

The Effect of Coating Thickness on the Electrochemical Properties of a Li-La-Ti-O-coated $\text{Li}[\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3}]\text{O}_2$ Cathode

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A $\text{Li}[\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3}]\text{O}_2$ cathode was modified by coating with Li-La-Ti-O, and the effect of the coating thickness on their electrochemical properties was studied. The thickness of the coating on the surface of $\text{Li}[\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3}]\text{O}_2$ was increased by increasing the wt % of the coating material. The rate capability of the Li-La-Ti-O-coated electrode was superior to that of the pristine sample. 1- and 2-wt %-coated samples showed considerable improvement in capacity retention at high C rates. However, the rate capability of a 5-wt %-coated sample decreased. All the coated samples showed a high discharge capacity and slightly improved cyclic performance under a high cut-off voltage (4.8 V) condition. Results of a storage test confirmed that the Li-La-Ti-O coating layer was effective in suppressing the dissolution of the transition metals as it offered protection from the attack of the acidic electrolyte. In particular, the 2- and 5-wt %-coated samples showed a better protection effect than the 1-wt %-coated sample.

Key Words: Cathode, Li-La-Ti-O, Surface coating, Lithium battery

Introduction

Surface modification by coating with stable materials has been applied to cathode materials of lithium batteries to improve their electrochemical and structural properties. Coating materials such as oxides (Al_2O_3 , ZrO_2 , La_2O_3),¹⁻⁵ phosphates (AlPO_4 , LiCoPO_4),⁶⁻¹⁰ and fluorides (AlF_3 , LaF_3)¹¹⁻¹³ have been used to improve the properties of cathode materials. The surface coating suppresses the formation of an unwanted surface layer originating from the dissolution of cations (e.g., Co, Ni, and Mn) and/or the attack of HF in the electrolyte.⁵ However, these coating materials are basically non-conductive to lithium ions and electrons, so it is possible that the surface coating layer itself is a hindrance to the diffusion of the lithium ions and electrons. If the surface of the cathode is coated by a material having not only structural stability but also good electronic and ionic conductivity, the surface coating layer can facilitate lithium ion and electron diffusion as well as protect from the acidic electrolyte. In the present study, a solid electrolyte (Li-La-Ti-O type) with good ionic conductivity was used as a coating material. Li-La-Ti-O electrolyte is considered to have not only high ionic conductivity ($\sim 10^{-3} \text{ Scm}^{-1}$) but also high electronic conductivity.¹⁴⁻¹⁷ The high electronic conductivity of Li-La-Ti-O presents a major problem in using it as a solid electrolyte. However, this property offers a great advantage in using it as a coating material. Although a lot of surface coating materials for cathode were studied, adoption of solid electrolyte as a coating materials was scarcely reported. In this study, the surface of a $\text{Li}[\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3}]\text{O}_2$ cathode was coated with a Li-La-Ti-O electrolyte, which is promising as a cathode material for lithium secondary batteries, and the coating effect was examined and characterized. A hydrothermal coating method was adopted to achieve uniform coating. In particular, we focused on the effect of coating thickness on the electrochemical properties of the cathode

Experimental

Pristine $\text{Li}[\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3}]\text{O}_2$ powder was supplied by Daejung Chemicals & Metals. To prepare the Li-La-Ti-O coating solution, lithium nitrate [LiNO_3] (Aldrich), lanthanum(III) nitrate hexahydrate [$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$] (99.99%, Aldrich), and titanium(IV) isopropoxide [$\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$] (97%, Aldrich) were dissolved in isopropanol and an ammonium solution was added while the mixture was continuously stirred at 50 - 60 °C on a hot plate. The molar ratio of the Li:La:Ti sources was 0.5:0.5:1 (thus, the coating material was $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$). Pristine $\text{Li}[\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3}]\text{O}_2$ powder was added to the coating solution and mixed well. The mixture was introduced into a Parr bomb and heated to 120 °C for 15 h to produce a hydrothermal reaction. Afterwards, the slurry was dried and heat-treated in a furnace at 400 °C for 6 h to obtain Li-La-Ti-O-coated $\text{Li}[\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3}]\text{O}_2$ powder. X-ray diffraction (XRD) patterns of the powders were obtained using a Rigaku X-ray diffractometer in the 2 θ range of 10 - 70° with monochromatized Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The microstructure of the powder was observed by field-emission scanning electron microscopy (FE-SEM, JEOL-JSM 6500F). Transmission electron microscopy (FE-TEM, JEOL-JEM 2100F) was also carried out with an electron microscope operating at 200 kV.

