Surface-Modified Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ for Li-Ion Batteries

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ABSTRACT

Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has received great attention as one of the most outstanding cathode materials for Li-ion batteries (LIBs) because of its high energy density resulting from the operating voltage of ~ 4.7 V (*vs.* Li^+/Li) based on the $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox reaction. However, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is known to suffer from undesirable side reactions with the electrolyte at high voltage as well as Mn dissolution from the structure. These issues prevent the realization of the optimal electrochemical performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Extensive research has been conducted to overcome these issues. This review presents an overview of the various surface-modification methods available to improve the electrochemical properties of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and provides perspectives on further research aimed at the application of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as a cathode material in commercialized LIBs.

Key words : Spinel, Batteries, Electrodes

1. Introduction

To overcome environmental issues such as global warming and air pollution, the development of sustainable energy technologies that are clean, affordable, and effectively infinite is required.¹⁻³⁾ Energy produced using renewable energy resources such as solar and wind energies is appealing; however, efficient energy storage systems (ESSs) are needed to compensate for the resulting intermittent energy production.¹⁻⁵⁾ To cope with the ever-increasing demands for the power sources to be used in grid-scale ESSs as well as portable electronic devices and electric vehicles (EVs), there have been many efforts to develop an efficient rechargeable battery system with high energy and power densities.¹⁻¹²⁾ Among known rechargeable batteries, Li-ion batteries (LIBs) offer the highest gravimetric and volumetric energy densities, which makes them the optimal choice for portable electronic devices and an appealing option for EVs and grid-scale ESSs.³⁻¹¹⁾ LIBs have dominated the portable electronic device market in the past two decades, and various types of EVs using LIB as power sources as well as prototype grid-scale ESSs have come to market during the past several years. In the pursuit of extended driving distances for EVs and lowered costs and long-lasting cycle per-

formance for grid-scale ESSs, extensive efforts have been made to find potential candidates for next-generation cathode materials for LIBs.¹³⁻²⁷⁾

Since Sony succeeded in commercializing the LIB system based on a LiCoO_2 cathode and carbon anode, various types of cathode materials (e.g., layered, spinel, Li-rich, and polyanionic compounds) have been introduced and commercialized for LIBs. Among them, layered-type cathode materials, LiMO_2 ($\text{M} = \text{Co}, \text{Mn}, \text{Ni}, \text{Ni}_x\text{Co}_y\text{Mn}_{1-x-y}$, or $\text{Ni}_x\text{Co}_y\text{Al}_{1-x-y}$), have received great attention for EVs and grid-scale ESSs because of their high gravimetric energy density (> 500 Wh kg^{-1}) and good cycling performance.^{19,28-36)} However, these electrode materials generally suffer from structural instability in the charged state or at high temperature due to transition metal migration and high oxygen activity, which can result in severe safety issues in practical applications. These safety concerns triggered the exploration of various polyanionic compounds (i.e., LiMPO_4 , $\text{Li}_2\text{MPO}_4\text{F}$, LiMSO_4F , $\text{Li}_2\text{MP}_2\text{O}_7$, where $\text{M} = \text{Fe}, \text{Mn}, \text{or Co}$) as cathode materials for LIBs because of the strong covalent bond of the polyanion, which stabilizes the oxygen ion within the crystal structure.^{23-25,37-57)} However, these electrodes exhibit low energy density and low ionic and electronic conductivities, which limit their further development and application. Spinel-structured LiMn_2O_4 has been the focus of much attention because of its high structural stability, low cost, low toxicity, and relatively high energy density.⁵⁸⁻⁶⁷⁾ LiMn_2O_4 has a face-centered cubic structure (space group $Fd\bar{3}m$), with Mn and Li located at 16d octahedral and 8a tetrahedral sites, respectively. The spinel structure provides three-dimensional (3D) Li conduction pathways, which enable fast Li de-

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insertion upon electrochemical cycling. However, the electrochemical reaction of LiMn_2O_4 in Li-ion cells involves severe Jahn-Teller distortion and disproportionation due to existing Mn^{3+} , resulting in poor cycle performance.⁶⁴⁻⁶⁷ Many previous studies have suggested that the electrochemical performance of LiMn_2O_4 can be improved by doping with different cations and anions.

Among doped $\text{LiMMn}_{2-x}\text{O}_4$ ($M = \text{Co}, \text{Fe}, \text{Cr}, \text{Cu}$, and Ni) materials, high-voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, which utilizes the redox couples of $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Ni}^{3+}/\text{Ni}^{4+}$, is considered a promising cathode for next-generation LIBs for EV and grid-scale ESS applications because of its high operating voltage of ~ 4.7 V (*vs.* Li^+/Li), low cost, and good cycle and high-rate performances.⁶⁸⁻⁸³ However, several issues and challenges must be addressed in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$: i) the unstable solid electrolyte interphase (SEI) formation at high operating voltage (*vs.* Li^+/Li), ii) the Mn dissolution upon electrochemical cycling, and iii) the structural transition from the LiM_2O_4 -type spinel structure to M_3O_4 -type spinel and rock-salt structures at the particle surfaces. Many efforts have been made to enhance the electrochemical properties of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ by cation doping, applying electrolyte additives, controlling the particle size and morphology, controlling the degree of cation ordering, and surface modification.^{34,68-117} Among these solutions, the most efficient and simple way to prevent deleterious side reactions upon electrochemical cycling of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is surface modification, which can enhance the overall capacity and cycle life.^{34,68-106} Efficient surface passivation prevents the direct contact of active particles with the electrolyte solution and suppresses the phase transition and side reactions at the particle surface, resulting in marked improvements in the electrochemical performance of electrode materials.

