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Oxidation Behavior of Electrolytes Used in Lithium Ion Batteries

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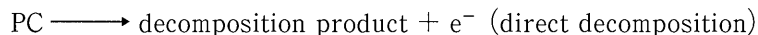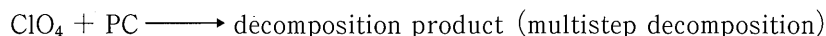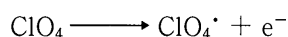
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The current - potential relationships for the electrochemical oxidation of organic solvent electrolytes on microelectrodes are confirmed for various lithium salts, namely $LiClO_4$, $LiBF_4$, $LiCF_3SO_3$ and $LiPF_6$. The oxidation is expected to occur by means of a two stage process; the chemical degradation of the solvent followed by the electrochemical generation of anion radical species, and the direct electrochemical oxidation of the solvent. The dependence of the oxidation current on temperature and the lithium salt concentration confirms this two step reaction feature. In other words, a reaction based on electrochemically generated anion radicals seems to occur below 4.8V vs. Li/Li^+ and direct oxidation of the solvent occurs above 4.8V. Above 4.8V, we cannot disregard the distribution of the diffusion-limiting current of the anion radical into the whole oxidation current.

1. INTRODUCTION

Electrolytes with organic solvent have been investigated and used for lithium battery applications because their electrochemical window is wider than that of aqueous electrolyte. In particular, their excellent tolerance to electrochemical oxidation is an intrinsic requirement for the utilization of 4-V cathode materials[1]. The electrolytes of practical lithium ion batteries contain $LiPF_6$ salt dissolved in mixtures of several carbonates[2]. These practical electrolytes are believed to be sufficiently stable for high voltage cathodes, but their reaction behavior has not been accurately evaluated.

Arakawa et al. proposed the following reaction pathway for the anodic oxidation of $LiClO_4$/propylene carbonate (PC) electrolyte based on GC-MS (gas chromatography-mass spectroscopy) results[3].

<Reaction Scheme I>
$ClO_4 \longrightarrow ClO_4^{\cdot} + e^-$
$ClO_4 + PC \longrightarrow$ decomposition product (multistep decomposition)
$PC \longrightarrow$ decomposition product $+ e^-$ (direct decomposition)

The solvent molecule has two chances to oxidize. First, a salt anion may oxidize electrochemically and form radical species, that attack the solvent molecule. In addition, the solvent molecule is capable of being oxidized directly. Other electrolytes are expected to decompose by means of the same scheme, for example, Dubois et al. have proposed a similar scheme for $LiClO_4$/THF electrolyte from ex situ FT-IR measurements[4]. However, few reports have provided proof of this multi-step reaction.

In this study, we investigated the anodic behavior of several electrolytes by varying the temperature and salt concentration. In order to clarify the distribution of salt species, we fixed the solvent used in this study with propylene carbonate (PC) and employed various salts. In a previous paper, we proposed a novel method that uses a microelectrode for the observation of reaction currents by preventing double-layer current distribution[5]. We expect to be able to

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use this method to analyze anodic current based on a Tafel approach. We also used this method here to confirm the precise anodic behavior of electrolyte salts.

2. EXPERIMENTAL

The microelectrode used in this study was obtained from NTT Advanced Technology Co. It was prepared by sputtering and a mask with a small conductive hole, as described in a previous paper[5]. Lithium foil (Honjo Metal) was cut into 5×5mm pieces and used as reference and counter electrodes. The electrolytes chosen for this study were obtained by dissolving $LiClO_4$, $LiCF_3SO_3$, $LiBF_4$ or $LiPF_6$ salt in PC. $LiClO_4/PC$ and $LiPF_6/PC$ electrolytes were purchased in 1M solution from Tomiyama Chemical Co., and diluted with PC (Mitsubishi Chemical Co., battery grade). $LiCF_3SO_3$ and $LiBF_4$ salts were dissolved in PC at prescribed concentrations. The water content of all the electrolytes was below 50ppm, which we confirmed with a Karl-Fischer Aquacounter (Hiranuma, AQ-7). The electrodes and electrolyte were constracted in a closed 2-electrode cell in a glove box filled with argon gas.

