

# Effect of acid on passivation of a copper electrode in $\text{LiCF}_3\text{SO}_3$ /propylene carbonate in underpotential region

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Received 7 April 1999; accepted 22 April 1999

## Abstract

The electrochemical behaviour of a copper electrode is examined using microelectrode (diameter = 0.025 mm) techniques over a wide potential range (+3.5 to  $-0.2$  V vs.  $\text{Li}/\text{Li}^+$ ) in  $\text{LiCF}_3\text{SO}_3$  which contains propylene carbonate (PC). Cyclic voltammetry and differential pulse voltammetry suggest that water may be the cause of passivation of a copper electrode. Small amounts of strong acid can prevent this passivation by changing the reduction mechanism of oxygen and water in the underpotential region. X-ray photoelectron spectroscopic analysis reveals that lithium compounds precipitate on copper, even in the underpotential region, when no acid is added to the organic solution. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Lithium; Copper; Underpotential deposition; XPS; Differential pulse voltammetry

## 1. Introduction

Contaminants in the electrolyte solution can strongly affect the surface of a lithium electrode [1–4]. This is because most compounds can be reduced on lithium near its equilibrium potential. While a great deal of attention has been paid to lithium electrodes [5,6], the electrochemistry of non-lithium electrodes, such as nickel [7], gold [8–13], platinum [13], silver [11,12,14] and copper [11], in lithium-containing electrolyte solutions has been of minor interest. Non-lithium electrodes are, however, excellent probes to investigate the contaminant-related reaction which occurs at potentials positive to lithium deposition.

Cyclic voltammograms for a nickel electrode in propylene carbonate (PC) containing 0.1 M  $\text{LiAsF}_6$  show three peaks at potentials positive to bulk lithium deposition [7]; this appears to be common behaviour for non-lithium electrodes. The peaks are attributable to oxygen and water-related reactions, except for the pair of peaks appearing around 0.4 V (cathodic) and 0.9 V (anodic). To date, underpotential deposition (UPD) and underpotential stripping (UPS) are assumed to be responsible for these peaks, but without any proof. We have recently questioned this hypothesis [15] by conducting experiments on a nickel

electrode. In this study, similar investigations with a copper electrode generalize the previous results with a nickel electrode. Since copper is used as a current-collector in lithium-ion batteries, its passivation behaviour at cathodic potentials in organic solutions is of interest. In particular, exfoliation of carbon from a copper current-collector may be caused by passivation. The objectives of this work are to clarify the relationship between the voltammetric peaks and the passivation of a copper electrode and to determine the role of trace amounts of water and acid in lithium deposition.

## 2. Experimental

All electrolytes were purified in a glove box (M-Brown) filled with recycling argon gas (dew-point  $< -80^\circ\text{C}$ ,  $\text{O}_2 < 1$  ppm). Battery-grade lithium triflate  $\text{LiCF}_3\text{SO}_3$  (Tomiya Pure Chemical Industries) was recrystallized twice in dry dimethoxy carbonate containing less than 10 ppm water, then vacuum-dried in an oven at  $100^\circ\text{C}$  for 10 h. 99% pure  $\text{LiPF}_6$  (Kishida Reagents Chemicals) was used after drying at  $100^\circ\text{C}$  for 24 h. All dry organic solvents (water content less than 10 ppm) were obtained from Kishida Reagents Chemicals. The amount of the residual water in the solvents was confirmed by the Carl Fisher method.

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The surface of the copper electrode (disc of diameter 13 mm) was analyzed by X-ray photoelectron microscopic (XPS) measurements on a Model ESCA 5300 system (Perkin-Elmer). The electrode was washed with dimethoxy ethane in the glove box after electrochemical treatment in a sealed cell, then transferred to the XPS chamber without exposure to the air.

A three-electrode glass cell was fabricated and sealed in the glove-box for electrochemical measurements. Cyclic voltammetry and differential pulse voltammetry were performed by means of a potentiogalvanostat Model 283 (EG and G Instruments, Princeton Applied Research). A copper micro-disc electrode (99.99% pure, 0.025 mm diameter, Niraco) was used as the working electrode and lithium metal (Honjoh Metal) as the counter and reference electrodes.