The cathodes for electrochemical studies were prepared using a doctor-blade coating method with a slurry of 80-wt %-coated active material, 12-wt % conductive carbon (Super-P), and 8-wt % poly vinylidene fluoride (PVDF) in *N*-methyl-2-pyrrolidone (NMP), as the solvent for the mixture. The electrochemical performances of the discs were evaluated with coin-type cells of the 2032 configuration and the discs were assembled in an argon-filled glove box. Cells were subjected to galvanostatic cycling using a WonAtech system. The pristine and coated samples were tested before and after storage using inductively

coupled plasma-atomic emission spectroscopy (ICP-AES) and glow discharge optical emission spectroscopy (GD-OES). The samples were charged to 4.8 V and then stored with electrolyte at 50 °C for 7 days. Then, the electrolyte was analyzed with ICP-AES to measure the transition metal dissolution during storage. GD-OES was applied for characterization of the electrodes during storage, to obtain a depth profile of the constituent elements from the surface to the interface with the current collector. The sample was sputtered in an argon atmosphere by applying radio frequency. The Radio Frequency Glow Discharge Spectrometer (JY 10000 RF, KBSI-PA314) at the Korea Basic Science Institute (Busan Center) was used for the measurement.

Results and Discussion

The surface morphology of pristine and Li-La-Ti-O-coated $\text{Li}[\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3}]\text{O}_2$ powder was examined through SEM images. As shown in Fig. 1a, the surface of the pristine sample was clean and smooth. In contrast, the coated sample showed a very rough surface covered by very small particles (Figs. 1b-1d). The size of the surface particles was about 10 - 50 nm. The surface of the 1-wt %-coated sample was not completely covered by the coating particles. However, as the amount of coating material increased, most of the surface of the powder was encapsulated by the coating layer. The Li-La-Ti-O coating layer on the $\text{Li}[\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3}]\text{O}_2$ powder was observed by TEM analy-

sis. Figure 2a shows the smooth surface of a pristine sample. The surface of the coated sample, however, clearly shows a coating layer (Figs. 2b-2d). The thickness of the coating layer was not uniform, but it increased with the increase in wt % of the coating material. Even though some parts of the surface were exposed, most of the surface of the 1-wt %-coated sample was covered by a thin coating layer (< 50 - 60 nm). The 2-wt %-coated sample showed a thicker coating layer (> 100 nm) than the 1-wt %-coated sample. The coating layer of the 5-wt %-coated sample was considerably thicker, as shown in Fig. 2d. From these images, it is confirmed that the coating thickness on the cathode depends on the wt % of the coating material. The spot pattern of the coating layer is shown on the right side of Figs. 2b-d. The whole coating layer was confirmed to be in an amorphous phase. Generally, most solid electrolytes are in an amorphous phase because the flexible structure of the amorphous phase can facilitate the diffusion of ions. Therefore, this amorphous coating layer may facilitate intercalation and deintercalation of Li ions during the charge and discharge process.

The electrochemical properties of the pristine and coated $\text{Li}[\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3}]\text{O}_2$ electrodes were characterized, to examine the coating effect. Figure 3 shows the discharge capacity and cyclic performance of the pristine and coated $\text{Li}[\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3}]\text{O}_2$ electrodes as a function of charge-discharge rates. The measurement was carried out at 0.5 C, 1 C, 2 C, 3 C and 6 C rates in the voltage range of 4.6 - 3.0 V. The discharge capacities of

