

Short communication

Enhanced electrochemical properties of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material by coating with LiAlO_2 nanoparticles

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Abstract

Surface coating of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ with LiAlO_2 nanoparticles has been attempted to improve the electrochemical properties of these materials as cathodes in lithium-ion batteries. The coating is undertaken by a sol–gel method that uses $\text{C}_9\text{H}_{21}\text{O}_3\text{Al}$, $\text{LiOH}\cdot\text{H}_2\text{O}$ and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. X-ray diffraction analysis shows that the LiAlO_2 is composed of both α - and β - LiAlO_2 phases. The average size of the particles is about 15 nm. The structure of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is not affected by the LiAlO_2 nanoparticle coating. A 3 wt.% LiAlO_2 -coating increases the specific discharge capacity, provides excellent cycling performance (i.e. 96.7% capacity retention after 50 cycles at the 1 C rate) and improves the rate capability. By contrast, heavier coatings (5 wt.%) on $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ dramatically decrease both the discharge capacity and the rate capability, but enhance the cycle life.

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1. Introduction

LiCoO_2 , which is one of many hexagonal α - NaFeO_2 -type materials such as LiNiO_2 [1] and LiMnO_2 [2], has been widely used as a positive electrode (cathode) material in commercial lithium-ion batteries because of its good electrochemical properties and ease of preparation [3,4]. The specific capacity of LiCoO_2 does, however, decrease significantly when the material is cycled to over 4.2 V. This is because extracting more Li ions from $\text{Li}_{0.5}\text{CoO}_2$ (by raising the charge cut-off voltage over 4.2 V) leads to a decrease in the lattice constant c via a transition from the hexagonal to the monoclinic phase, and thereby collapses the structure [5]. Hence, the practical specific capacity of LiCoO_2 is limited to below 140 mAh g^{-1} by charging along up to 4.2 V versus Li ($\text{Li}_{0.5}\text{CoO}_2$) even though the theoretical capacity is 274 mAh g^{-1} .

To overcome this drawback, which limits the use of LiCoO_2 cathode material in batteries that are required to have a high

energy density, new materials such as $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ [6], $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ [7], $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [8], $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ [9] and $\text{LiNi}_{0.6}\text{Co}_{0.4-x}\text{Mn}_x\text{O}_2$ [10] have been synthesized by substituting an electrochemically-active metal (e.g., Ni, Mn) at the Co-site in LiCoO_2 . Among these alternative materials, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ has attracted significant attention on account of its many advantages over LiCoO_2 , namely, high capacity, structural and thermal stability, and excellent cycleability [11–14]. Moreover, it has found that electrochemically-inactive metals such as Mg, Nb, Si, and Zr can be doped into the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ matrix to enhance further its electrochemical properties and thermal stability. For example, Si (or Zr)-doped $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ displays improvements in rate capability, specific capacity and cycle life compared with undoped material [15].

For similar reasons, coating of the surface of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ with AlPO_4 , Al_2O_3 and LiAlO_2 has been attempted using a sol–gel method that is analogous to the preparation of metal oxide or metal phosphate-coated LiCoO_2 [16,17] for which excellent capacity retention was observed at charge cut-off voltages of over 4.2 V. The present study has focused on the preparation and electrochemical properties of LiAlO_2 -coated

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$\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. To the authors' knowledge this is the first time that such coating has been attempted as a means to improve the electrochemical properties. The effects of the coating on rate capability and cycle life are investigated.

2. Experimental methods

$\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}(\text{OH})_2$ starting powders were prepared by co-precipitation through addition of NaOH and NH_4OH solutions to a solution that contained stoichiometric amounts of nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), cobalt sulfate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$), and manganese sulfate ($\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$). The pH was maintained between 11 and 12 by controlling the amount of NaOH. The solution was strongly stirred at 400–1000 rpm. The particle size was controlled by the pH, reaction time and stirring speed. Spherical particles ($\sim 10 \mu\text{m}$ diameter) were uniformly produced for a pH of 11, a reaction time of 12 h, and a stirring speed of 1000 rpm. To prepare $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powders, stoichiometric amounts of the as-prepared $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}(\text{OH})_2$ and $\text{LiOH} \cdot \text{H}_2\text{O}$ were mixed, calcined and sintered at 1000°C for 10 h.