### 3. Results and discussion

#### 3.1. Cyclic voltammetry

Reversible electrodeposition and dissolution of lithium on a copper substrate was virtually unachievable in available battery-grade electrolyte solutions, e.g., 1 M LiClO<sub>4</sub>, LiPF<sub>6</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, dissolved in PC. This was due to passivation by precipitation on the electrode of reduced electrolytes, PC, or contaminants such as LiF, lithium alkyl carbonate and LiOH [1–6]. To conduct experiments under controlled contamination, we prepared a dilute electrolyte solution just before use with dry PC (water < 10 ppm) and purified electrolytes. This purification only marginally improved the cycling performance. Typical cyclic voltammograms for a copper electrode (diameter = 0.025 mm) in 10 mM LiCF<sub>3</sub>SO<sub>3</sub>/PC with and without the addition of 100 volume ppm water (hereafter "volume" will be omitted). The peaks for lithium electrodeposition and dissolution decrease during cycling in a dry electrolyte solution containing less than 10 ppm water (Fig. 1(A)). The addition of 100 ppm of water obviously accelerates the decrease in peaks (Fig. 1(B)). The decrease in the peaks for lithium deposition–dissolution is most likely due to the formation of a passive film as a result of the reaction between lithium and the electrolyte solution, and water stimulates the growth of the film. The reduction in the peaks was observed, however, even when the potential was previously cycled between 1.2 and 0.1 V, without bulk lithium deposition. Thus, formation of a resistive film should occur even in the underpotential region.

A possible cause of passivation in the underpotential region is the formation of a lithium hydroxide film on the surface of the copper electrode through the reaction hypothesized by Pletcher et al. [7], i.e.,



The alkaline environment near the electrode surface that is caused by the cathodic decomposition of contaminated

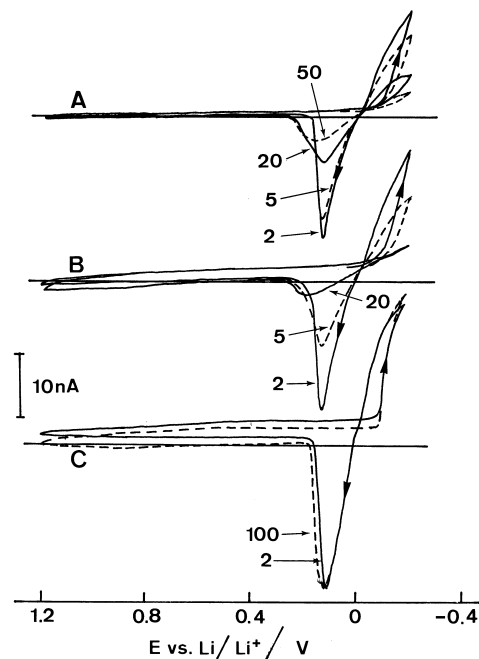


Fig. 1. Typical cyclic voltammogram for a copper electrode ( $\phi = 0.025$  mm) in 10 mM LiCF<sub>3</sub>SO<sub>3</sub>/PC intentionally contaminated with: (A) nothing; (B) 100 ppm water; (C) 100 ppm CF<sub>3</sub>COOH + 100 ppm water. Scan rate: 10 mV s<sup>-1</sup>. Cycle number as indicated.

water appears to be essential in the passivation process. Thus, the effects of acid in an electrolyte solution on lithium electrodeposition on copper have been investigated.

A typical cyclic voltammogram for a copper electrode in 10 mM LiCF<sub>3</sub>SO<sub>3</sub>/PC contaminated with 100 ppm CF<sub>3</sub>COOH + 100 ppm water is shown in Fig. 1(C). The cycleability of lithium electrodeposition on copper is greatly improved. This strongly suggests that the surface of an electrode in organic solutions is exposed to an alkaline environment at cathodic potentials through the presence of water. Furthermore, the pH-control of residual water in the organic solvent by adding strong acid may provide the means to preserve the activity of the copper electrode.

#### 3.2. X-ray photoelectron spectroscopy (XPS)

The film formation, which promotes passivation, increases greatly the resistance for lithium electrodeposition. This is confirmed by ex situ XPS measurements. XPS spectra are presented in Fig. 2 for Cu<sub>2p1/2</sub>, Cu<sub>2p3/2</sub>, F<sub>1s</sub>, O<sub>1s</sub>, C<sub>1s</sub> and Li<sub>1s</sub> on a copper electrode surface after 100 cycles between 1.2 and -0.2 V vs. Li/Li<sup>+</sup> in 10 mM LiCF<sub>3</sub>SO<sub>3</sub>/PC contaminated with 100 ppm water (Fig. 2A), or with 100 ppm CF<sub>3</sub>COOH + 100 ppm water (Fig. 2B). Some lithium compounds are found on the electrode surface in water-contaminated solution, but no lithium compounds are present on the electrode after potential-cycling in acidic solution. The atomic concentration of a copper electrode surface after cycling in acidic solution is

