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著者(和文)	OhGwangseok
Author(English)	Gwangseok Oh
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論文題目

**Interfacial reactions in high-voltage type all solid-state batteries with  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  electrolyte**

物質電子化学専攻 菅野・平山研究室  
Gwangseok Oh

**Chapter 1. Introduction**

All solid-state batteries using inorganic solid electrolytes are attracting because of its high safety and reliable characteristics. As the most promising solid electrolyte,  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  shows the high lithium ionic conductivity of  $\sim 10^{-2} \text{ S cm}^{-1}$ , which is comparable with that of organic liquid electrolytes. Moreover,  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  is electrochemically stable from around 0 V to 5 V (vs.  $\text{Li/Li}^+$ ). Therefore, 5 V class cathode materials can be used for the improvement of energy density of batteries. On the other hand, interfacial reactions among components in all solid-state batteries have been becoming new great challenges for development of high-performance bulk-type all solid-state batteries. An elucidation of the phenomena occurring at the interface will give important suggestions for realization of all solid-state batteries as the next generation energy storage device. In this study, bulk-type all solid-state batteries with the 5 V-class  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cathode and the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  solid electrolyte were fabricated, and their electrochemical properties were investigated. Interfacial reaction analyses were performed using diffractometry, microscopy, and electrochemical impedance spectroscopy (EIS).

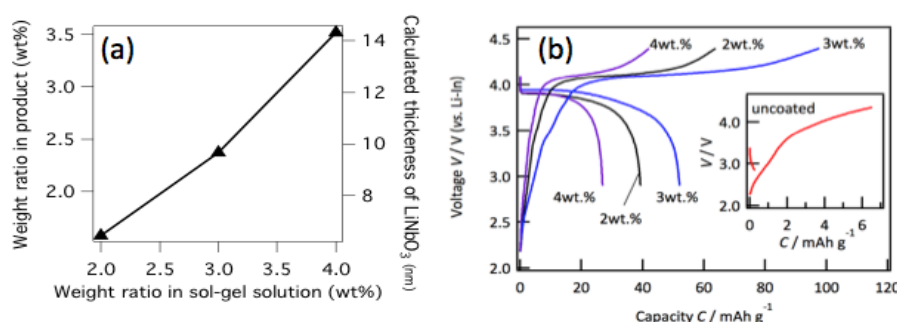
**Chapter 2. Experimental**

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powder was annealed at 1023, 1073, and 1123 K for 10 h in air to prepare oxygen-deficient  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$  with higher electronic conductivity. Then, the surface of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$  was modified with a  $\text{LiNbO}_3$  buffer layer by a sol-gel method. The morphologies and the thickness of  $\text{LiNbO}_3$  coating were characterized by scanning electron microscopy (SEM)/energy dispersive X-ray spectroscopy (EDS) and inductively coupled plasma emission spectrometry (ICP). The all solid-state batteries were assembled

with the cathode composite of  $\text{LiNbO}_3$ -coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}/\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ /acetylene black (AB), the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  solid electrolyte, and Li-In alloy or Li metal anode. The electrochemical properties of the batteries were evaluated by charge–discharge measurements using a multichannel potentiostat/galvanostat. The interfacial resistances at the electrode/electrolyte interface were measured by EIS. The interfacial species formed during electrochemical cycling were characterized by XRD and SEM/EDS measurements.

### Chapter 3. Effect of surface modification and oxygen deficiency

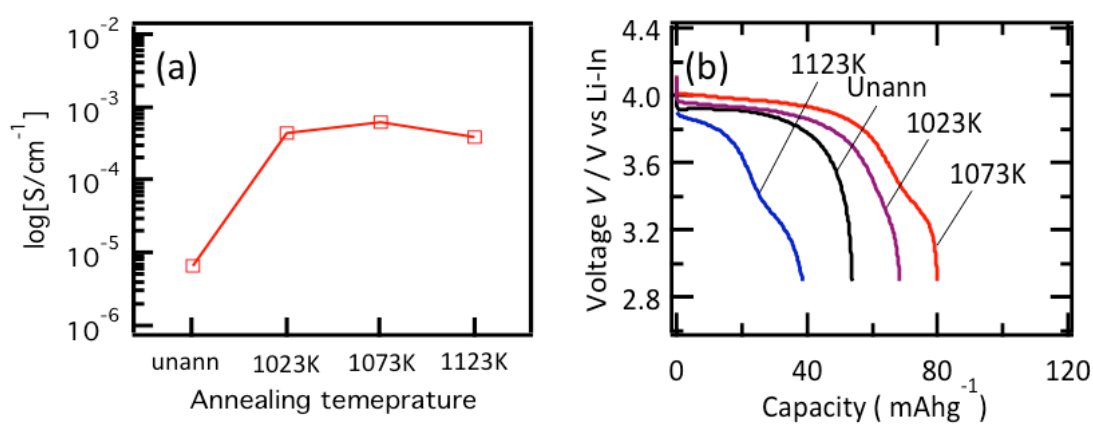
In all-solid-state batteries, forming an intimate interface in composite electrode is necessary for Li ions and electron conduction for reversible battery operation. The surface coating of  $\text{LiNbO}_3$  on  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  particle is an effective method to form an electrochemically active interface with the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  electrolyte. SEM/EDS observation revealed that the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  surface was uniformly covered with the  $\text{LiNbO}_3$  layer. **Figure 1(a)** indicates that the coating thicknesses were found to be 6.5, 9.7, and 14.3 nm for the 2, 3, and 4wt.%  $\text{LiNbO}_3$  coating, respectively. Although the pristine electrode shows slight charge/discharge capacities, discharge capacities over  $25 \text{ mAh g}^{-1}$  are observed for the  $\text{LiNbO}_3$ -coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrodes as shown in **Figure 1(b)**. This result indicates that the  $\text{LiNbO}_3$ -coating layer sufficiently reduce the interfacial resistance between the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  and the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ . However, the highest discharge capacity of  $53 \text{ mAh g}^{-1}$  for the coated-electrodes is still smaller than that of the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  using the conventional liquid-type cell system ( $120 \text{ mAh g}^{-1}$ ). One possible reason is the low electronic conductivity of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  ( $10^{-6} \text{ S cm}^{-1}$  at room temperature), which could provide high resistance of the charge transfer reaction.