The preparative procedure for LiAlO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was modified from the method reported for LiCoO_2 [18]. To produce a 3 wt.% (5 wt.%) LiAlO_2 coating on 30 g of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powder, 0.9 g (1.5 g) of $\text{C}_9\text{H}_{21}\text{O}_3\text{Al}$ and 0.185 g (0.308 g) of $\text{LiOH} \cdot \text{H}_2\text{O}$ were dissolved in 25 ml of distilled water and stirred for 1 h at 50°C . The $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powder was slowly added and thoroughly mixed for 10 min. The mixture was dried at 120°C for 10 h and then calcined at 600°C for 3 h.

Powder XRD data for finely-ground samples were collected at 298 K using a Philips PW1830 diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). It was operated at 40 kV and 30 mA over a 2θ range of $10\text{--}80^\circ$ in a continuous scan mode with a step size 0.02° and scan rate $1.0^\circ \text{ min}^{-1}$. Scanning electron microscope (SEM) images of the particle shapes and morphologies of bare and LiAlO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ were obtained by means of a Hitachi S-4800 machine.

The electrodes were fabricated from a 85:6:8 (mass %) mixture of active material:polyvinylidene difluoride (PVDF, Aldrich) as binder:super-P carbon black (MMM Carbon) as current conductor. The PVDF was dissolved in *N*-methylpyrrolidinone (NMP, Kanto) and the active material and conductor mixture were added. After homogenization, the slurry was evacuated for 20 min to remove the retained air. The slurry was then coated on a thin aluminum foil ($15 \mu\text{m}$ thick) and dried overnight at 120°C . The electrode was pressed ($600\text{--}800 \text{ kg cm}^{-2}$) and punched into 15-mm diameter disks.

Electrochemical cells were prepared in the form of the standard 2032 coin configuration with lithium metal foil used as both the counter and reference electrodes. The cells were assembled in a dry room (dew point below -55°C). The electrolyte was 1.15 M LiPF_6 in ethylene carbonate:ethyl methyl carbonate:diethyl carbonate (EC:EMC:DEC = 3:5:2). The cells were taken out of the dry room and connected to a battery testing system (TOSCAT 3000). The cells were aged for 12 h before the first charge to ensure full absorption of electrolyte into the electrodes.

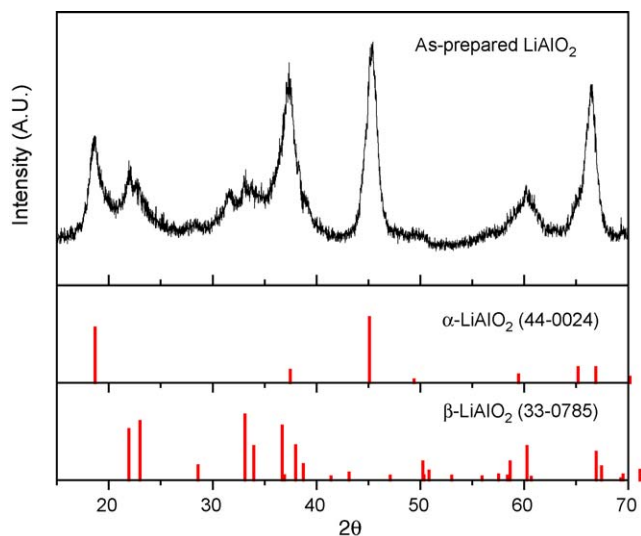


Fig. 1. X-ray diffraction pattern of LiAlO_2 nanoparticles after heat treatment at 600°C for 3 h. Peaks can be indexed to rhombohedral and orthorhombic structures of LiAlO_2 . Average size of particles is about 15 nm.

