

Improving Cyclability of 5 V Cathodes by Electrochemical Surface Modification

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A simple electrochemical procedure is proposed for surface modification of cathode materials. A metal oxide-retaining layer deposited electrochemically on the electroactive material avoids its direct contact with the electrolyte. For 5 V cathodes, which are extremely oxidant at charged state, this action significantly enhances the cyclability. In addition, the own stability of the metal oxide-retaining layer deposited on the cathode surface has a significant effect on the cyclability, which can be enhanced by inducing a mechanical force during the electrodeposition process.

Surface modification is an efficient method to reduce capacity fading of cathode materials in lithium batteries. Capacity fading of 5 V cathode materials is due to the generation of extremely active oxidant during high-voltage performance resulting in electrolyte oxidation. Very recently, surface modification has been applied to improve cyclability of 5 V cathode materials.^{1,2} However, further attention should be paid to this issue.

In the present paper, it is aimed to propose a simple method for surface modification of cathode materials. This method is typically examined for three well-known 5 V cathode materials, namely $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$,¹⁻⁴ $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$,^{5,6} and LiCoPO_4 .^{7,8} The first two belong to the class of $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ 5 V cathode materials, which is the most known class of 5 V cathode materials. LiCoPO_4 is an example of another class of 5 V cathode materials namely olivine-type compounds.

Three known samples were synthesized according to the methods reported in the literatures: $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$,¹ $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$,^{5,6} LiCoPO_4 .^{7,8} The cathode materials synthesized were deposited onto an Al current collector with a 100 W sputtering method to prepare film-based cathodes and examined in a coin-type cell containing the cathode and a lithium foil as both anode and reference electrode. The electrolyte solution was a 1 M LiPF_6 in ethylene carbonate–dimethyl carbonate (EC/DMC) 3:7. Charge–discharge profiles of the cathodes were recorded with a rate $C/2$ at room temperature using a battery cycler to determine the specific capacity at each cycle number.

The first aim of the present study is to show the usefulness (and indeed importance) of metal-oxide coating of 5 V cathode materials to achieve acceptable cyclability. Secondly, it is aimed to use a simple electrochemical procedure instead of current physical techniques such as rf sputtering for the surface modification of the cathode materials.

It has been reported^{9,10} that metal oxides can be incorporated within LiMn_2O_4 film during an electrochemical process. Indeed, this electrochemical process can also be used for the deposition of a thin film of metal oxide on the cathode material. A thin film of Al_2O_3 (ca. 10 nm) was deposited on the cathode surface from an electrolyte solution containing 0.1 M $\text{Al}(\text{NO}_3)_3$ in 1 M LiOH by applying a constant current density (ca. 1 mA/cm^2). Since the metal oxide is very thin, the time required for this process is very

short (<1 s), and this action cannot affect Li intercalating system of the cathode.

Figure 1 compares cyclability of different 5 V cathode mate-

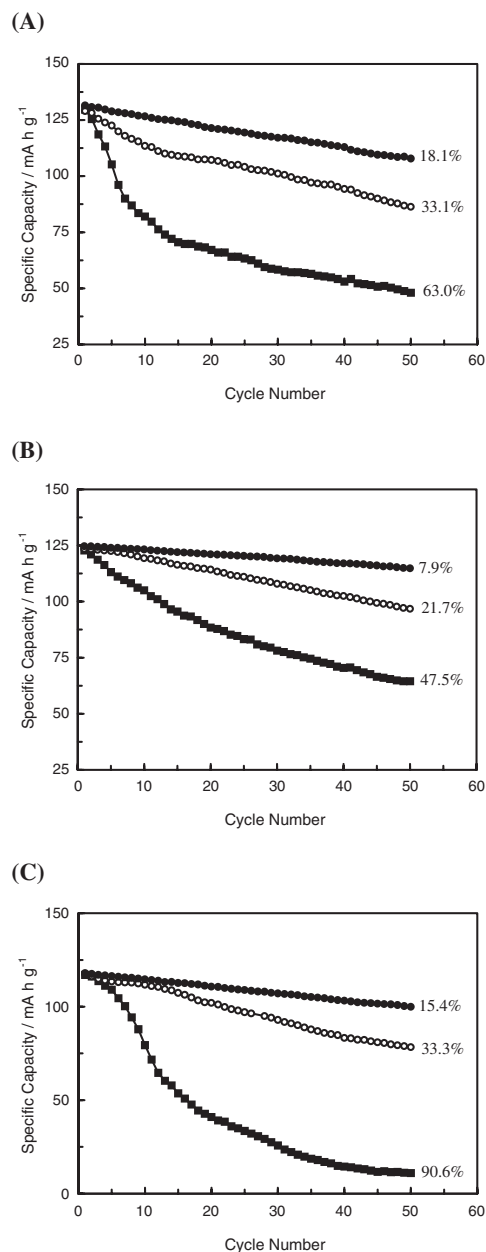


Figure 1. Cyclability data for different cathodes: (A) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, (B) $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$, and (C) LiCoPO_4 . The data correspond to conventional cathodes (■), cathodes coated by Al_2O_3 (○), and cathodes coated by Al_2O_3 under an applied centrifugal force (●).

