



# Enhanced electrochemical properties of $\text{Li}(\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3})\text{O}_2$ cathode by surface modification using $\text{Li}_3\text{PO}_4$ -based materials

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## ABSTRACT

The surface of a commercial  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  cathode is modified using  $\text{Li}_3\text{PO}_4$ -based coating materials. The electrochemical properties of the coated materials are investigated as a function of the pH value of the coating solution and the composition of coating materials. The  $\text{Li}_3\text{PO}_4$  coating solution with pH 2 is found to be favorable for the formation of stable coating layers having enhanced electrochemical properties. The  $\text{Li}_3\text{PO}_4$ ,  $\text{Li}_{1.5}\text{PO}_4$ , and  $\text{PO}_4$  coating layers are formed as amorphous phases. However, the  $\text{Li}_{3-x}\text{Ni}_{x/2}\text{PO}_4$  coating layers are composed of small particles with a crystalline phase covered with an amorphous phase.  $\text{Li}_3\text{PO}_4$  and  $\text{Li}_{1.5}\text{PO}_4$  coatings considerably enhance the rate capability of the  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  electrode. In contrast, the  $\text{Li}_{3-x}\text{Ni}_{x/2}\text{PO}_4$  coating material, which contained Ni, has an inferior rate capability compared to the  $\text{Li}_x\text{PO}_4$  series ( $x = 1.5$  and  $3$ ), although the  $\text{LiNiPO}_4$ -coated electrode shows a better rate capability than a pristine one.  $\text{Li}_3\text{PO}_4$ -based coating materials are effective at enhancing the cyclic performance of the electrode in the voltage range of 3.0–4.8 V. DSC analysis also confirms the improved thermal stability attained by coating the cathode with  $\text{Li}_3\text{PO}_4$ -based materials.

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## 1. Introduction

A cathode is one of the key components of lithium secondary batteries that can affect the discharge capacity, cyclic performance, rate capability, thermal stability, and safety of the batteries. Therefore, extensive research has been carried out to develop an optimum cathode material that offers high discharge capacity, a long cycle life, good rate capability, and excellent thermal stability. Unfortunately, such a perfect cathode material has not yet been found. However, several cathode materials such as spinel  $\text{LiMn}_2\text{O}_4$ , olivine  $\text{LiFePO}_4$ , and layered  $\text{Li}(\text{Ni}, \text{Co}, \text{Mn})\text{O}_2$  have been commercialized; among these materials, although layered  $\text{LiCoO}_2$  is still the most widely used cathode material. Moreover, several treatment methods have been developed to enhance the electrochemical properties of cathode materials. One approach to improve the properties of cathodes is the surface modification of cathodes by coating them with stable materials. Several studies have reported that the physical and chemical properties of cathodes can be improved by coating them with oxides [1–7] and phosphates [8–16]. However, the effect of coating on cathodes is highly dependent on the specific

coating material [17–19], coating content, and heat treatment conditions [20,21]. Phosphate is often used as a coating material. The strong P=O bond of phosphate may lead to good chemical resistance of the cathode to acidic electrolytes [11]. In addition, the strong covalency of the  $\text{PO}_4$  polyanions with the metal ions may improve the thermal stability of the coated cathode [11]. Therefore, several metal phosphates such as  $\text{AlPO}_4$  and  $\text{Co}_3(\text{PO}_4)_2$  have been used as coating materials. These metal phosphates were effective at preventing unwanted reactions between cathodes and electrolytes, and this resulted in an improved cycle life and thermal stability. However, these coating materials do not conduct lithium ions and electrons; therefore, they may prevent the diffusion of lithium ions and electrons.

Our study was motivated by the notion that if the coating material could have good ionic conductivity, the surface coating, in addition to its protective effect, could facilitate ionic diffusion of Li in the interface between the cathode and electrolyte. In principle,  $\text{Li}_3\text{PO}_4$  (or a  $\text{Li}_3\text{PO}_4$ -based structure) is a stable lithium-ion-conducting solid electrolyte with a stable P=O bond. In this work,  $\text{Li}_3\text{PO}_4$  and  $\text{Li}_3\text{PO}_4$ -based materials were introduced as coating materials for a  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  cathode.  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$ , a series of  $\text{Li}[\text{Ni}, \text{Co}, \text{Mn}]\text{O}_2$ , is one of the most promising cathode materials because its electrochemical property is comparable or superior to the properties of other alternative cathode materials [22–28]. However,  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  still requires an enhanced rate capability, stable cyclic performance at

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a high voltage range, and high thermal stability to satisfy industrial needs. In this study, a  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  cathode was coated with  $\text{Li}_3\text{PO}_4$  and  $\text{Li}_3\text{PO}_4$ -based materials, and the electrochemical and structural properties of the coated electrode were investigated. In particular, the effect of the composition of the coating material and the pH of coating solution was carefully examined.

## 2. Experimental

The pristine  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  powder was a commercial product of ECOPRO. To prepare the coating solution, lithium nitrate [ $\text{LiNO}_3$ ] (Aldrich), nickel nitrate [ $\text{Ni}(\text{NO}_3)_2$ ] (Aldrich), and diammonium hydrogen phosphate [ $(\text{NH}_4)_2\text{HPO}_4$ ] (JUNSEI) were dissolved in isopropanol with continuous stirring for 24 h at 21 °C. Ammonium was diluted and added drop by drop into the coating solution to adjust pH value. Subsequently,  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  powder was added to the coating solution and mixed thoroughly for 24 h at 21 °C. The slurry was dried in an oven at 100 °C for 12 h and heat-treated in a furnace at 400 °C for 4 h. The estimated concentration of  $\text{Li}_x\text{PO}_4$  in the  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  powders was varied by using the following values of  $x$ : 0, 1.5, and 3. The pristine sample was also heat treated at 400 °C for 4 h before the electrochemical tests to prevent effects caused by heating on the electrochemical property of the cathode powder. X-ray diffraction (XRD) patterns of powders were obtained using a Rigaku X-ray diffractometer in the  $2\theta$  range of 10° to 70° with monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The microstructure of the powder was observed using a field-emission scanning electron microscopy (FESEM, JEOL-JSM 6500F). A transmission electron microscopy (TEM, JEOL-JEM 2100F) study was also carried out using an electron microscope, operating at 200 kV.

The electrochemical performance of the coated  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  cathodes was examined using two-electrode test cells (of 2032 configuration) consisting of a cathode, metallic lithium anode, polypropylene separator, and an electrolyte of 1 M  $\text{LiPF}_6$  in EC/DMC (1:1, vol%). The cathode contained 80 wt% active materials, 12 wt% carbon black, and 8 wt% PVDF binder. The components were ball-milled for homogeneous mixing and then coated on aluminum foils and dried at 90 °C for 2 h. The cells were assembled in an Ar-filled glove box. Cells were subjected to galvanostatic cycling using a WonAtech system in the voltage range of 3.0–4.6 V or 3.0–4.8 V at various rates between 0.5 and 6 C. The impedance measurement was carried out by electrochemical workstation (CH instrument, CHI 660A), where an AC voltage of 5 mV amplitude was applied over the frequency range of 0.1 Hz to 100 kHz. To prepare samples of the cathodes for differential scanning calorimetry (DSC, Mettler Toledo), the coin cells were charged to 4.6 V at 0.2 C. The cells were then disassembled in a dry room to remove the charged positive electrode. Next, 5 mg of the positive electrode containing the electrolyte was sealed in a high pressure DSC pan. The heating rate and temperature range in the DSC tests were 5 °C  $\text{min}^{-1}$  and 100–300 °C, respectively.

