

Electrochemical and quartz microbalance technique studies of anode material for secondary lithium batteries

Shinji Koike *, Takuya Fujieda, Noboru Wakabayashi, Shunichi Higuchi

Department of Energy Conversion, Osaka National Research Institute, AIST, 1-8-31 Midorigaoka, Ikeda, Osaka 563, Japan

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Abstract

The lithium metal anode for secondary lithium batteries was studied using the electrochemical and the quartz crystal microbalance (QCM) techniques. The solutions studied were: (i) propylene carbonate (PC) containing LiClO_4 , and (ii) γ -butyrolactone (γ -BL) containing LiPF_6 . Surface film formation on the electrodes in these solutions was investigated during galvanostatic electrodeposition of lithium. Moreover, the influence of the surface films upon the electrodeposition of lithium and the electrodeposited lithium through surface films were investigated in these solutions. The molecular weights of the species precipitated on the electrode surface were estimated from the QCM data. The deposited lithium on the electrodes made surface films instantaneously in both solutions. The surface films grew continuously in LiClO_4/PC even after the electrodeposition of lithium stopped. By contrast, the surface film made in $\text{LiPF}_6/\gamma\text{-BL}$ was thin and close, and prevented the decomposition of electrolyte and consumption of deposited lithium. © 1997 Elsevier Science S.A.

Keywords: Quartz crystal microbalance studies; Surface films; Lithium

1. Introduction

It is well known that there is considerable difficulty in obtaining high cycling efficiencies for lithium anodes in secondary lithium batteries. This lack of cycleability is related to passivating films at the electrode/electrolytic solution interface [1]. A consequence of the presence of the thick surface film is an increased tendency for growth of dendrites during lithium deposition, which is related to the nonuniform current density distribution at the electrode/electrolytic solution interface [2].

Recently, the application of the electrode mass monitoring change during electrochemical measurements by quartz microbalance techniques (QCM) has been reported. QCM is an extremely sensitive technique for mass measurements on metal electrodes [3,4]. In this method, mass is monitored simultaneously with electrochemical measurements and it provides a large amount of information about electrochemical and surface processes. Indeed, there are recent reports on the study of underpotential deposition (UPD) of lithium on noble metal electrodes using this technique [5,6].

In the studies described herein, QCM was employed for monitoring the mass change of the surface films on electrodeposited lithium. We will discuss the effect of electrolytes in forming the passivating layer.

2. Experimental

All experimental work was carried out in a glove box under a high-purity argon atmosphere. The electrochemical and the QCM experiments were carried out in three-electrode cells using a Hokuto Denko Model HA-501G potentiostat/galvanostat and a Model HQ-101B QCM control unit with a Model HQ-201 QCM oscillator unit interfaced to a NEC PC9801 personal computer. Six MHz AT-cut quartz crystal with 1.5 cm^2 active area of nickel was employed for electrochemical and QCM measurements. Lithium metal was used as the counter and the reference electrodes. The galvanostatic electrodeposition of lithium was performed in PC containing a 1.0 M LiClO_4 solution (Mitsubishi Chemical) and γ -BL containing a 1.0 M LiPF_6 solution (Mitsubishi Chemical). The galvanostatic electrodeposition current was 0.5 mA/cm^2 . All solutions initially contained less than 20 ppm of H_2O measured by the Karl-Fischer method.

* Corresponding author

3. Results and discussion

3.1. Lithium deposition on nickel

Fig. 1 shows typical results of the potential (E) and the change in the quartz resonance frequency (Δf) responses during the constant current measurements of nickel electrodes coated on quartz. The Δf was continuously decreased during electrolysis; this signifies an increase in the electrode mass. At a potential from open-circuit voltage (OCV) to 0 V versus Li/Li⁺ (first process), the Δf was much smaller than at below 0 V (second process). During the first process, bulk deposition of lithium did not occur. The reactants were electrolytes, residual oxygen, residual water and/or lithium (due to UPD). During the second process, first, Δf was very large but it decayed with elapse of electrodeposition. During the first large Δf decrease, the decomposition of electrolytes occurred on the surface of deposited lithium, leading to the formation of a passivating layer that reduced another formation of surface films. In comparing these two electrolytes, LiClO₄/PC and LiPF₆/γ-BL, both E and Δf were almost the same profiles excepted for the volume of Δf during the second process.

