Electrochemical performance of a newly-designed all-solid-state Li ion battery with a LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$–LiVO$_3$ mono-particle layered cathode and a lamellar LiVO$_3$ anode

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All-solid-state Li ion battery (ASS-LIBs) with a LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$–LiVO$_3$ mono-particle layered (NCMLVO-MPL) cathode was newly developed by blade coating method with a mixture of NCM and deliquescent-LiVO$_3$ (LVO). The electrode was fabricated by coating the aqueous slurry containing the LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ (NCM) particles and the liquefied LVO on the Al foil and drying it at low temperature below 150°C. By controlling the gap of blade coater, we successfully fabricated “mono-particle layered structure”, where NCM particles are highly dispersed in the LVO matrix and the thickness was almost same as the diameter of the particles. The ASS-LIB with the NCMLVO-MPL cathode exhibited high discharge retention of 84% after 50 cycles. In the MPL structure, the well-dispersed NCM mono-particles functioned as the ion and electron conductive path in the direction perpendicular to the electrode, which kept charge–discharge capacity during the cycle test. Moreover, the all-solid-state Li ion battery incorporated with the NCMLVO-MPL composite cathode and a lamellar LVO anode was designed, also exhibiting high discharge retention of 92% after 50 cycles.

Key-words : All-solid-state, Li ion battery, Mono-particle layered cathode, Deluquescent-LiVO$_3$

1. Introduction

All-solid-state Li ion batteries (ASS-LIBs) have attracted a lot of attention in recent years because its desirable possibility for improving volumetric energy density and safety of a liquid-based LIBs. A non-flammable solid electrolyte is generally used as an electrolyte in ASS-LIBs, having higher safety relative to a conventional flammable electrolyte solution. In addition, all-solid-state LIBs will realize a high volumetric energy density by stacking assemblies including a solid electrolyte and electrodes.¹ All-solid-state LIBs with active material particles have the advantage of a high energy density but face the task of being difficult to form a dense active material layer with a good electrical conductive path. Sulfur-based electrolytes²–⁴ are promising materials because of its high Li ion conductivity and high flexibility. However, the sulfur-based electrolytes carry the risk of emitting the toxic gas when reacting with moisture. Oxide-based solid electrolytes⁵–⁷ are another attractive materials because of their chemical stability in the atmosphere and high Li ion conductivity. Though, the oxide-based solid electrolytes have low flexibility compared to the sulfur-based electrolytes resulting in insufficient interfacial contact between the solid electrolyte and active materials. The insufficient interface degrades Li ion and electron conductive path at the interface, which leads to electrical resistance and poor charge–discharge cycle performance.

We recently developed the dense active material layers with no toxic effect and sufficient interfacial contact by liquefaction approach using deliquescent-LiVO$_3$ (LVO).⁸–⁹ The LVO has been known as one of candidate for active materials⁹–¹² but we focused on its deliquescent characteristics and first demonstrated the validity of the deliquescent material to form the favorable solid-solid interface in ASS-LIBs. The active material layers were fabricated by applying the slurry containing LVO dissolved in aqueous-organic solution to Al foil and drying as 150°C in air. As for anode, the LVO active material layer with a lamellar structure was developed in our latest research, exhibiting a superior charge–discharge cycle performance.¹⁰ In anode, LVO worked as active material whose the charge–discharge potential of the lamellar LVO electrode was about 2.4 V. As for cathode, we fabricated a composite electrode containing the LVO and 4 V class active materials such as LCO and NCM, where the LVO functioned as a Li ion conductive path.¹¹ The issue of the cathode was poor cycle performance which was due to the interfacial delamination between stacked active material particles and the solid electrolyte. It has not been reported about relationships between a thickness of active material layer as same size as active material particles and cycle performance.

This paper firstly reported the influence of a thickness of an active material layer as same size as LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ active material particles on cycle performance. Also, an electrochemical performance of the newly-designed all-solid-state LIBs incorporated with a mono-particle layer LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$–LiVO$_3$ (NCMLVO-MPL) cathode and the lamellar LVO anode was investigated.