3. Results and discussion

3.1. Characterization of LiAlO_2 nanoparticles and LiAlO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$

Isolated LiAlO_2 nanoparticles were prepared using identical heat treatment to that for LiAlO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. The material was dried at 120°C for 10 h and then heated at 600°C for 3 h to determine whether the LiAlO_2 phase is actually synthesized by this preparative procedure. X-ray diffraction patterns of the as-prepared LiAlO_2 nanoparticles are shown in Fig. 1. Broad peaks are observed and the major peaks can be indexed to $\alpha\text{-LiAlO}_2$ phase (JCPDS no. 44-0024), while the minor peaks correspond to $\beta\text{-LiAlO}_2$ phase (JCPDS no. 33-0785). The average size of the LiAlO_2 nanoparticles is calculated to be about 15 nm from the half-width of the diffraction peaks using the Scherrer equation [19].

The X-ray diffraction patterns of bare and 3 and 5 wt.% LiAlO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, after heat treatment at 600°C for 3 h are given in Fig. 2. The data reveal that only the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ single phase in the R-3 m space group and no other impurity phases are present. This suggests that the structure of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is not affected by the LiAlO_2 coating. The XRD pattern of the LiAlO_2 coating layer is not observed and this is probably because LiAlO_2 nanoparticles have broad and low intensity (~ 250 counts) peaks that are covered by the sharp and high intensity peaks (~ 4500 counts) of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (~ 4500 counts).

Scanning electron microscope (SEM) images of bare and 3 and 5 wt.% LiAlO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ particles are presented in Fig. 3. Bare $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ consists of rod-shaped particles of sub-micron size that form spherical aggregates of $\sim 10 \mu\text{m}$ in diameter. The bare particles have smooth and clean surface so with a 3 wt.% LiAlO_2 coating, the surfaces of the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ particles are partially covered with nano-sized LiAlO_2 particles. When the coating is increased

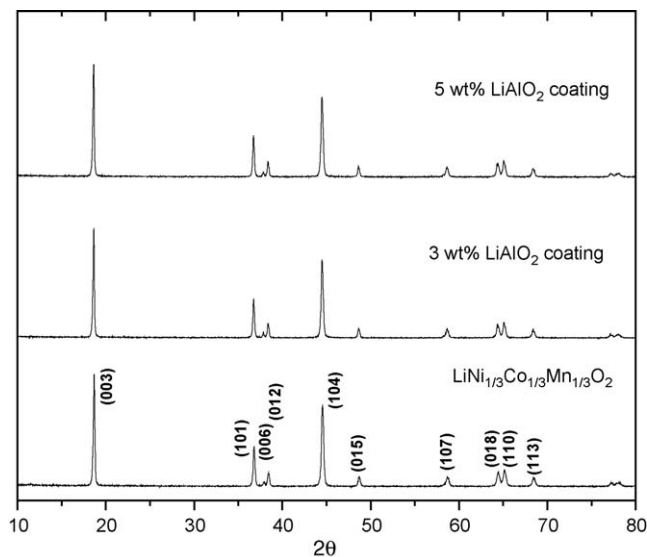


Fig. 2. X-ray diffraction patterns of bare and 3 and 5 wt.% LiAlO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ powders after heat treatment at 600 °C for 3h.

to 5 wt.%, the aggregated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ particles are completely encapsulated by LiAlO₂ nanoparticles, as shown in Fig. 3(c). Similar SEM images have been observed for AlPO₄-coated Li(Ni_{0.8}Co_{0.2})O₂ [20] and Al₂O₃-coated LiCoO₂ [21].

In the former study, Li(Ni_{0.8}Co_{0.2})O₂ particles were heavily, but not uniformly, coated at ≥5 wt.% AlPO₄.