The potential of the working electrode was raised stepwise from 3.5V to about 5.5V using a highly sensitive potentiostat (Fuso Electric, SECS-318C) connected to a function generator (Hokuto Denko, HB-104). The potential was maintained until the applied current reached a steady state to remove the double-layer capacitance contribution. We placed the cell in a temperature chamber (Tabai Espec Co., SU-240) and controlled the measurement temperature at -20, 0, 25, 40 and 60-C by controlling the chamber temperature.

In-situ Raman spectra were measured using a conventional laser Raman Spectrometer (Nippon Bunko Co.; NRS-2000, laser wavelength was 514nm). The cell we used here was a 2-electrode cell containing the microelectrode described above, lithium foil (3×3mm) and a quartz cell. This cell was connected to a DC power supply (Metronix, 532B) and placed on the sample stage of the Raman spectrometer. The potential was increased in 0.5V steps and the spectrum was measured at the surface of the electrode at room temperature.

3. RESULTS

1) Temperature Dependence of Electrolyte Oxidation **Fig. 1** shows the log |current density (i)| -potential (E) relationships of the oxidation of (a) 1M $LiClO_4/PC$ and (b) 1M $LiCF_3SO_3/PC$ electrolytes at various cell temperatures. All the current density values at the same potential increased with increases of temperature, including some results not shown here. Some plots, e.g. the 25°C data for 1M $LiClO_4/PC$, show linear relationships on the given scale, while others, e.g. the -20°C and 60°C data for the same electrolyte, have a plateau region around 4.5 ~5.0V vs. Li/Li+.

In each electrolyte, the current density values in relation to potential during oxidation should obey the following Arrehnius type
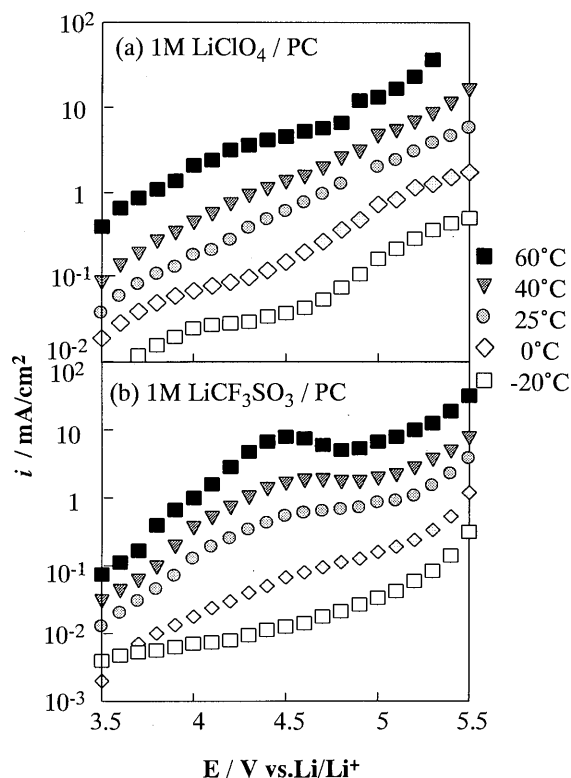
Fig. 1 The log i-E plots of the oxidation of (a) 1M $LiClO_4/PC$ and (b) 1M $LiCF_3SO_3/PC$ electrolytes at various temperatures.
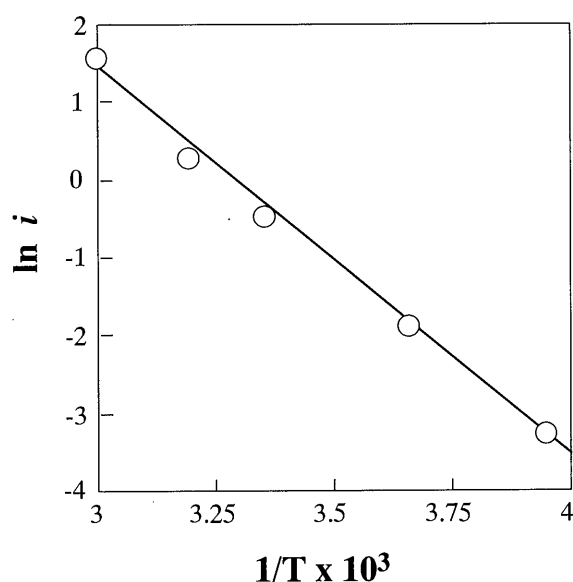
Potential: 4.5V vs. Li/Li$^+$.