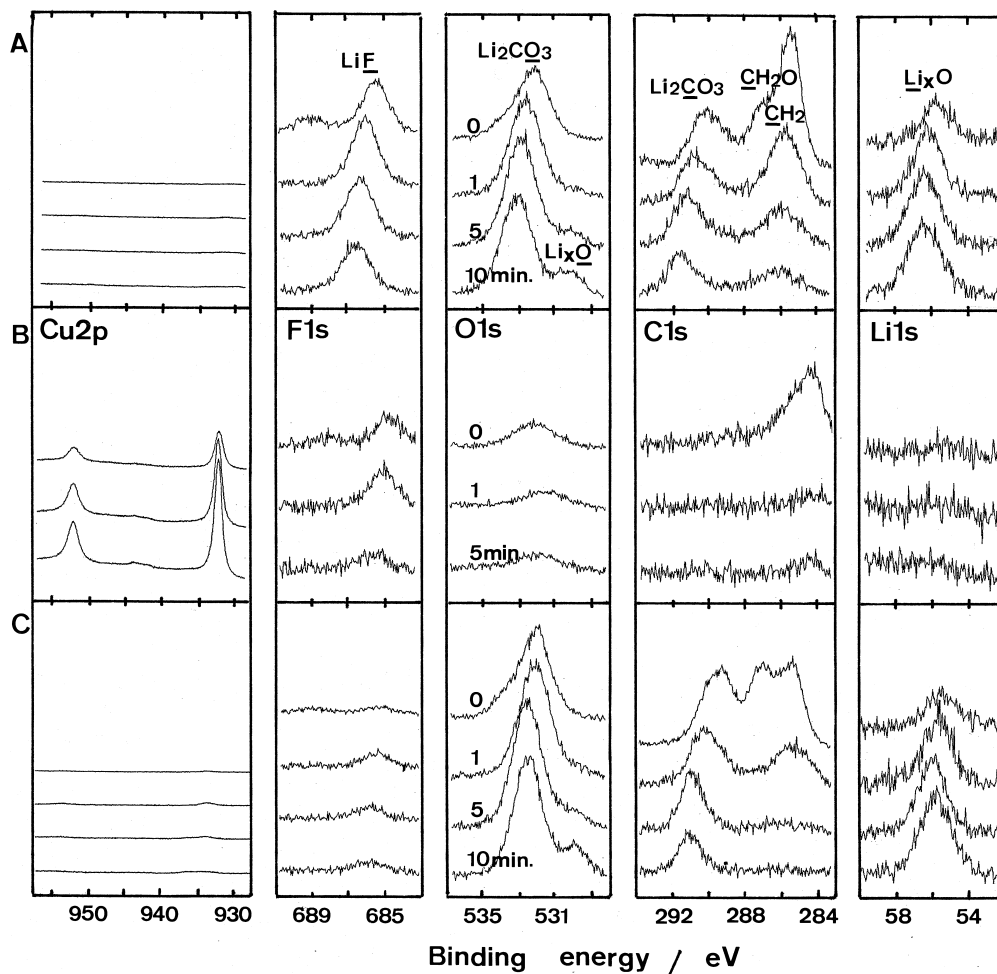


Fig. 2. XPS spectra for copper electrodes after cycling between 3.2 and  $-0.2$  V vs.  $\text{Li}/\text{Li}^+$  in 10 mM  $\text{LiCF}_3\text{SO}_3/\text{PC}$  contaminated with: (A) 100 ppm water; (B) 100 ppm water + 100 ppm  $\text{CF}_3\text{COOH}$ ; (C) after potential cycling between 3.2 and 0.1 V vs.  $\text{Li}/\text{Li}^+$  in 10 mM  $\text{LiCF}_3\text{SO}_3/\text{PC}$  contaminated with 100 ppm water.  $\text{Ar}^+$  sputtering time (min) as indicated.

typically  $\text{Cu}:\text{Li}:\text{O}:\text{C}:\text{F} = 75:0:16:0:9$ . The appearance of strong peaks for  $\text{Cu}_{2p_{1/2}}$  and  $\text{Cu}_{2p_{3/2}}$  in Fig. 2(B) suggests that the bare copper electrode surface is still exposed to the electrolyte solution after cycling without any films in the acidic solution. These results agree well with the behaviour of cyclic voltammograms in Fig. 1.

