

Anodic oxidation of nonaqueous electrolytes on cathode materials and current collectors for rechargeable lithium batteries

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Abstract

Oxidation of propylene carbonate on Al and LiCoO₂ electrodes was observed by using cyclic voltammetry and in situ FTIR spectroscopy combined with potential step experiment. From these measurements, two points were discussed in this study. The oxidation of solvents on LiCoO₂ occurred at 4.2 V vs. Li/Li⁺ that corresponds to the cut-off potential of rechargeable lithium ion batteries, because of high catalytic activity of transition metal oxide materials. On the other hand, the oxidation on Al as a current collector was strongly influenced by passivation phenomena in nonaqueous electrolyte. The passivation phenomena depend on a kind of electrolyte salt. Among four electrolyte salts used in this study [LiClO₄, LiPF₆, Li(CF₃SO₂)₂N, and Li(CF₃SO₂)(C₄F₉SO₂)N], Li(CF₃SO₂)(C₄F₉SO₂)N exhibited several interesting features which were useful to suppress the anodic oxidation of nonaqueous electrolytes and dissolution of Al. Furthermore, a mixed solvent of ethylene carbonate and dimethoxyethane with Li(CF₃SO₂)(C₄F₉SO₂)N was not oxidized at 4.8 V vs. Li/Li⁺ on both LiCoO₂ and Al electrodes. In addition, the anodic corrosion of Al in this electrolyte was suppressed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Nonaqueous electrolyte; Imide; LiCoO₂; Al; FTIR

1. Introduction

Some excellent electrochemical materials, such as transition metal oxides, carbons, and lithium metal have been used in rechargeable lithium batteries. Nonaqueous electrolytes are also important elements of this battery. Many researchers have prepared various types of nonaqueous liquid and solid electrolytes. Among them, aprotic organic solvents containing lithium inorganic or organic salts are the most popular electrolyte. For example, ester or ether compounds have been used as solvents and LiPF₆, LiClO₄, or LiCF₃SO₃ have been used as electrolyte salts [1]. In general, nonaqueous electrolytes have wider electrochemical potential windows than aqueous electrolytes [2]. However, higher stability of nonaqueous electrolytes is needed to obtain higher reliability of lithium ion batteries [3]. This is due to very positive operation potential of cathode materials used in lithium ion batteries [4–8]. For example, the discharge and charge potential of LiCoO₂ and LiNiO₂ are around 4.0 V vs. Li/Li⁺ [4]. Possibly, such a high

electrode potential leads to oxidative decomposition of nonaqueous electrolytes. Therefore, electrochemical oxidation of nonaqueous electrolytes has to be studied in order to obtain high safety and reliability of rechargeable lithium batteries [9–12].

Several reports on this subject have been published elsewhere. In most of the researches, Pt and Au electrodes were used as working electrodes [13–15]. However, positive electrodes in rechargeable lithium batteries were constructed from various materials (active material, conducting material, current collector, and binding material). Considering catalytic activity of those materials, stability of nonaqueous electrolytes has to be examined by using each material separately. We have investigated the stability of various nonaqueous electrolytes on Pt, Ni, Al, LiMn₂O₄ and LiCoO₂ electrodes [16–19]. In these previous researches, LiClO₄, LiBF₄, or LiPF₆ were used as electrolyte salts. These inorganic electrolyte salts are slightly unstable in a sense of both chemical and thermal decomposition. On the other hand, organic electrolyte salts, such as imide salts, are fairly stable, compared with inorganic electrolyte salts [20]. In this study, we discussed the stability of various nonaqueous electrolytes containing inorganic or organic electrolyte salts on LiCoO₂ and Al electrodes.

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2. Experimental

Propylene carbonate (PC), diethyl carbonate (DEC), and dimethoxy ethane (DME) were supplied from Mitsubishi Chemical Co. Imide salts, such as $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ and $\text{Li}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)\text{N}$, were supplied from Central Glass Co. Other electrolytes were also supplied from Mitsubishi Chemical Co. The water contents in these electrolytes were determined to be less than 20 ppm with Karl Fischer titration method before all experiments.