3.2. Electrochemical properties of LiAlO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂

The initial charge and discharge curves of bare, 3 and 5 wt.% LiAlO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ in a coin-type cell between 4.5 and 2.8 V at the 0.2 C rate are shown in Fig. 4. The bare sample gave an initial discharge of 173.9 mAh g⁻¹, which compares well with values reported by other workers [15,22]. The 3 wt.% LiAlO₂-coated sample provides a slightly larger specific capacity, namely, 177.2 mAh g⁻¹. With increasing C rate, much larger capacity retention is observed with the 3 wt.% LiAlO₂-coated sample, i.e., 90.3% versus 86.7%, see Fig. 5. This enhanced rate capability is important for battery performance because fast Li⁺ extraction/intercalation from/into cathodes reduces the charge time of batteries in portable electric devices. By contrast, a 5 wt.% coating dramatically decreased both the initial discharge and the rate capability, as shown in Fig. 5.

The cycle-life performances of bare, 3 and 5 wt.% LiAlO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ operated at 1 C rate between 4.5 and 2.5 V are presented in Fig. 6. The initial discharge capacity

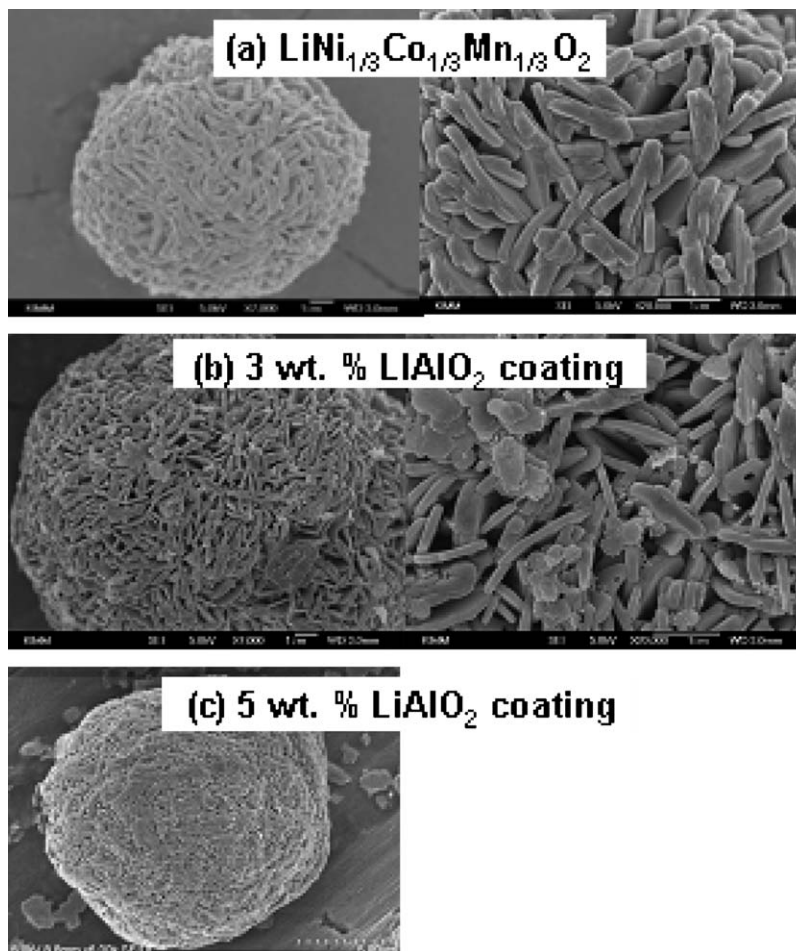


Fig. 3. Scanning electron micrographs of (a) bare; (b) 3 wt.%; and (c) 5 wt.% LiAlO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ powders after heat treatments at 600 °C for 3h.