2. Experimental

2.1 Preparation of the LiVO$_3$ powder

The LVO powder was obtained by conventional solid state reaction. Li$_2$CO$_3$ and V$_2$O$_5$ were uniformly mixed, and the mixture was heated at 650°C in air for 10 h. The LVO aqueous solution was prepared by dissolving the LVO powder in the water-organic mix solvent with N-methylpyrrolidone. The experimental detail of

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the preparation of the LVO powder and LVO aqueous solution referred to our latest papers.3,9

2.2 Fabrication and characterization of the LiNi_{1/3}Co_{1/3}Mn_{1/3}O_{2–LiVO₃} composite electrode

The NCM-LVO composite electrodes were prepared via blade coating method. The slurry consisting of 0.6 g of NCM powder, 0.7 g of the LVO aqueous solution, and 0.01 g of Ketjen Black EC 300J (KB) was coated on Al foil by using a blade with a gap of 50 or 100 μm. The thickness of the NCMLVO composite electrodes was controlled by changing a gap of a blade. The slurry-coated Al foil was dried in an oven at 150°C for 6 h and was pressed under a pressure of 40 MPa. The lamellar LVO electrode was also prepared by the same manner of the NCMLVO electrode preparation except not adding NCM powder. The electrode morphology was observed by scanning electron microscopy (SEM, Hitachi S-4800).

2.3 Electrochemical measurements

For evaluating electrochemical performance of the NCMLVO composite electrodes with different thickness of active material layer, the NCMLVO composite electrode (10 mm in diameter), Li foil, and polyethylene oxide (PEO) polymer membrane with Lithium bis(trifluoromethanesulfonyl)imide were used as a cathode, anode, and solid electrolyte layer, respectively. The lamellar LVO electrode was used as an anode in the all-solid-state cell with the NCMLVO cathode. All-solid-state cells were assembled in an Ar-filled glove box. The charge–discharge cycle tests were performed at 25°C under current constant condition, corresponding to C/25 using a potenti-galvanostat (Solartron, 1480). Design capacity of cathode material in this paper was set 150 mAh g⁻¹. Charge–discharge rate property of the cell was evaluated by changing a charge–discharge rate (1C, C/3, C/10, and C/25). The lower and upper voltage limits on using Li foil as an anode were 3.0 and 4.25 V, respectively. The limits were 0 and 2.25 V when the lamellar LVO electrode was used as an anode, and the cathode and the anode capacities were designed 0.148 and 0.300 mAh cm⁻², respectively. The internal resistance of the cells was analyzed by using frequency response analyzer (Solartron, FRA 1252A) with the frequency ranging from 0.1 Hz to 0.3 MHz with the amplitude of 10 mV.

3. Results and discussion

3.1 Characterization of the LiVO₃ powder and the LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂–LiVO₃ composite electrode

The obtained powder was light green color and its X-ray diffraction (XRD) pattern is shown in Fig. 1. The XRD pattern coincides with the LiVO₃ (LVO) of the ICDD card No. 33-0835 without impurity. The LVO powder was dissolved in water-organic solvent, being used as an electrolyte binder in the NCMLVO composite electrodes. Figure 2 shows the XRD pattern of the NCMLVO composite electrode fabricated by using a blade with a gap of 50 μm. The XRD pattern is basically a superposition pattern of the LVO powder and the NCM powder. However, one XRD peak emerges at 26.5°, which attributes to the LVO, disappears in the XRD pattern of the NCMLVO electrode. Furthermore, small peaks located at 17.0, 26.0, and 27.3° can be observed in the XRD pattern. The appearance of these unknown peaks and the disappearance of the LVO peak may be originated with the change of the LVO crystallite structure via dissolution and recrystallization process or the decomposition of the NCM by soaking into the solvent or the evolution of the solid solution phase of the NCM and LVO.