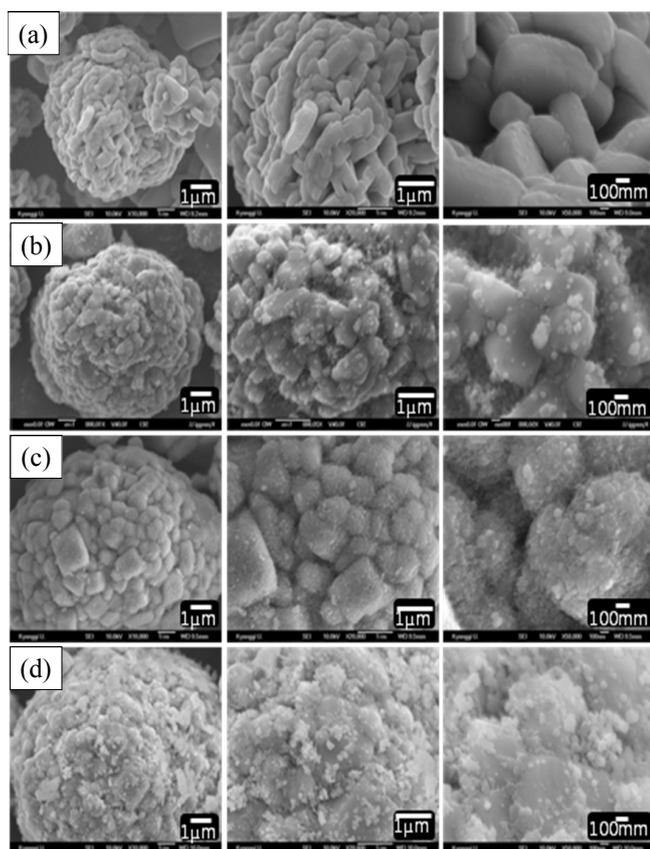


Figure 1. SEM images of (a) pristine and (b) 1-wt %, (c) 2-wt %, and (d) 5-wt %-Li-La-Ti-O-coated $\text{Li}[\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3}]\text{O}_2$ powders.

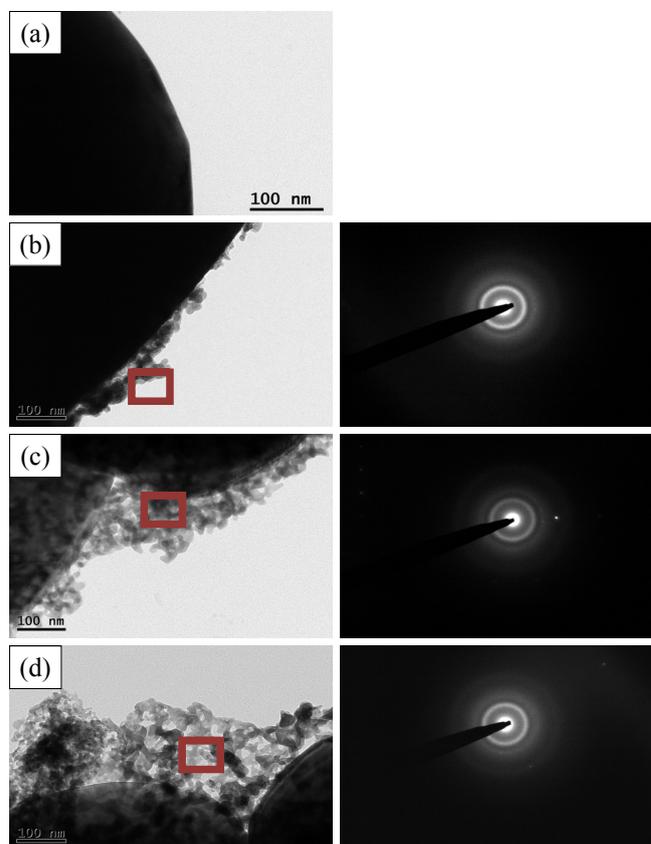


Figure 2. TEM images of (a) pristine and (b) 1-wt %, (c) 2-wt %, and (d) 5-wt %-Li-La-Ti-O-coated $\text{Li}[\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3}]\text{O}_2$ powders. Right images of (b)-(d) show the spot pattern of the coating layer.

