Abstract #438, 224th ECS Meeting, © 2013 The Electrochemical Society

Stable Interfaces of Solid Electrolytes with $LiFePO_4$ Cathode during Charge and Discharge Operations

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1. Introduction

One of the important matters for rechargeable batteries is the stability of interfaces of electrolytes with electrodes. Degradation of these interfaces causes reduction of the capacity and the operating voltage. However, there are only a few reports of the degradation in atomic scale. In this research, we apply an ultrathin-film cathode to the battery to focus on the stability of the interface. The electrode material we selected is lithium iron phosphate ($LiFePO_4$)[1]. Its electrochemical and structural features have been well-clarified by many researchers. The batteries is fabricated employing three electrolyte materials, $LiPF_6$ (in solution), $Li_9Al_3(P_2O_7)_3(PO_4)_2$ (LAPP, solid)[2], and $Li_3PO_{4-x}N_{2/3x}$ (LiPON, solid). We evaluated the charge and discharge characteristics and analyzed the details of the interface reactions.

2. Experiment

$LiFePO_4$ thin films of 0.1 μm thick were deposited to $Pt/Ti/SiO_2/Si$ substrate using Ar-plasma-sputtering equipment, then heated at 500°C under the Ar atmosphere.

For $LiPF_6$-employed battery, $LiFePO_4$ film, 1 M $LiPF_6$ solution in EC and DEC (3:7, v/v), and 0.3 mm-thick Li foil were employed as the cathode, the electrolyte and the anode, respectively. The distance between the cathode and the anode was set to 4 mm.

For LAPP-employed battery, 1.0 μm-thick LAPP was sputtered to the $LiFePO_4$ film using Ar plasma and a LAPP disk as the target. For LiPON-employed battery, 1.2 μm-thick LiPON was sputtered to the $LiFePO_4$ film using N_2 plasma and a Li_3PO_4 disk as the target. Finally, 2 μm-thick Li metal was vapor-deposited.

These batteries were galvanostatically charged and discharged at 20°C.

3. Results and Discussion

XRD analysis showed that the heat treatment at 500°C successfully produced a crystalline $LiFePO_4$ film with weak preferential orientation to the substrate surface.

Figures 1 and 2 show the charge-discharge curves of the $LiFePO_4/LiPF_6$ in solution/Li battery and the $LiFePO_4$/LAPP solid/Li battery, respectively. Both battery potentials are 3.43 V, which is that of the bulk $LiFePO_4$, confirming the electrochemical quality of the $LiFePO_4$ film. The first discharge capacity of $LiFePO_4/LiPF_6$ in solution/Li was estimated to be 5.0 μAh cm^{-2}, ~80% of the theoretical capacity. The capacity decreased and the overpotential increased with the charge-discharge cycle.

To analyze the capacity decline and the overpotential increment, we performed the XPS analysis of the $LiFePO_4$ film in a step-by-step manner during charge-discharge cycle. It demonstrated that partial electrochemical deactivation of Fe atoms and the penetration of fluorine atoms into the surface of the electrode proceed during the charge-discharge cycle. It suggests that the fluorine atoms chemically react with the Fe atoms. This phenomenon might form the resistive layer at the interface.

On the other hand, the first cycle capacity of the $LiFePO_4$/LAPP solid/Li battery was estimated to be 5.7 μAh cm^{-2}, more than 90% of the theoretical capacity. The capacity is comparable to that of the $LiFePO_4/LiPF_6$ in solution/Li battery. The charge and discharge characteristic showed neither the capacity reduction nor the overpotential increase, as clearly seen in Figure 2. The $LiFePO_4$/LiPON solid/Li battery represented the similar cycle characteristic (data not shown). The improvement of the cycle characteristics is explained by the formation of stable interfaces with fluorine-atom-free electrolytes.

4. Conclusion

The XPS analysis revealed that the insertion of fluorine atoms in the electrolyte ($LiPF_6$) to $LiFePO_4$ cathode is a trigger of the capacity decrease and the overpotential increase during charge-discharge cycle. The battery employing the solid electrolyte (LAPP and LiPON) without fluorine atoms revealed interface stability, resulting in excellent cycle characteristics.

References

[1] A. K. Padhi *et al.*, *J. Electrochem. Soc.*, **144** (1997), 1188-1194
[2] S. Poisson *et al.*, *J. Solid State Chem.*, **138** (1998), 32-40

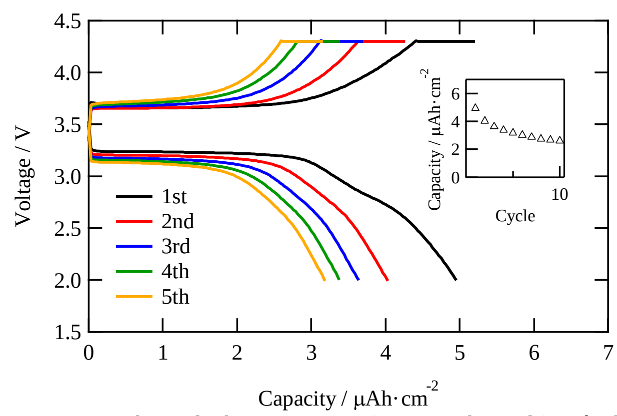

Figure 1. Charge-discharge curves (1st ~ 5th cycle) of the $LiFePO_4/LiPF_6$ in solution/Li battery. Current density was set to 2 μA·cm^{-2}. Inset: Discharge capacity per cycle.

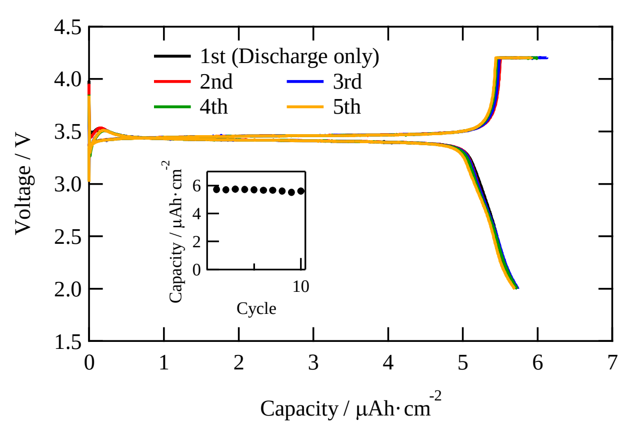

Figure 2. Charge-discharge curves (1st ~ 5th cycle) of the $LiFePO_4$/LAPP solid/Li battery. Current density was set to 1 μA·cm^{-2}. Inset: Discharge capacity per cycle.