**Figure 1** (a) Weight ratio of  $\text{LiNbO}_3$  to  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  and calculated thickness of the  $\text{LiNbO}_3$  layer and (b) the first charge/discharge curves of all-solid-state batteries with uncoated and  $\text{LiNbO}_3$ -coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ .

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders were annealed to introduce oxygen deficiency in  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  to improve the electronic conductivity. **Figure 2(a)** shows the temperature

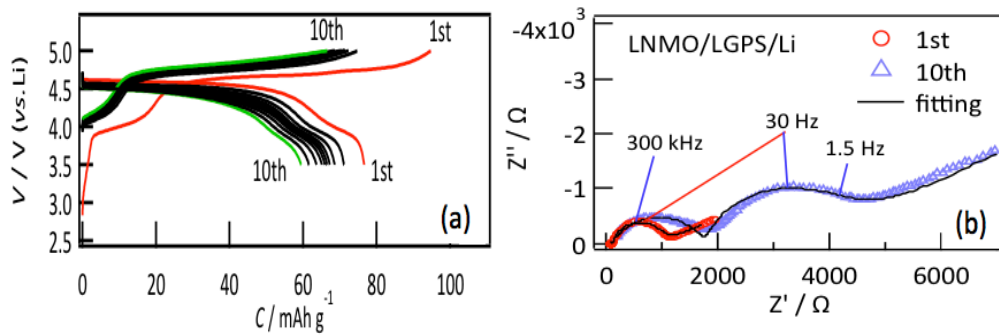
dependence of the lattice parameter and electronic conductivity for the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ . The annealed samples exhibited much higher electronic conductivities than the unannealed sample. The highest electronic conductivity of  $8.9 \times 10^{-4} \text{ S cm}^{-1}$  was obtained for the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$  annealed at 1073 K. **Figure 2(b)** illustrates discharge curves of the all solid-state batteries using  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrode.  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$  annealed at 1073 K showed the largest discharge capacities of  $80 \text{ mAh g}^{-1}$ , which is higher than that of the unannealed  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  ( $53 \text{ mAh g}^{-1}$ ). This result indicates that the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$  with high electronic conductivity promotes the charge transfer reaction at the electrode surface.



**Figure 2** (a) Electric conductivities of unannealed  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  and  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$  annealed at various temperatures and (b) the first discharge curves of all-solid-state batteries using unannealed  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  and annealed  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ .

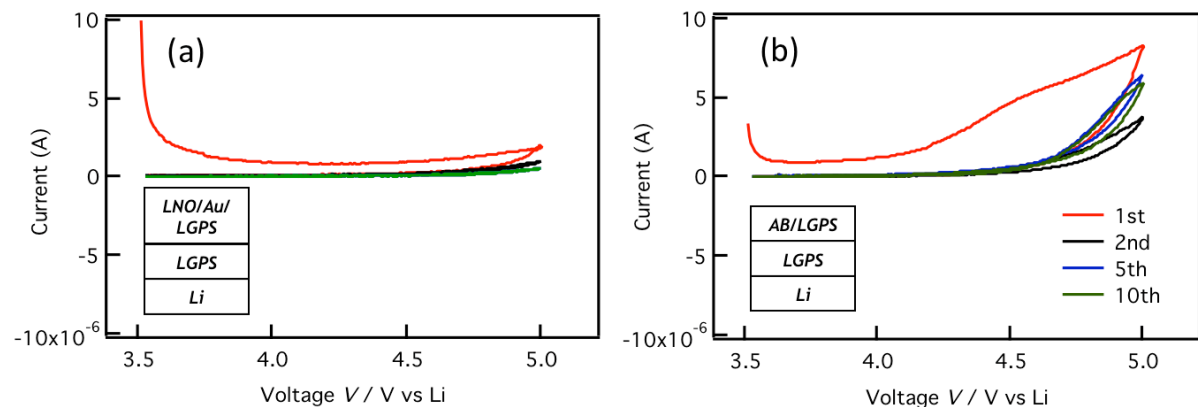
#### Chapter 4. Interfacial reactions between $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ and $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ solid electrolyte