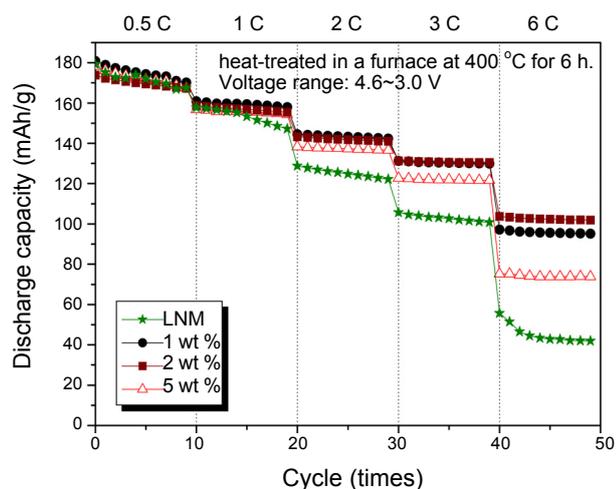


Figure 3. Discharge capacities and cyclic performances of pristine and Li-La-Ti-O-coated $\text{Li}[\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3}]\text{O}_2$ electrodes in voltage range of 4.6 - 3.0 V at 0.5, 1, 2, 3, and 6 C rates.

Table 1. Discharge capacity and capacity retention of $\text{Li}[\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3}]\text{O}_2$ electrode at various C rates (values of the first cycle). Percentages refer to the capacity retention compared with the discharge capacity at 0.5 C rate.

	Pristine	(%)	1 wt %	(%)	2 wt %	(%)	5 wt %	(%)
0.5 C	179.25	100.0	180.83	100	173.86	100	178.23	100
1 C	157.71	88.0	161	89	158.69	91.27	156.81	87.98
2 C	128.81	71.9	144	79.6	143.25	82.39	138.32	77.6
3 C	105.73	59.0	131.28	72.6	131.27	75.5	122.71	68.84
6 C	55.72	31.1	97.2	53.75	103.73	59.66	75.21	42.19

all the samples showed similar values at 0.5 C and 1 C rates. However, as the C rates increased, the discharge capacity of the pristine sample rapidly dropped. The coated samples also showed a loss of capacity at high C rates, however, they had a higher discharge capacity than that of the pristine sample at high C rates. In particular, the 1- and 2-wt %-coated samples showed a much enhanced rate capability. The increased discharge rate capability of cathode material due to surface coating has been reported. However, the interface region formed from the unwanted surface reaction between the electrode and the electrolyte hinders the fast diffusion of lithium ions and transfer of electrons during the charge and discharge processes. A stable coating layer can prevent the formation of the interface region by protecting the cathode from the electrolyte, so it can facilitate the movement of lithium and electrons during the charge and discharge process. When the coating concentration increases beyond the optimum concentration, the charge/discharge rate capability deteriorates. Our experiments showed that the optimum rate capability can be obtained with a 2-wt %-coated sample. If the coating layer is too thick, it will obstruct the fast lithium and electron movement during cycling. However, it is notable that the 5-wt %-coated electrode still showed better rate capability than the pristine electrode. In the TEM images (Fig. 2), the thickness of the coating layer is over 200 - 300 nm, which is very high compared to previously reported layers.¹⁻¹⁰ Most of the coating layer had a thickness range of 10 - 100 nm,

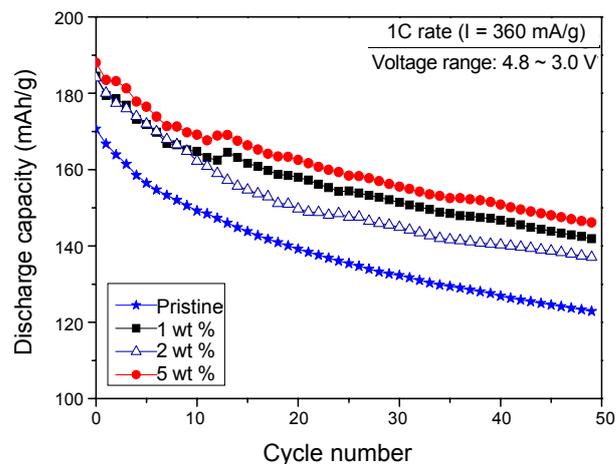


Figure 4. Cyclic performances of pristine and Li-La-Ti-O-coated $\text{Li}[\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3}]\text{O}_2$ electrodes in voltage range of 4.8 - 3.0 V at 1 C rate.