In this review, we will introduce the various surface modification techniques as well as the detailed synthesis methods used to stabilize the surface of the high-voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode material for LIBs. This review also covers the current state-of-the-art coating techniques based on metal oxides (i.e., ZnO , ZnAl_2O_4 , Al_2O_3 , TiO_2 , MgO , Fe_2O_3 , CuO , RuO_2 , SiO_2 , SnO_2 , etc.), polyanionic compounds (i.e., $\text{Li}_4\text{P}_2\text{O}_7$, Li_3PO_4 , LiPO_3 , $\text{Li}_{0.1}\text{B}_{0.967}\text{PO}_4$, LiFePO_4 , LiCoPO_4 , FePO_4 , Li_2SiO_3 , LiAlSiO_4 , etc.), polymers (polyimide (PI), polyacrylate, polypyrrole (PPy), poly(ethyl α -cyanoacrylate)), and carbon-based materials (amorphous carbon, graphene oxide, carbon nanotubes (CNTs)). In addition, various characterization techniques used to evaluate coating layers on electrodes such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy will be discussed. Finally, we will provide perspectives on the outlook of surface modification of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ materials.

2. Surface Modification Using Metal Oxide Compounds

Various metal oxides have received great attention as

coating materials for spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Several studies have reported on the use of ZnO coatings to protect the surface of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ against HF attack. Sun *et al.* reported that ZnO coating could improve the electrochemical properties of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.⁸⁴ 1.5 wt% ZnO -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ delivered a charge capacity of 137 mAh g^{-1} , and its capacity was maintained without any significant capacity degradation over 50 cycles at 55°C . Arrebola *et al.* also reported the effect of ZnO on nanosized spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was easily wrapped by ZnO by mixing $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ in ethanol followed by heat treatment.⁸⁵ The capacity of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{ZnO}$ at the current rate of $\text{C}/4$ was $\sim 128 \text{ mAh g}^{-1}$ and was stably retained over 50 cycles. Sun *et al.* reported further enhancement of the electrochemical properties of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ through improvement of the electrical properties of ZnO by Al doping.⁸⁶ The presence of the Al-doped ZnO coating was verified through TEM analyses, and the thickness of the coating was determined to be approximately 1 - 2 nm. The discharge capacity of the Al-doped ZnO -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at 0.1C was $\sim 128.9 \text{ mAh g}^{-1}$ and, surprisingly, that at 10C was $\sim 114.3 \text{ mAh g}^{-1}$, which is $\sim 77\%$ of its theoretical capacity. Electrochemical impedance spectroscopy (EIS) analyses revealed that the Al-doped ZnO -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ had a lower charge transfer resistance than bare $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and ZnO -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, which might affect the improvement of the power capability of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Furthermore, up to $\sim 99\%$ of the initial capacity of the Al-doped ZnO -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was maintained for over 50 cycles at 50°C as well as at 25°C . Lee *et al.* modified the surface of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ through coating with ZnAl_2O_4 , which provides low surface acidity, high thermal and chemical stability, and high mechanical resistance.⁸⁷ For the ZnAl_2O_4 coating, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles were added to a solution in which $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved, and the solution was stirred at 80°C to form a gel. The gel was heated at 180°C for further esterification followed by annealing at 900°C for 12 h. TEM analysis revealed the formation of a coating layer with a thickness of less than 100 nm on the surface of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles, and the presence of Zn and Al in the coating layer was confirmed through elemental analyses using TEM coupled with energy-dispersive X-ray spectroscopy (EDS). The capacity of the ZnAl_2O_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at 1C was $\sim 130 \text{ mAh g}^{-1}$, which is $\sim 88\%$ of its theoretical capacity. In addition, the ZnAl_2O_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ delivered a capacity of $\sim 97.3\%$ of its initial capacity after 100 cycles at the current rate of 1C , whereas the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ only provided $\sim 89.0\%$ retention of the initial discharge capacity. The thermal stability of the fully charged state of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was also enhanced with the addition of the ZnAl_2O_4 coating. The exothermic reaction temperatures of the pristine cathode were $\sim 181.8^\circ\text{C}$ and $\sim 267.1^\circ\text{C}$, whereas the exothermic reactions of the ZnAl_2O_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ occurred at $\sim 192.1^\circ\text{C}$ and 273.8°C , respectively.

Aluminum oxide (Al_2O_3) has also been used as a coating

material for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Wang *et al.* reported Al_2O_3 -modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ thin-film electrodes prepared by pulsed laser deposition (PLD).⁸⁸⁾ The $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ thin-film electrodes contained grains smaller than 200 nm covered with extremely small Al_2O_3 particles. The Al_2O_3 -modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibited enhanced cyclability with high coulombic efficiencies compared with pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, which means that the surface modification using Al_2O_3 resulted in improvement of the structural stability of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Whereas the discharge capacity of the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at the 50th cycle was $\sim 13.1 \text{ mAh g}^{-1}$, which is $\sim 10.6\%$ of its initial capacity at 55°C , $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ coated with 20-nm-thick Al_2O_3 exhibited $\sim 89.3\%$ capacity retention under the same conditions. Kim *et al.* also reported improvement of the electrochemical properties of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ by coating with Al_2O_3 .⁸⁹⁾ They used atomic layer deposition (ALD) to achieve a homogenous coating of Al_2O_3 on the surface of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles. The deposition of an $\sim 2\text{-nm}$ -thick amorphous layer on the particles was confirmed by TEM analysis. The SEI layer on the surface of the Al_2O_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was much thinner and contained fewer organic species than that on the surface of the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ because of the prevention of side reactions at high voltage provided by the Al_2O_3 coating. Thus, the Al_2O_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibited significantly improved capacity retention compared with the

pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The coulombic efficiency of the Al_2O_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ after the 80th cycle was $\sim 99.5\%$, whereas that of the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was 97.9% . Furthermore, it was verified that the Al_2O_3 coating could prevent the dissolution of transition metals in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The Mn amount dissolved from the Al_2O_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was ~ 6.6 times less than that from the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, indicating the successful protection from HF attack provided by the Al_2O_3 coating. It has also been reported that a combination of nanostructuring and Al_2O_3 coating could improve the properties of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Cho *et al.* prepared a $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ nanowire electrode using the sol-gel-based template method. The average diameter and length of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ nanowires were $\sim 140 \text{ nm}$ and $\sim 13 \mu\text{m}$, respectively.⁹⁰⁾ As observed in Fig. 1(a), the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ nanowires were uniformly coated by Al_2O_3 using ALD, and the thickness of the coating layer was $\sim 1.2 \text{ nm}$. The ALD coating on the nanowire electrode enhanced the electrochemical properties of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Fig. 1(b) shows that whereas the capacity of the uncoated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ nanowire was less than 10 mAh g^{-1} at a current rate of 1C and was significantly degraded over prolonged cycles, the Al_2O_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ nanowire exhibited a high coulombic efficiency of $\sim 98.8\%$ over 25 cycles with a capacity at 1C of $\sim 99 \text{ mAh g}^{-1}$ (10 times that of the uncoated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ nanowire).