3.2 Morphologies of the LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂–LiVO₃ composite electrode

The morphology of the NCMLVO composite electrodes prepared by changing the gap of a blade (50 or 100 μm) is shown in Fig. 3. In the active material layer fabricated by conventional method using a blade with the gap of 100 μm, the NCM particles are randomly stacked. The thickness of the active material layer is about 20 μm [Fig. 3(a)]. On the other hand, by decreasing the blade gap to 50 μm, the thickness of the active material layer was almost same as the diameter of NCM particle size (8 μm) [Fig. 3(b)]. The NCM mono particles are highly dispersed in the LVO matrix and aligned in the direction parallel to the electrode layer, hereinafter being described the NCMLVO mono-particle layered (NCMLVO-MPL) electrode. Figure 4 shows the illustration of the NCMLVO-MPL formation mechanism. Slight dissolving state of the LVO in the active material layer during the pressing process is important to fabricate the NCMLVO-MPL. By the slight dissolving state, the NCM particles move in the
active material layer during the pressing process, form a line without stacking. Applying in a thin layer is obviously important to fabricate the NCMLVO-MPL.

3.3 Electrochemical performance

Li intercalation/de-intercalation properties of the NCMLVO electrodes with different thickness were investigated by cyclic voltammetry (CV) technique. Shape and peak position of CV curve have a sensitive reaction to the difference of the electrical conductive rate. Figure 5 shows the CV curves of the cells with the NCMLVO electrodes as cathode. The anodic current of either cell increased from about 3.6 V and the cathodic current peak was also 3.6 V. This redox current is associated with the redox reaction of Ni$^{2+}$/Ni$^{4+}$ and Co$^{3+}$/Co$^{4+}$ in the NCM particles. In addition, the redox peak of V$^{4+}$/V$^{5+}$ in the LVO was not observed in this region of between 3.0 and 4.5 V. These results indicate that the NCM particles in the NCMLVO composite electrode functioned as a cathode active material in the range between 3.0 and 4.5 V and the LVO functioned as a Li ion conductive path. Here, the anodic curve of the cell with the NCMLVO electrode using the stacked NCM particles was warped in a direction toward higher potential, and the significant peak was not confirmed under the scanning rate of 0.05 mV s$^{-1}$ [Fig. 5(a)]. This shape of the CV curve means that electrical conductivity is not enough to keep up with a scanning rate. In contrast, the anodic and cathodic peaks were clearly observed in the CV curve of the cell with the NCMLVO-MPL composite electrode, and the anodic and cathodic peak positions were about 3.90 and 3.61 V, respectively [Fig. 5(b)]. Moreover, the cell with the NCMLVO-MPL composite electrode exhibited higher current densities relative to the cell with the stacked NCM particles. That is, the electrical conductive rate of the NCM particles improves by reducing the thickness of the active material layer like the NCMLVO-MPL. To clear the improvement of the electrical conductive rate directly, the difference of the internal resistance including charge transfer resistance was evaluated by using electrochemical impedance technique. Figure 6 shows impedance properties of the cells using the NCMLVO electrodes with the different thickness as cathodes. Li foil and PEO membrane with LiTFSI were used as an anode and a solid electrolyte, respectively. The Nyquist plots for the cells are separated into two components, which are a resistance component at approximately 0.1 MHz and semicircle component between 0.1 MHz and 1 Hz. The resistance component was approximately 100 $\Omega$ cm$^2$, can be identified the resistance of the PEO bulk ($R_{PEO}$). The semicircle resistance, was assumed to be a complex resistance, including the following resistance components, LVO bulk ($R_{LVO}$), NCM bulk ($R_{NCM}$), the interface between NCM and LVO ($R_{LCO/LVO}$), the interface between LVO and PEO ($R_{LVO/PEO}$), the interface between NCM and PEO ($R_{NCM/PEO}$), and the interface between Li foil and PEO.
(R_{Li/PEO}). The resistance of the cell with the NCMLVO-MPL cathode, which appears as the semicircle, was approximately 370 Ω cm². On the other hand, the resistance drawn as the semicircle of the cell with the NCMLVO composite cathode with the stacked NCM particles was 520 Ω cm². R_{Li/PEO} which was measured in our previous research was 280 Ω cm². That is, the internal resistances of the NCMLVO-MPL cathode and of the NCMLVO composite cathode with the stacked NCM particles were 90 and 240 Ω cm², respectively. The internal resistance of the NCMLVO cathode drastically decreased by forming the mono-particle layered structure.