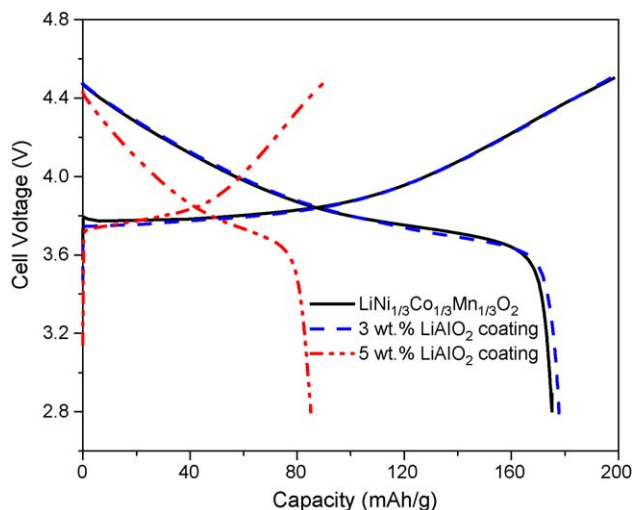


Fig. 4. Initial charge and discharge curves of bare and 3 and 5 wt.% LiAlO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ operated between 2.8 and 4.5 V at 0.2 C rate.

(131.1 mAh g⁻¹) of bare LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ decreases gradually with cycling; it finally reaches 109.7 mAh g⁻¹ after 50 cycles, i.e., 82.3% of its initial discharge capacity. This appears to be an excellent performance compared with that of commercial LiCoO₂ as reported by Xu et al. [14]. The improvement is attributed to the fact that the phase transformation from a hexagonal to monoclinic phase, which is commonly found with LiCoO₂ [5], has been suspended by the substitution of Ni and Mn and is not observed in Li_{1-x}Ni_{1/3}Mn_{1/3}Co_{1/3}O₂ (0 ≤ x ≤ 0.78) [23] during charge–discharge cycling. There remain, however, minor changes in the lattice parameter during cycling [23] at high rates that result in a gradual loss of electrical contact with other particles and with the current collector. This is believed to be responsible for the capacity fading of bare LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ on cycling at the 1 C rate. When LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ is coated with 3 wt.% LiAlO₂ nanoparticles, however, the cycle-life reten-

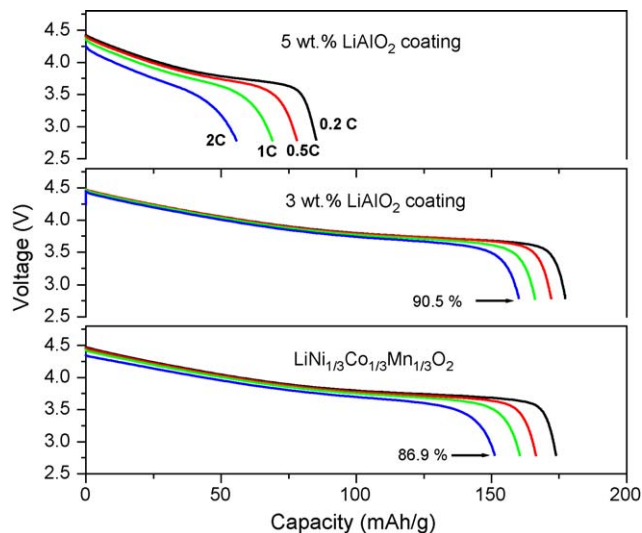


Fig. 5. Rate capabilities of coin-type cells using bare and 3 and 5 wt.% LiAlO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂. Cells charged at 0.2 C and discharged at 0.2, 0.5, 1 and 2 C, respectively, between 4.5 and 2.8 V.

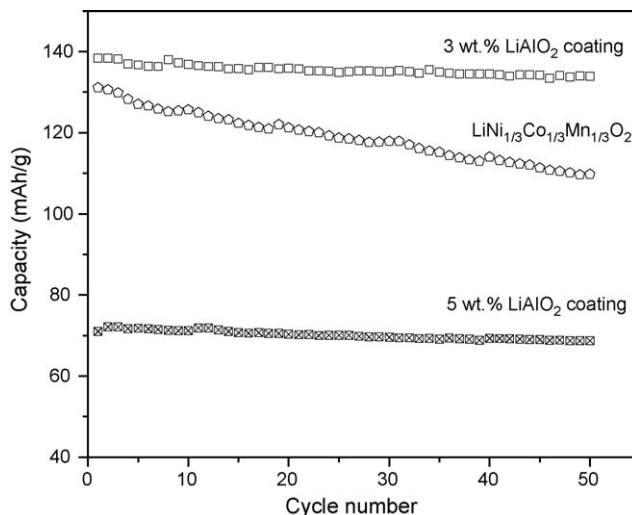


Fig. 6. Cycle-life performances of bare and 3 and 5 wt.% LiAlO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ operated between 2.8 and 4.5 V at 1 C rate.

