $\text{ClO}_2$  could not be identified.  $\text{ClO}_2$  may be too unstable for the reaction with electrolyte to detect with the current measurement system. A strong mass peak was observed at  $m/e=87$ .



is the first candidate for this peak because it is generated by the ionization process of PC in the mass spectrometer. However, this mass spectrum was obtained by subtracting the background as mentioned above, so the mass peak ( $m/e=87$ ) did not result from PC ionization. The gas from the lithium electrode was identified as hydrogen by using the quadropole mass spectrometer. This suggests that water or some Brønsted acids were produced during the reaction.

To investigate the PC oxidation mechanism, the products in the electrolyte due to galvanostatic oxidation

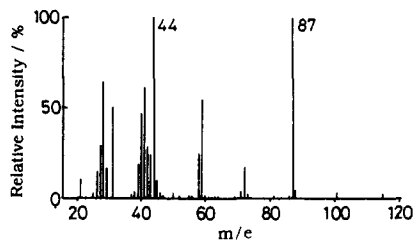


Fig. 5. Mass spectrum of gas generated by anodic oxidation of 1 M  $\text{LiClO}_4$ -PC.

were analysed in detail with the GC-MS. Fig. 6 is a gas chromatogram of the electrolyte after galvanostatic oxidation. Six new species were observed after oxidation. Fig. 7 shows their mass spectra. Species 1 was identified as  $\text{CO}_2$  ( $m/e=44$ ). Species 2 was identified as propanal ( $m/e=58$ ) by comparing retention times, although there are three alternatives for the species: propylene oxide, acetone and propanal (see Table 1). Species 5 showed a strong mass peak at  $m/e=87$ , which was also observed in direct introduction of the evolved gas into the mass spectrometer. It was identified as 2-ethyl-4-methyl-1,3-dioxolane by comparing its fragmentation pattern with the reported one [10] (see Table 2). Determination of the molecular formula by using high resolution mass

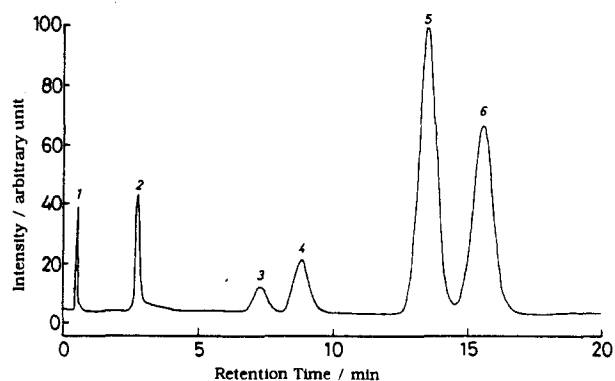


Fig. 6. Gas chromatogram of oxidized 1 M  $\text{LiClO}_4$ -PC. Column = PEG 20 M glass column (3 m); oven temperature = 30 °C, and carrier gas flow rate = 30 ml/min.

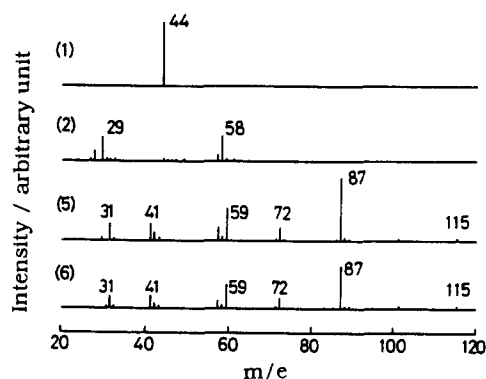


Fig. 7. Mass spectra of chemical species in oxidized 1 M  $\text{LiClO}_4$ -PC. Numbers on left side of each mass spectrum match the chemical species number in Fig. 6.