Fig. 1. (a) TEM image of Al_2O_3 -coated (15 ALD cycles) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ nanowire. Reproduced with permission.⁹⁰⁾ Copyright 2015, American Chemical Society. (b) Measurement of power capability of several $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ samples. Black: Pristine, Blue: TiO_2 -coated, Red: Al_2O_3 -coated. Reproduced with permission.⁹⁰⁾ Copyright 2015, American Chemical Society. (c) Schematic illustrations of the Li_2TiO_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and the role of Li_2TiO_3 . Reproduced with permission.⁹²⁾ Copyright 2014, Royal Society of Chemistry. (d) Comparison of cycling performance between pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and Li_2TiO_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at 55°C . Reproduced with permission.⁹²⁾ Copyright 2014, Royal Society of Chemistry.

Titanium-based compounds have also been used as coatings for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Tao *et al.* reported the improvement of the electrochemical stability of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ by surface modification with TiO_2 .⁹¹ The crystal structure of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was not affected by the TiO_2 coating, and no XRD peaks related to TiO_2 were observed, which indicates the low loading amounts and thin layer of TiO_2 . Protective TiO_2 layers were chemically coated on the surface of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles using a simple wet chemical method. The thickness of the coating layer of TiO_2 was ~ 2 nm, and titanium and oxygen were homogeneously distributed throughout the TiO_2 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles. The TiO_2 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ delivered a high discharge capacity of 74.5 mAh g^{-1} at 15C, which is a very fast current rate, and up to $\sim 88.5\%$ of its initial capacity was maintained over 500 cycles. In contrast, the capacity retention of the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was only $\sim 33\%$. Li_2TiO_3 has also been considered as a coating material for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Deng *et al.* reported the highly enhanced electrochemical performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ resulting from coating with Li_2TiO_3 .⁹² As observed in Fig. 1(c), Li_2TiO_3 has received great attention because of its 3D Li diffusion path and great structural stability in organic electrolytes. The Li_2TiO_3 coating did not affect the structural deformation of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ or the formation of impurities. The thin and uniform Li_2TiO_3 coating on the surface of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles was verified by TEM coupled with elemental mapping. Elemental Ti was homogeneously distributed throughout the particles, and the thickness of the coating layer was ~ 8 nm. At a fast current rate of 5C, 3 wt% Li_2TiO_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibited a discharge capacity of 95 mAh g^{-1} , which is $\sim 65\%$ of its theoretical capacity, whereas the capacity of pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was 70 mAh g^{-1} under the same conditions. Furthermore, 3 wt% Li_2TiO_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibited better capacity retention than pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. As shown in Fig. 1(d), at 55°C , up to $\sim 94.1\%$ of the initial capacity of Li_2TiO_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was maintained over 50 cycles. In contrast, the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ only exhibited 77.1% capacity retention under the same conditions.

Alva *et al.* studied the surface modification of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ using MgO .⁹³ Elemental Mg was primarily applied as an inhomogeneous MgO coating on the surface of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles *via* heat treatment at 500°C and was then doped into the crystal structure at the subsurface of the particles at 800°C . Using EDS elemental mapping coupled with SEM, the uniform encapsulation of each particle of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ by Mg was clearly verified. XPS analyses also supported the presence of Mg on the surface of the particles. At 50°C , the capacity of the Mg-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was $\sim 70 \text{ mAh g}^{-1}$ at 5C, whereas that of pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was $\sim 50 \text{ mAh g}^{-1}$.

Wang *et al.* reported the surface coating of Fe_2O_3 for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.⁹⁴ The $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was modified by Fe_2O_3 through a simple chemical precipitation method using polyvinyl pyrrolidone polymer as a surfactant. The existence of

elemental Fe in the Fe_2O_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was confirmed through atomic absorption spectroscopy (AAS) and XPS. No Fe_2O_3 peaks were detected in the XRD pattern of the Fe_2O_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, which indicated that the Fe_2O_3 coating layer might be amorphous or that the amount of Fe_2O_3 was too small to be detected. Although the initial discharge capacity of the Fe_2O_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was $\sim 126 \text{ mAh g}^{-1}$, which was slightly lower than that of pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($\sim 131 \text{ mAh g}^{-1}$), the Fe_2O_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibited better cycle performance than pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Fe_2O_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibited excellent capacity retention of $\sim 98.6\%$ at room temperature (RT) over 100 cycles and $\sim 92\%$ capacity retention at 50°C over 50 cycles, whereas the capacity retention of pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was $\sim 86.5\%$ at RT and 79% at 50°C . Additionally, Fe_2O_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ also exhibited excellent power capability, delivering $\sim 67\%$ of its theoretical capacity at 10C.

CuO has also been considered as a potential coating material for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Li *et al.* reported enhanced properties of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ resulting from CuO coating.⁹⁵ For the CuO coating, pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{Cu}(\text{H}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ were mixed in distilled water with vigorous stirring, and the mixture was heated at 500°C for 6 h in air. TEM analyses revealed the uniform coating of 3 wt% amorphous CuO on the surface of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles with a coating thickness of ~ 3 nm. The CuO -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibited great power capability compared with that of pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The capacity of the 3 wt% CuO -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was 98.7 mAh g^{-1} at 10 C, which was ~ 1.7 times higher than that of pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and was stably retained over 100 cycles without any significant capacity degradation.