## 3. Results and discussion

The surface potential of the oxide powder is dependent upon the pH value of the solution. At low pH values (acidic solution), oxides have a positive surface charge, whereas, they have a negative surface charge at high pH values [7]. As a result, their charge could affect the formation of the coating layer. To determine the optimal pH value, the surface coating of the pristine powder was carried out at various pH values of the coating solution. The surface morphology of the pristine and  $\text{Li}_3\text{PO}_4$ -coated  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  powder was investigated using FE-SEM. As shown in Fig. 1, a smooth and clean surface was observed for the pristine powder. How-

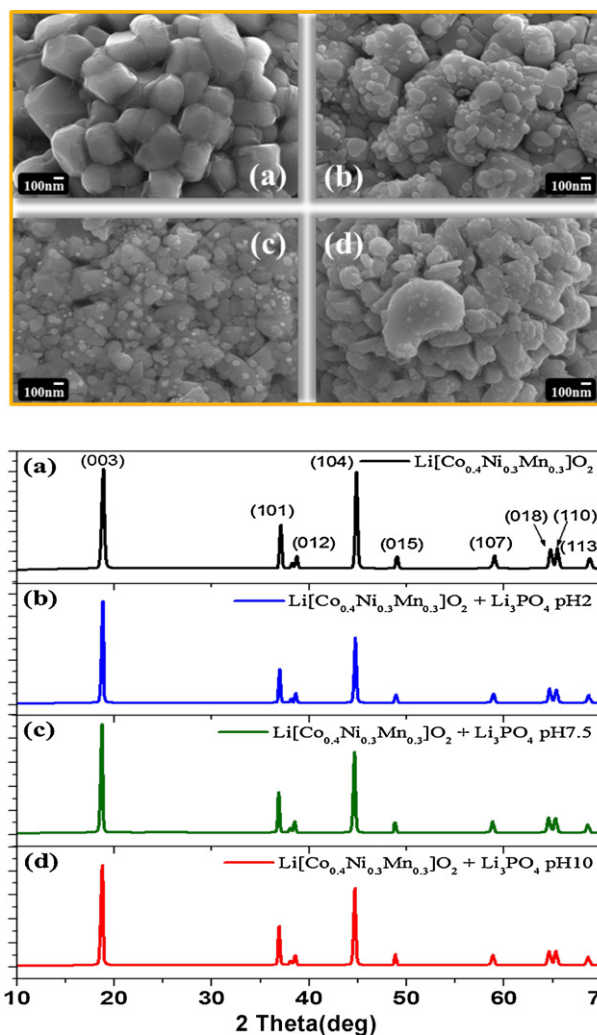
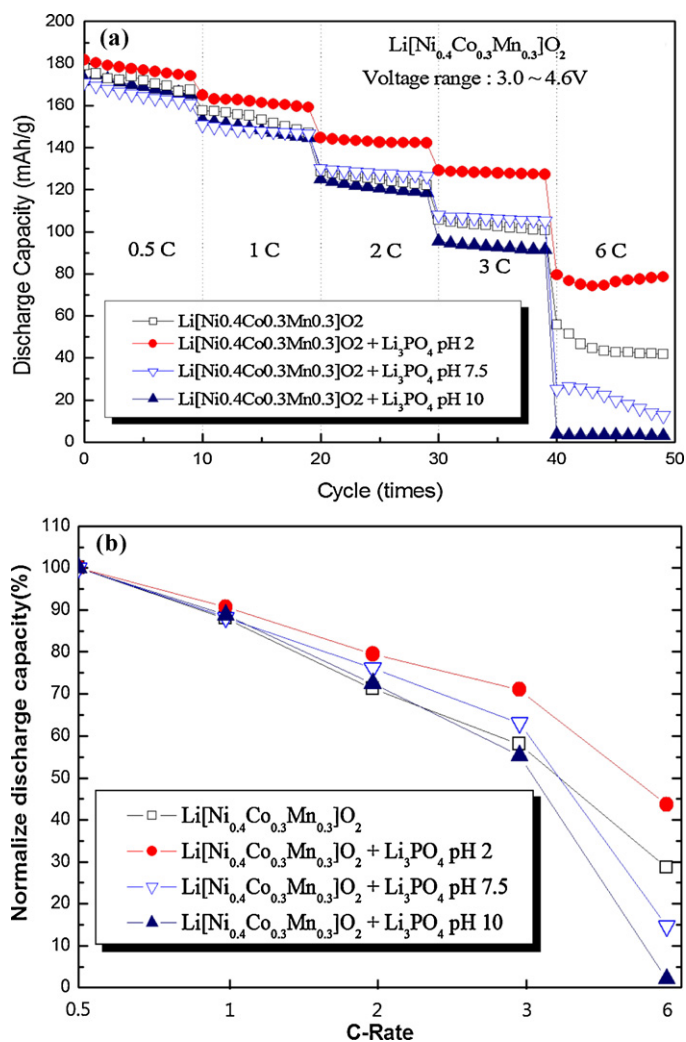


Fig. 1. SEM images and XRD data of  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  powder. (a) Pristine powder and  $\text{Li}_3\text{PO}_4$ -coated powders prepared by (b) pH 2, (c) pH 7.5, and (d) pH 10 coating solutions.

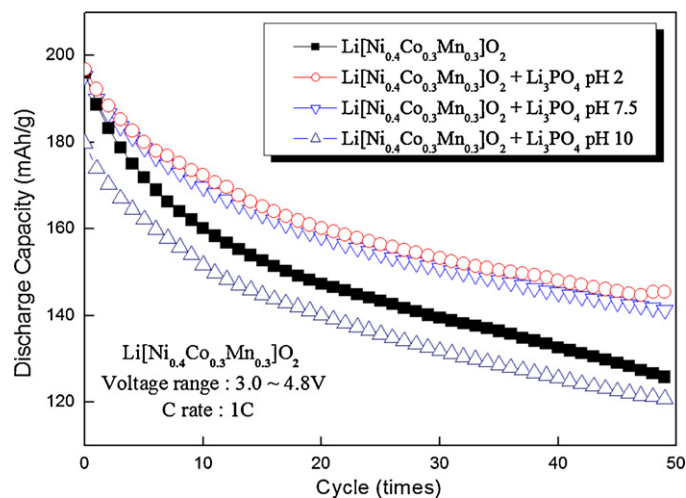
ever, numerous nanosized particles appeared on the surface of the coated powder. The coating layer was formed on the surface of the pristine powder for every coated sample. However, it is noticeable that the size of coating particles decreased as the pH value of the coating solution increased. In addition, it seemed that the coated area of the surface of the parent powder decreased as the pH value of the coating solution increased. This may suggest that an alkalic coating solution is not favorable for the formation of a stable coating layer. The XRD patterns of the pristine and  $\text{Li}_3\text{PO}_4$ -coated  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  powder were obtained to investigate the structural change after coating (Fig. 1). However, the diffraction patterns of coated powders were identical to those of the pristine sample, even though a coating layer was formed on the surface by different coating solutions. It appears that the surface coating layer is an amorphous phase because the heating temperature of 400 °C is not high enough to form a crystalline coating phase. Moreover, it is likely that the coating process does not affect the crystalline phase of the pristine powder.

The coating effect on the electrochemical properties of the pristine and coated electrode was characterized. Fig. 2a shows the discharge capacities and the cyclic performances of the pristine and  $\text{Li}_3\text{PO}_4$ -coated electrode at 0.5, 1, 2, 3, and 6 C rates in the voltage range of 3.0–4.6 V. The coated sample prepared using a pH 2 coat-



**Fig. 2.** Rate capability of pristine and  $\text{Li}_3\text{PO}_4$ -coated  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  electrodes in the voltage range of 3.0–4.6 V at 0.5, 1, 2, 3, and 6 C rates. (a) Comparison of discharge capacities and cyclic performances during cycling at various C rates. (b) Initial discharge capacity at various C rates normalized to the discharge capacity at 0.5 C rate.

ing solution showed higher discharge capacity at all C rates than those of pristine powder. Specially, at high C rates, it had a remarkably superior discharge capacity compared with the capacity of the pristine sample. However, the other coated electrodes showed inferior discharge capacities and rate capabilities as compared to the pristine powder. It is clear that  $\text{Li}_3\text{PO}_4$  coating could be effective in achieving a higher rate capability. However, the pH value of the coating solution is a very sensitive condition that is necessary to obtain a desirable coating layer. To illustrate the rate capability more directly, the discharge capacity values at various C rates are normalized to the discharge capacity value at a rate of 0.5 C and plotted in Fig. 2b. As shown in Fig. 2b, the capacity retention for the pristine electrode at the 6 C rate was only 29% of the capacity at a rate of 0.5 C. In contrast, the coated samples prepared using a pH 2 coating solution retained more than 43% of their original capacity



**Fig. 3.** Cyclic performance of pristine and  $\text{Li}_3\text{PO}_4$ -coated  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  electrodes in the voltage range of 3.0–4.8 V at 1 C rate.

under the same conditions. However, the coated samples prepared using high pH (7.5 and 10) coating solutions showed a rapid drop of discharge capacity at high C rates.