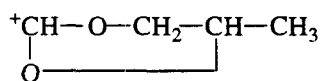
Table 1  
Retention time of species 2, propylene oxide, acetone and propanal

Compound	Retention time (min)
Species 2	2.77
Propylene oxide	2.06
Acetone	3.4
Propanal	2.83

Table 2  
Mass spectra of 2-ethyl-4-methyl-1,3-dioxolane (Ref. [10]), species 5 and 6

Compound	Relative intensity (%)									
	<i>m/e</i>	87	59	31	41	57	42	43	72	115
2-Ethyl-4-methyl-1,3-dioxolane	100	71	66	55	38	28	23	17	2	
Species 5	100	52	32	27	22	13	6	22	6	
Species 6	100	47	26	26	15	13	5	22	4	

spectrometry indicated that the  $m/e=87$  peak came from  $C_4H_7O_2^+$  which strongly supports the identification. That is,



was generated during the ionization process of 2-ethyl-4-methyl-1,3-dioxolane in the mass spectrometer. Species 6 was also identified as 2-ethyl-4-methyl-1,3-dioxolane. This suggests that species 5 and 6 are geometric isomers, as shown in Fig. 8. Species 5 identified as *cis*-isomer and species 6 as *trans*-isomer by comparing their reported retention times [10]. Species 3 and 4, unfortunately, could not be identified.

### 3.2. Decomposition mechanism of propylene carbonate

The reaction scheme proposed on the basis of the above discussion is shown in Fig. 9. Anion intercalates into graphite and produces graphite intercalation compounds (Eq. (1)). These compounds may have a catalytic effect and decompose the PC (Eq. (2)). This reaction is probably a backward PC synthesis reaction [11]. Propanal and 2-ethyl-4-methyl-dioxolane are produced by reactions (3) and (4). Hydrogen gas may be generated by the reaction between propanal and lithium (Eq. (5)). Other reactions produce species 3 and 4.

### 3.3. Anodic oxidation of ethylene carbonate

Fig. 10 shows the voltage profile and the volume of gas generated by galvanostatic oxidation of 2 M  $\text{LiClO}_4\text{-EC}$  at  $3.77 \text{ mA/cm}^2$ . 2 M  $\text{LiClO}_4\text{-EC}$  was liquid

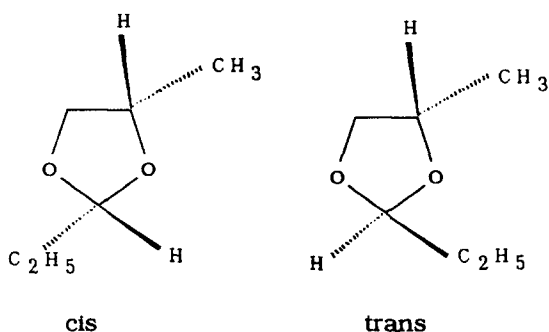


Fig. 8. *Cis* and *trans*-conformers of 2-ethyl-4-methyl-1,3-dioxolane.

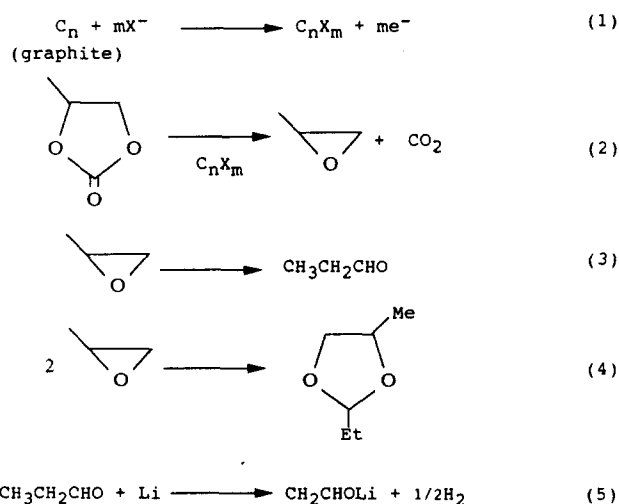


Fig. 9. Proposed mechanism for the oxidation of propylene carbonate.  $X^-$  is anion such as  $\text{ClO}_4^-$ .