Table 2. Discharge capacities and capacity retentions of pristine and Li-La-Ti-O-coated $\text{Li}[\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3}]\text{O}_2$ electrodes during 50 cycles in voltage range of 4.8 - 3.0 V at 1 C rate. Percentages refer to the capacity retention during 50 cycles.

	Pristine	(%)	1 wt %	(%)	2 wt %	(%)	5 wt %	(%)
1st	170.6		184.5		184.07		188.05	
50th	122.9	72.03	141.9	76.9	137	74.42	146	77.6

because too thick a coating layer would deteriorate the electrochemical property significantly. Although the discharge rate capability of the 5-wt %-coated electrode is lower than other coated samples, it still shows an improved rate over the uncoated sample. This is likely owing to the high ionic conductivity of the Li-La-Ti-O coating layer. Table 1 summarizes the discharge capacity and capacity retention at various C rates (the values are shown for the initial cycles at respective C rates).

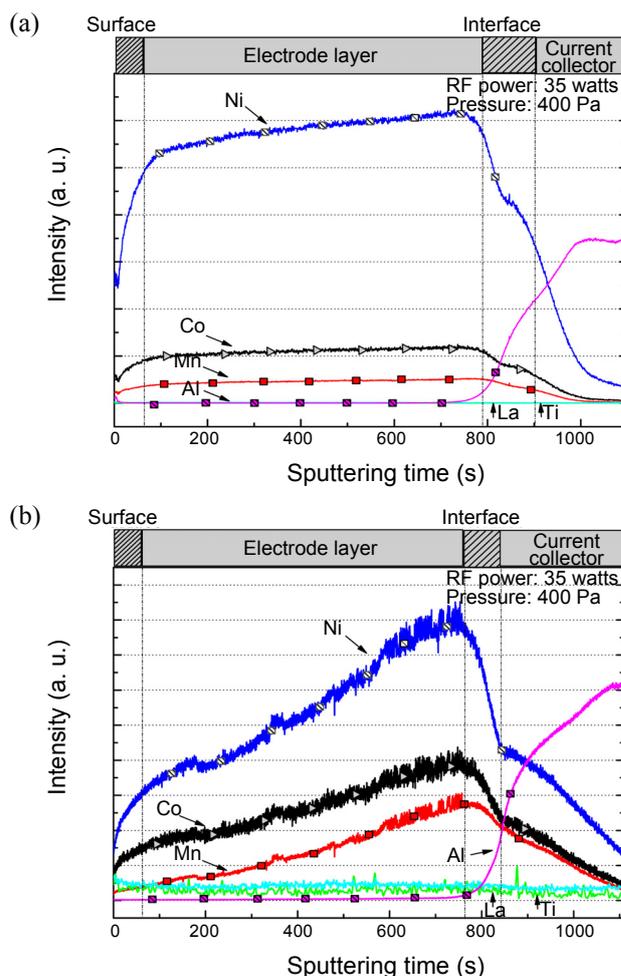
Figure 4 shows the cyclic performance of the pristine and Li-La-Ti-O-coated $\text{Li}[\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3}]\text{O}_2$ electrodes. The cut-off charge voltage was increased to 4.8 V to investigate the cyclic behavior under a structurally unstable condition. The $\text{Li}(\text{Ni}, \text{Co}, \text{Mn})\text{O}_3$ cathode, $\text{Li}[\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3}]\text{O}_2$ showed rapid capacity loss during cycling when the cut-off voltage increased above 4.7 V because of structural instability.¹⁸ As reported in previous work, the discharge capacity of the pristine and coated samples decreased considerably during cycling. However, the discharge capacity of the coated sample was higher than that of the pristine sample. It is interesting that the discharge capacity of the 5-wt %-coated sample was a little higher than that of the other coated samples at the high voltage range. In the Fig. 3, it was confirmed that a thick coating layer was not favorable for improving the rate capability. However, for obtaining a high discharge capacity in the high cut-off voltage range, the 5 wt % coating layer was slightly more effective than the other coating layers. It is speculated that the thick coating layer will encapsulate the vulnerable surface of the pristine powder more effectively. Thus, it is more efficient in protecting the surface of the

