Mass Transport of Li^+ Ion Accompanied with Electrodeposition of Li in $LiClO_4$-PC Solution

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Introduction

The rechargeable batteries are widely used as the power source for electronic devices. Metallic lithium is an interesting material for the negative electrode in rechargeable batteries. However, the performance of metallic lithium anode is limited by the occurrence of dendritic growth during battery charging and discharging operation. These phenomena are deeply related to the surface inactive layers on the active lithium metal electrode. Many studies have been reported about these surface layers called solid electrolyte interphase (SEI), but not many have been argued form the view point of ionic mass transfer in nonaqueous electrolyte. This paper describes the approach to clarify the ionic mass transfer in $LiClO_4$-PC solution by the holographic interferometer.

Experimental

Two different types of electrolytic cells were used. One is the conventional electric cell with vertical plane electrodes. Working electrode(6x15mm x 0.2mm), counter electrode were prepared with lithium metal foils (0.2mm thickness). The distance between working electrode and counter electrode is set to 2mm. The conventional Li metal reference electrode(3x3mm). Another cell configuration is cathode over anode. The electrodes were immersed in the electrolyte(0.5M LiClO4-PC) contained in optical glass cell. These electrolytic cell were assembled in the glove box filled with highly pure Ar gas. The galvanostatic electrolysis was conducted in both electrolytic cells. The concentration boundary layer thickness was in-situ measured for the conventional electrolytic cell configuration by the holographic interferometer.

Results and Discussion

When the electrolytic cell with horizontal electrode in the cathode-over-anode position was used, no natural convection is induced. Metal ions are transferred to the cathode in the diffusional mode such a configuratiuon. Experimental results are expected to agree with the theoretical prediction by the Sand equation.

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

$C=C_b$ at t=0

$$\frac{\partial c}{\partial x} = \frac{i(1-{}^*t_1)}{zFD} \quad \text{at } x=0$$

$C=C_b$ at $x=\infty$

The validity of this calculation has been confirmed in CuSO4 by McLarnon[1].

When the electrolytic is carried out in the conventional electrolytic cell with the vertical electrode configuration, the natural convection is induced accompanied with the electrodeposition of Li+ ion. Fig.1 shows the time variation of the concentration boundary layer thickness(δ) with square root of time determined at various current densities in the cell with vertical electrodes. The curves of solid lines are calculations by below equations.

$$\frac{\partial c}{\partial t} + u\frac{\partial c}{\partial x} + v\frac{\partial c}{\partial y} = D\frac{\partial^2 c}{\partial y^2}$$

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} = \nu\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right) + g\alpha\left(c - c^*\right)$$

$$\frac{\partial v}{\partial t} + u\frac{\partial v}{\partial x} + v\frac{\partial v}{\partial y} = \nu\left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2}\right)$$

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0$$

The initial conditions are expressed as
u=v=0, c=c* at t=0
The boundary conditions are
u=v=0, c=c* at x=0
u=v=0, $j = \frac{i(1-{}^*t_1)}{zF} = -D\left(\frac{\partial c}{\partial y}\right)_{y=0}$ at y=0
u=0, c=c* at y= δ_u

A good agreement is illustrated between the measured values and the calculated curve, as long as the transient variation concerns. However, some discrepancies exist in the absolute value of the steady state.

Reference

[1] F.R.McLarnon, et al., Electrochimica Acta, 21, 101 (1976)

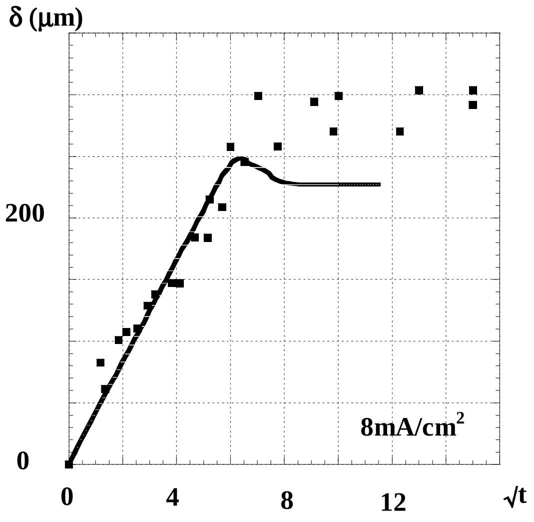

Fig.1 Time Transition of the Concentration Boundary Layer Thickness