It should be noted that a thick film was formed on the surface of the copper electrode after 100 cycles in the underpotential region between 1.2 and 0.1 V in 10 mM  $\text{LiCF}_3\text{SO}_3/\text{PC}$  contaminated with 100 ppm water, as shown in Fig. 2(C). The films consist of  $\text{Li}_2\text{CO}_3$ ,  $\text{Li}_x\text{O}$ , a trace of  $\text{LiF}$ , and contaminated hydrocarbon. It should be emphasized, however, that the detected  $\text{Li}_2\text{CO}_3$  may be formed from the reaction of  $\text{Li}_2\text{O}$  or  $\text{LiOH}$  with  $\text{H}_2\text{O}$  and  $\text{CO}_2$  in a glove box atmosphere according to:



To examine the potential dependence of the film formation on the copper surface, the XPS measurement was

conducted for the electrodes cycled in the solution between various potentials. A new copper electrode gave a potential between 3.1 and 3.3 V vs.  $\text{Li}/\text{Li}^+$  in 10 mM  $\text{LiCF}_3\text{SO}_3/\text{PC}$  solution contaminated with 100 ppm water. The electrode potential was cycled between this potential and 2.9, 1.8, 1.2, 0.1 and  $-0.2$  V, respectively, at  $10 \text{ mV s}^{-1}$  prior to ex situ XPS analysis. Figs. 3 and 4 show changes in the relative atomic concentration of copper and lithium on the surface of the electrode after the first and 100th cycle. The relative atomic concentrations were calculated from the intensity of the corresponding peaks in the XPS spectra after 1, 5 and 10 min of argon-ion sputtering and were plotted as a function of the cathodic limit of the potential cycling. Even on the first scan, precipitates of lithium compounds are clearly observed on the surface of the electrode. In particular, the film begins to grow fast between 1.8 and 1.2 V and covers most of the surface of the electrode. The atomic ratio in the film at 1.2 and 0.1 is typically  $\text{Cu}:\text{Li}:\text{O}:\text{C}:\text{F} = 10:28:52:7:3$ . The F-content increased markedly, to over 10%, when the potential was scanned to  $-0.2$  V. This means that deposition of

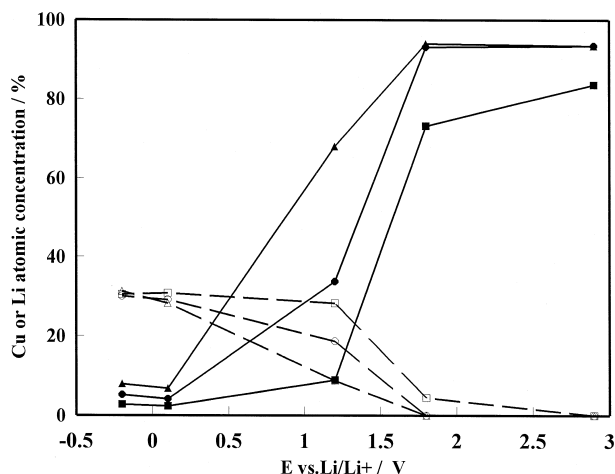


Fig. 3. Plot of relative atomic concentration of copper ( $\text{Ar}^+$  sputtering time:  $\blacksquare$  0;  $\bullet$  1;  $\blacktriangle$  5 min) or lithium ( $\square$  0,  $\circ$  1,  $\triangle$  5 min) on the surface of a copper electrode vs. negative limit of potential,  $E$ , during a cycle between 3.2 and  $E$  V in 10 mM  $\text{LiCF}_3\text{SO}_3/\text{PC}$  contaminated with 100 ppm water. The concentration is calculated from the area of the corresponding peaks in the XPS spectra.

bulk-lithium facilitates the decomposition of the electrolyte ( $\text{LiCF}_3\text{SO}_3$ ) on the electrode. The relatively high oxygen content observed in the film may be explained by the existence of oxygen-rich compounds such as  $\text{LiO}_2$  [7].

### 3.3. Differential pulse voltammetry

Fig. 5 (the first scan) and Fig. 6 (the third scan) show typical differential pulse (DP) voltammetry (DPV) for a copper electrode in 10 mM  $\text{LiCF}_3\text{SO}_3/\text{PC}$  with or without intentional contamination. For a deeper insight, the potential was scanned to higher positive potentials. The DP voltammogram displays more conspicuous peaks than a cyclic voltammogram in this potential region, since DP voltammetry eliminates most of the interference which results from the non-Faradaic charge current. This seriously hinders our understanding, particularly in the case of

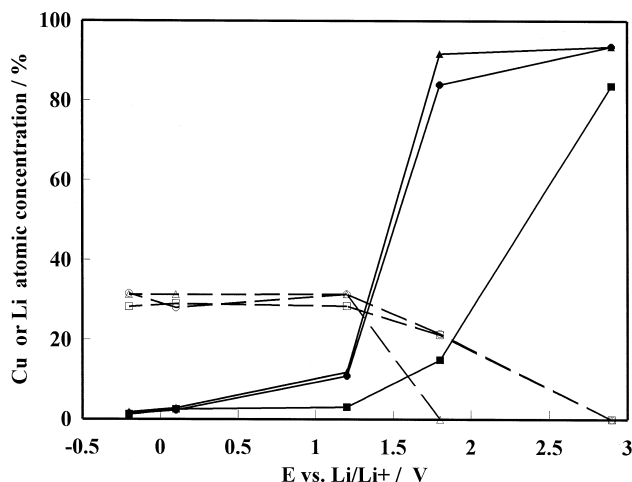


Fig. 4. Same plot as Fig. 3 for electrode after 100 cycles.