The charge-discharge profiles of the cells using each NCMLVO electrode as a cathode were investigated by use of galvanostatic charge-discharge technique, as shown in Fig. 7. Li foil and PEO membrane with LiTFSI were used as an anode and a solid electrolyte, respectively. The either cell exhibited the charge-discharge behavior derived from Li intercalation and deintercalation of NCM active material, as described above. In the charge process, the cell voltage rapidly raised to circa 3.7 V and moderately rose to about 3.8 V. The oxidation of Ni^{2+} to Ni^{3+} occurred in this region of between 3.7 and 3.8 V. In the region of up to 3.8 V, the oxidation of Ni^{3+} to Ni^{4+} and Co^{3+} to Co^{4+} also occurred. The redox reaction of Ni^{2+}/Ni^{4+} and Co^{3+}/Co^{4+} proceeded in the range of between 3.0 and 4.25 V without proceeding V^{4+}/V^{5+} redox reaction of the LVO in the NCMLVO electrode. The coulombic efficiency at first charge-discharge process was low, being associated with oxidation of impurities in the PEO membrane. The cell with the NCMLVO-MPL electrode exhibited 104.4 mAh g⁻¹ of the first discharge capacity [Fig. 7(b)], being higher than 91.4 mAh g⁻¹ of the cell with the NCMLVO electrode using the stacked NCM particles [Fig. 7(a)]. The comparison of the cycle performance of the cell is shown in Fig. 8. The cell with the NCMLVO electrode using the stacked NCM particles exhibited the drastic decrease in discharge capacity from 91.4 to 70.7 mAh g⁻¹ in mere 5 cycles, and its discharge retention rate was 77%. In contrast, the discharge capacity of the cell with the NCMLVO-MPL electrode moderately decreased only from 104.4 to 87.5 mAh g⁻¹ during 50 cycles, and the discharge retention and the coulombic efficiency were 84 and 99%, respectively. These results demonstrated that cycle performance drastically improved by reducing the thickness of the active material layer as same size as the NCM active material particles. The NCM active materials are known to exhibit not only ionic conductivity but also electronic conductivity. Therefore, in the MPL structure, the well-dispersed NCM mono-particles functioned as the ion and electron conductive path in the direction perpendicular to the electrode. In the thick electrode, the ionic paths were degraded by delamination at the interface between active materials and LVO owing to volume change of active material during charge-discharge test. On the other hand, in the MPL electrode, the ionic/electron path was kept even if the interface was delaminated.

It requires higher cycle property as well as higher charge-discharge rate property to achieve the practical use of ASS-LIBs. The mono-particle layered structure has inherently superior charge-discharge rate property because the NCM particles in the ideal NCMLVO-MPL cathode directly transfer Li ion and electron. The charge and discharge profiles of the NCMLVO-MPL/PEO/Li cell at different charge-discharge rate of 1C, C/3, C/10, and C/25 are shown in Fig. 9. The charge and discharge capacities decreased with increasing the charge-discharge rate. The discharge capacities of the cell at 1C, C/3, C/10, and C/25
are 5, 16, 77, and 118 mAh g$^{-1}$, respectively. The discharge capacity at 1C was very low but the surface of the NCM particles in the NCMLVO-MPL cathode is possibly contaminated with the LVO from the cross-sectional SEM image of the NCMLVO-MPL electrode [Fig. 3(b)]. That is, by removing the LVO on the NCM surface, the NCMLVO-MPL cathode has the possibility of conducting decent charge-discharge cycle at higher rate.