Coating of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with RuO_2 has been studied by several researchers because of the high electronic conductivity and catalytic functions for electrochemical oxidation processes of RuO_2 . Hong *et al.* reported a mechanism to improve the cycle performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ by RuO_2 surface modification.⁹⁶ The electrochemical properties of pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and RuO_2 -modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ were evaluated at various cut-off potentials ranging from 3.0 to 4.5 V. The specific capacity of pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at a cut-off voltage of 3 V was severely degraded to 18.0 mAh g^{-1} after 1000 cycles, which is only 13.8% of its maximum specific capacity, with $\sim 59 \text{ mAh g}^{-1}$ retained at the cut-off voltage of 4.5 V over 1000 cycles, which represents $\sim 50.9\%$ of its maximum capacity. The cyclability of RuO_2 -modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was significantly improved when the cut-off potential was 4.5 V, with RuO_2 -modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ delivering a specific capacity of 77.3 mAh g^{-1} after 1000 cycles, corresponding to $\sim 70.1\%$ of its maximum capacity. Jung *et al.* also reported on RuO_2 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ prepared by a wet chemical route with heat treatment at 450°C .⁹⁷ The existence of elemental Ru was identified through SEM elemental mapping. In addition, TEM analyses confirmed that the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles were coated

by polycrystalline RuO_2 with a coating thickness of ~ 10 nm. The cyclabilities of the pristine and RuO_2 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes were evaluated through charge/discharge tests at 0.1C for the first two cycles and then at 0.5C for subsequent cycles. The capacity retention of RuO_2 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with a loading weight of 9 mg cm^{-2} was $\sim 96.1\%$, which was higher than the $\sim 85.7\%$ capacity retention of pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ measured under the same test conditions.

Several researchers have used SiO_2 for improvement of the electrochemical performances of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Fan *et al.* prepared SiO_2 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.³⁴ No significant structural change was observed with the SiO_2 coating in the XRD analysis, and the TEM analyses confirmed that a porous nanostructured SiO_2 layer with a thickness of ~ 30 nm wrapped the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles. The capacity retention of the pristine sample and the 0.5, 1.0, and 3.0 wt% SiO_2 -coated samples over 100 cycles was $\sim 59\%$, 69% , 86% , and 87% , respectively, which indicated that the SiO_2 coating improved the cycle stability of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. To verify the effect of the SiO_2 coating on the electrochemical performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, the XPS spectra of the pristine and 1.0 wt% silica-coated samples measured at 55°C over 100 cycles were compared. The amount of LiF on the surface of the SiO_2 -coated sample was much lower than that on the surface of the pristine sample because of the reaction between SiO_2 and HF. Because the LiF resulted in high impedance, preventing fast Li-ion diffusion, the SiO_2 -coated

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with the smaller LiF content exhibited lower polarization during charge/discharge as well as better cycle performance than the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Shin *et al.* prepared $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode materials encapsulated by a cross-linked composite polymer layer containing SiO_2 nanoparticles through a chemical cross-linking reaction.⁹⁸ Fig. 2(a) shows the synthesis process for SiO_2 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Whereas the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibited an initial coulombic efficiency of $\sim 85.2\%$, the 3 wt% SiO_2 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ delivered better coulombic efficiency of $\sim 90.7\%$. As observed in Fig. 2(b), at 55°C , the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode suffered from severe capacity degradation, and its capacity after 100 cycles was $\sim 55\%$ of its initial capacity. However, the 3 wt% SiO_2 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode exhibited improved capacity retention of $\sim 81\%$ over 100 cycles. Furthermore, the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode experienced higher Mn and Ni dissolution from the SiO_2 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was detected. This finding indicates that the cross-linked composite polymer layer containing SiO_2 particles provided effective protection from HF attack.

Ma *et al.* prepared SnO_2 -modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ synthesized *via* a facile synthesis method.⁹⁹ The average particle size of the SnO_2 -modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was smaller than that of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ because of the inhibition of crystal growth resulting from the formation of a thin SnO_2 layer on

Fig. 2. (a) Schematic illustration of SiO_2 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Reproduced with permission.⁹⁸ Copyright 2014, Royal Society of Chemistry. (b) Comparison of cyclability of pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and several SiO_2 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ structures. Reproduced with permission.⁹⁸ Copyright 2014, Royal Society of Chemistry. (c) Comparison of power capability of pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and several SnO_2 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ structures. Reproduced with permission.⁹⁹ Copyright 2017, Royal Society of Chemistry.

the surface of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles. EDS elemental mapping of the SnO_2 -modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ revealed a homogeneous distribution of Ni, Mn, and Sn on the particles. As observed in Fig. 2(c), the capacity of the SnO_2 -modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at a current rate of 20C was $\sim 112.2 \text{ mAh g}^{-1}$, which is $\sim 77.2\%$ of its theoretical capacity, whereas the capacity of the pristine sample at 20C was $\sim 64.3 \text{ mAh g}^{-1}$. Over 500 cycles, the capacity of the SnO_2 -modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was maintained up to $\sim 103 \text{ mAh g}^{-1}$, representing retention of $\sim 75\%$ of its initial capacity, whereas that of the pristine sample decreased to 55 mAh g^{-1} , which is only $\sim 50\%$ of its initial capacity. These electrochemical results indicated the improved power capability and greater cyclability of the SnO_2 -modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ compared with those of the pristine sample.

Y_2O_3 coating has also been used for improvement of the electrochemical performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Wen *et al.* prepared Y_2O_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ using a heterogeneous nucleation method.¹⁰⁰ No significant structural differences were observed in the XRD patterns of the Y_2O_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and pristine samples. The elemental mapping performed using SEM/EDS analyses revealed a homogeneous distribution of Y on the surface of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The thickness of the coating layer was determined to be $\sim 6\text{--}8 \text{ nm}$ based on TEM analyses. The Y_2O_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibited better power capability than the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Whereas the capacity of the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was 56 mAh g^{-1} at 10C rate, the Y_2O_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibited a remarkable capacity of 102 mAh g^{-1} at the same current rate, which corresponds to $\sim 70\%$ of its theoretical capacity despite the fast current rate. Furthermore, the capacity retention of the Y_2O_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was $\sim 91.6\%$ over 100 cycles at 55°C , which is much greater than that of the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, which was only $\sim 77.9\%$.