The interface reactions in bulk-type all-solid state batteries composed of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$  cathode,  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  electrolyte, and Li metal anode were investigated. **Figure 3(a)** shows the charge-discharge curves of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}/\text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{Li}$  cell. The plateau regions around 4.6 V were observed in the discharge curves, which is comparable to the liquid battery system using the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrode. Charge and discharge capacities of 101 and  $80 \text{ mAh g}^{-1}$ , respectively, were observed at the first cycle and the capacities gradually decreased to 71 and  $57 \text{ mAh g}^{-1}$  at the 10th cycle. Formation of the  $\text{Li}_2\text{S}$  layer was confirmed at the interface between  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  and Li metal by *ex situ* XRD, which could act as a SEI (solid electrolyte interphase) layer to suppress the further decomposition of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ .



**Figure 3** (a) Charge and discharge curves and (b) Cole-Cole plots of the 3wt.% LiNbO<sub>3</sub> coated LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4-δ</sub> / Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub>/Li battery.

To elucidate the mechanism of the capacity fading during cycling, EIS analyses were performed after battery reactions. Cole-Cole plots are shown in **Figure 3 (b)**. Considering that the resistance value of cathode part (30 Hz) is much larger than that of anode (1.5 Hz) and SEI (300 kHz) parts, the cathode-electrolyte interface might be the dominant factor of deterioration in the cell performance during cycling. These results suggest that the capacity fading could be associated with the high resistive layer formation of lithium conduction between LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4-δ</sub> and Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> throughout the LiNbO<sub>3</sub> coating layer and/or electron conduction between LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4-δ</sub> and the conductive AB additive. To clarify the interfacial reactions of LiNbO<sub>3</sub> and AB with Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub>, CV measurements were conducted for the LiNbO<sub>3</sub>/Au/Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> and AB/Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> composite electrodes (**Figure 4**).



**Figure 4.** CV curves of (a) LiNbO<sub>3</sub>/Au/LGPS and (b) AB/LGPS composite electrodes. LGPS and Li were used as the solid electrolyte and counter electrode, respectively.

AB/Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> exhibits larger oxidation current at over 4.0 V in the first cycle comparing to LiNbO<sub>3</sub>/ Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> and shows no significant decrease in the current upon cycling. These results reveal that the interfacial side-reaction proceeds at the AB/Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub>

interface. The interfacial layer could suppress electron and/or lithium ion conduction between the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$  domain and  $\text{AB/Li}_{10}\text{GeP}_2\text{S}_{12}$ , which leads capacity fading of the battery.

## **Chapter 5. General conclusion**

This study has demonstrated the development of high voltage type all solid-state lithium batteries using  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  spinel and  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  solid-electrolyte. The interface investigation and modification are considered as the most important challenges in all solid-state batteries, which are consisted of solid/solid contacts. This study discussed the interfacial reactions among the components in all solid-state batteries using high voltage cathode.

In chapter 3, the  $\text{LiNbO}_3$  coating delivered reversible lithium intercalation of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  through an electrochemical interface with the  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ . Introduction of the oxygen deficiency into the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  improved the electronic conductivity of the electrode, which contributed to the higher intercalation activity.

In chapter 4, at the interface between  $\text{Li/Li}_{10}\text{GeP}_2\text{S}_{12}$ ,  $\text{Li}_2\text{S}$  layer acted as ionic passivation layer to suppress further decomposition of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ . At the interface between  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  solid-electrolyte/carbon, the decomposed  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  layer with AB at 5 V acted as resistive layer, which is disrupting Li ions and electron paths.

The interfacial layers formed by side reactions between components are considerably important for the conduction of the Li ions and electrons in composite cathodes. The elucidation and controlling of the interfacial reactions at high voltage region could allow the development of high voltage type all solid-state batteries. Until now, improvement of the ionic conductivity has been mainly focused for development of the solid-electrolytes. According to this research, it is needed to develop novel solid-electrolyte with stability against components in the batteries such as anode, cathode and electric conductive materials. Coating layer for solid-electrolyte might be another solution to protect solid-electrolyte at high voltage. Therefore, this research is indicating a new perspective for the development of solid-electrolytes applied in 5 V-class all solid-state batteries.