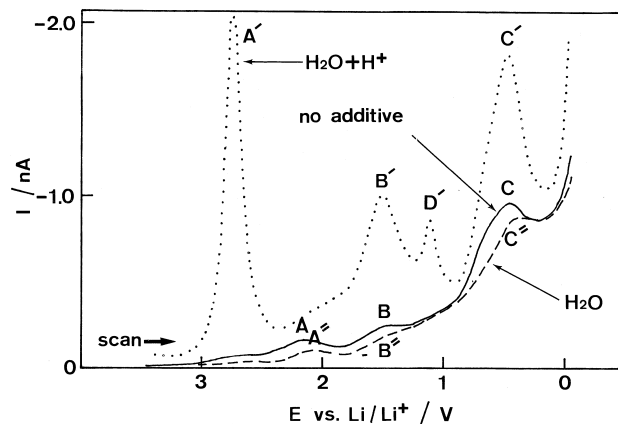


Fig. 5. Typical differential pulse voltammetry (the first scan) for a copper electrode ( $\phi = 0.025$  mm) in 10 mM  $\text{LiCF}_3\text{SO}_3/\text{PC}$  intentionally contaminated with: (—) nothing; (---) 100 ppm water; ( $\cdots$ ) 100 ppm  $\text{CF}_3\text{COOH}+100$  ppm water. Scan rate:  $5 \text{ mV s}^{-1}$  in negative-going direction.

acid contamination. The curves are characterized by three pronounced peaks (A, B and C) with monotonically increasing cathodic current as the potential is scanned in negative-going direction. When the same measurement is repeated with the same electrode in water-contaminated solution, all the cathodic peaks become less pronounced with cycling; this reflects passive behaviour of the electrode in this solution. By contrast, in the acid–water–

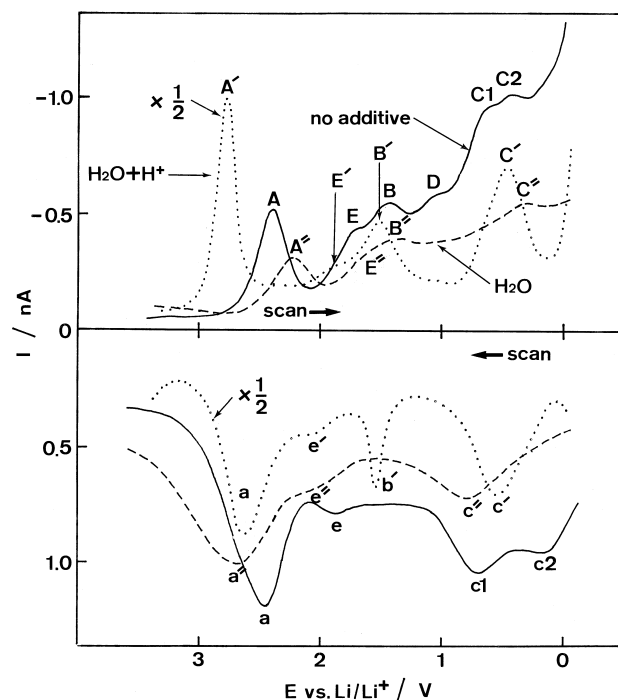
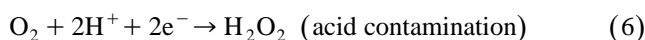
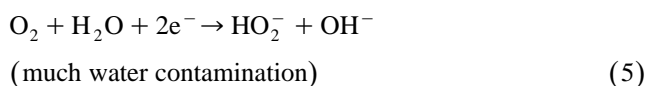


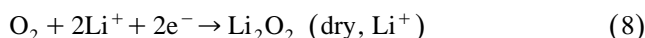
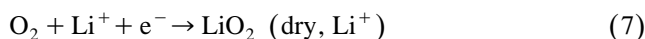
Fig. 6. Typical differential pulse voltammetry (third scan) for a copper electrode ( $\phi = 0.025$  mm) in 10 mM  $\text{LiCF}_3\text{SO}_3/\text{PC}$  intentionally contaminated with: (—) nothing; (---) 100 ppm water; ( $\cdots$ ) 100 ppm  $\text{CF}_3\text{COOH}+100$  ppm water (reduced  $1/2$ ). Scan rate:  $5 \text{ mV s}^{-1}$  in a negative-going (top graphs) and positive-going (bottom graphs) direction.

contaminated solution, peaks **A**, **B** and **C** do not change with cycling, but peak **D** disappears after the first scan. Three of the cathodic peaks (**A**, **B**, **C**) are identical to those observed by other research groups [2,7–14]. These peaks are attributed to reduction of oxygen (peak **A**) and water (peak **B**), and underpotential deposition (UPD) of lithium (peak **C**). Although common contaminants of oxygen and water are considered to cause the surface films, the reduction mechanism in the acid-contaminated solutions should be modified as follows.