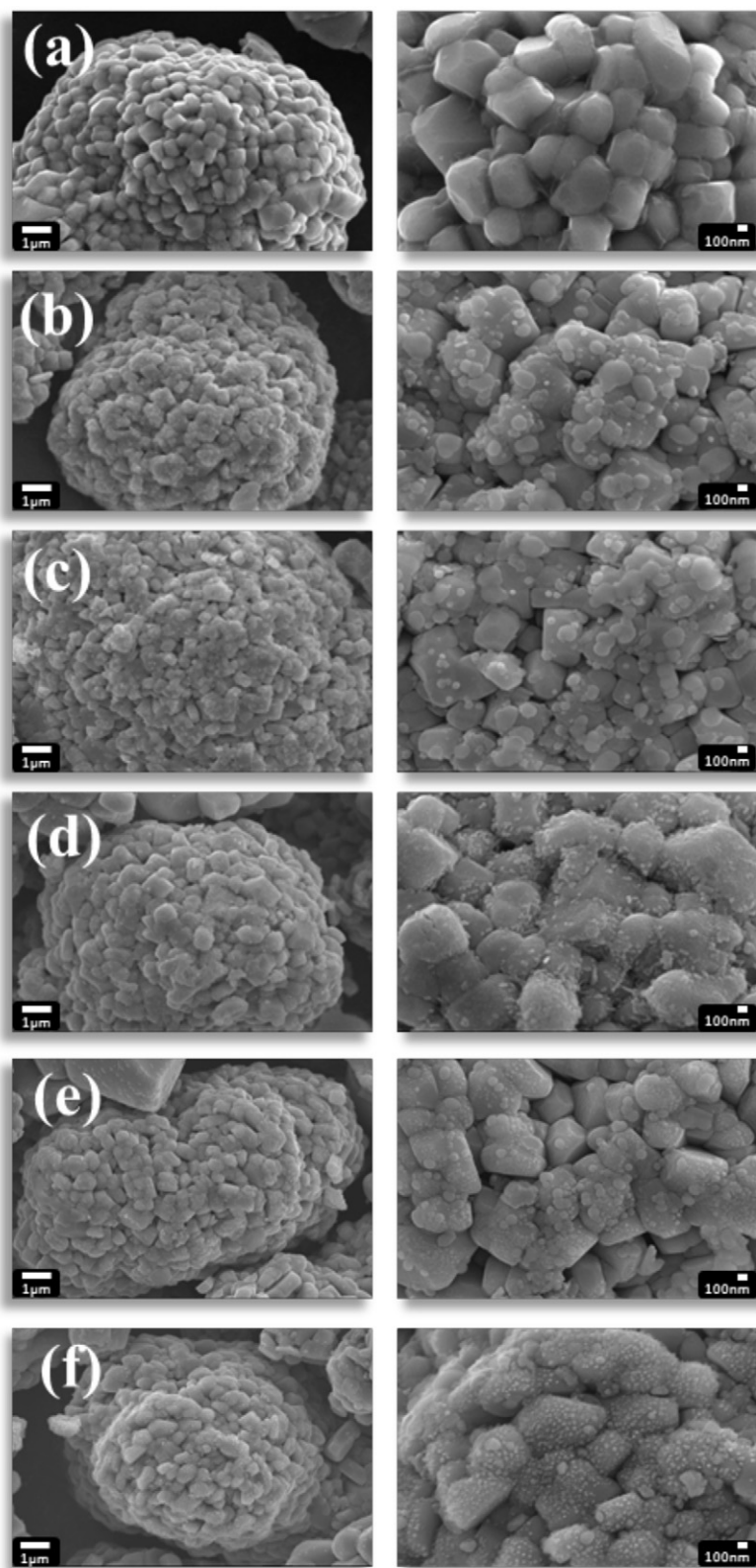
To identify the effect of coating on the discharge capacity and cycling behavior at high voltage, the upper cut-off voltage was increased to 4.8 V. Chemical or structural instability begins in the high voltage range above 4.6 V for the  $\text{Li}[\text{Ni}, \text{Co}, \text{Mn}]\text{O}_2$  cathode [7]. Fig. 3 shows the discharge capacity and cyclic performances in the voltage range of 3.0–4.8 V at 1 C rate. As shown in Fig. 3, the cyclic performance of the  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  electrode at the high cut-off voltage was improved by surface coating. During cycling, the coated samples prepared using pH 2 and 7.5 coating solutions sustained superior discharge capacities than that of pristine samples. However, the capacity of a coated sample prepared using a pH 10 coating solution decreased. Table 1 summarizes the discharge capacity and capacity retention in the voltage range of 3.0–4.8 V. With regard to the discharge capacity and rate capability, a coating solution with pH 2 is desirable for effective surface modification. However, as shown in Figs. 2 and 3, when the pH was increased to higher values, the performance of the surface coating layer became unsatisfactory. Therefore, the pH value of the coating solution was determined from this work.

Another important factor for determining coating effects is the exact composition of the coating material. The coating material is likely to easily diffuse into the surface and react with the elements of the bare material such as Li, Co, Ni, and Mn because of the high surface free energy of nanoparticles, which is attributed to their size. Therefore, it is difficult to analyze the exact composition of the coating layer. In addition, it has been reported that a small amount of lithium constituents such as  $\text{Li}_2\text{O}$ , which are formed during the storage of powder, can easily react with coating materials [16]. Herein, the lithium content of the coating material was controlled to be  $\text{Li}_3\text{PO}_4$ ,  $\text{Li}_{1.5}\text{PO}_4$ , and  $\text{Li}_0\text{PO}_4$  (only  $\text{PO}_4$ ). In addition,  $\text{Li}_{3-x}\text{Ni}_{x/2}\text{PO}_4$ , a series of  $\text{Li}_3\text{PO}_4$ -based material containing Ni, were introduced for surface coating of  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  because they could act as stable lithium-ion-conducting solid elec-

**Table 1**

Discharge capacities and capacity retentions of pristine and  $\text{Li}_3\text{PO}_4$ -coated  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  electrodes during 50 cycles in the voltage range of 3.0–4.8 V at 1 C rate. Percentages indicate the capacity retention during 50 cycles.

Cycle	Pristine ( $\text{mAh g}^{-1}$ )	%	$\text{Li}_3\text{PO}_4$ pH 2 ( $\text{mAh g}^{-1}$ )	%	$\text{Li}_3\text{PO}_4$ pH 7.5 ( $\text{mAh g}^{-1}$ )	%	$\text{Li}_3\text{PO}_4$ pH 10 ( $\text{mAh g}^{-1}$ )	%
1st	196	100	196.7	100	190.1	100	179.7	100
50th	125.8	64.1	145.4	73.9	141.4	74.3	120.7	67.1



**Fig. 4.** SEM images of (a) pristine  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  powder and  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  powder coated with (b)  $\text{Li}_3\text{PO}_4$ , (c)  $\text{Li}_{1.5}\text{PO}_4$ , (d)  $\text{PO}_4$ , (e)  $\text{LiNiPO}_4$ , and (f)  $\text{Li}_{0.5}\text{Ni}_{1.25}\text{PO}_4$ .