Table 3. ICP AES measurements of dissolution of transition metals (Ni, Co, and Mn) into electrolyte used for storage (at 50 °C for 7 days) of pristine and coated electrode charged at 4.8 V

Sample	Analysis	Result	
(a) pristine	Ni (mg/kg)	25.5	ICP-AES Perkin-Elmer OPTIMA 5300 DV
	Co (mg/kg)	15.7	
	Mn (mg/kg)	20.3	
(b) 1 wt %	Ni (mg/kg)	17.6	
	Co (mg/kg)	11.8	
	Mn (mg/kg)	14.7	
(c) 2 wt %	Ni (mg/kg)	8.1	
	Co (mg/kg)	5.7	
	Mn (mg/kg)	7.3	
(d) 5 wt %	Ni (mg/kg)	9.1	
	Co (mg/kg)	6.2	
	Mn (mg/kg)	8.2	

electrode from the attack of the acidic electrolyte. This improves the structural stability in the highly charged state and facilitates lithium intercalation/deintercalation in the high voltage range. The cyclic stability also improved a little because of the surface coating. Table 2 summarizes the discharge capacity and capacity retention in the voltage range of 4.8 - 3.0 V.

In the following test, the pristine sample and the three coated samples were tested after storage, by ICP-AES and GD-OES. At first, the samples were charged to 4.8 V and stored in the electrolyte at 50 °C for 7 days. Then, the electrolyte used for the storage test was analyzed by ICP-AES to measure the dissolution of the transition metals (Co, Mn, and Ni). As shown in Table 3, the surface coating obviously suppressed the dissolution of the transition metals, which correlates with the enhanced electrochemical performance of the coated electrode at a highly charged state (over 4.6 V). Specifically, the 2- and 5-wt %-coated samples were more effective at suppressing the dissolution of the transition metals than the 1-wt %-coated sample. This is most likely related to the fact that not all the surface area of the 1-wt %-coated sample is covered by the coating layer, as shown in Fig. 1. To obtain more information about the dissolution of the transition metals during storage, the concentration profile vs. depth of the electrode was investigated by Glow discharge optical emission spectroscopy (GD-OES). GD-OES is an essential and convenient technique for elemental surface analysis and depth profiling.^{19,20} In this method, a pristine and a coated sample were sputtered from the surface in glow discharge conditions, and then the optical emission of the sputtered atoms in Ar plasma was analyzed by spectroscopy. Since the sputter progresses deeper into the electrode with time, a depth profile of the constituent elements of the sample can be obtained. Figure 5a shows the variation of optical emissions from the constituent elements depending on sputtering time, derived from the GD-OES measurement of the pristine electrode before storage. Some deviation of intensity was observed for several seconds; then a strong emission was observed from Ni, Co, and Mn, which are the main metal elements in the electrode. The deviation of emission intensity at the surface may be due to the roughness of the electrode. The emission of Li was not measured because the intensity of Li was too low (since the electrode

**Figure 5.** Depth profiles of optical emission from constituent elements depending on sputtering time in GD-OES measurements of pristine Li[Ni_{0.3}Co_{0.4}Mn_{0.3}]O₂ electrode, which is charged at 4.8 V, (a) before storage, and (b) after storage at 50 °C for 7 days.