Referring to the literature [16], peaks **A**, **A'** and **A''**, which are enhanced by O<sub>2</sub>-addition, are attributed to oxygen-related reactions, e.g.,



or, precipitation of lithium superoxide or peroxide [7,17],



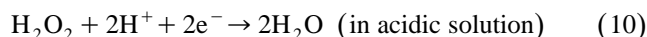
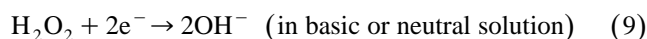
The peaks observed around 2–3 V can be ascribed to a mixture of the above reactions that depends on the concentration of residual water and the pH of the solutions. The addition of 100 ppm of water to the dry solution shifts peak **A** to less positive potentials (peak **A'**) and decreases its intensity. On the other hand, the addition of 100 ppm water + 100 ppm CF<sub>3</sub>COOH shifts the peak to more positive potentials (peak **A'**) and increases its intensity. Reaction (6) will predominate over the other reactions in acidic solution, and give rise to a film-free electrode surface. Insoluble lithium compounds may precipitate on copper by reactions (7) or (8) in the other solutions. The XPS results in Fig. 3 and 4 suggest, however, that film formation is negligible around this potential.

In Fig. 6, the anodic peaks **a'** and **a''** both shift to more positive potentials compared with peak **a** in additive-free solution. The shift in the water-contaminated solution can be easily explained by a change in the reversibility of the electrochemical reactions due to film formation on copper at cathodic potentials. The reduced reversibility of the electrochemical reactions on the electrode will shift all peaks in the scanned directions, particularly, peak **a** to **a''**.

On the other hand, it is difficult to explain the shift of peak **a'** in terms of formation of a film, because no film is formed in the acidic solution as demonstrated by XPS. Furthermore, the anodic peak **a'** should appear at more positive potentials than the corresponding cathodic peak **A'**. This shift possibly originates from a change in pH near the electrode surface. Since the scan in the positive-going direction on the DP voltammogram starts from a potential which is sufficiently negative for hydrogen evolution, the

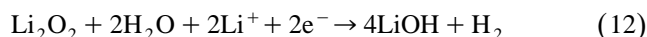
acidity near the electrode surface may be weakened by reduction of protons. Thus, the change in both pH and electrochemical reversibility leads to complicated behaviour of oxygen-related peaks around this potential.

The pH-dependent minor peak **E**, at more a negative potential than peak **A** by 0.6–0.7 V, is due to the reduction of hydrogen peroxide via reaction (5') or (6), according to [18]:



The intensity of the peak **E** (**E''**) increases when the same measurement is repeated in the same cell, probably due to accumulation of the reduced intermediate, H<sub>2</sub>O<sub>2</sub>, in the solution.

Peaks **B** (in dry solution) and **B''** (in water-added solution) near 1.5 V are identical to those reported by Pletcher et al. [7], and are attributed to the decomposition of water to form lithium hydroxide on the copper surface by reaction (1) or:



These reactions can be the cause of passivation of a copper electrode in a water-contaminated solution. The fact that no corresponding anodic peaks are observed during the reverse scan suggests that the reduced product, LiOH, accumulates on the copper electrode in these solutions. In agreement with the appearance of this peak, the thickness of the film on copper increases sharply when the potential is scanned to potentials over 1.5 V, as shown by XPS in Fig. 4.

Although cathodic peaks **B'** and **B** appear at similar potentials in dry and acidic solution, the corresponding anodic peak **b'** is observed only in acidic solution. Thus, peak **B** and **B'** originate from different electrochemical phenomena. Peak **B'** should not be attributed to the irreversible formation of a LiOH film, according to reaction (1) or (12), because no compounds are observed by XPS on copper cycled in acidic solution. Given that increase in acid concentration enhances the relative height of both peaks **B'** and **C'**, these peaks might be related to proton-related reactions such as adsorption of hydrogen atoms on copper. This possibility will be further discussed later.