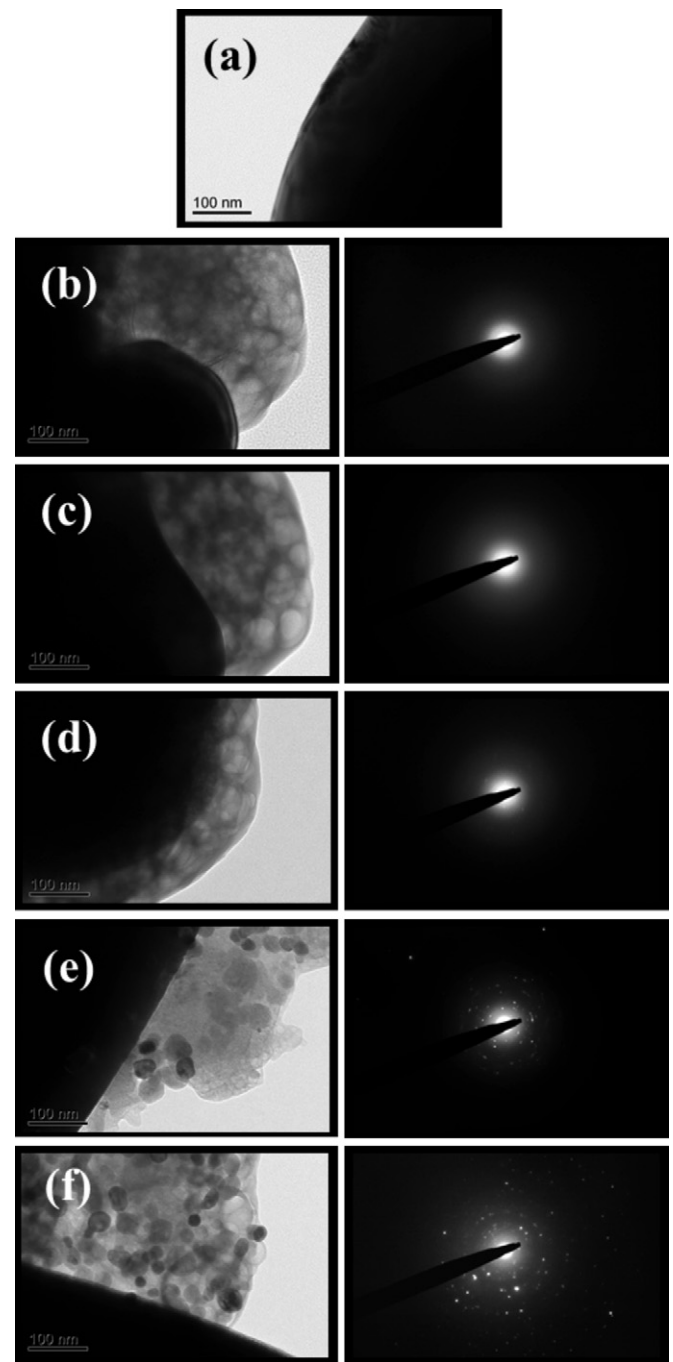
trolytes [15]. Fig. 4 shows SEM images of pristine and coated  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  powders. Five  $\text{Li}_3\text{PO}_4$ -based materials were used as coating materials. Morphological changes to the surfaces of the coated samples were observed. The surfaces of the  $\text{Li}_{1.5}\text{PO}_4$  coated samples were covered by fine nanoparticles approximately

100 nm in size. The changes were very similar in shape to the surface morphology of the  $\text{Li}_3\text{PO}_4$  coated samples. In contrast, the coating layer of the  $\text{PO}_4$ -coated sample consisted of smaller particles and (or) kinds of film. It is clear that the surface morphology of  $\text{PO}_4$ -coated samples was distinctly different with the  $\text{Li}_3\text{PO}_4$ -

and  $\text{Li}_{1.5}\text{PO}_4$ -coated samples. The  $\text{PO}_4$  coating layer was expected to react with several elements (Li, Co, Ni, and Mn) in the surface of pristine powder. However, if the reaction between  $\text{PO}_4$  polyanions and the metal ions in the surface was insufficient, a suitable coating layer will not form on the surface. In some cases, the reaction between  $\text{PO}_4$  polyanions and the metal of pristine powder can deteriorate the structural stability of the parent phase, which may degrade the electrochemical property of the electrode. The  $\text{Li}_3\text{PO}_4$ -based coating layer containing Ni also contained nanoparticles. The  $\text{LiNiPO}_4$ -coated sample showed similar surface morphology as the  $\text{Li}_3\text{PO}_4$ - and  $\text{Li}_{1.5}\text{PO}_4$ -coated samples. The size of the nanoparticles in the coating layer was approximately 100 nm. However, the  $\text{Li}_{0.5}\text{Ni}_{1.25}\text{PO}_4$  coating layer consisted of much smaller nanoparticles.

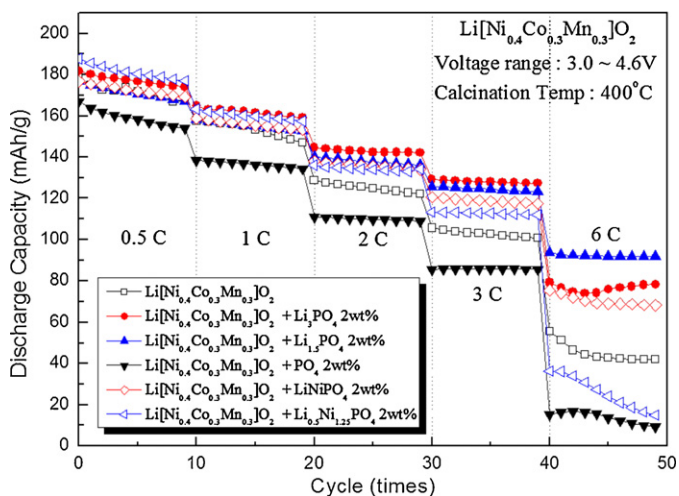
To investigate the shape and crystallinity of the coating layer in detail, TEM images and spot patterns of coating layers were obtained. As shown in Fig. 5a, the pristine particles had a smooth surface, whereas the surfaces of coated  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  particles contained a coating layer.  $\text{Li}_3\text{PO}_4$ ,  $\text{Li}_{1.5}\text{PO}_4$ , and  $\text{PO}_4$  coating layers were an amorphous phase, which was confirmed by the spot patterns shown in the panels on the right in Fig. 5b–d. However, it is noticeable that the  $\text{Li}_{3-x}\text{Ni}_{x/2}\text{PO}_4$  coating layer seemed to be composed of small particles with a crystalline phase covered with an amorphous phase, as shown in Fig. 5e and f. The spot pattern of the right side also shows the coating layer is a mixture of crystalline (or quasi-crystalline) and an amorphous phase. It is clear that the addition of Ni facilitates the formation of the crystalline phase of the  $\text{Li}_3\text{PO}_4$ -based coating material. In this work, all samples were treated at  $400^\circ\text{C}$  after coating, which is not hot enough to form a perfect oxide crystalline phase. Moreover, many solid electrolytes are amorphous phases because the flexible structure of an amorphous phase can facilitate the diffusion of ions. The phase of the coating layer may affect the electrochemical properties such as the rate capability.

