

Improvement of Electrochemical Properties of Surface Modified $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ Cathode Material for Lithium Secondary Battery

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In this study, nano-crystallized LiCoO_2 was coated on the surface of $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ powders via sol-gel method. The influence of coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ about electrochemical behavior was discussed. The surface morphology characterization was achieved by transmission electron microscopy (TEM). Nano-crystallized LiCoO_2 was clearly observed on the surfaces of $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$. It showed that LiCoO_2 coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ cathode exhibited distinct surface morphology. Cyclic voltammetry (2.8–4.6 V) shows that the characteristic voltage transition on cycling exhibited by the bare compound are suppressed by 5 wt% LiCoO_2 coating. This behavior implies that LiCoO_2 prevent structural change of $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ or reaction with electrolyte on cycling. In addition, LiCoO_2 coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ compound shows highly improved area-specific impedance (ASI), one of the important battery performances. From the correlation between these characteristics of bare and coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$, the role of LiCoO_2 coating played on the electrochemical performance of $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ was probed.

Key Words : Cathode material, $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$, Sol-gel coating, LiCoO_2 , Lithium ion battery

Introduction

Li-ion batteries with high energy density and power capability has become an important power sources for portable electronic devices, such as cellular phones and computers and, more recently, hybrid electric vehicle (HEV).¹ Most of commercialized Li-ion batteries use LiCoO_2 as cathode material due to its ease of production, stable electrochemical cycling, and acceptable specific capacity.^{2,3} The relatively high cost of cobalt and the lure of large capacity have, however, lead to the study of other possible alternatives.

Recently, we found a new layered cathode material of $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$.⁴ This compound can be classified as $\alpha\text{-NaFeO}_2$ structure type and delivers an initial discharge capacity of 165 and 190 mAh/g at 2.8–4.5 and 2.8–4.8 V. The discharge capacities at 2.8–4.5 and 2.8–4.8 V decrease with cycling and remained at 142 and 102 mAh/g after 20 cycles, which are 87 and 55 % of initial capacities, respectively.⁴

Recently, it is testified that surface chemistry and surface reactions of cathode material strongly affect its electrochemical performance.⁵ Surface modification by thin layer coatings of cathode materials with metal oxides (Al_2O_3 , ZrO_2 , ZnO , etc.) and metal phosphate (AlPO_4) are substantially effective approaches for enhancing the electrochemical performances.^{6–12} Therefore, to retaining discharge capacity and preventing reaction with electrolyte, surface modification of particle has been adapted in this work. These studies reveal that the surface modification of the cathode materials by coating thin layers of LiCoO_2 increases discharging capacity and decreases area-specific impedance (ASI). LiCoO_2 is chosen for coating of these particles; because LiCoO_2 has excellent cycleability, good stability

with electrolyte and same structure with $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ material.

Experimental

$\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ (calcined 1000 °C for 10 hr) was made by simple sol-gel method according to a preparation procedure previously reported.⁴ For the 5 wt % coating of LiCoO_2 on to the particles of the cathode material, the procedure adopted for coating is as follows. Cobalt acetate tetrahydrate [$\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$] and Lithium acetate dihydrate [$\text{Li}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] was dissolved in distilled water and stirred continuously at 80 °C for 4 h until a transparent sol was obtained. Then $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ was added into this solution during stirring at 80 °C. The amount of LiCoO_2 in the solution was 5 wt% of $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ powders.

To remove water, the solution was heated at 100 °C for 6 hrs, accompanied by vigorous mechanical stirring (1000 rpm). When the mixture had become thick slurry, it was transferred to oven for drying at 140 °C for 12 hr. The dried compound was ground to ensure proper mixing. The coated black powder was first heated at 500 °C for 5 h in air, and it was calcined at 800 °C for 12 h in air to obtain LiCoO_2 coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ powder.

The surface morphology of the coated powder was observed with transition electron microscope (TEM).

To prepare the positive electrode, 72% LiCoO_2 coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ powder., 10% SFG6 graphite, 10% acetylene black, *N*-methyl-2-pyrrolidone and 8% PVdF (Kureha KF100) binder were added in crucible. After two hours of grinding, viscous slurry was coated on an aluminum

foil using a doctor blade and a film of uniform thickness was obtained. The film was then dried 60 °C for 6 h and 120 °C for 6 h in vacuum oven. The thickness of cathode film was about 40 μm . The swage-lock cell was assembled in a glove box using the above cathode film, lithium, porous polyethylene film and 1.2 M LiPF_6 solution in 1:1:3 volume ratio of ethylene carbonate (EC)/poly carbonate (PC)/dimethyl carbonate (DMC). Lithium metal foil was used as both the counter and reference electrode. After swage-lock cell assembly, the test cells were charged to 4.5 versus Li/Li^+ with a current density of 0.5C (170 mA g^{-1} was assumed to be 1C rate) and then discharged to 2.8 V with the same current density.