In this study, Al and LiCoO_2 were used as working electrodes. An Al plate (1 cm \times 1 cm, 99.9%) was polished by alumina powders (0.05 μm) and then washed by H_2O and methanol. After this treatment, the Al electrode was treated with an ultrasonic bath to remove residual alumina powders. Finally, the Al electrode was washed with acetone and dried under 60°C for 24 h. LiCoO_2 electrode was prepared by a sputtering method. The detailed preparation procedures have been already reported in our previous paper [19]. The electrochemical property and

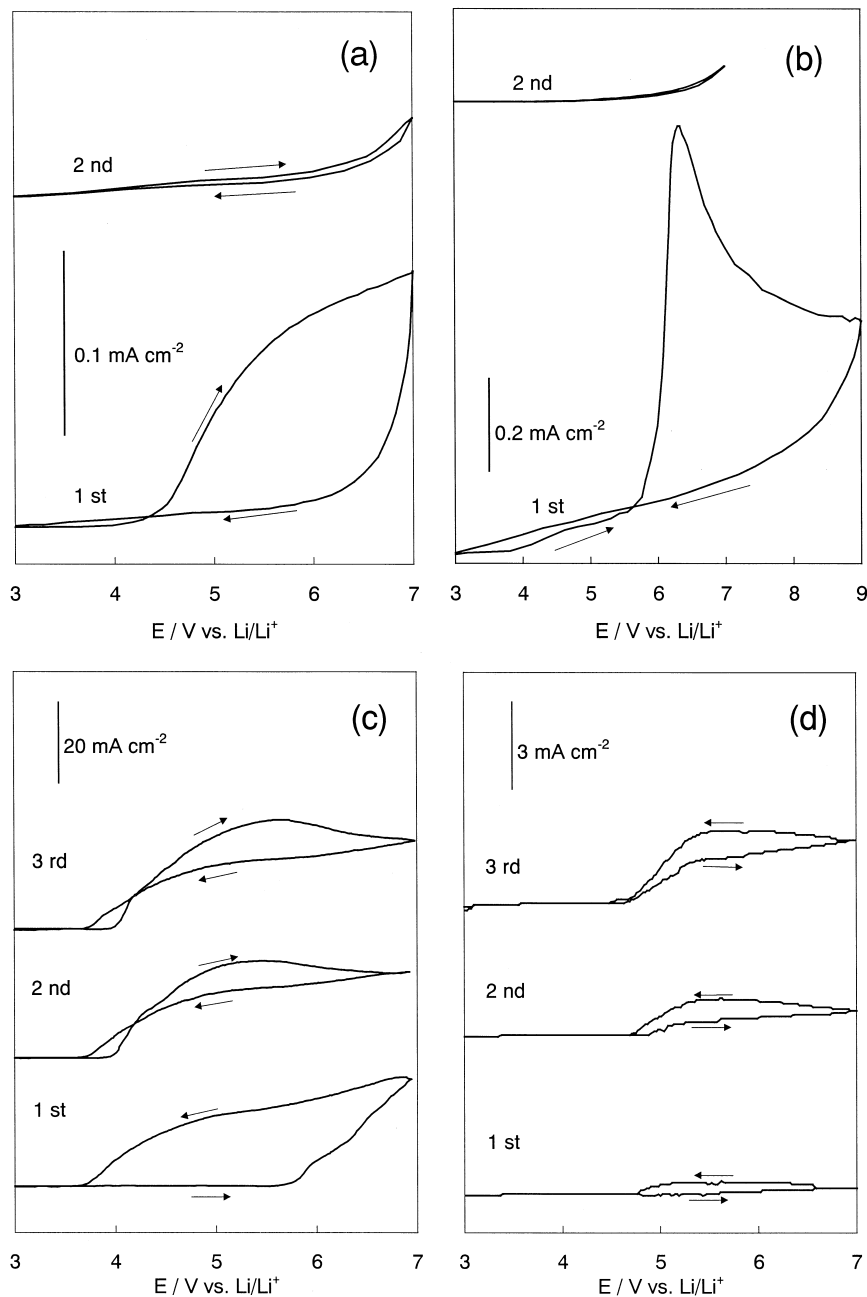


Fig. 1. Cyclic voltammograms on the Al electrode in propylene carbonate containing (a) $1.0 \text{ mol dm}^{-3} \text{ LiClO}_4$, (b) $1.0 \text{ mol dm}^{-3} \text{ LiPF}_6$, (c) $1.0 \text{ mol dm}^{-3} \text{ Li}(\text{CF}_3\text{SO}_2)_2\text{N}$, and (d) $1.0 \text{ mol dm}^{-3} \text{ Li}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)\text{N}$, at 50 mV s^{-1} .

crystal structure of this film were examined in order to confirm the formation of LiCoO_2 having the same characteristics with LiCoO_2 powders.

Anodic oxidation of nonaqueous electrolytes was investigated by using cyclic voltammetry and in situ FTIR spectroscopy. Subtractively normalized interfacial FTIR (SNIFTIR) spectra were obtained from two reflectance spectra measured at two different electrode potentials, according to Ref. [19]. In SNIFTIR spectra, upward peaks and/or downward peaks were observed. An upward peak corresponds to a disappearance of solvent adsorbed on an electrode surface. A downward peak corresponds to a formation of new compounds derived from the oxidation of solvents. A peak at 2400 cm^{-1} corresponds to CO_2 remaining in an analysis chamber of FTIR equipment used in this study. Therefore, this peak was not discussed in this paper.

3. Results and discussion