was in a highly charged state, most of the Li ions were removed from the electrode). The emission of La and Ti was not detected. After over 700 s of sputtering, a rapid increase of Al emission and a drop in emission for the transition metals was observed because of the sputter of the Al current collector. The interface between the electrode and the Al current collector is not perfectly flat, and a concentration gradient was observed in that interface range. As shown in Fig. 5b, the GD-OES profile of the pristine electrode was dramatically changed after storage at 50 °C for 7 days. The emission intensities of all the transition metals showed a steep gradient from the Al current collector to the surface. This result clearly displays that the transition metals had dissolved into the electrolyte during the cycling. Figure 6a shows the GD-OES profile of the 2 wt % Li-La-Ti-O-coated sample before storage. The intensity of the La and Ti emission was clearly detected, which shows the existence of the coating layer. The optical emission profiles of the transition metals are similar to those of the pristine sample. As shown Fig. 6b, the GD-OES profile of the coated electrode had also changed after storage. However, it is noticeable that the gradient of the optical emission intensities of all the transition metals is much slower

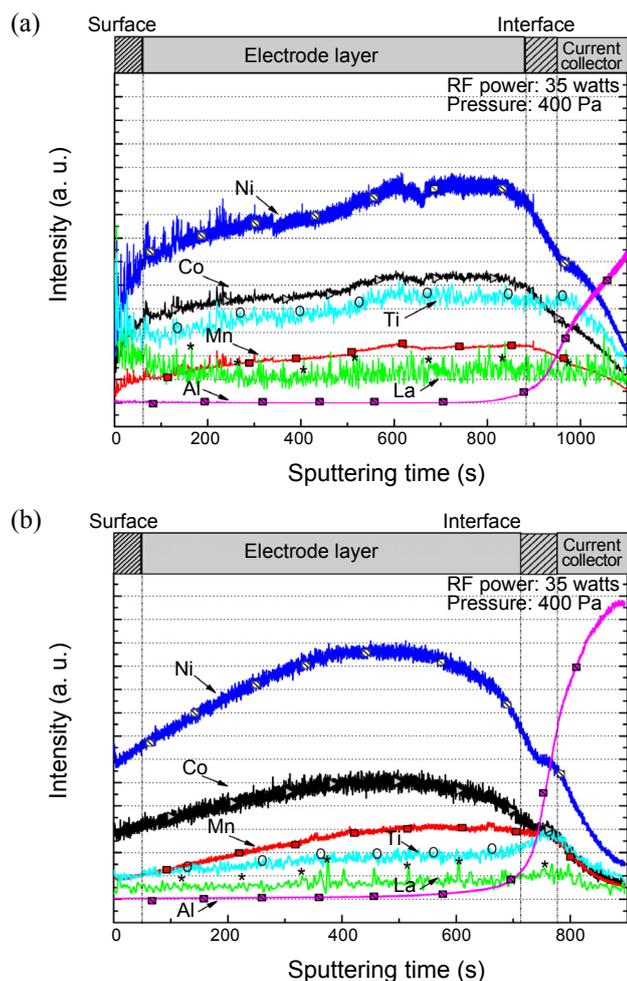


Figure 6. Depth profiles of optical emission from constituent elements depending on sputtering time in GD-OES measurements of 2-wt % Li-La-Ti-O-coated $\text{Li}[\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3}]\text{O}_2$ electrode, which is charged at 4.8 V, (a) before storage, and (b) after storage at 50 °C for 7 days.

compared with the steep gradient of Fig. 5b. This means that the dissolution of the transition metals into the electrolyte was suppressed by the Li-La-Ti-O coating. From the ICP-AES and GD-OES analysis, it is confirmed that the Li-La-Ti-O coating is a very effective method to decrease the dissolution of transition metals. This is obviously associated with the enhanced electrochemical properties of the coated sample such as high discharge capacity and improved cyclic performance and discharge rate capability.