Fig. 2 presents the mass accumulated per mole of electrons transferred (mpe) [6] versus the charge per unit area (Q). The mpe is

$$mpe = (d\Delta m/dQ)F(d\Delta f/dQ)(F/C_f) \quad (1)$$

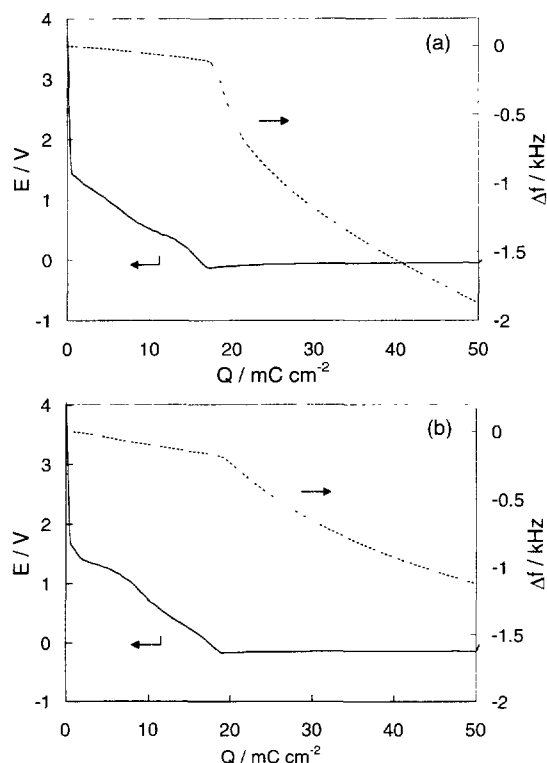


Fig. 1. (—) E and (· · ·) Δf vs. Q during the constant current measurements on nickel electrode in (a) LiClO₄/PC and (b) LiPF₆/γ-BL.

where Δm is the mass accumulation per unit area, F is the Faraday number and C_f is the correlation coefficient between Δf and Δm . It is difficult to evaluate the real mass change of the electrodes from Δf , since the resonance frequency is changed by many factors. But it is possible to roughly estimate Mw/n (the average molecular weight of the forming surface species divided by the number of electrons transferred) from mpe . Table 1 shows the theoretical Mw/n values for several considering surface species.

Comparing Fig. 2 and Table 1, the additional product (mpe is about 8) during the first process is lithium in both electrolytes. A recent paper [7] reported the UPD of lithium begins about 0.4 V and the oxygen reduction occurs at 1.58 and 1.76 V in the absence and presence of lithium salt, respectively. Therefore, the surface product before 0.4 V is assumed to be either LiO₂ or Li₂O₂. The lithium salt is presumably formed by an EC or an ECE mechanism (E and C represent 'electrochemical' and 'chemical' reaction) where the lithium ion interacts with the electrochemical reduction product of the initially absorbed oxygen and/or the oxide film on the nickel electrode since the mpe value indicates only the lithium value.

During the second process, the bulk deposition of lithium, the mpe value differs with the electrolytes. Many researchers have studied the surface films formed on lithium and suggest organic lithium compounds such as RCO₂Li and inorganic lithium compounds by Fourier-transform infrared [8], X-ray photoelectron spectroscopy [2,9], etc. In the case of the LiClO₄/PC solution, most of the deposited lithium reacts with the electrolyte to make up surface films of RCO₂Li since its mpe value is very large. On the other hand, the surface films made in the LiPF₆/γ-BL solution consist of small

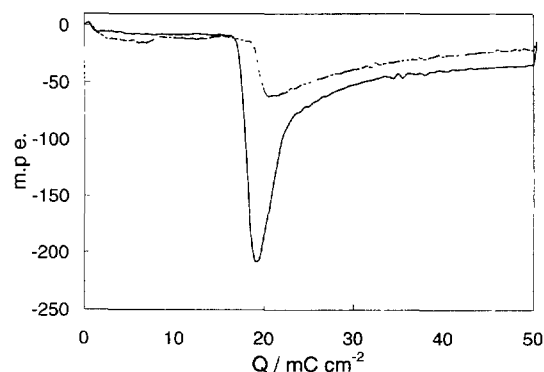


Fig. 2. mpe evaluated from Fig. 1 vs. Q in (—) LiClO₄/PC and (· · ·) LiPF₆/γ-BL.

Table 1
 Mw/n values of possible compounds formed on lithium surface

Compound	Mw/n	Compound	Mw/n
Li	7	Li ₂ CO ₃	37
Li ₂ O	15	LiOH·H ₂ O	42
Li ₂ O ₂	23	LiF·H ₂ O	44
LiOH	24	LiOH·2H ₂ O	60
LiF	26	RCO ₂ Li	83

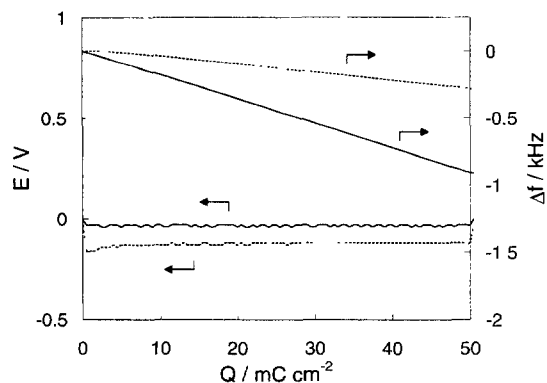


Fig. 3. E and Δf vs. Q during the constant current measurements on lithium electrode in (—) LiClO_4/PC and (· · ·) $\text{LiPF}_6/\gamma\text{-BL}$.

amounts of RCO_2Li and inorganic compounds such as Li_2O , Li_2O_2 , LiOH and LiF because of their small mpe values.

