

Short communication

Characterization of LiCoO₂ coated Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O₂ cathode material for lithium secondary cells

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Abstract

In this study, nano-crystalline LiCoO₂ was coated onto the surface of Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O₂ powders via sol–gel method. The influence of the coating on the electrochemical behavior of Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O₂ is discussed. The surface morphology was characterized by transmission electron microscopy (TEM). Nano-crystallized LiCoO₂ was clearly observed on the surfaces of Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O₂. The phase and structural changes of the cathode materials before and after coating were revealed by X-ray diffraction spectroscopy (XRD). It was found that LiCoO₂ coated Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O₂ cathode material exhibited distinct surface morphology and lattice constants. Cyclic voltammetry (2.8–4.6 V versus Li/Li⁺) shows that the characteristic voltage transitions on cycling exhibited by the uncoated material are suppressed by the 7 wt.% LiCoO₂ coating. This behavior implies that LiCoO₂ inhibits structural change of Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O₂ or reaction with the electrolyte on cycling. In addition, the LiCoO₂ coating on Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O₂ significantly improves the rate capability over the range 0.1–4.0C. Comparative data for the coated and uncoated materials are presented and discussed.

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Keywords: Cathode material; Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O₂; Sol–gel coating; LiCoO₂; Lithium ion battery

1. Introduction

At present, the most widely used commercial cathode material for lithium ion cells is LiCoO₂ due to its ease of production, stable electrochemical cycling, and acceptable specific capacity [1–3]. The relatively high cost of cobalt and the lure of larger specific capacity have, however, led to the study of possible alternatives.

Recently, we synthesized a new layered cathode material of Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O₂ [4]. This compound has the α-NaFeO₂ structure and delivers initial discharge capacities of 165 and 190 mAh g⁻¹ at 2.8–4.5 and 2.8–4.8 V, respectively. The discharge capacities at 2.8–4.5 and 2.8–4.8 V decreased with cycling and remained at 142 and 102 mAh g⁻¹ after 20 cycles, which are 87 and 55% of the initial capacities, respectively [4].

It has been reported that the surface chemistry and surface reactions of cathode materials strongly affect their electrochem-

ical performance [5]. Surface modification (or coating) by Ag [6], Al₂O₃ [7], AlPO₄ [8], SnO₂ [9], MgO [10] and other metal oxides [11] has been widely investigated. Therefore, in an attempt to retain the initial discharge capacity and prevent reaction with the electrolyte, surface coating of the active material has been utilized in this work. These studies reveal that the surface modification of the cathode material by coating with thin layers of LiCoO₂ increases the rate capability, and hence the discharge capacity at high rates. LiCoO₂ is chosen for coating of these particles because LiCoO₂ has excellent cycleability, good stability in contact with electrolyte and the same structure as Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O₂.

2. Experimental equipment and procedures

Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O₂ (calcined at 1000 °C for 10 h) was made by a simple sol–gel method according to a preparation procedure previously reported [4]. Based on our previous experience with active material coatings, we chose 7 wt.% for this investigation. For a 7 wt.% coating of LiCoO₂ on the particles of the cathode material, the procedure adopted for

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coating is as follows: 0.390 g of cobalt acetate tetrahydrate $[\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$ and 0.160 g of lithium acetate dihydrate $[\text{Li}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$ were dissolved in distilled water and stirred continuously at 80°C for 4 h until a transparent sol was obtained. Then about 2 g of $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ were added to this solution while stirring at 80°C . To remove water, the solution was heated at 100°C for 3 h. When the mixture had become a thick slurry, it was transferred to an oven for drying at 140°C for 12 h. The dried material was ground with a mortar and pestle. The coated black powder was first heated at 500°C for 5 h in air, and then 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.

X-ray diffraction patterns for the cathode materials were obtained using a Siemens D-5000 diffractometer in the 2θ range from 10° to 70° with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The lattice parameters were determined by whole pattern fitting. The surface morphology of the coated powder was observed with a transmission 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 placed in a mortar. After 2 h of mixing and grinding, the viscous slurry was coated onto 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 a vacuum oven. The thickness of the cathode film was about $40 \mu\text{m}$. A Swagelok cell was assembled in a glove box using the above cathode film, lithium metal foil, porous polyethylene film and 1.2 M LiPF_6 solution having a 1:1:3 volume ratio of ethylene carbonate (EC)/propylene carbonate (PC)/dimethyl carbonate (DMC). Lithium metal foil was used as both the counter and reference electrode. After assembly, the test cells were charged to 4.5 V versus Li/Li^+ at a current density of $0.1C$ (170 mA g^{-1} was assumed to be $1C$ rate) and then discharged to 2.8 V at the same current density. The rate performance was measured by varying only the discharge rate, using the values 0.1, 0.2, 0.5, 1.0, 2.0 and $4.0C$.