The effect of  $\text{Li}_3\text{PO}_4$ -based coating on the rate capability was investigated. The discharge capacities of the pristine and coated electrodes are shown in Fig. 6. The five coating materials,  $\text{Li}_3\text{PO}_4$ ,  $\text{Li}_{1.5}\text{PO}_4$ ,  $\text{PO}_4$ ,  $\text{LiNiPO}_4$ , and  $\text{Li}_{0.5}\text{Ni}_{1.25}\text{PO}_4$ , were tested in the voltage range of 3.0–4.6 V at 0.5, 1, 2, 3, and 6 C rates. To compare the discharge capacity, the initial discharge profile of pristine and coated electrodes at 0.5 C, 3 C, and 6 C rates are shown in Fig. 7. The  $\text{PO}_4$ -coated sample showed inferior discharge capacity to the pristine sample at all C rates. It is speculated that  $\text{PO}_4$  coating without metal ions may consume positive elements, such as the Li, Co, Mn, and Ni of the pristine electrode, which leads to deterioration of the electrochemical properties of the  $\text{PO}_4$ -coated sample. However, a slightly Li-deficient coating material,  $\text{Li}_{1.5}\text{PO}_4$ , was a very effective coating material that enhanced the rate capability of the  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  electrode.  $\text{Li}_{1.5}\text{PO}_4$ -coated samples had similar discharge capacities to that of the pristine sample at a 0.5 C rate. Compared with the  $\text{Li}_3\text{PO}_4$ -coated samples, the  $\text{Li}_{1.5}\text{PO}_4$ -coated sample showed a slightly smaller discharge capacity, which may be due to the consumption of positive elements on the surface of  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  particles. However, the  $\text{Li}_{1.5}\text{PO}_4$ -coated sample had a superior discharge capacity as compared to the pristine sample at high C rates. With the increase of C rate, the capacity difference between the pristine and  $\text{Li}_{1.5}\text{PO}_4$ -coated samples was more prominent, indicating that  $\text{Li}_{1.5}\text{PO}_4$  coating enhanced the rate capability of the  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  electrode. Moreover, it is remarkable that the  $\text{Li}_{1.5}\text{PO}_4$ -coated sample had a superior rate capability to the  $\text{Li}_3\text{PO}_4$ -coated samples. Theoretically, the surface coated sample should have a lower discharge capacity and rate capability because of the coating material, which does not participate in the lithium intercalation–deintercalation process. However, the stable surface coating layer can “protect” the electrode from unwanted reactions with the electrolyte, so it may



**Fig. 5.** TEM images of (a) pristine  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  powder and  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  powder coated with (b)  $\text{Li}_3\text{PO}_4$ , (c)  $\text{Li}_{1.5}\text{PO}_4$ , (d)  $\text{PO}_4$ , (e)  $\text{LiNiPO}_4$ , and (f)  $\text{Li}_{0.5}\text{Ni}_{1.25}\text{PO}_4$ . Right-side images of (b)–(f) are spot patterns of the coating layer.

facilitate lithium diffusion or electron movement. This can explain the enhancement in rate capability through surface modification by coating. However, as shown in Figs. 4 and 5, the morphology of the  $\text{Li}_{1.5}\text{PO}_4$  coating layer was very similar to the  $\text{Li}_3\text{PO}_4$  coating layer, which may imply that the coated area of the parent particles were also similar. If the protection effect prevents direct contact between electrode and electrolyte, the enhanced rate capability of the  $\text{Li}_{1.5}\text{PO}_4$ -coated sample compared to the  $\text{Li}_3\text{PO}_4$ -coated samples may not be clearly explained by only the protection effect. The other possible explanation for the improved rate capability is that the coating layer acts as a lithium ion conductor.

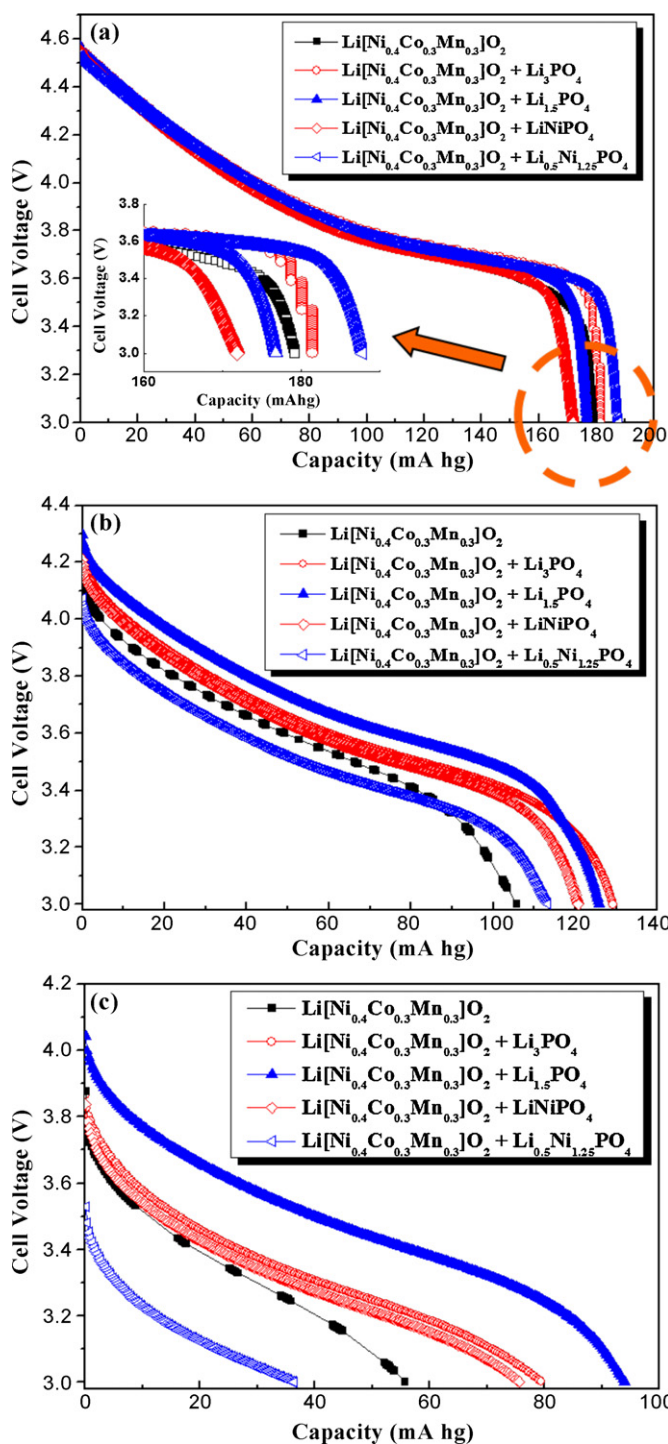


**Fig. 6.** Comparison of discharge capacities and rate capabilities of pristine electrode and Li[Ni<sub>0.4</sub>Co<sub>0.3</sub>Mn<sub>0.3</sub>]O<sub>2</sub> electrodes coated with Li<sub>3</sub>PO<sub>4</sub>, Li<sub>1.5</sub>PO<sub>4</sub>, PO<sub>4</sub>, LiNiPO<sub>4</sub>, and Li<sub>0.5</sub>Ni<sub>1.25</sub>PO<sub>4</sub> in the voltage range of 3.0–4.6 V.