Mou *et al.* reported the improved electrochemical performance of BiFeO_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.¹⁰¹ The coating of 1.0 wt% BiFeO_3 on the surface of the particles was shown to considerably enhance the power capability and cyclability of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The 1.0 wt% BiFeO_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ delivered discharge capacities of ~ 85.8 and $\sim 74.8 \text{ mAh g}^{-1}$ at current rates of 5C and 10C, respectively, whereas the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ delivered discharge capacities of 77.5 and 60.9 mAh g^{-1} , respectively, under the same conditions. The capacity retention of the 1.0 wt% BiFeO_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ over 50 cycles at 55°C ($\sim 92.9\%$) was higher than that of the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($\sim 80.3\%$).

Surface modification using a $\text{LiCoO}_2/\text{Co}_3\text{O}_4$ composite has also been considered for the enhancement of the properties of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ because of the fast Li-ion transport into the LiCoO_2 structure and the cubic spinel structure of Co_3O_4 , which is similar to that of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Qiao *et al.* prepared $\text{LiCoO}_2/\text{Co}_3\text{O}_4$ -modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ using a simple liquid-phase process.¹⁰² No LiCoO_2 or Co_3O_4 XRD peaks were detected, which indicates the absence of any structural deformation resulting from the surface modification. TEM

analyses revealed that the thickness of the coating layer was $\sim 10\text{--}60 \text{ nm}$, and the d -spacing values measured in the coating layer were ~ 0.200 and $\sim 0.243 \text{ nm}$, corresponding to the (104) plane of LiCoO_2 and (311) plane of Co_3O_4 , respectively. The power capability and cyclability of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ were significantly improved after coating with $\text{LiCoO}_2/\text{Co}_3\text{O}_4$. Up to $\sim 85.5\%$ of the theoretical capacity of the $\text{LiCoO}_2/\text{Co}_3\text{O}_4$ -modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was maintained at 5C, and its capacity over 200 cycles was $\sim 97.8\%$ of the maximal attainable capacity.

3. Surface Modification Using Polyanion Compounds

Various polyanion compounds have been used as coating materials for spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Many researchers have reported on the coating effect of phosphate-based compounds for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Chong *et al.* reported improvement of the electrochemical performance of $\text{Li}_4\text{P}_2\text{O}_7$ -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ resulting from the high ionic conductivity of $\text{Li}_4\text{P}_2\text{O}_7$.¹⁰³ The $\text{Li}_4\text{P}_2\text{O}_7$ -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was synthesized using the conventional solid-state method, and using XRD analysis, the main phase of this compound was identified as $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with the cubic spinel structure with the coexistence of $\text{Li}_4\text{P}_2\text{O}_7$. The TEM analyses confirmed that the thickness of the $\text{Li}_4\text{P}_2\text{O}_7$ coating on the surface of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was $\sim 8\text{--}10 \text{ nm}$. The $\text{Li}_4\text{P}_2\text{O}_7$ -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ retained $\sim 86.7\%$ of its initial capacity at the current rate of 40C, whereas pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ only retained $\sim 34.4\%$ of its initial capacity at 40C. Furthermore, the cycle retention of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was significantly improved by coating with $\text{Li}_4\text{P}_2\text{O}_7$.

Li_3PO_4 has also been considered as a coating material for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Konishi *et al.* reported the effect of Li_3PO_4 coating on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ using PLD.¹⁰⁴ In the XRD analysis, besides for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, other peaks related to Li_3PO_4 were not detected, which indicates that the coating consisted of the amorphous phase of Li_3PO_4 . X-ray reflectometer (XRR) analysis verified that the thickness of the Li_3PO_4 coating layer was $\sim 0.7\text{--}3.6 \text{ nm}$. The Li_3PO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibited a larger specific capacity and reduced capacity degradation compared with pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Chong *et al.* also prepared Li_3PO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as a stable high-voltage cathode material for LIBs.¹⁰⁵ An $\sim 5\text{--}6\text{-nm-thick}$ Li_3PO_4 coating was homogeneously applied on the surface of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ using a solid-state synthesis method. The Li_3PO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibited much more stable cyclability than the uncoated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The Li_3PO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ retained 80% of its initial capacity ($\sim 122 \text{ mAh g}^{-1}$) over 650 cycles. To further characterize the phase change after long cycles, dQ/dV plots of the Li_3PO_4 -coated and uncoated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at the first cycle and 200th cycle were compared. The Li_3PO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ did not experience a phase change, which indicates that the redox reactions of $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Ni}^{3+}/\text{Ni}^{4+}$ were well retained even after 200 cycles.

Fig. 3. (a) Schematic illustration demonstrating the effects of LiPO_3 coating on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Reproduced with permission.¹⁰⁶ Copyright 2016, Royal Society of Chemistry. (b) Rate performance of LiPO_3 -coated and uncoated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes charged at 0.1C then discharged at various C rates. Reproduced with permission.¹⁰⁶ Copyright 2016, Royal Society of Chemistry.

LiPO_3 has also been used as a coating material for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ because of its good ionic conductivity and chemical passivation properties. Chong *et al.* prepared $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ coated with 1-nm-thick LiPO_3 using the solid-state synthesis method.¹⁰⁶ As shown in Fig. 3(a), the LiPO_3 coating provided many advantages for improvement of the electrochemical performance of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The existence of the LiPO_3 coating layer verified using XRD and Raman spectroscopy. Two Raman shifts were detected at 1077 and 1172 cm^{-1} , representing the P-non-bridging oxygen in the LiPO_3 phase. Fig. 3(b) shows that with increasing C rate, the LiPO_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibited significantly improved power capability compared with the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Furthermore, the LiPO_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibited 77% capacity retention at the fast current rate of 30C. These results indicate that the enhanced ionic conductivity resulting from the LiPO_3 coating could efficiently lower the cell impedance and result in the superior power capability of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

$\text{Li}_{0.1}\text{B}_{0.967}\text{PO}_4$, which has been investigated as a solid electrolyte for LIBs because of its high Li ionic conductivity, was also applied as a coating material for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Yang *et al.* prepared $\text{Li}_{0.1}\text{B}_{0.967}\text{PO}_4$ -coated and Cr-doped $\text{LiNi}_{0.45}\text{Cr}_{0.1}\text{Mn}_{1.45}\text{O}_4$ using the soft combustion reaction.⁶⁸

Fig. 4. (a) Schematic illustration of the synthetic process for LiCoPO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Reproduced with permission.⁶⁹ Copyright 2016, Royal Society of Chemistry. (b) Comparison of cycle of pristine and LiCoPO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ structures measured at various C-rates ranging from 0.5C to 20C. Reproduced with permission.⁶⁹ Copyright 2016, Royal Society of Chemistry.

No significant structural change was detected with the addition of the $\text{Li}_{0.1}\text{B}_{0.967}\text{PO}_4$ coating, which indicated the presence of a separate layer of $\text{Li}_{0.1}\text{B}_{0.967}\text{PO}_4$ on the surface of the $\text{LiNi}_{0.45}\text{Cr}_{0.1}\text{Mn}_{1.45}\text{O}_4$ particles. The $\text{Li}_{0.1}\text{B}_{0.967}\text{PO}_4$ -coated and Cr-doped $\text{LiNi}_{0.45}\text{Cr}_{0.1}\text{Mn}_{1.45}\text{O}_4$ exhibited outstanding cyclability with a capacity retention of $\sim 85.4\%$ over 400 cycles and excellent power capability with a capacity of $\sim 90.7 \text{ mAh g}^{-1}$ at 20C. These results indicate that the $\text{Li}_{0.1}\text{B}_{0.967}\text{PO}_4$ coating layer provided a fast Li^+ diffusion channel with low charge transfer resistance and served as a protective layer to achieve a more stable surface chemistry.

LiCoPO_4 has also been applied as a coating material for spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ using a hydrothermal reaction synthesis method. Li *et al.* showed that the olivine LiCoPO_4 -shell-coated structure could significantly enhance the electrochemical performance by inducing the production of an appropriate amount of Mn^{3+} .⁶⁹ The synthesis process for the LiCoPO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is illustrated in Fig. 4(a). The XRD peaks of the prepared samples were well indexed to the cubic spinel structure of the $Fd\bar{3}m$ space group with no impurity phase. It was identified through inductively coupled plasma-atomic emission spectrometry (ICP-AES) that increasing the coating amount of LiCoPO_4 on the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles led to an increase in the Mn^{3+} con-

tent in the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. As observed in Fig. 4(b), the 5 wt% LiCoPO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibited outstanding cyclability with 98.5% charge/discharge efficiency after 100 cycles and great power capability, delivering 130 mAh g^{-1} at a high current rate of 20C, compared with pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

Jang *et al.* attempted to prepare LiFePO_4 -modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ via a scalable sol-gel technique.⁷⁰⁾ No structural change occurred with the LiFePO_4 coating, and the existence of LiFePO_4 in the compound was verified through elemental mapping based on TEM measurements. At elevated temperature conditions of 55°C , the LiFePO_4 -modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ delivered excellent cyclability with $\sim 89\%$ retention of its initial capacity after 50 cycles, whereas the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ experienced severe capacity degradation under the same measurement conditions. The authors reported that this outstanding improvement of the electrochemical performances of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ resulted from the protective coating of LiFePO_4 , which prevented severe HF attack, because at high temperature, the reaction is prone to be accelerated compared with that at ambient conditions. EIS analysis revealed the lower charge-transfer resistance of the LiFePO_4 -modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ than the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ after 50 cycles at 55°C , demonstrating the benefit of the LiFePO_4 coating for enhanced electrochemical activity of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at high temperature.

Amorphous FePO_4 was also considered as a coating material for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Xiao *et al.* proposed the use of a novel ALD-derived ultrathin amorphous FePO_4 coating.⁷¹⁾ After applying the FePO_4 coating using ALD, no peaks of FePO_4 were detected in the XRD pattern because of the ultrathin and amorphous nature of the FePO_4 phase. The intensity of the P 2p spectra decreased during ALD cycling, indicating that the amount of elemental P on the surface of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ increased with increasing number of ALD cycles. After 40 ALD cycles, no P 2p spectra was observed because of the surface saturation. HRTEM images revealed that the ultrathin FePO_4 coating layer was $\sim 2\text{-nm}$ thick, and the lattice fringe of $\sim 0.24 \text{ nm}$ distance was consistent with the (222) spacing of spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The FePO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ prepared using 10 ALD cycles exhibited great electrochemical performance, including a capacity of more than 80 mAh g^{-1} at 5C and retention of $\sim 91.96\%$ of the initial capacity after 100 cycles. Whereas pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ suffers from side reactions upon direct contact with the electrolyte, such as Mn dissolution and continuous electrolyte decomposition, the resistivity of the FePO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ prevented the direct contact of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with the electrolyte, helping to prevent the reduction and dissolution of Mn ions caused by oxidation. Yi *et al.* also prepared FePO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ via a sol-gel method.⁷²⁾ XRD measurements indicated that the FePO_4 coating did not change the structure of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. EDS mapping based on SEM imaging revealed the presence of Fe and P as well as Ni, Mn, and O, indicating the presence of FePO_4 in the coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. TEM analyses veri-

fied that $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles were uniformly encapsulated by the $\sim 1\text{-nm}$ -thick FePO_4 layer, which indicates that FePO_4 might have acted as an effective coating layer between the electrolyte and surface of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. In addition, 1 wt% FePO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibited great power capability with a capacity of $\sim 120 \text{ mAh g}^{-1}$ at the fast current rate of 2C. After 80 cycles, the reversible discharge capacity of the 1 wt% FePO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was $\sim 117 \text{ mAh g}^{-1}$, whereas that of the pristine sample was only $\sim 50 \text{ mAh g}^{-1}$.

Li_2SiO_3 , a novel and typical Li^+ -ion conductor, has also been considered as a coating material for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Deng *et al.* reported novel composites of $(1-x)\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \cdot x\text{Li}_2\text{SiO}_3$ prepared via a citric acid-assisted sol-gel method.⁷³⁾ The XRD peaks of the layer-structured Li_2SiO_3 and spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ were simultaneously detected in all the $(1-x)\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \cdot x\text{Li}_2\text{SiO}_3$ composites, indicating the coexistence of Li_2SiO_3 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The HRTEM images and selected area diffraction (SAED) patterns revealed that all the samples exhibited clear lattice fringes, indicating the good crystallinity of the materials. In addition, a thin layer was observed on the edge of the grains, which indicates the existence of amorphous Li_2SiO_3 on the surface of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles. The Li_2SiO_3 coating could enhance the cyclic performance and power capability of the spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The composite with $x = 0.1$ exhibited excellent power capability with a capacity of 107 mAh g^{-1} at the fast current rate of 2C and a capacity retention of $\sim 85.3\%$ over 50 cycles at 1C.

Fig. 5. (a) Schematic illustration of synthetic route used to produce LiAlSiO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNM) microparticles. Reproduced with permission.⁷⁴⁾ Copyright 2016, Royal Society of Chemistry. (b) Cyclic performance of pristine and 3 wt% LiAlSiO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at 1C and 55°C . Reproduced with permission.⁷⁴⁾ Copyright 2016, Royal Society of Chemistry.

Deng *et al.* reported the coating of microporous LiAlSiO_4 with good Li ionic conductivity on the surface of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles using a citric-acid-based sol-gel method.⁷⁴ Fig. 5(a) presents a schematic illustration of the synthetic route used to produce the LiAlSiO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles. The XRD peaks of LiAlSiO_4 were not detected for coatings containing 0–5 wt% LiAlSiO_4 . HRTEM analyses revealed that all of the samples had lattice fringes of ~ 0.48 nm, corresponding to the d -spacing of the (111) plane of spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. In addition, the samples except pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ were encircled by the coating layer of LiAlSiO_4 . The 3 wt% and 5 wt% LiAlSiO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ displayed outstanding cyclability of 96.7% and 97.1% over 150 cycles at 25°C, respectively. Furthermore, the capacity of the 3 wt% LiAlSiO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was maintained up to $\sim 94.3\%$ over 150 cycles at 55°C, whereas the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ only exhibited capacity retention of $\sim 76.5\%$ under the same conditions (Fig. 5(b)).

4. Surface Modification Using Polymers

Cho *et al.* proposed coating $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles with a polyimide (PI) gel polymer electrolyte (GPE) to prevent serious interfacial side reactions at high voltage, as shown in Fig. 6(a).⁷⁵ The surface of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles was encircled with PI *via* thermal curing of a four-component (pyromellitic dianhydride (PMDA)/biphenyl dianhydride (BPDA)/phenylenediamine (PDA)/oxydianiline (ODA)) polyamic acid. TEM measurements indicated that the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles were well encapsulated by an ~ 10 -nm-thick PI layer. Fourier-transform infrared (FT-IR) spectroscopy peaks corresponding to the C=O bond of the PI layer were observed at 1723 cm^{-1} , whereas the peak of the C=O bond of the pristine polyamic acid appears at 1650 cm^{-1} . This shift of the C=O bond indicated that the polyamic acid was successfully imidized to form the polyimide wrapping the surface of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles. No substantial differences were detected in the XRD patterns of the PI-coated and pristine samples. Compared with the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, the PI-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibited significantly improved cyclability. Up to $\sim 120\text{ mAh g}^{-1}$ of the capacity of the PI-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was retained after 50 cycles, whereas that of the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was only $\sim 98\text{ mAh g}^{-1}$ after 50 cycles. Pang *et al.* also reported enhanced electrochemical properties of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with PI coating.⁷⁶ The PI-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was prepared *via* a co-precipitation method and exhibited a spinel structure with P4332 symmetry, indicating that no structural change occurred as a result of the coating process. The PI coating prevented severe capacity fade of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at the high temperature of 55°C, and the capacity retention of the PI-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ over 180 cycles was $\sim 85\%$, which indicates the excellent thermal stability, good chemical resistance, and mechanical properties of the PI.

A polyacrylate coating was also applied to improve the electrochemical properties of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Zhang *et al.*

Fig. 6. (a) Schematic of PI-wrapping layer formed on the surface of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) and its role as an ion-conductive protection layer in suppressing side reactions. Reproduced with permission.⁷⁵ Copyright 2012, Royal Society of Chemistry. (b) Cycling performance of pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and 3 wt%, 5 wt%, and 8 wt% PPy-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at 1C and 55°C. Reproduced with permission.⁷⁸ Copyright 2014, Royal Society of Chemistry.

prepared lithium polyacrylate (PAALi)-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.⁷⁷ The $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles were uniformly surrounded by a thin disordered 1% PAALi layer, unlike the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles without any coating layers. The 1% PAALi-coated and pristine samples retained up to $\sim 90.0\%$ and $\sim 78.2\%$ of their initial capacities over 200 cycles at 1C, respectively, which indicates the highly enhanced electrochemical performances of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ resulting from the PAALi coating. Furthermore, SEM analysis of the cycled electrodes of the 1% PAALi-coated and pristine samples showed that PAALi could encourage the formation of a SEI layer, which was compatible between $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and the electrolyte.

Conductive PPY coatings have also been applied to improve the electrochemical properties of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Gao *et al.* prepared conductive PPY-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ composites using simple chemical oxidative polymerization in an aqueous solution.⁷⁸ No structural differences were detected in the XRD patterns of the pristine and PPY-coated

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ composites. SEM analysis indicated that the size of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles was $\sim 200 - 500$ nm. TEM and EDS analyses revealed that the ~ 3 -nm-thick porous PPy layer containing N well wrapped the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles. As observed in Fig. 6(b), whereas the pristine sample only exhibited capacity retention of 76.7% over 300 cycles, the 5% PPy-coated sample retained up to $\sim 91\%$ of its initial capacity after 300 cycles.