3. Results and discussion

3.1. Physical characterization of

$\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ coated with LiCoO_2

The XRD patterns of bare (uncoated) and LiCoO_2 coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ are presented in Fig. 1. It is observed that the LiCoO_2 coating does not change the structure of $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$. All the samples have a well-defined $\alpha\text{-NaFeO}_2$ structure with no minor phases. Distinct splitting of the $[(108), (110)]$ and $[(006), (102)]$ peaks is observed in these patterns. This indicates that the metal and oxygen atoms are perfectly layered before and after surface modification [12]. The least squares fitted lattice parameters, calculated from the d spacing and Miller indices are given in Table 1. It is evident that the lattice constant a for the coated material decreased, and the lattice parameter c was smaller for coated material than for bare material, which suggests that the phase on the surface of the

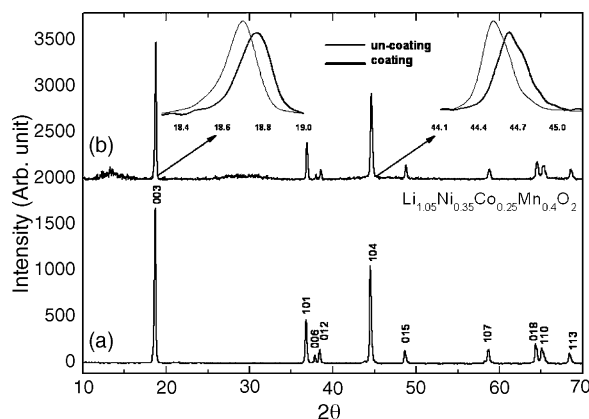


Fig. 1. XRD patterns of (a) bare and (b) LiCoO_2 coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$.

Table 1

Hexagonal lattice parameters for bare and LiCoO_2 coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$

X (wt.%) LiCoO_2 coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$	a (\AA)	c (\AA)	c/a
$x = 0$: bare	2.8670 ± 0.0004	14.279 ± 0.003	4.98
$x = 0.07$	2.8587 ± 0.007	14.245 ± 0.006	4.98

powder is LiCoO_2 crystal formed on the surface of the coated particles. The coated LiCoO_2 was synthesized at a low temperature (800°C for 12 h) compared to $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ (1000°C for 10 h). Therefore, the lattice parameter of the surface material on the powder will be smaller.

Fig. 2 shows the TEM photograph of 7 wt.% LiCoO_2 coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$. The coated material can be seen to be about 10–30 nm in size with a compact, pore-free, uniform film on the surface.

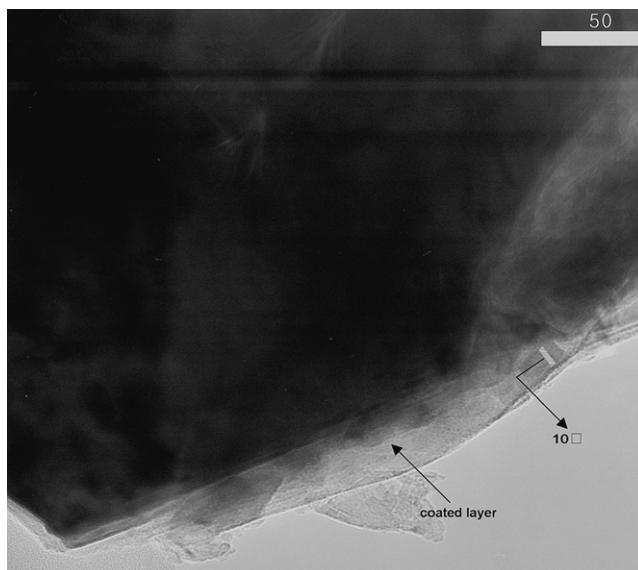


Fig. 2. TEM image of 7.0 wt.% LiCoO_2 coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$.