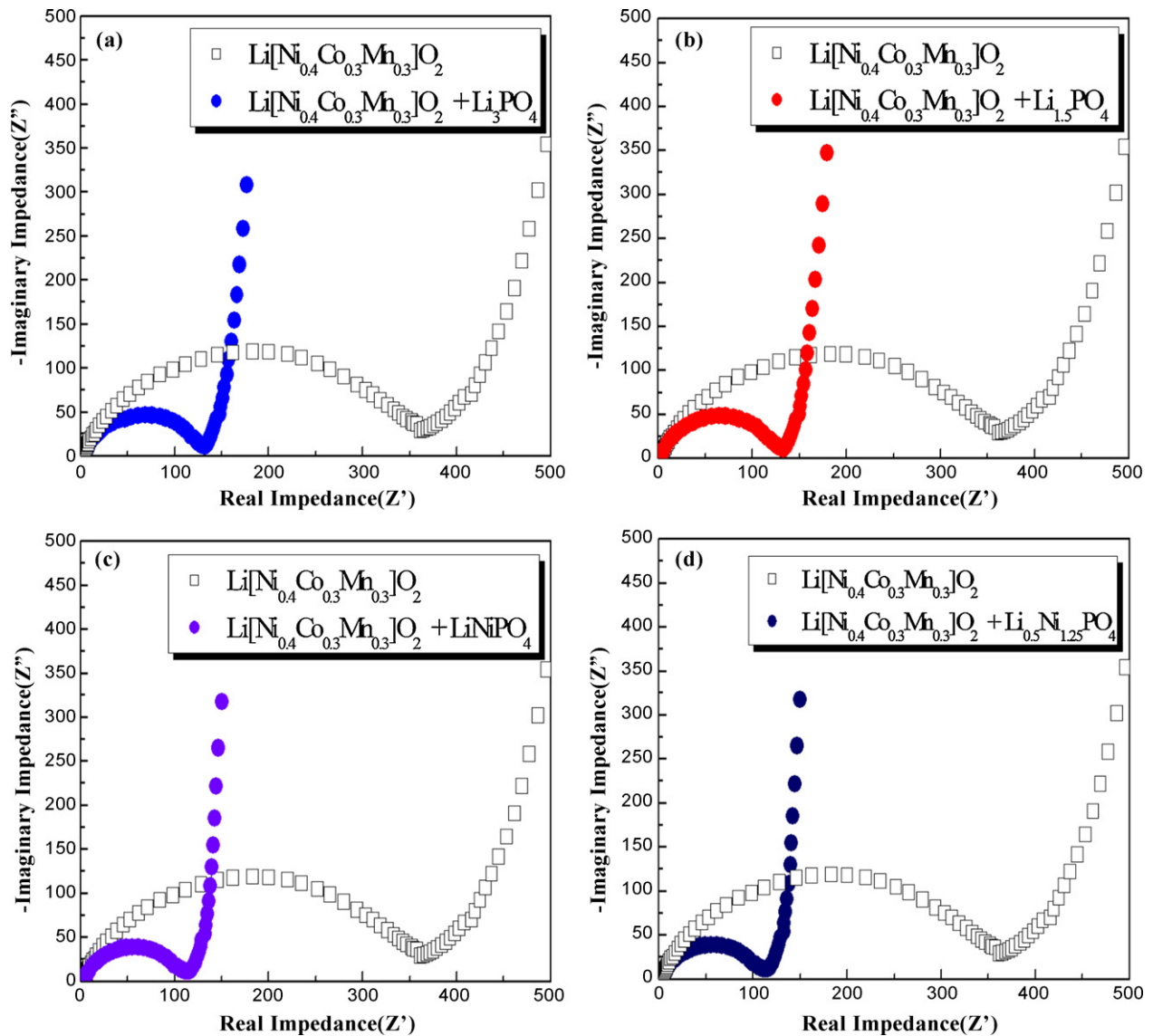
Specially, Li<sub>3</sub>PO<sub>4</sub>-based materials are a series of solid electrolytes with high lithium ion conductivity. Moreover, it is speculated that the Li<sub>1.5</sub>PO<sub>4</sub> coating materials could form a Li-deficient solid electrolyte having numerous defects and vacancies. This is likely lead to enhancement of lithium diffusivity of the interface between the electrode and electrolyte. In contrast, the Li<sub>3-x</sub>Ni<sub>x/2</sub>PO<sub>4</sub>-coated sample showed an inferior rate capability to the Li<sub>3</sub>PO<sub>4</sub>-coated sample. Considering that the morphology of the LiNiPO<sub>4</sub> coating layer is very similar to that of the Li<sub>3</sub>PO<sub>4</sub> and Li<sub>1.5</sub>PO<sub>4</sub> coating layers, it is also suspected that LiNiPO<sub>4</sub> coating layer have lower lithium diffusivity than other coating layers. In Fig. 5e, the LiNiPO<sub>4</sub> coating layer was a mixed phase that contained a crystalline phase. Generally, the amorphous phases would favor lithium diffusion due to their flexible structures. The crystalline phase could disturb the fast lithium ion diffusion through the coating layer. The Li<sub>0.5</sub>Ni<sub>1.25</sub>PO<sub>4</sub>-coated sample had an inferior rate capability compared to the LiNiPO<sub>4</sub>-coated sample, which supports fact that the Li<sub>0.5</sub>Ni<sub>1.25</sub>PO<sub>4</sub> coating layer showed a more distinct spot pattern, indicating superior crystallinity than LiNiPO<sub>4</sub> coating layer. In addition, considering the differences in the surface morphologies of LiNiPO<sub>4</sub> and Li<sub>0.5</sub>Ni<sub>1.25</sub>PO<sub>4</sub> coating layers, as shown in Fig. 4e and f, surface protection might also affect the difference in the rate properties of the samples. Table 2 summarizes the discharge capacity and capacity retention of pristine and coated electrodes at various C rates (the values of initial cycles at respective C rates). The capacity retention for the pristine electrode at the 6 C rate was only ~29% of the capacity at a 0.5 C rate. However, the Li<sub>3</sub>PO<sub>4</sub>- and Li<sub>1.5</sub>PO<sub>4</sub>-coated samples had ~44% and ~53% capacity retention under the same conditions, respectively. Although the LiNiPO<sub>4</sub>-coated sample showed a slightly lower capacity retention of ~43%, it was greater than the capacity of the pristine sample. However, the capacity retention of Li<sub>0.5</sub>Ni<sub>1.25</sub>PO<sub>4</sub> dropped to ~19%.

**Table 2**  
Discharge capacity and capacity retention of Li[Ni<sub>0.4</sub>Co<sub>0.3</sub>Mn<sub>0.3</sub>]O<sub>2</sub> electrode at various C rates (values of the first cycle). Percentages indicate the capacity retention compared with the discharge capacity at a 0.5 C rate.

	Pristine (mAh g <sup>-1</sup> )	%	Li <sub>3</sub> PO <sub>4</sub> (mAh g <sup>-1</sup> )	%	Li <sub>1.5</sub> PO <sub>4</sub> (mAh g <sup>-1</sup> )	%	PO <sub>4</sub> (mAh g <sup>-1</sup> )	%	LiNiPO <sub>4</sub> (mAh g <sup>-1</sup> )	%	Li <sub>0.5</sub> Ni <sub>1.25</sub> PO <sub>4</sub> (mAh g <sup>-1</sup> )	%
0.5C	179.2	100	181.8	100	176.7	100	167	100	176.8	100	187.8	100
1C	157.7	88	164.9	90.7	158.3	89.5	138.6	82.9	158.8	89.8	163.3	86.9
2C	127.7	71.2	144.6	79.5	140.1	79.2	110.9	66.4	138	78	136	72.4
3C	104.6	58	129.2	71	125.7	71.1	85.7	51.3	120.7	68.2	113.3	60.3
6C	51.4	28.6	79.4	43.6	93.8	53	15.2	9.1	75.6	42.7	36.3	19.3



**Fig. 7.** Initial discharge profiles of pristine electrode and Li[Ni<sub>0.4</sub>Co<sub>0.3</sub>Mn<sub>0.3</sub>]O<sub>2</sub> electrodes coated with Li<sub>3</sub>PO<sub>4</sub>, Li<sub>1.5</sub>PO<sub>4</sub>, LiNiPO<sub>4</sub>, or Li<sub>0.5</sub>Ni<sub>1.25</sub>PO<sub>4</sub> in the voltage range of 3.0–4.6 V at (a) 0.5 C, (b) 3 C, and (c) 6 C rates.