Cyclic voltammograms of Al in PC containing 1.0 mol dm^{-3} of four different electrolyte salts are shown in Fig. 1. Anodic currents were observed in all electrolytes, but the on-set potential for the anodic current depended on the kind of electrolyte salt. In LiClO_4/PC , the anodic current rapidly increased at 5.8 V vs. Li/Li^+ and then decreased through a maximum anodic current. The current peak was observed at 6.2 V vs. Li/Li^+ . During the cathodic scan, the anodic current was very small. In the second cathodic and anodic scans, the anodic current was very small. These current–potential curves exhibit the passivation phenomena of the Al electrode. Usually, Al electrode has many pores in a surface film, so that the anodic current observed in Fig. 1a may correspond to a passivation of such a pore. The anodic current in LiPF_6/PC as shown in Fig. 1b was much smaller than that in LiClO_4/PC , indicating that a passivation film was easily produced in LiPF_6/PC . On the other hand, a drastic anodic current (roughly 20 mA cm^{-2}) was observed in $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}/\text{PC}$, as shown in Fig. 1c. Many researchers have recognized this result, as a corrosion of Al in nonaqueous electrolytes containing imide salts. The anodic current was very small at the first anodic scan in the potential range less than 4.5 V vs. Li/Li^+ . When the electrode potential was more anodic than 4.5 V vs. Li/Li^+ , a large anodic current was observed, which was 100–1000 times as large as those observed in Fig. 1a or b. This means that a corrosion of Al takes place during the anodic polarization. In order to confirm the corrosion of Al, the Al electrode after the anodic oxidation at 5.0 V vs. Li/Li^+ for 1 h was observed with scanning electron microscopy (SEM). From the SEM photographs in Fig. 2a, it can be seen that a corrosion of the Al electrode proceeds with a large pit formation. In $\text{Li}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)\text{N}/\text{PC}$ (Fig. 1d), the anodic current was much smaller than that observed in Fig. 1c, indicating that the corrosion of the Al electrode did not proceed in this electrolyte. 3M has

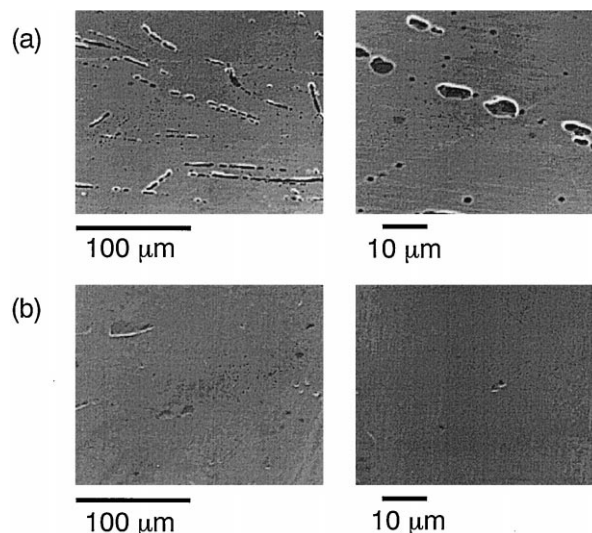


Fig. 2. SEM photographs of the Al electrodes after the anodic oxidation in (a) $1.0\text{ mol dm}^{-3}\text{ Li}(\text{CF}_3\text{SO}_2)_2\text{N}/\text{PC}$, and (b) $1.0\text{ mol dm}^{-3}\text{ Li}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)\text{N}/\text{PC}$ at 5.0 V vs. Li/Li^+ for 1 h.

reported a similar result [21]. After the anodic oxidation of the Al electrode for 1 h, the electrode surface was observed with SEM. Fig. 2b shows the SEM photographs obtained for the Al electrode polarized at 5.0 V vs. Li/Li^+ for 1 h in $\text{Li}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)\text{N}/\text{PC}$. In this case, any pits produced by the dissolution of Al were not observed. From a comparison of these photographs with those in Fig. 2a, it can be seen that $\text{Li}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)\text{N}$ has an excellent effect for suppressing the corrosion of Al in the nonaqueous electrolyte.

Thus, the anodic polarization behavior of Al electrode strongly depends on the kind of electrolyte salt. This is due to the surface change of Al electrode during the anodic polarization. Such a change also influences an anodic oxidation behavior of nonaqueous electrolytes on the Al electrode. This is very important for reliability of rechargeable lithium batteries. In this study, the stability of PC solvent on the Al electrode was examined by using in situ FTIR spectroscopy.

Fig. 3 shows the SNIFTIR spectra for (a) LiClO_4/PC , (b) LiPF_6/PC , (c) $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}/\text{PC}$, and (d) $\text{Li}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)\text{N}/\text{PC}$. In the potential region less than 5.0 V vs. Li/Li^+ , there were no clear peaks in the spectra obtained for LiClO_4/PC and LiPF_6/PC electrolytes. At more anodic potential than 5.0 V vs. Li/Li^+ , or 6.2 V for LiClO_4/PC or LiPF_6/PC , respectively, a typical peak showing a decomposition of solvent was observed at a wavenumber of 1700 cm^{-1} . A wavenumber for $\text{C}=\text{O}$ in PC is 1780 cm^{-1} , so that the peak at 1700 cm^{-1} is assigned to $\text{C}=\text{O}$ stretching vibration mode in oxidation products of PC. A ring-opening reaction of PC can explain this peak shift [16–18]. These spectra indicate PC is not oxidized on the Al electrode at the operation potential region of rechargeable lithium batteries when using LiClO_4/PC or LiPF_6/PC . On the other hand, when