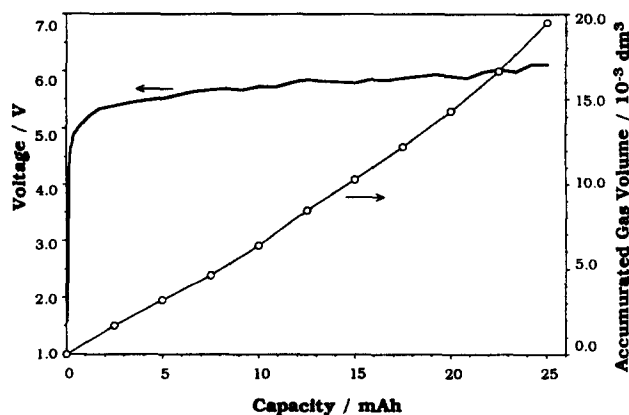


Fig. 10. Potential curve and gas volume due to anodic oxidation of electrolyte (2 M  $\text{LiClO}_4\text{-EC}$ ).

at room temperature. The voltage profile has a plateau at around 5.5 V. An approximately constant gas generation rate was observed over this voltage plateau.

The mass spectrum of the generated gas at the voltage plateau is shown in Fig. 11. The spectrum was obtained by subtracting the background spectrum (volatile EC and traces of air) from the generated gas spectrum, as described above. This analysis of the generated gas indicated that the main species is  $\text{CO}_2$ . However, other species ( $m/e=81, 154$ , etc.), which were not observed

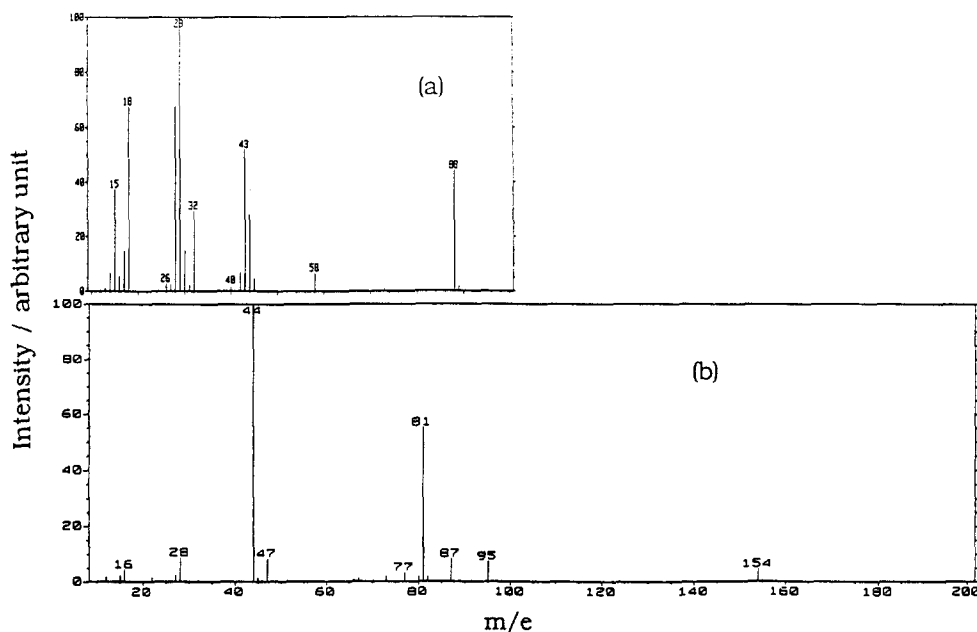


Fig. 11. Mass spectra of (a) background, and (b) gas.

before anodic oxidation, were also observed. Unfortunately, these species have not been identified.

Moreover, new species were not observed in the oxidized electrolyte when the electrolyte was analysed after anodic oxidation by GC-MS. This suggests the formation of non-volatile products in the electrolyte during sample preparation, that is, disassembling the cell and filtration of the electrolyte in an argon-filled glove box. Considering the similarities between this mechanism and the PC one, the difference in results between PC and EC may be due to the stability of intermediate products, which may be propylene oxide for PC and ethylene oxide for EC.

#### 4. Conclusions

Investigating the electrochemical oxidation of PC and EC is quite important to the understanding of the cell performance and safety when these solvents are used in high voltage lithium cells. We found that  $\text{CO}_2$  was generated during PC oxidation. When PC is oxidized, it may therefore decompose into  $\text{CO}_2$  and propylene oxide, which in turn react to form other by-products, such as propanal and 2-ethyl-4-methyl-1,3-dioxolane. This reaction may be caused by the catalytic effect of anion-intercalated graphite. Carbon dioxide and other species were generated during EC oxidation. Oxidation

mechanism of EC may be similar to that of PC, although reaction products have not been identified yet.

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