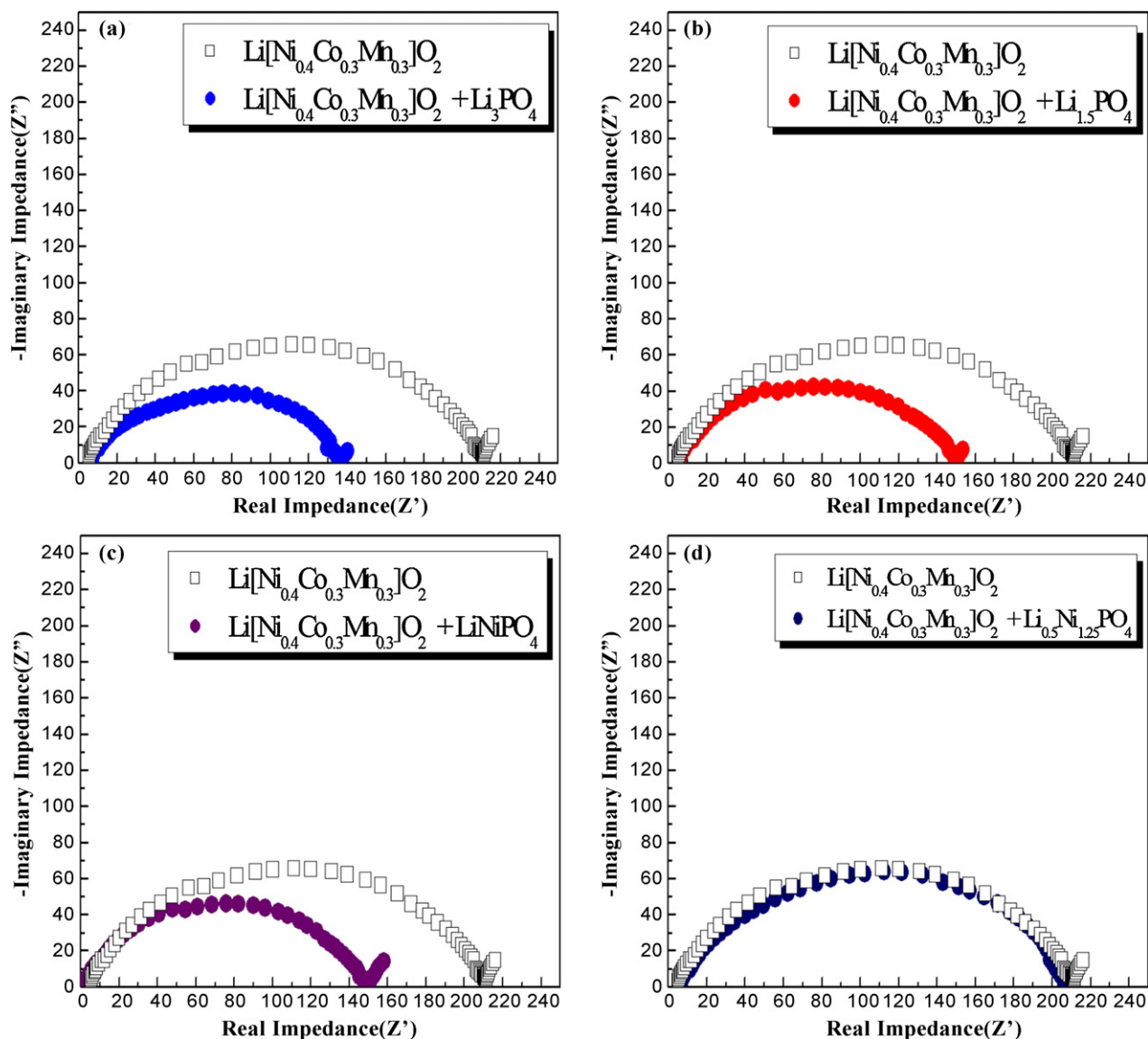


**Fig. 8.** Impedance spectra of  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  electrode coated with (a)  $\text{Li}_3\text{PO}_4$ , (b)  $\text{Li}_{1.5}\text{PO}_4$ , (c)  $\text{LiNiPO}_4$ , and (d)  $\text{Li}_{0.5}\text{Ni}_{1.25}\text{PO}_4$  before electrochemical test. (All spectra were compared with that of pristine one.)

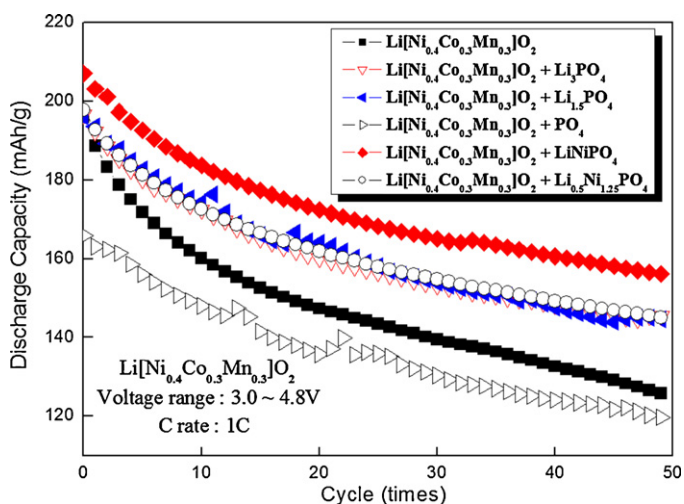
To obtain more information about electrodes, impedance analysis was introduced. Fig. 8 compares the impedance spectra of pristine and coated electrode before electrochemical test. The impedance plot shows two overlapped semicircles and a straight sloping line. The high frequency semicircle presents the impedance due to a solid electrolyte interface formed on the surface of the electrode, and the intermediate frequency semicircle is related to the charge-transfer resistance in the electrode/electrolyte interface [29]. A straight line in the low frequency region is related to a Warburg impedance arising from the semi-infinite diffusion of Li ions. As shown in Fig. 8, it was clear that all coated samples had significantly smaller semicircles in impedance spectra, compared with that of pristine samples. This indicates that both impedance values related with solid electrolyte interface and charge-transfer resistance are decreased by surface coating, which is correlated with enhanced rate capability of coated electrodes. To compare the impedance of the electrode after storage at charged state, pristine and coated electrode was charged to 4.6V and stored 3 days at 50°C. Fig. 9 shows the impedance spectra of the pristine and coated electrode after

storage. Except  $\text{Li}_{0.5}\text{Ni}_{1.25}\text{PO}_4$ -coated electrode,  $\text{Li}_3\text{PO}_4$ ,  $\text{Li}_{1.5}\text{PO}_4$ , and  $\text{LiNiPO}_4$  coated electrodes showed lower impedance value than that of the pristine one, which confirmed the coating treatment was effective on surface protection from acidic electrolyte at charge state. The relatively high impedance of  $\text{Li}_{0.5}\text{Ni}_{1.25}\text{PO}_4$ -coated electrode at charged state may explain its inferior rate capability.

The cyclic performance of pristine and  $\text{Li}_3\text{PO}_4$ ,  $\text{Li}_{1.5}\text{PO}_4$ ,  $\text{LiNiPO}_4$ , and  $\text{Li}_{0.5}\text{Ni}_{1.25}\text{PO}_4$  electrodes were compared in the voltage range of 3.0–4.8V at 1C rate. As shown in Fig. 10, except for the  $\text{PO}_4$ -coated electrode, all coated electrode showed similar or slightly higher discharge capacities during the initial cycle. Furthermore, all coated electrode showed better cyclic performance than the pristine sample. This result indicates that structural stability could be enhanced by coating electrodes with  $\text{Li}_3\text{PO}_4$ -based materials. It is interesting that the  $\text{LiNiPO}_4$ -coated sample showed a slightly higher discharge capacity than other samples in the voltage range of 3.0–4.8V. As shown in Figs. 6 and 7,  $\text{Li}_{1.5}\text{PO}_4$  was optimum coating material for enhancing the rate capability. In contrast,  $\text{LiNiPO}_4$  was not so good coating material



**Fig. 9.** Impedance spectra of  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  electrode coated with (a)  $\text{Li}_3\text{PO}_4$ , (b)  $\text{Li}_{1.5}\text{PO}_4$ , (c)  $\text{LiNiPO}_4$ , and (d)  $\text{Li}_{0.5}\text{Ni}_{1.25}\text{PO}_4$  after storage at  $50^\circ\text{C}$  for 3 days. (The electrodes were charged to 4.6V before storage. All spectra were compared with that of pristine one.)