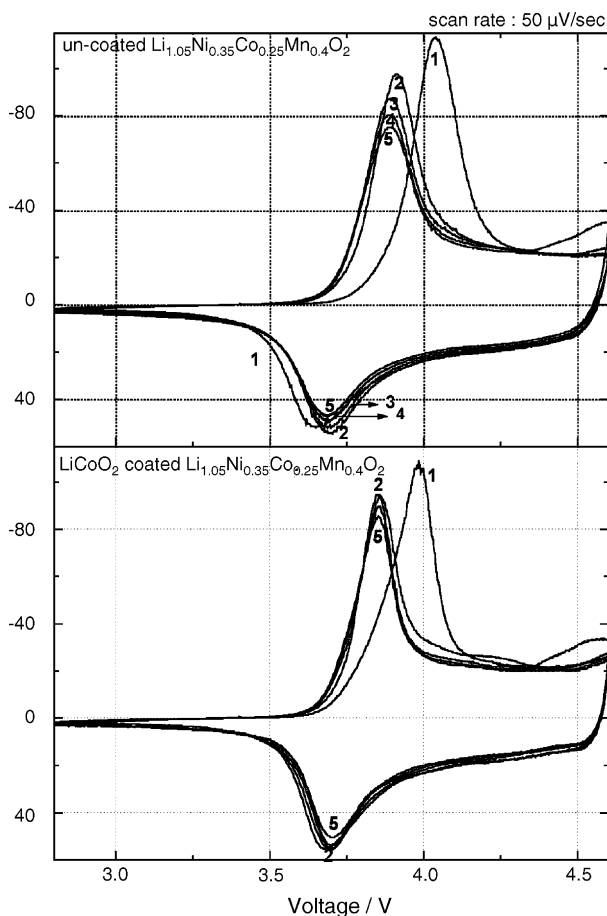


Fig. 3. Cyclic voltammetry of the bare and 7.0 wt.% LiCoO_2 coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ material between 2.8 and 4.6 V at a scan rate of $50 \mu\text{V s}^{-1}$.

3.2. Electrochemical behavior

Cyclic voltammetry is a technique well suited for evaluation of the electrochemical 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 material were recorded for the cells at room temperature with metallic lithium as the counter and reference electrodes. The cells were cycled in the range of 2.8–4.6 V versus Li/Li^+ . The CVs at a scan rate of 0.05 mV s^{-1} up to five cycles are shown in Fig. 3. An important feature is the difference between the first and subsequent cycles. In the case of the 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 at 4.04 V in the first anodic scan was shifted lower by 0.13 V in subsequent cycles. On the subsequent cycles, the oxidation and reduction processes show only one major peak centered 3.89 and 3.69 V, respectively. The effect of the LiCoO_2 coating is clearly revealed in the CV presented in Fig. 3(b). The first anodic scan has two oxidation peaks, a major peak centered at 3.96 V and a minor one at 4.5 V, slightly lower than to that of the bare material. In addition, capacity fading was dramatically depressed, as reflected by the decrease in the rel-

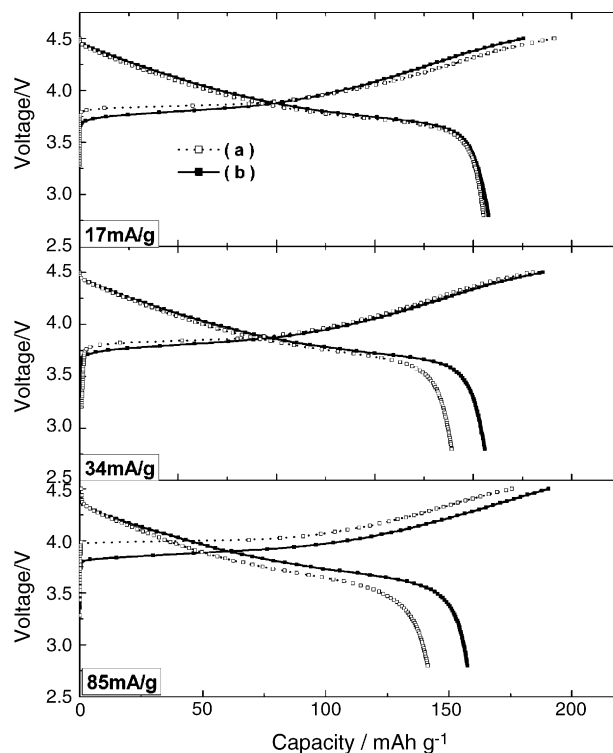


Fig. 4. First charge–discharge curves of (a) bare and (b) LiCoO_2 coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ samples at specific currents of $0.1C$ (17 mA g^{-1}), $0.2C$ (34 mA g^{-1}) and $0.5C$ (85 mA g^{-1}).