The all-solid-state cell using the LVO as an active material or a Li$^+$ conductive path newly designed to balance high cycle performance and safety, as illustrated in Fig. 10. The NCMLVO-MPL was used as a cathode where, the LVO functions as a Li$^+$ conductive path. Also, the lamellar LVO electrode, which exhibited remarkable cycle property in our latest research,9) was used as an anode (Fig. 11). The charge-discharge curves of the NCMLVO-MPL cathode and the lamellar LVO anode are shown in Fig. 12. The average voltage of the cell calculated by using the charge-discharge potentials at 50 mAh g$^{-1}$ (half of discharge capacity of the cathode) of the cathode and anode is about 1.4 V. Charge and discharge process proceeds according to the following cathodic and anodic reactions:

\[
\text{(Cathode)} \quad \text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2^- \rightarrow \text{Li}_{1-x-y}(\text{Ni}_{1/3}\text{Li}_{2-x-y}\text{Co}_{1/3}\text{O}_{3+y}^+)\text{Li}_{1/3}\text{Mn}_{1/3}\text{O}_2^- \\
+ (x+y)\text{Li}^+ + (x+y)e^-
\]  

\[
\text{(Anode)} \quad \text{LiVO}_3 + (x+y)\text{Li}^+ + (x+y)e^- \rightarrow \text{Li}_{1+x+y}\text{Vi}^{3+}x-y)\text{O}_3
\]

In addition, the cathode and the anode capacities were designed 0.148 and 0.300 mAh cm$^{-2}$, respectively. The charge-discharge profiles of the cell with the NCMLVO-MPL cathode and the lamellar LVO anode are shown in Fig. 13. The initial charge and discharge capacity of the cell were 150
and 125 mAh g\(^{-1}\), respectively. The coulombic efficiency was 83%. Figure 14 shows the cycle performance of the cell during 50 cycles. The discharge capacity of the cell decreased only 10 mAh g\(^{-1}\) during 50 cycles, and the discharge retention was 92%. The decrease in discharge capacity could be due to the deterioration of the NCMLVO-MPL cathode because the lamellar LVO anode exhibited discharge retention of 100% after 50 cycles in our latest research.\(^9\) The coulombic efficiency after 50 cycles increased from 83 to 98%. These results demonstrated the possibility of the performing charge and discharge with superior cycle performance and safety by using the NCMLVO-MPL cathode and the lamellar LVO anode.

4. Conclusions

A Li\(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2\)-LIVO\(_3\) mono-particle layered (NCMLVO-MPL) cathode, which was developed for the purpose of improving cycle performance, was prepared by blade coating method with the liquefied LVO. The NCMLVO-MPL cathode had an active material layer thickness of 8 μm, being similar in thickness with the NCM particles. In addition, the NCM particles in the NCMLVO-MPL cathode formed a line without being stacked on top of another. The cell with the NCMLVO-MPL cathode exhibited higher discharge retention relative to the cell with the stacked NCM active material particles, whose discharge retention and coulombic efficiency after 50 cycles were 84 and 99%, respectively. In addition, the cell in which the LVO was applied to both cathode and anode was newly designed for realizing both high cycle performance and safety, and the NCMLVO-MPL composite electrode and the lamellar LVO electrode were used as a cathode and anode, respectively. The LVO functioned as a Li conductive path in the NCMLVO-MPL composite electrode and functioned as an active material in the lamellar LVO electrode. The cell with NCMLVO-MPL cathode and the lamellar LVO anode exhibited 92% of the discharge retention after 50 cycles, whose coulombic efficiency was 98%. From the above results, we concluded that the LVO is a promising material for all-solid-state Li ion batteries, and the balance between high cycle performance and safety was realized by using the LVO as a Li conductive path or an active material.

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