tion is increased (96.7% initial discharge capacity) with a better initial discharge capacity of 138.4 mAh g⁻¹. 5 wt.% LiAlO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ exhibited the similar capacity retention, viz., 97.8% initial discharge capacity, but the heavier coating dramatically reduced the discharge capacity, as described above.

Similar results have been observed for other coated cathode materials such as metal oxide or metal phosphate-coated LiCoO₂ [16,17], AlPO₄-coated LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ [24], and AlPO₄-coated LiNi_{0.8}Co_{0.2}O₂ [20]. Extensive studies have been performed to understand the effects of coated cathode materials on the electrochemical properties. In the case of Al₂O₃-coated LiCoO₂ [21,25], it was reported that Al³⁺ ions diffuse into, and react with, the surface region of LiCoO₂, to form a thin layer of a Li–Al–O solid solution phase both during the heat-treatment stage of the coating preparation and during charge–discharge cycling. This reaction layer was reported to have a low electronic conductivity and a reasonably high Li-ion conductivity [21,25]. Additionally, it stabilizes the layered LiCoO₂ structure, which significantly improves the cycle-life performance above 4.3 V without affecting the high initial discharge capacity [26]. For AlPO₄-coated LiCoO₂ cathode material [17], a Li–Al–P–O solid-solution coating layer was formed on the surface of LiCoO₂. Nevertheless, the discharge capacity was reported to decrease as the coating thickness was increased because the reaction of Li becomes slower and less efficient with a thick coating layer.

In a similar way, a Li–Al–O solid-solution phase can be formed on the surface of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ by coating LiAlO₂ nanoparticles. Since this coating material contains Li⁺ ions, a much higher ionic conductivity is expected in the reaction layer. It can provide a better medium for the transport of Li⁺ ions during the Li⁺ extraction and intercalation process. This coating can minimize the resistance among particles and additionally stabilize the layered structure of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ to reduce strain or defects in particles during cycling. Therefore, the rate capability and cycle-life performance are improved

in 3 wt.% LiAlO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂. As seen above, however, these properties decrease with 5 wt.% LiAlO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ electrodes. It is believed that a 5 wt.% LiAlO₂ coating provides a thicker barrier to Li⁺ ion transport at the surface of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ so that electronic and ionic conduction among the particles becomes limited. Therefore, it is important to control the coating thickness by adjusting the amount of LiAlO₂ so as not to increase the interfacial resistance. The optimum coating thickness has been reported to be 10 to 15 nm in metal oxide-coated LiCoO₂ [16]. In LiAlO₃-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂, 3 wt.% LiAlO₂ coating may provide an optimum level of coating thickness to give high rate capability and good cycling performance without decreasing the initial high capacity.

4. Conclusions

3 and 5 wt.% LiAlO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ electrodes have been synthesized by a sol–gel method. The as-prepared LiAlO₂ material is composed of both α- and β-LiAlO₂ phases and the average size of the particles is about 15 nm. These nanoparticles of the mixed phases may react with the surface of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cathode to form a coating layer of a Li–Al–O solid-solution phase. A coating of 3 wt.% LiAlO₂ improves discharge rate capability and cycle-life performance by stabilizing the layered structure of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂. Therefore, the electrochemical properties of a bare LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cathode, which has many advantages over commercial LiCoO₂ cathode material, can be further enhanced by a 3 wt.% LiAlO₂ coating.

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