**Fig. 10.** Discharge capacity and cyclic performance of pristine electrode and  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  electrodes coated with  $\text{Li}_3\text{PO}_4$ ,  $\text{Li}_{1.5}\text{PO}_4$ ,  $\text{PO}_4$ ,  $\text{LiNiPO}_4$ , or  $\text{Li}_{0.5}\text{Ni}_{1.25}\text{PO}_4$  in the voltage range of 3.0–4.8V at 1C rate.

for rate capability. However, to obtain a higher discharge capacity in the high cut-off voltage range,  $\text{LiNiPO}_4$  coating was more effective.

In the following test, the thermal stability of the  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  electrode before and after coating was compared using DSC analysis. The electrodes were charged to 4.6 before the test and sealed in a high-pressure DSC pan. The DSC profiles of the pristine and  $\text{Li}_{1.5}\text{PO}_4$ - and  $\text{LiNiPO}_4$ -coated samples are shown in Fig. 11. The pristine sample showed a thermal reaction with the electrolyte at  $220^\circ\text{C}$  and heat was generated until  $270^\circ\text{C}$ . The  $\text{Li}_{1.5}\text{PO}_4$ -coated sample showed a thermal reaction with the electrolyte at  $240^\circ\text{C}$  and heat generation decreased. Moreover, the heat generation was more prominently decreased by  $\text{LiNiPO}_4$  coating. This improvement in thermal stability may be due to the suppression of the surface reaction between the electrode and electrolyte by the stable coating material. Considering that coated area of the parent particles of both coated samples are similar,  $\text{LiNiPO}_4$  coating is more favorable for improving thermal stability than  $\text{Li}_{1.5}\text{PO}_4$  coating.



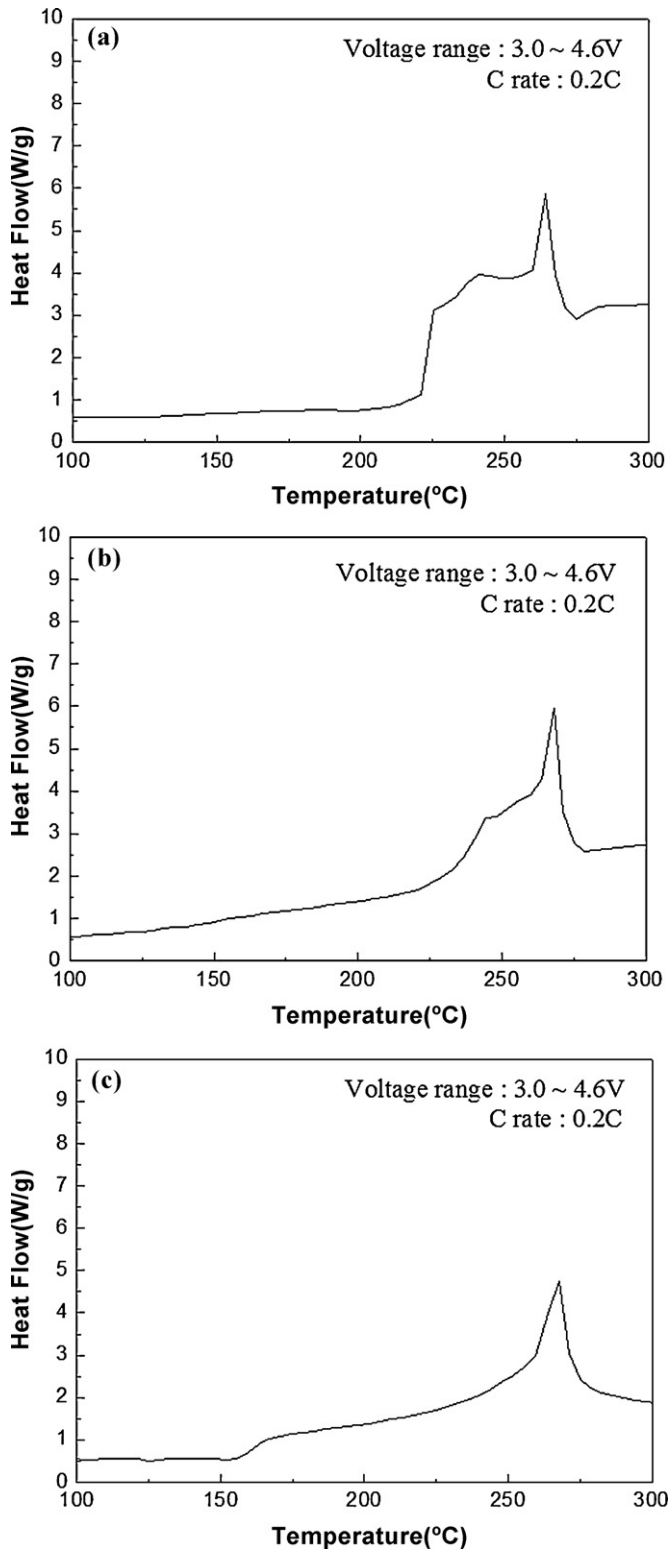


Fig. 11. DSC profiles of  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  electrode charged to 4.6 V. (a) Pristine sample, (b)  $\text{Li}_{1.5}\text{PO}_4$ -coated sample, and (c)  $\text{LiNiPO}_4$ -coated sample.

#### 4. Conclusions

$\text{Li}_3\text{PO}_4$ , which is a type of solid electrolyte, was introduced as a coating material for a  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  cathode. Three  $\text{Li}_3\text{PO}_4$  coating solutions with pH 2, 7.5, and 10 were used to modify the surface of  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  powder. The surface morphology

of the coated powder was dependent upon the pH value of the coating solution. The coated sample prepared using a coating solution with pH 2 showed enhanced discharge capacity, rate capability, and cyclic performance. However, if the pH value was high, the performance of the surface coating layer was not satisfactory. Five coating materials,  $\text{Li}_3\text{PO}_4$ ,  $\text{Li}_{1.5}\text{PO}_4$ ,  $\text{PO}_4$ ,  $\text{LiNiPO}_4$ , and  $\text{Li}_{0.5}\text{Ni}_{1.25}\text{PO}_4$ , at pH 2, were used to modify  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  powder.  $\text{Li}_3\text{PO}_4$ ,  $\text{Li}_{1.5}\text{PO}_4$ , and  $\text{PO}_4$  coating layers exhibited amorphous phases, whereas the  $\text{Li}_{3-x}\text{Ni}_{x/2}\text{PO}_4$  coating layers were composed of small particles with crystalline phases covered with amorphous phases.  $\text{Li}_{1.5}\text{PO}_4$ , a slightly Li-deficient coating material, was a very effective coating material that enhanced the rate capability of the  $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}]\text{O}_2$  electrode. This may be due to the formation of a Li-deficient solid electrolyte layer having numerous defects and vacancies, as well as the protection effect of a stable coating layer. In contrast, the  $\text{Li}_{3-x}\text{Ni}_{x/2}\text{PO}_4$ -coated sample showed a relatively inferior rate capability compared to the  $\text{Li}_{1.5}\text{PO}_4$ - and  $\text{Li}_3\text{PO}_4$ -coated samples. The surface modified electrode coated with  $\text{Li}_3\text{PO}_4$ -based materials showed enhanced cyclic performance in the voltage range of 3.0–4.8 V, which indicates that the structural stability was improved by surface coating. Although it was not so good for rate capability,  $\text{LiNiPO}_4$  coating was effective for obtaining higher discharge capacities in the high cut-off voltage range. Moreover, considering DSC analysis result,  $\text{LiNiPO}_4$  coating was more favorable for improving thermal stability than  $\text{Li}_{1.5}\text{PO}_4$  coating.

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