Results

Surface morphology characterization. The morphology of bare $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ was observed with a scanning electron microscope (SEM) as shown in Figure 1(a).⁴ The average particle size of the samples lies in the range 200–600 nm. The HRTEM (high-resolution TEM) image of $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ is presented in Figure 1(b).⁴ The (3 0 0) lattice can be seen in the HRTEM image. A schematic drawing of the Li, Ni, Co and Mn is given in Figure 1. The image of the atoms in (0 0 3) planes can be seen clearly. The image of the atoms in the (0 0 3) plane corresponds to an array of Ni, Co and Mn atoms, whereas the relatively light Li atoms are not seen. The 4.7 Å (d_{003}) layer distance obtained from HRTEM is in good agreement with that (4.74 Å) calculated from XRD measurements.⁴ Figure 2 shows the TEM photograph of 5 wt.% LiCoO_2 coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ oxides. The coating materials can

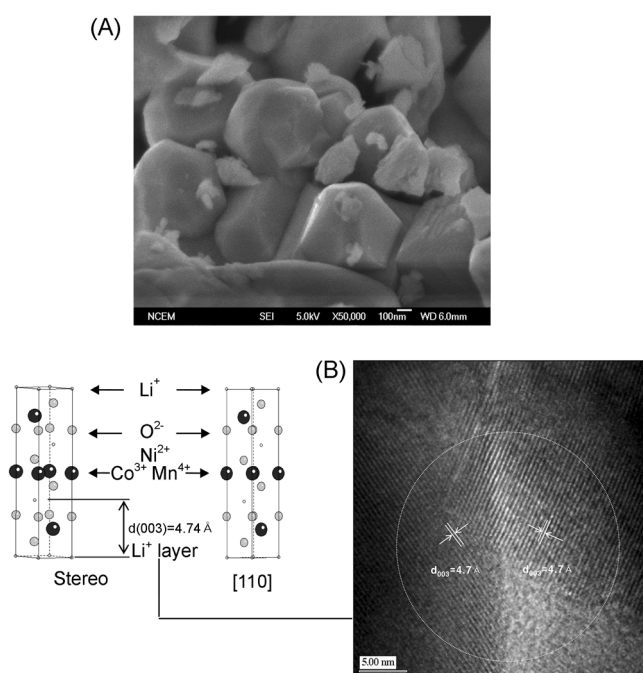


Figure 1. (a) SEM image and (b) TEM image of $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ compound prepared by simple sol-gel method calcined at 1000 °C for 10 h.⁴

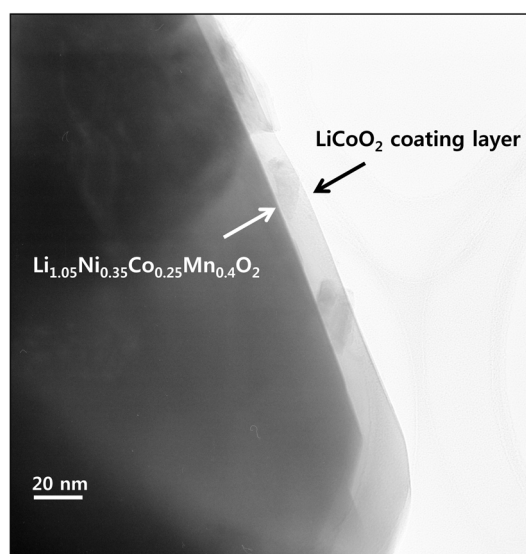


Figure 2. TEM image of 5.0 wt.% LiCoO_2 coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ compound prepared.

be seen to be about 20 nm in size and form compact, pore-free, uniform films on the cathode material.