3.2. Lithium deposition on lithium

Fig. 3 shows typical results of E and Δf responses during the constant current measurements on lithium electrodes in the two solutions. Lithium electrodes were prepared by electrodeposition on nickel electrodes from experimental solvents, the slopes of Δf are linear versus Q and the mpe values are 22 and 7 for LiClO_4/PC and $\text{LiPF}_6/\gamma\text{-BL}$, respectively. In the case of the LiClO_4/PC solution, the real Mw/n value of the decomposed product must be a few times larger than 22 because a part of the deposited lithium reacts with the electrolyte since $\sim 80\%$ of the deposited lithium is capable of anodic dissolution, therefore the major surface compounds will be RCO_2Li . On the other hand, deposited lithium from $\text{LiPF}_6/\gamma\text{-BL}$ did not react with the electrolyte since the mpe value was almost the Mw/n value of lithium. Comparing the potential during the electrodeposition of lithium from the LiClO_4/PC solution and the $\text{LiPF}_6/\gamma\text{-BL}$ solution, the $\text{LiPF}_6/\gamma\text{-BL}$ solution needs a larger overpotential than the LiClO_4/PC solution. This indicates that a more close surface film is made from the $\text{LiPF}_6/\gamma\text{-BL}$ solution than from the LiClO_4/PC solution.

3.3. Time dependence of deposited lithium

The stability of the surface films formed in the $\text{LiPF}_6/\gamma\text{-BL}$ solution and the LiClO_4/PC solution was investigated. Fig. 4 shows Δf measured at OCV against time after electrodeposition of lithium (150 mC) on nickel electrodes from the $\text{LiPF}_6/\gamma\text{-BL}$ solution and the LiClO_4/PC solution. The Δf continuously decreased (mass increasing) in LiClO_4/PC , on the other hand, it did not change in $\text{LiPF}_6/\gamma\text{-BL}$. The difference between Δf reflected the stability of the surface

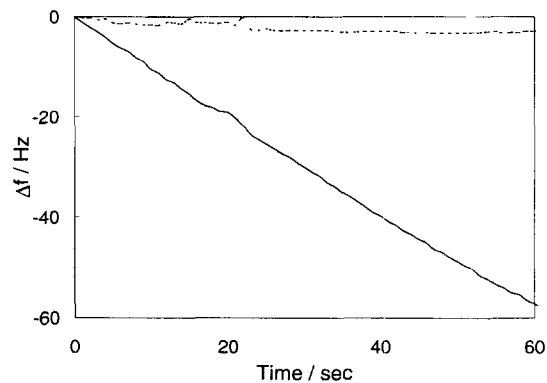


Fig. 4. Δf as a function of time, measured after electrodeposition of lithium at OCV in (—) LiClO_4/PC and (· · ·) $\text{LiPF}_6/\gamma\text{-BL}$.

films. The small part of lithium exposed the electrolyte in LiClO_4/PC then decomposed the electrolyte. The products caused by decomposition are not clear because of an unknown amount of lithium was reacted but that must be same products of initial surface films. The surface films formed from $\text{LiPF}_6/\gamma\text{-BL}$ solution protects the lithium against chemical reactions. These results are consistent with the result of lithium deposition on lithium electrodes.

4. Conclusions

The electrodeposited lithium reacts immediately with electrolyte and/or residual impurities in the electrolyte that makes surface films. The surface films made in the LiClO_4/PC solution are not enough to protect the deposited lithium from another chemical reaction with electrolytes. On the other hand, the surface films made in $\text{LiPF}_6/\gamma\text{-BL}$ solution are close and protective due to the consumption of deposited lithium by decomposition of the electrolytes.

References

- [1] J.O. Besenhard and G. Eichinger, *J. Electroanal. Chem.*, 68 (1976) 1–18.
- [2] K. Kanamura, H. Tamura and Z. Takehara, *J. Electroanal. Chem.*, 333 (1992) 127–142.
- [3] J.L. Jones and J.P. Meire, *Anal. Chem.*, 41 (1969) 484–490.
- [4] T. Nomura and M. Iijima, *Anal. Chim. Acta*, 131 (1981) 97–102.
- [5] N. Yamamoto, H. Hirasawa, H. Ishida, T. Tatsuma and N. Oyama, *Bull. Chem. Soc. Jpn.*, 67 (1994) 1296–1300.
- [6] D. Aurbach and A. Zaban, *J. Electrochem. Soc.*, 142 (1995) L108–L111.
- [7] D. Pletcher, J.F. Rohan and A.G. Ritchie, *Electrochim. Acta*, 39 (1994) 1369–1376.
- [8] D. Aurbach, Y. Gofer and J. Longzam, *J. Electrochem. Soc.*, 136 (1989) 3198–3205.
- [9] K. Kanamura, H. Tamura, S. Shiraishi and Z. Takehara, *J. Electroanal. Chem.*, 394 (1995) 49–62.