SEI Film on Lithium Metal Anode in Mixed-Salt System

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Introduction

Lithium metal is a potential anode material for a high energy battery system owing to its low electrode potential and high specific capacity. However, the low cycle life has been a serious issue, which can be attributed to its dendritic growth in the plating process. In this study, electrolyte salt effect on solid electrolyte interphase (SEI) is discussed to improve lithium metal anode for organic lithium-oxygen secondary battery.

Organic lithium-oxygen battery usually uses electrolyte comprising dimethylsulfoxide (DMSO) as solvent [1,2], since it shows good chemical stability against super oxide anions, and high dissolving ability of lithium salts. In this study, lithium bis(fluorosulfonyl)imide (LiFSI) and lithium nitrate ($LiNO_3$) were examined as the salt for DMSO solution, in which the ratios of $LiNO_3$:LiFSI (x:100-x mol%) were changed in the range of $0 \leq x \leq 100$. The electrochemical lithium plating/stripping were tested with different x-values. The results were discussed with respect of chemical compositions of SEI on the electrode.

Experimental

The electrochemical lithium plating/stripping were tested in a two-electrode 2025 type coin cell. Lithium metal and cupper foil were used as a counter and working electrode, respectively. The current density was 0.2 mA cm^{-2}. The plating/stripping time was 1 hour for each step. The volume of electrolyte solution was 75 µL.

XPS analyses were measured at the potential before and after the peaks of cyclic voltammogram that was kept for 2 hours. Mg Kα radiation was used as X-ray source. Acceleration voltage was 10 kV. Emission current was 20 mA. Ar ion gun etching was conducted at acceleration voltage of 2.0 kV and emission current of 20 mA.

Results and Discussions

$LiNO_3$ single salt was found effective to yield small polarizations in the initial several cycles. The polarization gradually became larger with cycle numbers. LiFSI single salt showed larger polarizations, but it was kept in a similar magnitude during extended cycles. $LiNO_3$ and LiFSI salt mixtures gave better cycle performances with low and stable polarizations.

XPS analyses demonstrated that $LiNO_3$ gave Li_2O-rich SEI film, while LiFSI gave LiF-rich one. In sweeping to the reduction direction in the mixed salt system, LiF was first formed by decomposition of LiFSI, then Li_2O was mainly produced by decomposition of $LiNO_3$. Moreover, it is considered that there is a decomposition potential of DMSO near the formation potential of Li_2O. Considering the polarization behaviors together, Li_2O is considered to give an ionic conductivity for the film and LiF suppresses continuous film growth. The mixture of Li_2O and LiF made stable lithium metal plating/stripping reaction possible and as a result it gave better cycle performance with low and stable polarizations.

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References:

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