Conclusions

Li-La-Ti-O coating effect on the electrochemical properties of $\text{Li}[\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3}]\text{O}_2$ was characterized as a function of the coating thickness. The thickness of the coating layer was in-

creased by increasing the wt % of the coating material. 1 and 2 wt % coating layer was very effective in improving the rate capability. Nevertheless, a 5-wt %-coated electrode, i.e., a coating layer thickness of 200 - 300 nm, also showed better rate capability than a pristine electrode. At high voltage, all the coated electrodes showed a higher discharge capacity than the pristine electrode; the 5-wt %-coated sample showed a slightly higher discharge capacity than the other coated samples. From ICP-AES and GD-OES analysis, it was confirmed that the Li-La-Ti-O coating was very effective in suppressing the dissolution of transition metals during storage at high temperature (50 °C). The 2 and 5 wt % coating layers were more favorable than the 1 wt % coating layer.

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References

1. Cho, J.; Kim, Y. J.; Kim, T.-J.; Park, B. *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 3367.
2. Myung, S.-T.; Izumi, K.; Komaba, S.; Sun, Y.-K.; Yashiro, H.; Kumagai, N. *Chem. Mater.* **2005**, *17*, 3695.
3. Thackeray, M. M.; Johnson, C. S.; Kim, J.-S.; Lauzze, K. C.; Vaughey, J. T.; Dietz, N.; Abraham, D.; Hackney, S. A.; Zeltner, W.; Anderson, M. A. *Electrochem. Commun.* **2003**, *5*, 752.
4. Ryu, J. H.; Kim, S. B.; Park, Y. J. *Bull. Korean Chem. Soc.* **2009**, *30*, 657.
5. Myung, S.-T.; Izumi, K.; Komaba, S.; Yashiro, H.; Bang, H. J.; Sun, Y. K.; Kumagai, N. *J. Phys. Chem.* **2007**, *C 111*, 4061.
6. Lee, H.; Kim, Y.; Hong, Y. S.; Kim, Y.; Kim, M. G.; Shin, N. -S.; Cho, J. *J. Electrochem. Soc.* **2006**, *153*, A781.
7. Ryu, K. S.; Lee, S. H.; Koo, B. K.; Lee, J. W.; Kim, K. M.; Park, Y. J. *J. Appl. Electrochem.* **2008**, *38*, 1385.
8. Wu, Y.; Murugan, A. V.; Manthiram, A. *J. Electrochem. Soc.* **2008**, *155*, A635.
9. Park, B.-C.; Kim, H.-B.; Myung, S.-T.; Amine, K.; Belharouk, I.; Lee, S.-M.; Sun, Y.-K. *J. Power Sources.* **2008**, *178*, 826.
10. Ryu, K. S.; Lee, S. H.; Park, Y. J. *Bull. Korean Chem. Soc.* **2008**, *29*, 1737.
11. Zheng, J. M.; Zhang, Z. R.; Wu, X. B.; Dong, Z. X.; Zhu, Z.; Yang, Y. *J. Electrochem. Soc.* **2008**, *155*, A775.
12. Yun, S. H.; Park, K. S.; Park, Y. J. *J. Power Sources.* **2010**, *195*, 6108.
13. Yun, S.; Park, Y. J. *Bull. Korean Chem. Soc.* **2010**, *31*, 355.
14. Inaguma, Y.; Chen, L.; Itoh, M.; Nakamura, T.; Uchida, T.; Ikuta, H.; Wakihara, M. *Solid State Commun.* **1993**, *86*, 689.
15. Lee, J. M.; Kim, S. H.; Tak, Y. S.; Yoon, Y. S. *J. Power Sources.* **2006**, *163*, 173.
16. Inaguma, Y.; Yu, J.; Shan, Y. J.; Itoh, M.; Nakamura, T. *J. Electrochem. Soc.* **1995**, *142*, L8.
17. Oguni, M.; Inaguma, Y.; Itoh, M.; Nakamura, T. *Solid State Commun.* **1994**, *91*, 627.
18. Choi, J.; Manthiram, A. *J. Electrochem. Soc.* **2005**, *152*, A1714.
19. Ui, K.; Yamamoto, K.; Ishikawa, K.; Minami, T.; Takeuchi, K.; Itagaki, M.; Watanabe, K.; Koura, N. *J. Power Sources* **2008**, *183*, 347.
20. Saito, Y.; Rahman, M. K. *J. Power Sources* **2007**, *174*, 877