Peaks **Cs** (**C'**, **C''**, **C1** and **C2**) near 0.5 V vs. Li/Li<sup>+</sup> in Figs. 5 and 6 appeared prior to the lithium bulk deposition and are attributed to the UPD of lithium [7–14]. Once oxygen and water are related to peaks **A** and **B**, respectively, there is no choice but to assign peak **Cs** to the UPD of lithium. In fact, most researchers believe the existence of UPD of lithium at this potential. The following experiment which shows a lack of lithium ions in the system arises us doubt on the possibility of UPD.

Fig. 7 presents a typical DP voltammogram for a copper electrode in PC solvent without any lithium salt, but contaminated with water, CF<sub>3</sub>COOH, or with both of them. Surprisingly, three conspicuous peaks (**A'**, **B'**, **C'**)

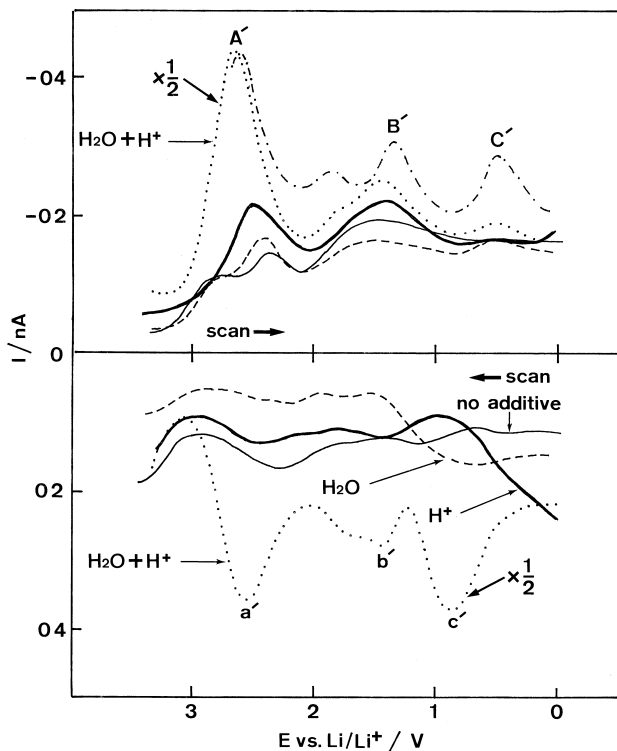


Fig. 7. Typical differential pulse voltammetry for a copper electrode ( $\phi = 0.025$  mm) in PC contaminated with: (—) nothing; (---) 100 ppm water; (· · ·) 100 ppm  $\text{CF}_3\text{COOH}$ +100 ppm water; (—) 100 ppm  $\text{CF}_3\text{COOH}$ ; (- - -) 200 ppm  $\text{CF}_3\text{COOH}$ +100 ppm water. Scan rate:  $5 \text{ mV s}^{-1}$ .

appear in  $\text{Li}^+$ -free PC containing a trace of both water and acid at the same potentials as those in the solution containing lithium salt. The existence of a pair of the peaks,  $\text{C}'$  and  $\text{c}'$  in the solution without  $\text{Li}^+$  ions excludes the possibility of reversible UPD and UPS of lithium at those potentials.  $\text{H}_3\text{O}^+$  intrinsically seems to contribute to the appearance of a pair of peaks.

To exclude the possibility that lithium ions dissolve from the reference or counter lithium electrode, and then contaminate the solution, we carried out an experiment with a complete lithium-free cell which was made up of a copper foil reference electrode (ca.  $16 \text{ cm}^2$ ) and a platinum counter electrode (ca.  $2 \text{ cm}^2$ ). The same results were obtained as in Fig. 7. The peaks  $\text{C}'$  and  $\text{c}'$  in the underpotential region are therefore not relevant to lithium ions but contaminants and their reduction products.

It should be noted that these peaks are commonly observed in various electrolyte solutions. Fig. 8 shows a typical DP voltammogram on the first scan for copper electrodes in 10 mM  $\text{LiCF}_3\text{SO}_3/\text{PC}$ ,  $\text{LiPF}_6/\text{PC}$  and  $\text{LiCF}_3\text{SO}_3/\gamma\text{-BL}$  contaminated with both water and acid. As these curves are quite similar and display four peaks, we can conclude that these peaks should be related to reactions involving contaminants or lithium ions that are commonly include in electrolyte solutions. Therefore, they

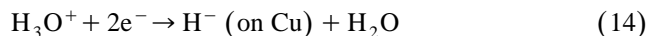
should not be attributed to the decomposition of PC, BL,  $\text{CF}_3\text{SO}_3^-$  or  $\text{PF}_6^-$ .