Electrochemical behavior. Cyclic voltammetry is a complementary and well-suited technique to evaluate the cathodic performance and electrode kinetics of oxide materials. The cyclic voltammograms (CV) of bare and LiCoO_2 coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ cathode were recorded

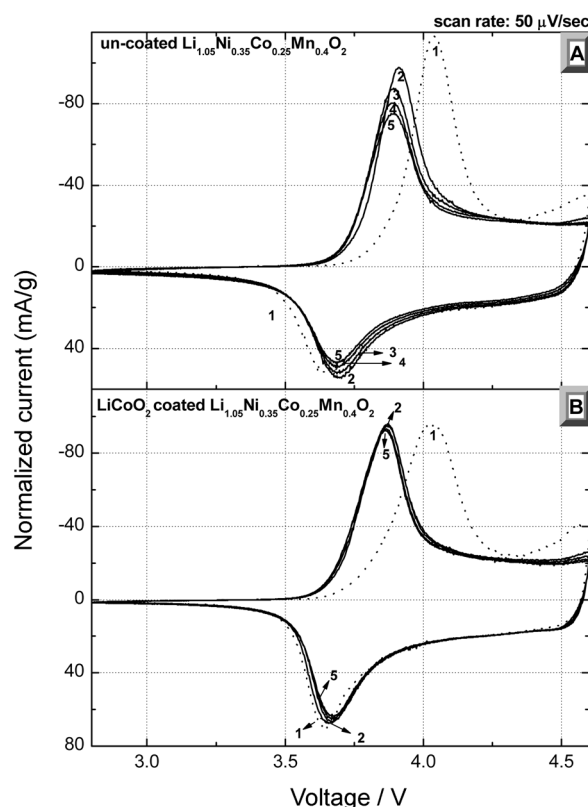


Figure 3. Cyclic voltammetry of the bare and 5.0 wt.% LiCoO_2 oxide coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ cell between 2.8 and 4.6 V at a scan rate of 50 $\mu\text{V s}^{-1}$.

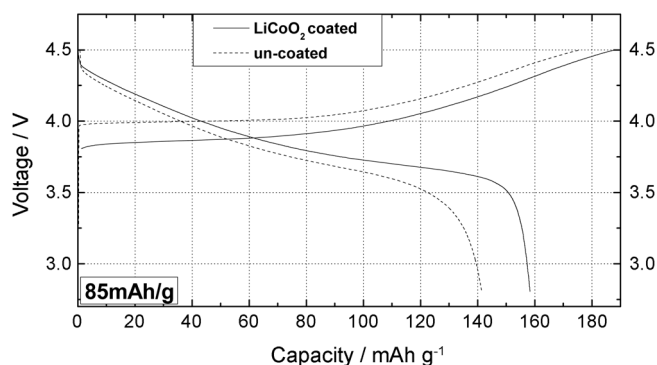


Figure 4. First charge-discharge curves of (a) bare and (b) LiCoO_2 coated the $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ samples at a current density of 0.5C (85 mA/g).

for the cells at room temperature with metallic lithium as the counter and reference electrodes in the range of 2.8–4.6 V. The CV at a scan rate of 0.05 mV/s up to 5 cycles is shown in Figure 3. The importance feature is the difference between the first and subsequent cycles. In the case of bare $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ cathode, the first anodic scan has two oxidation peaks, a major peak centered at 4.04 V and a minor one at 4.6 V corresponding to irreversible capacity observed in the first charge profile. The peak 4.04 V in the first anodic scanning was shifted by 0.13 V to lower voltage. On the subsequent cycle, the oxidation and reduction processes show only one major peak centered 3.89 and 3.69 V, respectively. The effect of LiCoO_2 coating is clearly revealed in the CV presented in Figure 3(b). The first anodic scan has two oxidation peaks, a major peak centered at 4.02 V and a minor one at 4.56 V is slightly lower than to that of the bare compound. In addition, capacity fading was dramatically depressed, as reflected in a decrease in the in the relative intensities of main redox peaks. Possibly, this behavior implies that LiCoO_2 at the surface layer prevent structural change of $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ or reaction with electrolyte on cycling.

Typical initial charge and discharge curves of cathodes for the bare and the LiCoO_2 coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ cell that contains a 1.2 M $\text{LiPF}_6\text{-EC/PC/DMC}(1:1:3)$ at a various current density are shown in Figure 4. These curves show that the cathode polarization for both charge and discharge is reduced substantially by LiCoO_2 coating. The discharge capacity and irreversible capacity also improved by the coating. LiCoO_2 coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ cell has a very smooth and monotonous voltage profile, similar to the voltage profiles of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cell reported by other researchers.^{12,13} LiCoO_2 coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ compound in the voltage range 2.8–4.5 V has a relatively large initial discharge capacity of 159 mAh/g with an irreversible capacity loss of 29 mAh/g. On the other hand, Bare $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ compound in the voltage range 2.8–4.5 V give a discharge capacity of 141 mAh/g with an irreversible capacity loss of 34 mAh/g. These results suggest that the irreversible capacity is improved by coating. The increased discharge capacity of electrode is may be

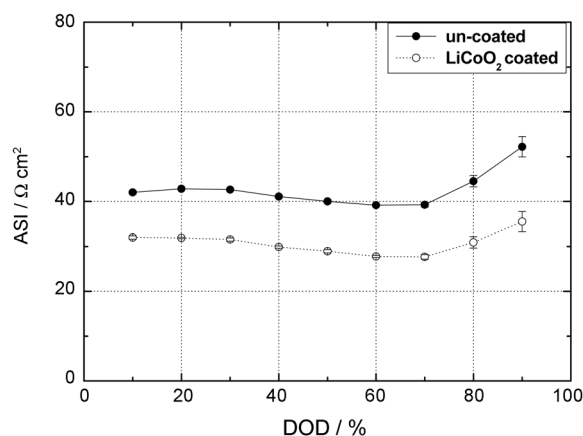


Figure 5. Area specific impedance (ASI) of bare and LiCoO_2 coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ as a function of state of discharge (DOD).

attributed to the presence of nano sized LiCoO_2 on surface of the particles. This coated layer minimized cell polarization due to have high electronic conductivity. Minimized cell polarization can be observed cyclic voltammetry in Figure 3 and charge-discharge curve in Figure 4.

To understand the superior electrochemical property of LiCoO_2 coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ cell, the area specific impedance (ASI) was measured as a function of the depth of discharge (DOD). During lithium insertion/extraction, a combination of electrode kinetics, ohmic drop and Li^+ ion diffusion cause a change in the overall cell voltage.¹⁴ The area specific impedance (ASI) was determined by $(A \cdot \Delta V)/I$,¹⁵ where A is the cross-sectional area of the electrode (1 cm^2), ΔV is the voltage variation during current interruption for 60s at each DOD, and I is a constant current density of 0.1 mA/cm^2 (The thickness of cathode film was about $40 \mu\text{m}$). As can be seen in Figure 5, the LiCoO_2 coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ cathode ($30\text{--}35 \Omega \text{ cm}^2$) exhibits much lower ASI values than that for un-coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ cathode ($40\text{--}50 \Omega \text{ cm}^2$). Again, the improved ASI characteristics could be ascribed to the reduced interfacial impedance between cathode and electrolyte, which confirms that LiCoO_2 coated layer on the

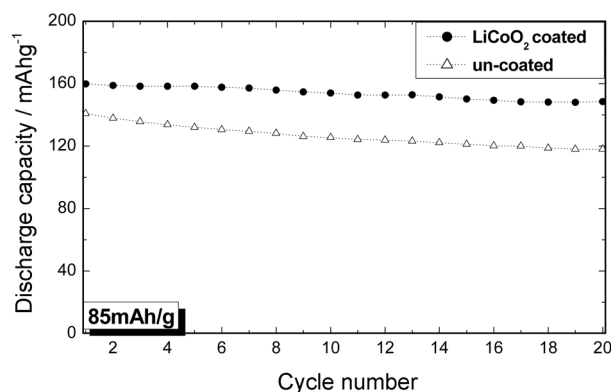


Figure 6. Cycle performance of bare and LiCoO_2 coated the $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ samples at a constant current density of 85 mA/g (0.5 C).

surface of the $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ works as interfacial stabilizer. However, the mechanisms such as cation mixing and interactions with the electrolyte involved with the LiCoO_2 coating need to be identified.

The cycle performance of cells with bare $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ and 5 wt.% LiCoO_2 coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ cathode material is presented in Figure 6. as a function of cycle number for a cell operated at 85 mA/g when cycled between 2.8–4.5 V. For the bare electrode, the discharge capacity decreases gradually with cycle number and reaches a 118 mAh/g at 2.8–4.5 at the end of 20 cycles. Thus, there is about 16% decrease in capacity. On the other hand, the decrease in capacity of LiCoO_2 coated electrode is small compare with that of bare material. At the end of 20 cycles, the discharge capacity value is 148 mAh/g at 2.8–4.5, which accounts to only about 7% decrease. This indicates that nano-sized LiCoO_2 particles coating is not effective increasing discharge capacity but increasing cycle performance.

Conclusions

The cycling behavior of $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ material is improved without sacrificing discharge capacity by coating 5 wt.% LiCoO_2 particles on the surfaces. In addition, the cathode polarization for both charge and discharge is reduced substantially by LiCoO_2 coating. The improved electrochemical performance of LiCoO_2 coated

$\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ electrode is partly attributed to the minimization of cell polarization and decrease ASI value that is caused by the uniform LiCoO_2 coating.

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