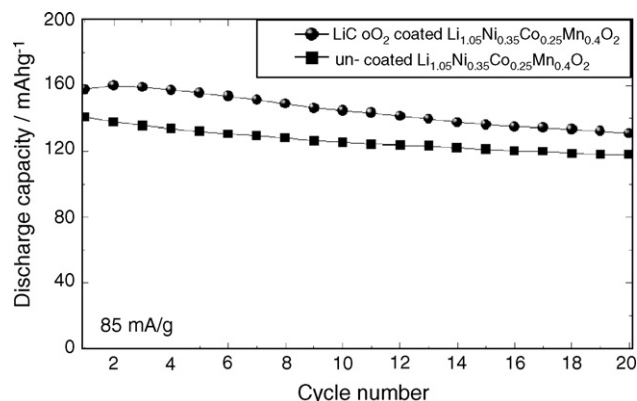
ative intensities of main redox peaks. Possibly this behavior implies that the LiCoO_2 surface layer prevents structural change of $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ or reaction with the electrolyte on cycling.

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 $1.2 \text{ M LiPF}_6\text{-EC/PC/DMC}$ (1:1:3) electrolyte at various current densities are shown in Fig. 4. The weight of the coating has been included in the calculations of specific currents and specific capacities. These curves show that the polarization for both charge and discharge is reduced substantially by the LiCoO_2 coating. The discharge capacity and irreversible capacity are also improved by the coating. The 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 monotonic voltage profile, similar to the voltage profiles of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cells reported by other researchers [13,14]. The LiCoO_2 coated $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ in the voltage range 2.8–4.5 V has a relatively large initial discharge capacity of 166 mAh g^{-1} with an irreversible capacity loss of 14 mAh g^{-1} . On the other hand, the bare $\text{Li}_{1.05}\text{Ni}_{0.35}\text{Co}_{0.25}\text{Mn}_{0.4}\text{O}_2$ in the voltage range 2.8–4.5 V shows a discharge capacity of 164 mAh g^{-1} with an irreversible capacity loss of 28 mAh g^{-1} . These results suggest that the irreversible capacity is improved by the LiCoO_2 coating. The exact mechanism of the reduction in irreversible capacity by means of the coating will be published after further work. Our current view is that the continuous coating of LiCoO_2 serves to protect the active material from the electrolyte, resulting in a decreased irreversible capacity loss.

Table 2

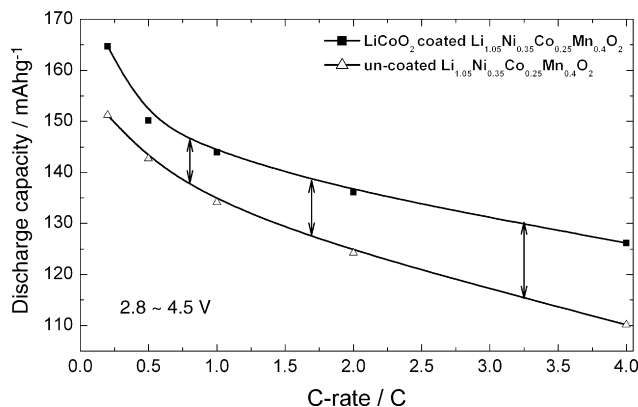
Comparison of rate capabilities bare and LiCoO₂ coated Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O₂ cathode cycled between 2.8 and 4.5 V

C rate	Bare		LiCoO ₂ coated Li _{1.05} Ni _{0.35} Co _{0.25} Mn _{0.4} O ₂	
	Discharge capacity (mAh g ⁻¹)	Ratio (%)	Discharge capacity (mAh g ⁻¹)	Ratio (%)
0.1	164.1	100.0	166.1	100.0
0.2	151.2	92.2	164.66	99.1
0.5	142.7	87.2	150.2	90.4
1	134.2	82.0	144.0	86.7
2	124.2	75.6	136.1	81.9
4	110.2	67.1	126.2	76.0

Fig. 5. Cycling stability of bare and LiCoO₂ coated Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O₂ samples at a constant specific current of 85 mA g⁻¹ (0.5C).

The cycling performance of cells with bare Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O₂ and 7 wt.% LiCoO₂ coated Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O₂ cathode material is presented in Fig. 5 as a function of cycle number for cells operated at 85 mA g⁻¹ when cycled between 2.8 and 4.5 V. For the bare electrode material, the discharge capacity decreases gradually with cycle number and reaches a 118 mAh g⁻¹ at the end of 20 cycles. Thus, there is about 16% decrease in specific capacity. The decrease in capacity of the LiCoO₂ coated electrode material is similar to that of the bare material. At the end of 20 cycles, the discharge capacity value is 130 mAh g⁻¹, which amounts to only about 17% decrease. This indicates that the LiCoO₂ coating is not effective for decreasing the capacity fade rate but is effective for increasing the discharge capacity, especially at high rates. This suggests that the capacity fade mechanism may be predominantly associated with subtle structural changes in the bulk of the active material, such as cation mixing, and not direct interactions with the electrolyte. The increased discharge capacity of the electrode (at the higher rates) may be attributed to the presence of nano-sized LiCoO₂ on the surface of the particles. This coating may minimize cell polarization due to high electronic conductivity and improved intercalation kinetics. Reduced cell polarization can be observed in the cyclic voltammetry of Fig. 3 and the charge/discharge curves in Fig. 4.

