THE EFFECT OF FLUORIDE ADDITIVES ON THE CORROSION OF ALUMINUM CURRENT COLLECTOR FOR LITHIUM ION BATTERY

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1. Introduction

Fluorine-containing imide and methide salts are attractive as new electrolyte with high thermal stability and high electrical conductivities. However, dissolution of aluminum cathode current collector occurs at high potentials in organic solvents containing these electrolytes. In this paper, we propose the corrosion mechanism of aluminum in organic solvents containing $LiCF_3SO_3$ and effect of fluoride additives on the corrosion of aluminum [1].

2. Experimental

Corrosion of aluminum was examined by cyclic voltammetry in an electrochemical cell with metallic lithium as counter and reference electrodes in 0.5 M (mon/dm^3) $LiCF_3SO_3$-EC/DEC (1:1) containing a complex fluoride or $LiClO_4$. The complex fluorides used were $LiBF_4$, $LiPF_6$, $LiAsF_6$ and $LiSbF_6$. The concentrations of additives were 0.05-0.2 M for $LiBF_4$ and 0.2 M for other additives. Aluminum plate (purity: 99.99%) was used after washing by ethanol and drying. The effect of surface fluorination of aluminum was also examined (fluorinated by 0.3 bar F_2 at 150°C, 250°C and 350°C for 20 min). Cyclic voltammetry measurements were made mainly at 10 mV/s in a potential range of 0 to 8 V vs Li/Li$^+$ at 25°C.

3. Results and discussion

The electrochemical oxidation of $CF_3SO_3^-$ anion would produce CF_2 and/or carbon atom which is formed by the disproportionation reaction of CF_2 [2]. These chemically active species would reduce the oxide layer of aluminum, which leads to the corrosion of aluminum [1]. In fact, large corrosion currents and vigorous dissolution of aluminum were observed in 0.5 M $LiCF_3SO_3$-EC/DEC. The corrosion currents were smaller in a fluoride- or $LiClO_4$-added solvent (0.5 M $LiCF_3SO_3$-EC/DEC), decreasing in the order, $LiSbF_6$>$LiAsF_6$>$LiClO_4$>$LiPF_6$>$LiBF_4$. It has been found that $LiBF_4$ is the most effective for preventing the corrosion of aluminum. The stability and oxidation potentials of these anions would obey the following order: $CF_3SO_3^-$≈ClO_4^-<BF_4^-<PF_6^-<AsF_6^-<SbF_6^- [3]. This means that a fluoride anion with a similar oxidation potential to that of $CF_3SO_3^-$ is preferable as an anti-corrosion material. It has been also revealed that fluorination is more effective than oxygenation and surface fluorination of aluminum has additional effect for prevention of the corrosion of aluminum.

References

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