Fig. 2　An Arrehnius plot of the oxidation of 1M LiClO$_4$/PC electrolyte.

equation[6].

$$i = (nFC/A)\ (kT/h)\ \exp\ (-\varDelta G^{\ddagger}/RT)\ *$$
$$\exp\ \{(1-\alpha)nFE/RT\} \qquad (1)$$

(where n is the number of electrons associated with the reaction, F is the Faraday constant, C is the surface concentration of the reactant, A is electrode area, (kT/h) is a pre-exponential factor, $\varDelta G^{\ddagger}$ is activation free energy, R is the gas constant, T is temperature, and α is a transfer coefficient.)
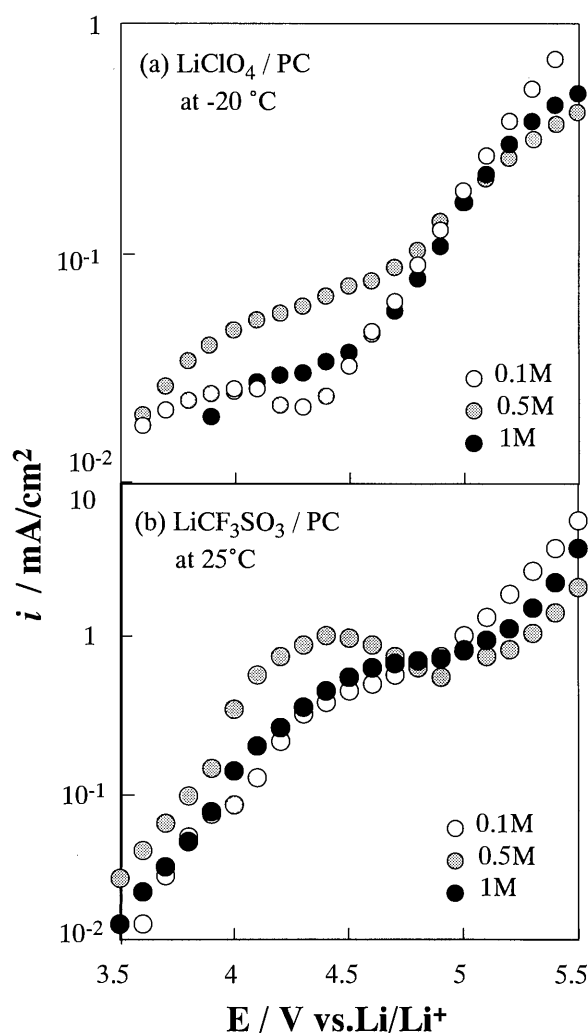

Temperature: (a) −20℃, (b) 25℃.

Fig. 3　The log i-E plots of the oxidation of (a) LiClO$_4$/PC and (b) LiCF$_3$SO$_3$/PC electrolytes with various salt concentrations.

According to Eq. (1) , log i should be proportional to T for a given potential.　**Fig. 2** shows the log i-T plot of 1M LiClO$_4$/PC at 4.5V.　It can be seen that there is a good linear relationship (correlation coefficient ＝ 0.995).　The slope value in this case is −4.96.　At almost all the potential points of all the electrolytes measured in this study, we observed linear relationships for log i and T.　Therefore the same reaction occurs at certain potential points regardless of temperature.

2) The Salt Concentration Dependence of Electrolyte Oxidation.

Fig. 3 shows the log i-E plots of oxidation of (a) LiClO$_4$/PC at −20℃ and (b) LiCF$_3$SO$_3$/PC at 25℃ with various salt concentrations.　The LiClO$_4$/PC system changed very little with salt concentration at 25℃, however, lower temperature measurements can reveal its salt concentration dependence.　In contrast, the LiCF$_3$SO$_3$ system showed salt concentration dependence even at 25℃.　In both cases, it was only possible to observe the differences in current density degree above 4.8V vs. Li/Li$^+$. The salt concentration of which the current density showed the highest value below 4.8V was 0.5M when both salts were employed.
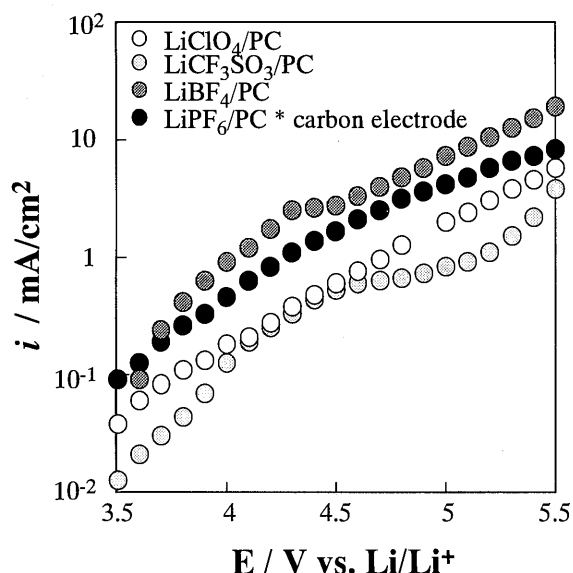
3) Oxidation Behavior of Various Salt Electrolytes

Fig. 4 shows the log i-E plots of the oxidation of electrolytes containing 1M of LiClO$_4$,

Temperature: 25℃, Salt concentration: 1M.

Fig. 4   The log i-E plots of the oxidation of various nonaqueous electrolytes.

Raman Shift / cm^{-1}

Laser wavelength: 514nm.

Fig. 5   An overview of Raman spectra of 1M LiClO$_4$/PC at a Pt microelectrode.

LiCF$_3$SO$_3$, LiBF$_4$ and LiPF$_6$. None of the plots for one electrolytes exactly fit a straight line except for 1M LiClO$_4$/PC. The electrolytes containing LiCF$_3$SO$_3$ and LiBF$_4$ have plateaus around 4.7V and 4.4V, respectively. The order of the current value is different from that previously reported by Koshiba et al., where an electrolyte containing LiPF$_6$ reacted least to anodic oxidation[7]. We assume our result to be the "initial" reactivity order where the reaction current is relatively low.
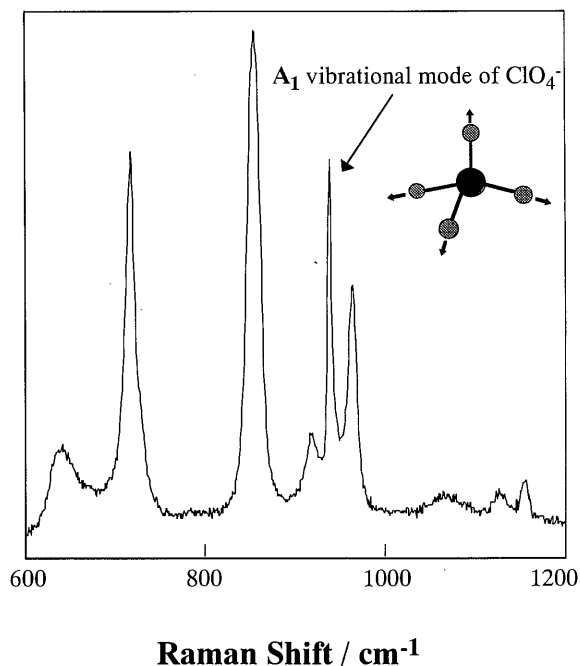
4) In-situ Raman Spectroscopy

Fig. 5 shows Raman spectra of 1M LiClO$_4$/PC on a Pt microelectrode. The peak at 937cm^{-1} is ascribed to the A$_1$ vibration mode of the ClO$_4^-$ anion[8]. We observed a change in this peak as the potential increased. **Fig. 6** shows the peak at potentials from 3.0V to 5.5V vs. Li/Li$^+$. Above 4.5V, the peak shifted slightly toward a higher wavenumber and the bandwidth was broadened.
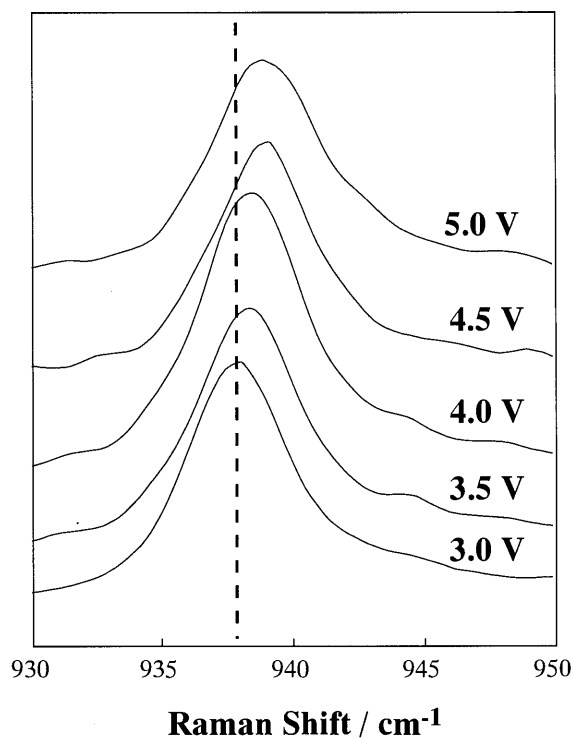
4. DISCUSSION

1) Oxidation Potentials of Electrolyte Salt Anions.

Raman Shift / cm^{-1}

Fig. 6   Raman spectra of 1M LiClO$_4$/PC on Pt microelectrode at various potentials.

As shown in **Fig. 1**, in many cases the Tafel plots of the anodic decomposition of electrolytes are not linear. Anodic processes seem to involve two reaction modes. We regard these distinct modes as multi-step decomposition and direct decomposition of the solvent, as shown in
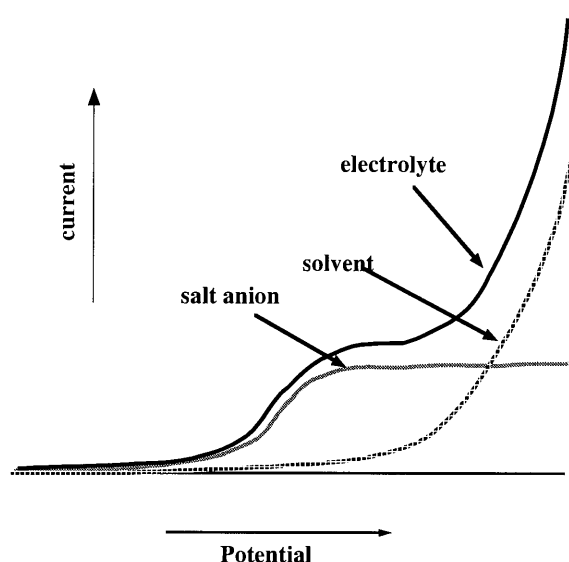
Fig. 7　A schematic model of the electrochemical oxidation of nonaqueous electrolyte.

