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Equivalent circuit model analysis on electrochemical impedance spectroscopy of lithium metal batteries

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HIGHLIGHTS

- 1,4-dioxane is proved to be a good pretreatment liquid for lithium electrode.
- The surface modification mechanisms are studied by FTIR, SEM and EIS methods.
- A reasonable equivalent circuit is designed for EIS analysis.
- The equivalent circuit model is analyzed theoretically.

GRAPHICAL ABSTRACT
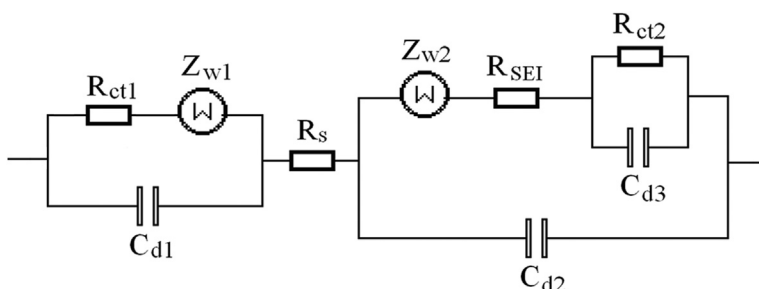
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ABSTRACT

Lithium metal electrode is pretreated with 1,3-dioxolane or 1,4-dioxane to improve its properties. The components and morphology of the surface films formed in the above two pretreatment liquids are studied using FTIR and SEM respectively. Li−LiCoO$_2$ coin cells are then fabricated and their cycle and discharge performance are tested. It is found that the battery performance is greatly improved by such pretreatment. Interestingly, the 1,4-dioxane pretreatment is more effective than 1,3-dioxolane in improving the lithium metal electrode performance. To explore the mechanism(s) behind, the electrochemical impedance spectroscopy (EIS) is employed and an equivalent circuit model is designed for EIS analysis. The fitting curves are aligned well with the experimental curves, suggesting that the proposed equivalent circuit model is an ideal model for lithium battery. Next, the corresponding relationship between the impedance components and every individual semicircle in the Nyquist curves is inferred theoretically and the result is satisfying. Based on the analysis using this model, we conclude that the structural stability of SEI film is increased and the interfacial compatibility between the lithium substrate and the SEI film is improved by 1,3-dioxolane or 1,4-dioxane pretreatment.

1. Introduction

Lithium metal is an ideal electrode material with a theoretical specific capacity of 3800 mAh·g^{-1} and a very negative redox potential of −3.04 V. Thus, the lithium metal secondary battery holds great promise for wide applications in the future. However, currently there are still some obvious difficulties in using lithium

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metal as electrode materials. For example, lithium dendrites can be easily formed in the charge–discharge process, resulting in dead Li and a potential internal short circuit in battery [1–4]. Therefore, its commercialization has been limited. To suppress the dendrite formation and improve the cycle life and the safety properties, much research efforts have been conducted, e.g., surface pretreatment on lithium metal to form better solid electrolyte interface [5,6], improvement on the interfacial compatibility by applying new electrolyte systems [7,8], supplement of additives in electrolyte to improve the surface properties [4] and optimization of the lithium electrode fabrication process [9].

Despite the common belief that lithium metal is unstable in organic solvents due to its high reactivity from thermodynamics point of view, lithium metal can be used as electrode materials in some organic solvents with the formation of a solid electrolyte interphase (SEI) film on its surface. In such conditions, the interfacial stability and electrochemical performance of lithium electrodes will be dominated by the SEI films. Thus, SEI film plays a key role in determining the performance of the lithium electrode in lithium metal battery [1,3,10–12].

To study the SEI film, electrochemical impedance spectroscopy (EIS) represents a powerful tool that is widely applied [1,4,6,13,14]. EIS plots can inform the deposition and dissolution process of SEI film reflected from the increase and decrease of impedance, respectively. Furthermore, through the equivalent circuit modeling of EIS Nyquist curves, the structure characteristics and electrochemical performance of SEI film can be further described in the perspective of electricity. If the equivalent circuit model matches to the real interface, a profound understanding of the electrode interface and SEI film would be achieved, this would facilitate both theoretical and applied research in lithium metal battery.

In this study, lithium metal electrodes were pretreated with two types of liquids, namely, 1,3-dioxolane (1,3-DOL) and 1,4-dioxane (1,4-DOA). To compare the electrochemical performance of the pretreated lithium metal electrodes with the untreated one in a battery setting, Li–LiCoO₂ coin cells were fabricated with untreated or pretreated Li as anode and LiCoO₂ as cathode. The cycle and discharge performance of the cells were then tested. In addition, the EIS spectroscopy was measured under various discharge voltages in a typical cycle process. Furthermore, to understand why the surface modified lithium electrodes have improved performance, the study offered an equivalent circuit model fit to lithium battery and theoretically inferred the corresponding relationship between the equivalent circuit components and each semicircle in the Nyquist curves.