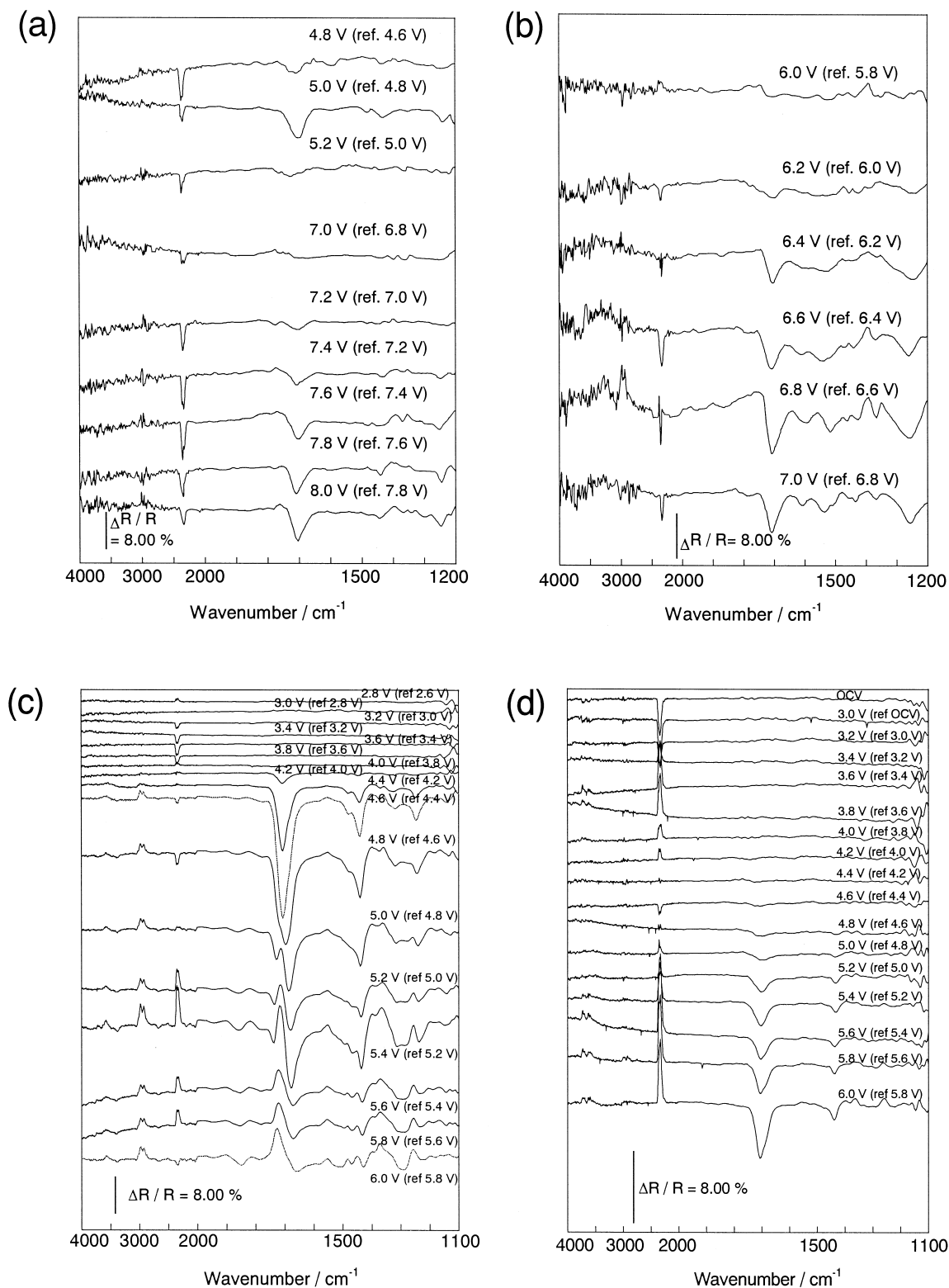


Fig. 3. In situ SNIPTIR spectra for propylene carbonate containing (a) $1.0 \text{ mol dm}^{-3} \text{ LiClO}_4$, (b) $1.0 \text{ mol dm}^{-3} \text{ LiPF}_6$, (c) $1.0 \text{ mol dm}^{-3} \text{ Li}(\text{CF}_3\text{SO}_2)_2\text{N}$, or (d) $1.0 \text{ mol dm}^{-3} \text{ Li}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)\text{N}$ on the Al electrode.

$\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ was used as the electrolyte salt, some clear peaks were observed even at relatively more cathodic potential, such as 4.2 V vs. Li/Li^+ . This means that the

electrochemical activity of the Al electrode can be changed by the kind of electrolyte salt. The passivation film of the Al electrode can be destroyed in this electrolyte, as dis-

cussed above. This may correspond to the formation of the active surface of Al during the anodic oxidation. By the way, when using $\text{Li}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)\text{N}$, the oxidation of PC on the Al electrode was surprisingly suppressed. From this result, it can be also seen that $\text{Li}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)\text{N}$ is highly effective to form the passivation layer on the Al electrode. The essential difference between these two imide salts may be due to their stereochemical structure and acidity. However, detailed understanding has not been obtained yet. In the near future, we will discuss this interesting point.