Scheme I. The salt concentration dependence of the reaction current should result in a salt influenced (i.e. multi-step) process below 4.8V. We believe from these results that the oxidation current can be divided in two parts at around 4.8V. The former is assigned to the anion oxidation to radical species, which in turn chemically decomposes the solvent, and the latter is assigned to the direct oxidation of the solvent. From the Raman spectra shown in **Fig. 6**, the peak shift is seen in the 4.0 ~ 4.5V region. The surface concentration of the oxidized species may increase and saturate above this potential region. The peak shift to a higher wavenumber can be associated with the bond loosening resulting from electron withdrawal from the charge center, Cl.

Low absolute current values in this potential region suggest the effect of the decomposition current of impurities, such as contaminated water. However, Karl-Fischer measurements revealed no correlation between water content and current value in this region. The similar salt concentration dependence of the two salts, $LiClO_4$ and $LiCF_3SO_3$, makes us think that the difference in the current values below 4.8V originated in the variation in the salt concentrations.

For both salts, the current in this region is largest when the salt concentration is 0.5M. Although the concentration points were too few to be described precisely, the quantity of dissociated anions may reflect the oxidation current.

　2) Effect of Diffusion Limiting Processes of Salt Anions on Oxidation Current

The log i-E plots of the two electrolytes, $LiBF_4$/PC and $LiCF_3SO_3$/PC, have plateaus around 4.8~5.0V at 25℃. The discussion in the previous section stated that the current below and above this plateau are expected to represent the anion oxidation and the direct oxidation of the solvent, respectively. This plateau may indicate the diffusion-limiting current of the anion oxidation. When a microelectrode is used as a working electrode, diffusion-limiting current can be expressed by the following equation[9].

$$I = 4\pi nFc^*Da \qquad\qquad\qquad (2)$$

(where I is diffusion-limiting current, c^* is the bulk concentration of the reactant, D is the diffusion coefficient of the reactant, and a is the electrode radius.)

The expected current-potential scheme is shown in **Fig. 7**. If the distributions of the anion oxidation and the solvent oxidation are completely independent, we can expect a diffusion-limiting current due to the finite salt concentration. When the salt concentration is too low or the anion diffusion coefficient is too small, a plateau should be observed. $CF_3SO_3^-$ and BF_4^- anions are suspected to have lower mobility than ClO_4^- and PF_6^-. The conductivity values of $LiCF_3SO_3$/PC ($1.7mScm^{-1}$) and $LiBF_4$/PC ($3.4mScm^{-1}$) at room temperature are smaller than those of $LiPF_6$/PC ($5.8mScm^{-1}$) and $LiClO_4$/PC ($5.6mScm^{-1}$)[10]. The correlation between the appearance of the plateau and the conductivity data may suggest that a diffusion-limiting process of salt anion oxidation may also affect the whole i-E curve together with the charge-transfer process. This effect may lower the apparent transfer coefficient value.

5. CONCLUSION

Our precise electrochemical measurements at various temperatures and salt concentrations of the oxidation of electrolytes used in lithium ion batteries revealed the salt anion contribution to overall oxidation. In terms of the salt anion contribution to the reaction, the i-E curves can be divided into two regions at around 4.8 V vs. Li/Li$^+$. Below 4.8V, the main process is expected to be anion oxidation into a radical species, which might cause a solvent molecule to decompose chemically.

Solvent also seems to be decomposed electrochemically above 4.8V. The diffusion-limiting process of salt anion oxidation has an effect on the reaction current over 4.8V.

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