2. Experimental

In a glove box full of argon gas, the lithium metal foil (battery grade, thickness 95 μm) and electrolytic copper wire mesh (thickness 50 μm, 100 meshes) was pressed in a flat press in order to fix them together. The lithium metal foils were then cut into circle lithium electrodes (diameter 14.0 mm) via die cutting process. Next, the prepared lithium electrode was soaked in 1,3-DOL (AR) or 1,4-DOA (AR) solution for 2 min followed by standing for 5 min in a glove box.

R2016 coin cells were fabricated using the lithium electrode as anode, LiCoO₂ electrode (LiCoO₂ 92wt%, PVDF 4wt%, acetylene black 4wt%, diameter 15.5 mm) as cathode, Celgard 2300 (diameter 18.5 mm) as separator and organic electrolyte (1M LiPF₆, EC:DMC:DEC = 1:1:1).

The charge and discharge performance test was conducted with LAND battery testing system (CT2001A type). The charge/discharge condition was described in the following: the cells were charged at a constant current intensity of 0.5 mA (current density is

0.325 mA cm⁻² in the lithium electrode) with an upper potential limit of 4.2 V, then charged at a constant voltage of 4.2 V for 1 h and with a lower current limit of 0.02 mA, standing for 5 min, and then discharged at a constant current intensity of 1.0 mA (current density is 0.65 mA cm⁻² in the lithium electrode) with a cutoff voltage of 2.7 V, standing for 5 min, cycled in this way for 100 times. The temperature was 24 ± 2 °C and the relative humidity was 55 ± 5 in the testing period.

The EIS measurements of coin cells were performed with ZAHNER IM6e electrochemical workstation. In order to study the change of interface impedance in the discharge process, we chose the coins after 10 cycles and measured EIS with four discharge voltage (i.e., 4.2 V, 3.9 V, 3.6 V and 2.7 V). For EIS testing, the following conditions were used: the coin cells were set at the open circuit state; the working electrode was lithium electrode; the counter electrode and reference electrode was LiCoO₂ electrode; the frequency range was set from 1 MHz to 20 mHz; the amplitude of voltage was 5 mV and the temperature was 24 ± 2 °C.

The components and morphology of the surface films formed in two pretreatment liquids were characterized using FTIR and SEM techniques, respectively. In a glove box full of argon gas, lithium metal foil was soaked in 1,3-DOL or 1,4-DOA for 2 min and standing in argon gas for 24 h, then FTIR and SEM were measured. Samples for FTIR were prepared in a glove box, lithium metal foil was pressed on a transparent KBr window and the reverse side was sealed with transparent adhesive tapes. The FTIR spectroscopy was measured with BRUKER fourier transform infrared spectrometer (VERTEX70), the resolving power was 0.4 cm⁻¹ and the measurement range was 2000-600 cm⁻¹. SEM measurements were carried out with JEOL scanning electron microscope (JSM-6390). Lithium metal foils were cut with a blade and their cross-sections were imaged. The electrodes prepared in glove box were transferred under argon protection to the sample chamber of SEM and were then imaged in vacuum.

3. Results and discussion

3.1. Components and morphology analysis of the surface films

Lithium metal is extremely active and reacts with most organic solvents [6]. Therefore, a film can be formed on its surface upon reacting with the pretreatment liquid. Aurbach et al. [15] treated lithium metal with 1,3-DOL for 2 h–24 h and reported that the major component of the formed surface film was $CH_3CH_2OCH_2OLi$. The reaction could follow the equation below:

$$DOL + Li + H^+ \rightarrow CH_3CH_2OCH_2OLi$$
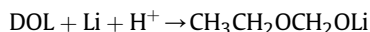
They thought that the hydrogen abstraction stages probably involve a dehydrogenation of 1,3-DOL molecules, but they didn't describe the details. Because the treatment time is only 2 min in the present study, which is much shorter than that in Ref. [15], so the components of the formed surface films need analyzing. Fig. 1 shows FTIR spectra obtained from lithium surfaces pretreated with 1,3-DOL or 1,4-DOA. The two spectra were similar with Li–O stretching bands at ˜650 cm⁻¹, CH_2=CH–O bands at ˜1020 cm⁻¹, CH_2–O bands at ˜1080 cm⁻¹, and CH_2–O–CH_2 bands at ˜1150 cm⁻¹ [15–17]. The intensities of peaks indicated that the major components of surface film formed in 1,3-DOL were CH_2=CHOCH₂OLi and $CH_3CH_2OCH_2OLi$, and the major components of surface film formed in 1,4-DOA were CH_2=CHOCH₂CH₂OLi and $CH_3CH_2OCH_2CH_2OLi$. Their corresponding reactions could follow the equations below: