



Lithium silicate–lithium phosphate ($x\text{Li}_4\text{SiO}_4 - (1 - x)\text{Li}_3\text{PO}_4$) coating on lithium nickel manganese oxide ($\text{LiNi}_{0.7}\text{Mn}_{0.3}\text{O}_2$) with a layered structure



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ABSTRACT

Solid solution of lithium silicate and lithium phosphate ($x\text{Li}_4\text{SiO}_4 - (1 - x)\text{Li}_3\text{PO}_4$, LSP) is coated on $\text{LiNi}_{0.7}\text{Mn}_{0.3}\text{O}_2$ using the reaction between the residual lithium compounds (Li_2CO_3 and LiOH) on the surface of $\text{LiNi}_{0.7}\text{Mn}_{0.3}\text{O}_2$ particles and the sol prepared from tetraethyl orthosilicate (TEOS) and anhydrous phosphoric acid. The physical properties of the samples are analyzed by powder X-ray diffraction (PXRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Electrochemical analyses, such as cyclic voltammetry (CV), galvanostatic intermittent titration technique (GITT) and galvanostatic cycling, are carried out for the samples. As a result, LSP-coating is found to be effective for improving the rate capability of $\text{LiNi}_{0.7}\text{Mn}_{0.3}\text{O}_2$ as a cathode material for lithium-ion batteries. The specific capacity of the LSP-coated sample retains 58% at high current density of 7 C-rate (vs. 0.5 C-rate) while the bare sample shows only 44% capacity retention. Higher Li^+ -chemical diffusion coefficient and fast charge transfer process at the interface of the LSP-coated sample estimated by GITT and CV analyses are believed to be the reasons for the better rate capability.

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1. Introduction

Recently, the market for lithium-ion batteries has expanded from power sources for portable electronics to vehicles and electric energy storage systems due to higher energy density, power capability and cycling stability. The evolution of cathode material is keeping pace with the market expansion of lithium-ion batteries. Nickel content in layered cathode materials has been raised to increase the specific capacity and cobalt content has been reduced to enhance the safety and lower the price. There have been many studies on the development of lithium nickel manganese oxide ($\text{LiNi}_x\text{Mn}_{1-x}\text{O}_2$) which does not contain cobalt [1–3]. However, it has also been reported that $\text{LiNi}_x\text{Mn}_{1-x}\text{O}_2$ suffers from poor structural stability, thermal stability, cycle life performance and rate capability, which have to be overcome for practical use of the material.

In order to overcome the problems in electrochemical performance of the cathode materials, surface modifications such as coating with Al_2O_3 , ZrO_2 and CuO , etc. have been extensively studied and the coating technologies have been proven to be effective on improving the cycle life performance and thermal stability [4–10]. Lithium-ion conducting

ceramics such as Li_3PO_4 and Li_4SiO_4 have also been adopted as a coating material to raise the rate capability as well as cycling stability of cathode materials, exploiting their ability to transport lithium-ions [11,12].

In this study, $\text{LiNi}_{0.7}\text{Mn}_{0.3}\text{O}_2$ cathode material is coated with a solid solution of lithium silicate and lithium phosphate (LSP), which has approximately a hundred times higher ionic conductivity than Li_4SiO_4 to investigate the effect of coating on the rate performance and cycling stability [13]. LSP was chosen as the coating material due to the high ionic conductivity of 10^{-5} S/cm at room temperature, electrochemical stability and low cost. The surface morphology, crystal structure and electrochemical characteristics of the bare and modified $\text{LiNi}_{0.7}\text{Mn}_{0.3}\text{O}_2$ materials are examined.

2. Experimental

LSP-coating was carried out on $\text{LiNi}_{0.7}\text{Mn}_{0.3}\text{O}_2$ supplied by POSCO ES Material. Our coating process uses the residual lithium compounds on the surface of the $\text{LiNi}_{0.7}\text{Mn}_{0.3}\text{O}_2$ particle as a reactant. The content of the residual lithium compounds was approximately 7300 ppm. The residual lithium compounds are composed of lithium hydroxide and lithium carbonate in a molar ratio of 3:7. The other reactants for preparing LSP (Si and P sources)—tetra ethyl orthosilicate (TEOS) and anhydrous phosphoric acid—were supplied by Sigma Aldrich and used

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without further purification. The amounts of TEOS and anhydrous phosphoric acid were controlled to the atomic ratio of Li (in the residual lithium compounds):Si:P = 3.7:0.7:0.3 to obtain a coating layer of $\text{Li}_{3.7}\text{Si}_{0.7}\text{P}_{0.3}\text{O}_4$.

In order to prepare a coating solution, TEOS and anhydrous phosphoric acid were dropped in anhydrous ethanol and vigorously stirred for 30 min. After stirring for 1 h, the coating solution was transferred into the flask of an evaporator. Subsequently, the cathode material was placed into the coating solution in the evaporator. The cathode material was uniformly dispersed in the coating solution by rotating the flask of the evaporator. The evaporator was connected to an aspirator and the temperature was adjusted to 80 °C to help the evaporation of ethanol. The dried powder was calcined at 600 °C for 4 h to form LSP layer on the surface of the $\text{LiNi}_{0.7}\text{Mn}_{0.3}\text{O}_2$ particles.

X-ray diffraction (XRD) analyses were carried out using an X-ray diffractometer (Rigaku, ULTIMA VI) over the 2θ range of 10° to 80° with monochromatized $\text{Cu-K}\alpha$ radiation. The morphology of the powder was observed using high-resolution scanning electron microscopy with an energy-dispersive spectrometer (HR-SEM/EDS, TESCAN-MIRA LMH).

In order to measure the electrochemical performances, 2016 coin-type half-cells were assembled in a glove box in which the moisture content was below 1 ppm. Lithium metal was used as a counterelectrode. The cathode was fabricated by casting a slurry with a formulation of 90 wt% active material, 5 wt% acetylene black and 5 wt% polyvinylidene difluoride (PVDF) binder on an aluminum foil. The electrolyte was 1.0 M LiPF_6 solution in 3:7 (vol%) ethylene carbonate (EC):diethyl carbonate (DEC). The coin-type cells were subjected to galvanostatic cycling and galvanostatic intermittent titration technique (GITT) measurement using a cycler (PNE Solution) in the voltage range of 3.0 to 4.3 V. The specific capacity was measured at 0.1 C-rate and a rate capability test was conducted at various current densities (0.1, 0.5, 1.0, 3.0 and 7.0 C-rate). The cells were cycled for 100 cycles, charging and discharging at 1.0 C-rate with a cutoff voltage from 3.0 to 4.3 and 4.5 V, to examine the cycling stability.

The cyclic-voltammetry (CV) measurements were carried out in the voltage range of 3.0 to 4.3 V at a scanning rate of 0.1 mA/s using a potentiostat/galvanostat (France, Bio-Logic, VSP).

3. Results and discussion

Powder XRD analysis were carried out to examine the change in crystal structure during LSP coating. Fig. 1 shows the XRD pattern of the bare and LSP-coated samples. Both samples showed similar patterns and no additional peaks for the impurities were observed after coating.

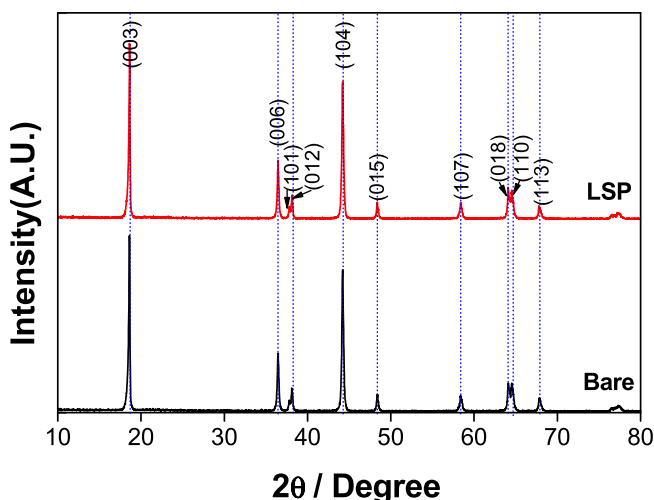


Fig. 1. Powder XRD patterns of the bare and LSP-coated samples.

The lattice parameters were estimated to be $a = 0.2886$ nm, $c = 1.4274$ nm for the bare sample and $a = 0.2886$ nm, $c = 1.4268$ nm for the LSP-coated sample, respectively. We can see that a noticeable change in crystal structure such as diffusion of Si or P into the bare material or the formation of new crystalline phase does not occur during the coating process from the negligible difference in the lattice parameter, peak positions and intensity after the coating process. Smaïhi et al. has reported a sol-gel preparation and lithium dynamics of LSP [13]. They prepared LSP powder by sol-gel reaction of LiOH and phosphoric acid in ethanol followed by calcination. Following their process with the addition of $\text{LiNi}_{0.7}\text{Mn}_{0.3}\text{O}_2$, an LSP-coated cathode material could be obtained successfully.

Fig. 2(a) to (d) shows SEM and EDS analysis results for the bare and LSP-coated samples. Both samples assumed a spherical shape and no morphological changes were observed after the coating process. The D_{50} of the bare and LSP-coated sample were almost same (11.27 μm for the bare sample and 11.83 μm for the LSP-coated sample). The EDS analysis result shows that the coating material (LSP) is uniformly dispersed throughout the surface of $\text{LiNi}_{0.7}\text{Mn}_{0.3}\text{O}_2$ particles as confirmed by the Si and P element mapping images. TEM analysis was conducted to investigate the shape and thickness of the coating layer. The dark and bright areas represent the $\text{LiNi}_{0.7}\text{Mn}_{0.3}\text{O}_2$ and coating layer, respectively. The thickness of the coating layer is in the range of 100 to 200 nm and the coating layer appears to be more film-like rather than particle-like.

The initial charge–discharge profiles of the bare and LSP-coated samples at 0.1 C-rate is displayed in Fig. 3. The LSP-coated sample delivered slightly lower specific discharge capacity (~151 mAh/g) than the bare sample (~156 mAh/g). Generally, the discharge capacities of the cathode materials coated with metal oxides is lower than the bare one because the coating material does not exhibit electrochemical activity (Al_2O_3 , MgO , etc.) [14]. LSP does not participate in an electrochemical reaction over the cycling voltage range as can be expected from the fact that LSP has no transition metal ions.

Fig. 4 shows cycling stability of the bare and LSP-coated samples at 0.5 C-rate (charge)/1 C-rate (discharge) with a charge cutoff voltage of 4.3 and 4.5 V. As can be seen in the figure, the LSP-coated sample retains better capacity at a high cutoff voltage (4.5 V) cycling, while a significant difference is not observed at 4.3 V. The cycling stability of the so-called ‘NMC cathode materials’— $\text{LiNi}_x\text{M}_y\text{Co}_z\text{O}_2$ —is greatly affected by solid electrolyte interface (SEI) layer formation and reversibility in the transformation of crystal structure [15]. It has been reported that the formation of metal oxides with SEI during cycling can deteriorate the cycling stability through an in-depth X-ray photoelectron spectroscopy (XPS) study [16]. Moreover, high potential at the charged state can accelerate the anodic decomposition of the electrolyte leading to the formation of a passivation layer on the surface of the electrode. We believe that the LSP-coating depressed the formation of the metal oxides on the surface of the electrode and reaction between the electrolyte and electrode, and thus contributed to the improvement in high-voltage cycling stability.

The rate capability of the samples is shown in Fig. 5. The measurement was conducted at various discharge current densities from 0.5 to 7.0 C-rate with a fixed charge rate (0.5 C-rate). The LSP-coated sample retains 58% of discharge capacity at 7.0 C-rate, while the bare sample shows only 45% of the capacity retention. It is quite a surprising result because LSP is known to be an electronic insulator and rate capability is closely related with the electronic conductivity of the cathode material [17]. To identify the reason for the enhancement in rate capability, galvanostatic intermittent titration (GITT) and cyclic voltammetry (CV) measurements were carried out.

The chemical diffusion coefficient of lithium ion is an important kinetic parameter for intercalation and de-intercalation in lithium ion batteries. The diffusivity of lithium ion has been measured with electro-chemical measurements such as GITT, potentiostatic intermittent titration technique (PITT) and electrochemical impedance spectroscopy

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