AC Impedance Spectroscopic Study of Electrodeposition Process of Lithium Metal

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Introduction

Lithium metal is an ideal anode active material for rechargeable lithium batteries, because of its theoretical capacity >3800 mAhg⁻¹. However the lithium metal anode has never been successfully applied to rechargeable batteries, because it easily forms dendrite which initiates the internal short-circuit of the cell resulting in the safety incidents, during the charging process.

Even though a lot of studies have been carried out to prevent the dendritic growth of lithium metal, it can never been completely prevented under critical conditions such as high deposition current or many cycling.

In this study, we conducted electrochemical analyses of the electrodeposition process of lithium metal using ac impedance spectroscopy to understand the key parameter of the lithium deposition process and also discussed the relationship between the deposition condition and the morphology of the electrodeposited lithium.

Experimental

The electrochemical analyses were carried out using a three-electrode Swagelok cell. Lithium metal was used for all the three electrodes; the working electrode (W.E.), the counter electrode (C.E.) and the reference electrode (R.E.). Ethylene carbonate (EC) and diethyl carbonate (DEC) 1:1vol% containing 1 mol dm⁻³ LiClO₄ was used as base electrolyte. In order to investigate the influence of SEI film, 5 vol% of fluoroethylene carbonate (FEC) was added to the above electrolyte solution for some measurements. The ac impedance spectra were taken at various temperatures and analyzed to calculate the activation energies.

Results and Discussion

Fig. 1 shows Nyquist plot of the lithium metal electrode in EC:DEC containing 1 mol dm⁻³ LiClO₄ with / without 5 vol% of FEC. Both spectra have two semicircles in the higher and lower frequency ranges. The semicircle at the higher frequency rages (10 kHz~10 Hz) was assigned to the lithium ion transfer in SEI film, because it got smaller in the case of the FEC containing electrolyte. Therefore, we suspect the other semicircle observed at the lower frequency range corresponds to the charge transfer of lithium ion.

Fig. 2 and Table 1 show Arrhenius plot of the impedance spectra and the activation energy of the lithium metal respectively. The calculated activation energy for the charge transfer process of the lithium (R4) was approximately 40 kJ mol⁻¹, while a graphite negative electrode shows 50-60 kJ mol⁻¹ [2]. It suggests that the rate-limiting factor of the lithium deposition process is different from that of a graphite negative electrode.

On the other hand, the impedance element corresponding to the lithium ion transfer in the SEI layer (R2 and R3) was 43.3-54.45 kJ mol⁻¹, indicating that the dendritic growth of the lithium metal was significantly affected by the properties of SEI layer.



Figure 1. Nyquist plots for the Li electrode in EC:DEC containing 1.0 M LiClO₄ without additives (\blacktriangle), with 5 vol% FEC (\blacksquare)



Figure 2. Arrhenius plot of lithium-ion transfer resistances at the interface between Li electrode and liquid electrolyte of EC:DEC containing 1.0 M LiClO₄

Table 1. The activation energy of the interface between the lithium metal and the electrolyte; EC:DEC containing 1.0 M LiClO₄.

	R1	R2	R3	R4
Ea (kJ mol ⁻¹)	14.42	43.30	54.45	39.99

Reference

1. K. Kanamura, S. Shiraishi, Z. Takehara, J. Electrochem. Soc., 143, 2187 (1996)

2. T. Abe, H. Fukuda, Y. Iriyama, Z. Ogumi, J. Electrochem. Soc., 151, A1120 (2004)