rials with and without metal oxide-retaining layer. It is obvious that the metal oxide-retaining layer significantly improves cyclability of the 5 V cathodes, avoiding direct contact of active oxidants generated during high-voltage performance.⁶ The results reported in Figure 1 for different 5 V cathodes indicate that the influence of the metal oxide-retaining layer is similar for all cases. This satisfactorily provides a strong evidence for usefulness of the procedure proposed for improving cyclability of 5 V cathode materials.

In addition to simplicity of the electrochemical procedure proposed for the surface modification of cathode materials, it has another advantage, i.e. flexibility for specified purposes by controlling electrodeposition process. For instance, inducing a mechanical force can improve the electrodeposition process. In a series of papers,^{11–15} it has been demonstrated that electrodeposition under centrifugal forces can improve stability and properties of materials deposited. For instance, transition metal hexacyanoferrate films deposited in the presence of gravitational¹³ or magnetic¹⁶ fields have enhanced stabilities. It is of great importance for the surface modification of cathode materials, since the stability of the own metal oxide-retaining layer deposited on the cathode surface is proportional to the cathode cyclability. On the other hand, it has been reported that electrodeposition under centrifugal forces leads to higher electrical conductivity of materials deposited owing to lower interfacial resistance of the particles.¹⁵ It is also of interest for the surface modification of cathode materials, since metal oxides are usually more resistive than electroactive material and also there is a significant interfacial resistance between the electroactive film and the metal oxide layer.

To gain this possibility, the electrochemical deposition of the metal oxide layer was performed in the presence of an applied centrifugal force. The detailed experimental procedure for this action has been reported in the literature.^{11,12} A typical centrifugal force of 210 g was used in the present study. The cyclability data of the 5 V cathode materials coated with a metal oxide layer under applied centrifugal force are also illustrated in Figure 1. It is obvious that electrodeposition of the metal oxide-retaining layer under centrifugal force is an efficient approach to additionally improve cyclability of the 5 V cathode

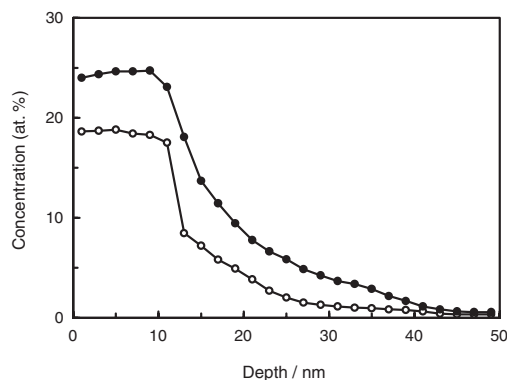


Figure 2. Depth analysis of the Al_2O_3 layer deposited without (○) and with centrifugal force (●) on the $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (as a typical cathode).

materials. It also indicates the importance of interfacial resistance for the surface modification of cathodes.

To understand the structure of the metal oxide layer deposited onto the cathode surface, it is useful to investigate its depth profile. Depth profiling by sequential Ar^+ -ion sputtering and XPS analysis is a common way to determine surface layer thickness and to measure elemental concentrations as a function of depth. For this purpose, depth profile data were obtained by Ar ion-beam sputtering (4 keV). Figure 2 displays depth profiles of the Al_2O_3 layers deposited on the $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode surface. It is obvious that aluminum also exists, out of the 10-nm thickness of the own film, within the cathode material. It might be attributed to the fact that electrolyte solution of the plating bath fills empty pores within the cathode material, and Al_2O_3 can be formed there.

The amount of aluminum is higher throughout the depth profile for the Al_2O_3 layer electrodeposited under centrifugal force. High amount of aluminum at the own Al_2O_3 layer is due to a denser film with lesser impurities deposited under the later condition. It has been described¹⁶ that inducing a mechanical force during electrodeposition process increases the film density and reduces the amount of impurities incorporated within the electroactive material from the electrolyte. Moreover, the mechanical force induced compelled the depositing particle to diffuse inside the cathode material.

In conclusion, the experimental procedure proposed for the surface modification cathode materials is an efficient method for improving their cyclability. Such improvement leads 5 V cathode materials toward practical performances. As stated, an important advantage of the procedure is its flexibility for controlling the surface modification. Therefore, further investigations in this direction may lead to peculiar results.

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