Fig. 6 shows the discharge capacity of bare and LiCoO₂ coated Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O₂ cathodes at various current densities and between the potential limits 2.8–4.5 V. The cells were charged using a current density of 17 mA g⁻¹ (0.1C rate) before each discharge test. The discharge capac-

Fig. 6. Rate capability of bare and LiCoO₂ coated Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O₂ cycled between 2.8 and 4.5 V. The cell was charged using a specific current of 17 mA g⁻¹ (0.1C rate) before each discharge test.

ity of the uncoated Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O₂ decreases with increasing current density when cycled between 2.8 and 4.5 V and reaches 82 and 67% at 170 mA g⁻¹ (1C rate) and 680 mA g⁻¹ (4C rate) compared with the specific capacity of 151 mAh g⁻¹ at 17 mA g⁻¹ (0.1C rate), respectively. On the other hand, the discharge capacity of the LiCoO₂ coated Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O₂ cathode material decreases to a smaller extent with increasing current density when cycled between 2.8 and 4.5 V and reaches 87 and 76% at 170 mA g⁻¹ (1C rate) and 680 mA g⁻¹ (4C rate) compared with the capacity of 165 mAh g⁻¹ at 17 mA g⁻¹ (0.1C rate), respectively. Discharge capacities of bare and LiCoO₂ coated Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O₂ obtained at various current rates are summarized in Table 2. This behavior shows that the rate capability of Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O₂, was significantly improved by the LiCoO₂ coating. The enhanced rate capability may be attributed to improvement in the electrical contact between the cathode particles and minimization of the interfacial impedance (associated with improved intercalation kinetics) that is provided by the uniform LiCoO₂ coating.

4. Conclusions

The rate capability and the specific capacity at the higher rates for the Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O₂ cathode material are improved by coating with 7 wt.% LiCoO₂. The overvoltage for both charge and discharge is reduced substantially by the LiCoO₂ coating. The enhanced rate capability may be attributed

to improvement in the electrical contact between the cathode particles and minimization of the interfacial impedance (associated with improved intercalation kinetics) that is provided by the uniform LiCoO₂ coating. Consequently the LiCoO₂ coating on the Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O₂ cathode allows fabrication of high-rate Li-ion cells based on Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O₂.

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References

- [1] K. Nagaura, Tozawa, Prog. Batteries Sol. Cells 9 (1990) 209.
- [2] K. Mizushima, T.P.C. Jones, P.J. Wiseman, J.B. Goodenough, Mater. Res. Bull. 15 (1980) 783.
- [3] D.D. MacNeil, Z. Lu, J.R. Dahn, J. Electrochem. Soc. 149 (2002) A1332.
- [4] J.-T. Son, E.J. Cairns, Electrochem. Solid-State Lett. 9 (2006) A27–A30.
- [5] G.G. Amatucci, J.M. Tarascon, J.C. Klein, Solid State Ionics 83 (1996) 167.
- [6] J.T. Son, G.S. Park, H.T. Chung, H.G. Kim, J. Power Sources 126 (2004) 182.
- [7] J. Cho, Y.J. Kim, B. Park, Chem. Mater. 12 (2000) 3788.
- [8] J. Cho, J.-G. Lee, B. Kim, B. Park, Chem. Mater. 15 (2003) 3190.
- [9] J. Cho, C.-S. Kim, S.-I. Yoo, J. Electrochem. Solid-State Lett. 3 (2000) 362.
- [10] Z. Wang, X. Huang, L. Chen, J. Electrochem. Soc. 150 (2003) A199.
- [11] Y.J. Kim, J. Cho, T.-J. Kim, B. Park, J. Electrochem. Soc. 150 (2003) A1723.
- [12] G.T.K. Fey, J.G. Chen, V. Subramanian, T. Osaka, J. Power Sources 384 (2002) 112.
- [13] T. Ohzuku, Y. Makihara, Chem. Lett. (2001) 642.
- [14] S.H. Na, H.S. Kim, S.I. Moon, Solid State Ionics 176 (2005) 313.