Poly(ethyl α -cyanoacrylate) (PECA) was also used as a coating material for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Liu *et al.* prepared surface-modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles *via in situ* polymerization of ethyl α -cyanoacrylate (ECA) to provide continuous surface coverage and a Li-ion transport channel.⁷⁹ The XRD pattern of the PECA-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was identical to that of pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, indicating that the polymer layer coating process did not affect the crystal structure of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles with a particle size of ~ 100 nm were encircled by an ~ 10 -nm-thick PECA layer. Whereas the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ delivered $\sim 74.7\%$ retention of its initial capacity over 100 cycles, the PECA-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ retained up to $\sim 92\%$ of its initial capacity under the same conditions. The polarization of the PECA-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ after 100 cycles was smaller than that of the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, which demonstrates the effectiveness of the PECA layer in preventing the formation of the interface layer that hindered the charge transport at the interface between $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and the electrolyte.

5. Surface Modification Using Carbon-Based Materials

Carbon-based materials are known as excellent coating materials for electrode materials for LIBs because of their high electronic conductivity. Yang *et al.* reported enhanced electrochemical performance of carbon-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ prepared by a sol-gel method.⁸⁰ The XRD pattern of the carbon-coated sample was characteristic of spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, and its particles were homogeneously wrapped by the carbon. The capacity of the carbon-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ modified with the addition of 1 wt% sucrose (sample c) remained up to ~ 130 mAh g^{-1} at 1 C and ~ 114 mAh g^{-1} at 5C. The carbon-coated sample also exhibited a high capacity retention of 92% after 100 cycles.

Graphene oxide was also applied as a coating material for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Fang *et al.* synthesized graphene-oxide-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ through simple mixing and annealing.⁸¹ The graphene-oxide-coated sample had a pure spinel crystal structure without any contamination, and the existence of graphene oxide was verified through elemental mapping based on SEM. As shown in Fig. 7(a), TEM analyses revealed that graphene oxide with a thickness of ~ 5 nm was coated on the outer surface of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The graphene-oxide-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at large current densities of 5C, 7C, and 10C retained up to $\sim 77\%$, $\sim 66\%$, and $\sim 56\%$ of the capacity measured at 1C (Fig. 7(b)), and its

Fig. 7. (a) HRTEM image of graphene-oxide-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with the graphene oxide on the surface of the particle. Reproduced with permission.⁸¹ Copyright 2013, Royal Society of Chemistry. (b) Comparison of power-capability between graphene-oxide-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Reproduced with permission.⁸¹ Copyright 2013, Royal Society of Chemistry.

capacity after 1000 cycles was $\sim 61\%$ of its initial capacity, indicating the enhanced electrochemical performances of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ resulting from the graphene-oxide coating.

Wang *et al.* synthesized a carbon-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ composite via pyrolysis of polyethylene glycol-400 (PEG) at high temperature.⁸² The carbon coating did not affect the crystal structure of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. A distinct coating layer was identified on the surface of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles through TEM observation. The Raman spectra of carbon in the carbon-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ composite clearly showed a disordered (D) band at 1366 cm^{-1} and the ordered graphite (G) band at 1575 cm^{-1} , verifying the existence of carbon in the composite. Over 500 cycles, the carbon-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ maintained up to $\sim 71\%$ of its initial capacity, whereas the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ only retained $\sim 55\%$ of its initial capacity.

Surface modification of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ using CNTs has also been attempted. Hwang *et al.* prepared CNT-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and oxidized CNT (OCNT)-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ composites *via* a mechano-fusion method to prevent unfavorable carbothermal reduction.⁸³ The D and G peaks were verified in each Raman spectra of the CNT- $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and OCNT- $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, verifying the existence of CNT and OCNT in each composite. The structures of the two composites were identical to that of the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ without any structural changes. TEM observation revealed

that the ~ 10 – 15 -nm thick CNT or OCNT layers encircled the surfaces of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles. The CNT-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and OCNT-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ delivered higher energy densities than the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ until the power density reached $\sim 1260 \text{ W kg}^{-1}$ at 2C.

6. Summary and Perspectives

Because of environmental problems such as air pollution and the greenhouse effect, considerable efforts have been made to design eco-friendly EVs, and LIBs have been considered one of the most attractive energy storage systems (ESSs) for EVs. To apply LIBs to these large-scale ESSs, however, their energy density must be improved. Thus, the development of electrode materials with theoretically high energy densities and high operation voltages is one of the major issues for LIBs in the world. Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has received great attention as an attractive cathode material for LIBs because of its high operating voltage of $\sim 4.7 \text{ V vs. Li}^+/\text{Li}$ based on the $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox reaction and relatively high theoretical capacity of $\sim 146.7 \text{ mAh g}^{-1}$. Recent studies on spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ have focused on surface coating using various compounds such as metal oxides, polyanion-based compounds, polymers, and carbon-based materials to improve the power capability and cyclability of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

The desired coating material should exhibit high stability to prevent side reactions between $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and the electrolyte as well as the HF attack accompanying Mn dissolution from $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Even though the cyclability of coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at room temperature is not significantly enhanced compared with that of pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibits higher stability than pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ during high-temperature cycle tests, which activate the side reactions and HF attack, because of the existence of the buffer layer for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Furthermore, coating of compounds containing Li ions in the structure or carbon-based materials simultaneously enables the achievement of great power capability and outstanding cyclability of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ because of the high ionic or electronic conductivity of the coating material as well as the encapsulation of the particle surfaces.

Various experimental processes have been applied to achieve uniform and homogenous coatings of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles. Many researchers have prepared coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ via heat treatment after mixing the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with a precursor containing the element desired in the solution base. Some researchers have attempted to apply deposition methods such as PLD or ALD to obtain more uniform and homogenous coatings on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The thickness of the coating layer is controlled by modifying the amount of reactants or the reaction time, and the existence of the coating layer in the composite is verified using SEM, TEM, XPS, or Raman spectra. It has been confirmed that the coating process does not affect the structure of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ regardless of the type of coating material.

To apply $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as a cathode material for LIBs,

more intensive research on the stability of electrolytes for LIBs is required despite numerous reports on the stable cyclability of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ over several hundred cycles. Previous studies on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ have generally used half-cell tests based on small-scale coin cells. However, for the practical application of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ in commercialized LIBs, it is essential to perform full-cell tests of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ based on large-scale pouch cells. Furthermore, various analyses of the modified electrolytes in the full-cell test should be performed to verify the stability of the LIBs at high operation voltage resulting from the redox reaction of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

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