From the comparison of the in situ FTIR spectra in Fig. 3 with the cyclic voltammograms in Fig. 1, it can be said that the stability of the passivation film on the Al electrode depends on the kind of anion involved in the nonaqueous electrolyte. Another important material of a positive electrode is a cathode active material. In this study, we also used in situ FTIR spectroscopy to see the anodic oxidation behaviors of nonaqueous electrolytes.

Fig. 4 shows the in situ FTIR for the LiCoO_2 electrode in (a) LiClO_4/PC , (b) LiPF_6/PC , (c) $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}/\text{PC}$, and (d) $\text{Li}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)\text{N}/\text{PC}$. Several upward and

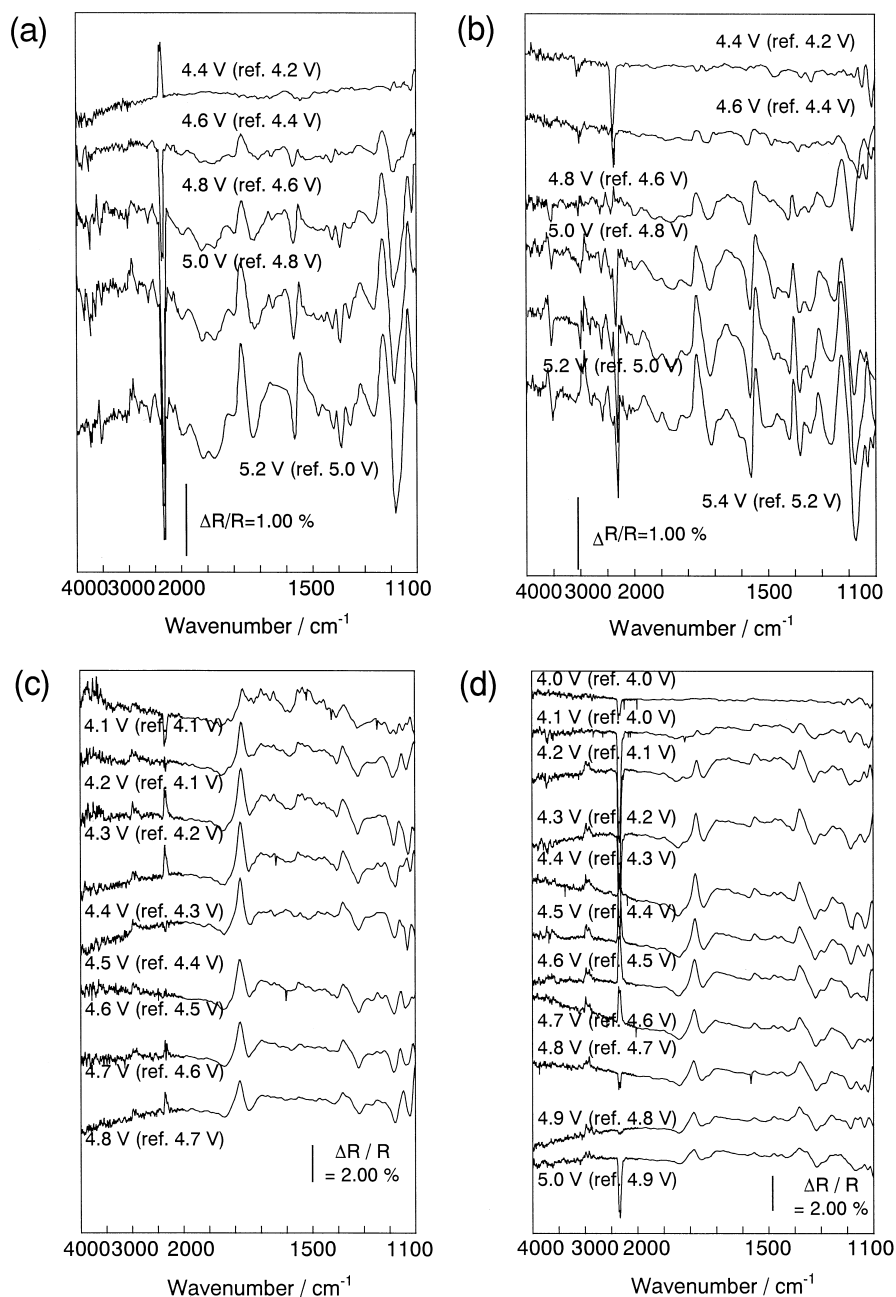


Fig. 4. In situ SNIFTIR spectra for propylene carbonate containing (a) $1.0 \text{ mol dm}^{-3} \text{ LiClO}_4$, (b) $1.0 \text{ mol dm}^{-3} \text{ LiPF}_6$, (c) $1.0 \text{ mol dm}^{-3} \text{ Li}(\text{CF}_3\text{SO}_2)_2\text{N}$, or (d) $1.0 \text{ mol dm}^{-3} \text{ Li}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)\text{N}$ on the LiCoO_2 electrode.

Table 1

Peak assignment for in situ FTIR spectra for the electrochemical oxidation of propylene carbonate containing $1.0 \text{ mol dm}^{-3} \text{ LiClO}_4$ on the LiCoO_2 thin film electrode

Upward peaks (cm^{-1})	Assignment	Downward peaks (cm^{-1})	Assignment
2900–3000	CH_3 or CH_2 stretching in PC	1990 ^a	C=O stretching in OP
1780	C=O stretching in PC	1920 ^a	
1550	O–C=O bending in PC	1880 ^a	
1310	CH_3 symmetrical bending in PC	1730	C=O stretching in OP
1230	C–O–C asymmetrical stretching in PC	1570	CO_2^- asymmetrical stretching in OP
1130	C–O–C symmetrical stretching in PC	1420	CO_2^- symmetrical stretching or CH_2 bending in OP
		1380	CH_3 symmetrical bending in OP
		1360	
		1270	C–O–C asymmetrical stretching in OP
		1180	C–O–C symmetrical stretching in OP

^aC=O bond in carboxylic acid anhydrides, OP: oxidation products of PC.

downward peaks were observed in all electrolytes. The upward and downward peaks appeared in the SNIFTIR spectra for LiClO_4/PC were summarized in Table 1. The peak assignments were also shown in this table. From the table, it can be said that PC adsorbed on the LiCoO_2 electrode is oxidized and changed to carboxylic like compounds with a ring-opening reaction of PC. Newly formed compounds are also adsorbed on the LiCoO_2 surface. The similar behavior of PC during the anodic polarization was observed in LiPF_6/PC . Since the original spectrum of this electrolyte is different from that of LiClO_4/PC , a slightly different feature from the SNIFTIR spectra in Fig. 4a was observed in Fig. 4b. However the peak assignments for the SNIFTIR spectra in Fig. 4b were almost the same with those in Table 1. When imide salts were used as electrolyte

salts, some peaks exhibiting the decomposition of PC were observed in (c) and (d). The essential explanation for the decomposition of PC in these electrolytes is not different from that obtained from Table 1. Thus, the electrochemical oxidation of PC electrolytes containing various salts on the LiCoO_2 thin films electrode actively proceeds. This may be due to a catalytic activity of the LiCoO_2 surface. When using Pt or Au electrode, which are inert metals, in nonaqueous electrolytes, we could not see any peaks corresponding to the electrochemical oxidation of PC at 5.0 V vs. Li/Li^+ in the SNIFTIR spectra.

In practical cells, ethylene carbonate, dimethyl carbonate, diethyl carbonate, and so on have been used as solvents. The in situ FTIR spectroscopy was also performed in these electrolytes. We have already obtained

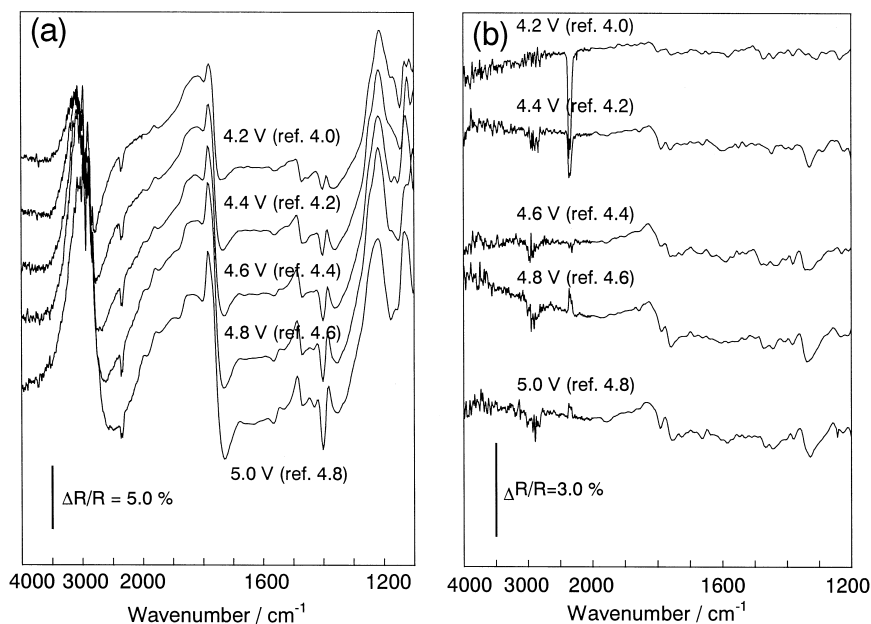


Fig. 5. In situ SNIFTIR spectra for mixed solvent of ethylene carbonate and dimethoxy ethane containing (a) $1.0 \text{ mol dm}^{-3} \text{ LiClO}_4$ or (b) $1.0 \text{ mol dm}^{-3} \text{ Li}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)\text{N}$ on the LiCoO_2 electrode.

similar results as shown in Figs. 3 and 4. The corrosion of Al and the oxidation of nonaqueous electrolytes can be suppressed by a proper choice of electrolyte salt, but the oxidation of nonaqueous electrolyte on the LiCoO_2 cannot be easily avoided by a selection of electrolytes. However, when thermal stability of nonaqueous electrolyte is considered as an important factor for a practical battery, a more stable anion is suitable. In this sense, $\text{Li}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)\text{N}$ is one of the very attractive materials.

The most interesting behavior of $\text{Li}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)\text{N}$ electrolyte salt was observed when using EC + DME solvent. Fig. 5 shows the SNIFTIR spectra during the anodic oxidation of (a) $\text{LiClO}_4/\text{EC} + \text{DME}$ and (b) $\text{Li}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)\text{N}/\text{EC} + \text{DME}$ on the LiCoO_2 electrode. In general, ether solvents are easily oxidized by an anodic polarization, as shown in Fig. 5a. In fact, when using LiClO_4 as the electrolyte salt, the decomposition of this solvent on LiCoO_2 electrode was easily observed at least 4.0 V vs. Li/Li^+ using in situ FTIR spectroscopy. However, as shown in Fig. 5b, the EC + DME with $\text{Li}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)\text{N}$ was not oxidized at more cathodic potential than 4.8 V vs. Li/Li^+ . This means that $\text{Li}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)\text{N}$ provides a high stability of EC + DME solvent.

4. Conclusion

The electrochemical oxidation of nonaqueous electrolytes on Al and LiCoO_2 electrodes was investigated by using in situ FTIR. Most of the electrolytes were oxidized even at 4.2 V vs. Li/Li^+ on the LiCoO_2 electrode. This is due to an undesirable catalytic activity of LiCoO_2 for the anodic oxidation of nonaqueous electrolytes. On the other hand, on the Al electrode, the anodic oxidation of nonaqueous electrolytes was related to the stability of the passivation film that is strongly dependent on the kind of anion. Therefore, the proper choice of electrolyte salt is effective and important to suppress the oxidation of Al.

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