

High-temperature Performance of Cathode with DLC Over-coating Layer

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Introduction

Lithium-ion battery has been widely applied for portable electronic devices, and will be good candidate of large-scale energy storage system, such as EV, HEV and stationary battery for renewable solar and wind powers. In these applications, severe performances are demanded; high-rate capability even at low operating temperature, high safety even at high operating temperature. It is well known that the cycle fading is remarkably accelerated at high operating temperature, because of the instability of the organic electrolyte and the electrode materials. Among them, the interface between the charged cathode and the organic electrolyte solution plays an important role. Therefore, many attempts have been carried out for the interfacial modification, especially for the surface of the cathode particles with electrochemical inactive oxide or fluoride coatings.

In this study, DLC (Diamond-like carbon) film, which has both chemical inertness and high electrical resistivity, was applied for the coating material. In addition, the coating process was applied not for the cathode particles but for the coated electrodes. The electrochemical performance of the cathode ($\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ particles as the active material) was studied with the galvanostatic charge-discharge cycling at high temperature and discussed, compared to those of the pristine cathode.

Experimental

$\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode electrodes (the active material loading of 13 mg/cm^2 and the film thickness of $60 \mu\text{m}$) were prepared by usual doctor blade technique. Generally, it is difficult to coat DLC film on a cathode sheet, because its surface has complex geometry and the binder contained in the cathode film has low melting point. Therefore, the DLC film (the effective thickness less than 5 nm) was deposited by a hybrid process of PBIID (Plasma-based ion implantation and deposition), which enables us to obtain uniform and thin coating at low processing temperature. Note that the DLC-layer is deposited not onto individual cathode particles (Fig. 1).

Using the cathode electrodes with DLC over-coating layer, Li-coin cells were constructed with Li anode and $\text{LiPF}_6/\text{EC-DMC}$ electrolyte solution. They were subjected to galvanostatic charge-discharge cycling in the voltage window from 2.5 to 4.5 V at a constant current rate of 0.5 C ($1 \text{ C} = 180 \text{ mAh/g}$). The cells were put in the electric oven in order to keep the operating temperature at 55°C .

Results and discussion

Fig. 2 shows high-temperature cycling performance of DLC-coated cathode in the half cells. The initial charge/discharge profiles were almost insensitive to the DLC film thickness. The initial discharge capacity was approximately 180 mAh/g , and almost independent of the DLC over-coating layer thickness. The discharge capacity of the pristine cathode significantly decreased after 30th cycles, and reached approximately 20 mAh/g after 100th cycles. On the contrary for the DLC-coated cathodes, the discharge capacity degradation was reduced. The

discharge capacity of the cathode with DLC layer of 2 nm suddenly decreased after 50th cycles, and the capacity remained after 100th cycles was about 30 mAh/g . Surprisingly it was found that the discharge capacity of cathode with DLC layer of 5 nm hardly decreased even after 100th cycles. Thus, the high-temperature cycling performance was improved with the optimum thickness of DLC over-coating, which may suppress the solid/liquid interfacial reaction between the cathode particle and the electrolyte solution, and also may not hinder the lithium ionic transfer at the solid/liquid interface.

From these experimental facts, the DLC over-coating film has an influence on the solid/liquid interfacial property of the cathode. Considering that it may protect the cathode film from HF attack, the full cell configuration test is required, especially for the Li-Mn spinel oxide cathode, in which the Mn dissolution from the cathode is remarkable and the Mn deposition onto graphite anode surface causes serious battery deterioration. These experiments are being carried out, and the results will be presented and discussed at the conference.

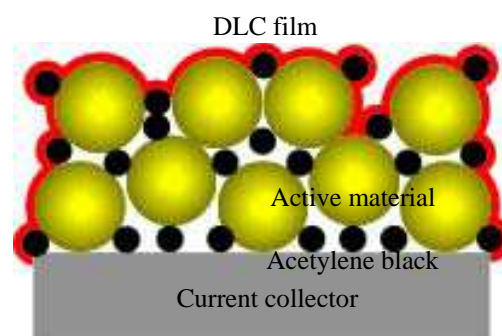


Fig. 1 Schematic diagram of DLC-coated cathode sheet.

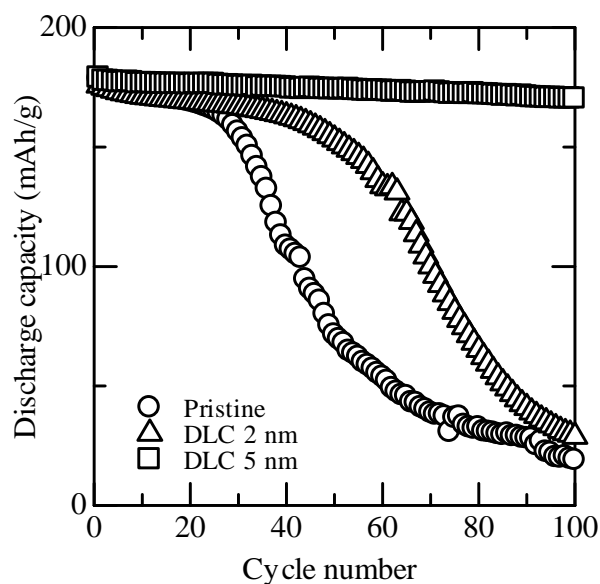


Fig. 2 High-temperature cycling performance of the cathodes with DLC over-coating layer.