It is highly possible that impurities, e.g., HCl, HF,  $\text{CF}_3\text{SO}_3\text{H}$ ,  $\text{H}_2\text{SO}_4$ , which are incorporated in lithium salts such as  $\text{LiClO}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiCF}_3\text{SO}_3$ , affect the electrochemical behaviour of a copper electrode in the underpotential region. Therefore, not only the peak  $\text{C}'$  but also peaks  $\text{C}$  and  $\text{C}''$  in Figs. 5 and 6 can be attributed to  $\text{H}_3\text{O}^+$ -related reactions.

It is thereby reasonable to hypothesize the deposition of both lithium ions and protons for the complicated behaviour of peaks around this potential. Wagner et al. [8,9] proposed the deposition of lithium hydride, LiH, on gold for the peaks around 0.5 V, i.e.,



and confirmed the presence of LiH by IR spectroscopy. Our results are more consistent with their hypothesis rather than that of the possibility of Li-UPD for peaks Cs. In solution lacking lithium ions, the deposition of  $\text{H}^-$  may occur instead of reaction (13) on the surface at this potential due to the low concentration of  $\text{H}_3\text{O}^+$  and the slow evolution of  $\text{H}_2$  in the organic solvent, according to:



When the concentration of acid was increased at 200 ppm, however, the peaks  $\text{B}'$  and  $\text{C}'$  were enhanced, as

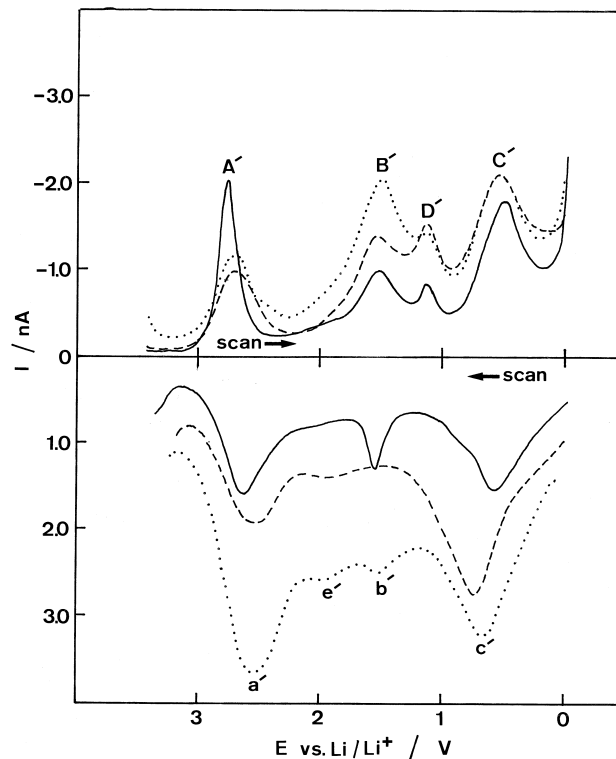
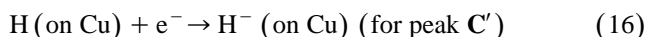
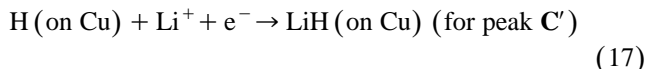


Fig. 8. Typical differential pulse voltammetry (first scan) for a copper electrode ( $\phi = 0.025$  mm) in: (—) 10 mM  $\text{LiCF}_3\text{SO}_3/\text{PC}$ ; (---) 10 mM  $\text{LiPF}_6/\text{PC}$ ; (· · ·) 10 mM  $\text{LiCF}_3\text{SO}_3/\text{GB}$  with contamination of 100 ppm water and 100 ppm  $\text{CF}_3\text{COOH}$ . Scan rate:  $5 \text{ mV s}^{-1}$ .

shown in Fig. 7. Therefore, both peaks should be related to protons. We suppose the following two-step one-electron reductions are responsible for the peaks in the absence of lithium ions:



However, the following reaction may occur in the presence of lithium ions and acid:



In dry (water < 10 ppm) solution (see Fig. 6), the splitting of peak **C** into **C1** and **C2** (similarly peak **c** into **c1** and **c2**) suggests a more complicated feature of the reactions around this potentials. We suggest heterogeneous reactions probably related to a heterogeneous film composed of lithium compounds on the electrode. The details are vague, however. The origin of peaks **D** and **D'** has also not been clarified.

#### 4. Conclusions

The behaviour of a copper electrode in organic solutions is strongly influenced by contaminated water and acid. Electrodes in organic solvents would be exposed to an alkaline environment at negative potentials in the presence of water, and this leads to the formation of a passive film, even in the underpotential region. The addition of a small amount of acid,  $\text{CF}_3\text{COOH}$  can effectively prevent

the passivation of a copper electrode in solutions containing lithium salts by keeping the electrode surface film-free.

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