

All-solid-state lithium secondary batteries using a layer-structured $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cathode material

Fuminori Mizuno, Akitoshi Hayashi, Kiyoharu Tadanaga, Tsutomu Minami,
Masahiro Tatsumisago*

*Department of Applied Materials Science, Graduate School of Engineering, Osaka Prefecture University,
1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan*

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Abstract

All-solid-state cells of $\text{In}/\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ using a superionic oxysulfide glass with high conductivity at room temperature of $10^{-3} \text{ S cm}^{-1}$ as a solid electrolyte were fabricated and the cell performance was investigated. Although a large irreversible capacity was observed at the 1st cycle, the solid-state cells worked as lithium secondary batteries and exhibited excellent cycling performance after the 2nd cycle; the cells kept charge–discharge capacities around 70 mAh g^{-1} and its efficiency was almost 100%. This is the first case to confirm that all-solid-state cells using manganese-based layer-structured cathode materials work as lithium secondary batteries.

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1. Introduction

Recently, lithium secondary batteries have been rapidly popularized as a power source for portable electronic devices such as notebook-type personal computers, cellular phones and video cameras, because these batteries have superior properties like high voltage, high energy density and light weight. In these commercially available batteries, liquid electrolytes with organic solvents are used. Since organic liquid electrolytes are flammable, they are easy to ignite with exposure to high temperatures. To solve this safety problem, it is strongly desired to replace flammable electrolytes with nonflammable electrolytes. Inorganic solid electrolytes are essentially nonflammable and thus the most promising electrolytes.

Lithium ion conducting sulfide glasses have been often investigated as inorganic solid electrolytes for lithium secondary batteries [1–3]. We have reported thermal, electrical and electrochemical properties of sulfide-based glasses in the systems $\text{Li}_2\text{S}\cdot\text{SiS}_2\cdot\text{Li}_x\text{MO}_y$ (Li_xMO_y : Li_4SiO_4 , Li_4GeO_4 , Li_3PO_4 , etc.) prepared by using the rapid quenching method [4–7]. The glasses with 5 mol% Li_xMO_y exhibit high thermal stability against crystallization, high lithium

ion conductivity of $10^{-3} \text{ S cm}^{-1}$ at room temperature and wide electrochemical window over 10 V. We have found that all-solid-state cells of In/LiCoO_2 using the oxysulfide glass as a solid electrolyte work at room temperature as lithium secondary batteries even under a large current density over 2 mA cm^{-2} [8].

Very recently, Ohzuku and Makimura have synthesized a novel $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cathode material with layer structure [9]. This material shows high rechargeable capacity of 150 mAh g^{-1} and has higher thermal stability even in the fully charged state than layer-structured LiCoO_2 , which is widely used as a positive electrode for lithium ion secondary batteries. $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ has little volume change during charge–discharge process [10], which is very important for all-solid-state cells to maintain close contact between electrode and electrolyte. Furthermore, from viewpoints of both economy and safety, manganese-based cathode materials have been intensively investigated to replace LiCoO_2 [11–13]. Thus, applying the manganese cathode material to all-solid-state lithium secondary batteries is highly desired.

In the present study, we have assembled all-solid-state cells of $\text{In}/\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ using the $95(0.6\text{Li}_2\text{S}\cdot 0.4\text{SiS}_2)\cdot 5\text{Li}_4\text{SiO}_4$ (mol%) oxysulfide glass with high conductivity of $1 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature as a solid electrolyte. Cell performances as lithium secondary batteries are examined under various current densities at room temperature.

* Corresponding author. Tel.: +81-722-54-9331; fax: +81-722-54-9913.
E-mail address: tatsu@ams.osakafu-u.ac.jp (M. Tatsumisago).

2. Experimental

Superionic conductive oxysulfide glasses for the electrolyte were prepared by a conventional press-quenching method and detail experimental procedure was described in our previous reports [4–8]. In order to obtain fine solid electrolyte powders, prepared oxysulfide glasses were pulverized by a planetary ball mill (Fritsch Pulverisette 7). A stainless-steel pot and zirconia balls were used and the glass powders were ball-milled at room temperature for 1 h under a constant rotating speed of 370 rpm.

Laboratory-scale solid-state cells were fabricated as follows. Composite electrodes were obtained by mixing of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ (Tanaka Chem. Co.), oxysulfide glass and acetylene-black powder with various weight ratios of $x:50 - x:y$ ($x = 10, 20, 30, 40, y = 1, 2, 3, 4, 6$). Two layers of the composite powder (20 mg) as a positive electrode and the oxysulfide glass powder (80 mg) as a solid electrolyte were together pressed under 3700 kg cm^{-2} in a polycarbonate tube ($\phi = 10 \text{ mm}$), and then an indium foil with a thickness of 0.1 mm as a negative electrode was pressed under 2500 kg cm^{-2} on the obtained pellet. After releasing the pressure, the obtained pellet was sandwiched by two stainless-steel rods as current collectors. These cells were charged and discharged in the potential range from 2 to 3.7 V under various constant current densities from 64 to $1280 \mu\text{A cm}^{-2}$ to evaluate cycling performance. The measurements were carried out at room temperature in an Ar atmosphere.

3. Results and discussion

In the present study, we have prepared composite electrodes from following three kinds of powders: the active material ($\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$), the oxysulfide glass providing lithium ion conduction path and the acetylene-black providing electron conduction path. In order to achieve smooth electrochemical reaction in all-solid-state cells, it is very important not only to make close contact among those powders but also to optimize the ratio of them.

Fig. 1 shows the first charge and discharge curves of all-solid-state cells using composite electrodes with various weight ratios of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$:oxysulfide glass:acetylene-black = $x:50 - x:3$ ($x = 10, 20, 30, 40$). Current density in this measurement was $64 \mu\text{A cm}^{-2}$. The cells with $x = 10, 20$ and 30 are charged and discharged although they have large irreversible capacities. To our knowledge, this is the first case to confirm that all-solid-state cells using manganese-based layer-structured cathode materials work as lithium secondary batteries. The cell with $x = 20$ exhibits larger charge and discharge capacities and a higher discharge voltage plateau than the cells with $x = 10$ and 30. The cell with $x = 40$ does not exhibit an obvious plateau.

Fig. 2 shows the first charge and discharge curves of all-solid-state cells using composite electrodes with various

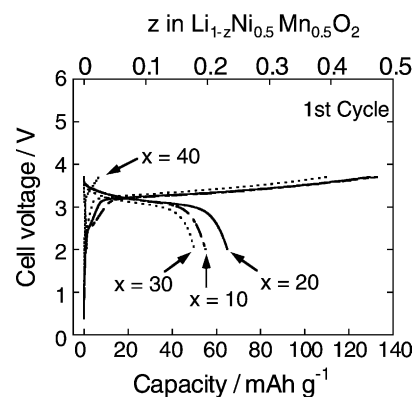


Fig. 1. First charge and discharge curves for all-solid-state cells of $\text{In}/\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ with the 95(0.6 Li_2S :0.4 SiS_2):5 Li_4SiO_4 (mol%) oxysulfide glass as a solid electrolyte. Composite electrodes with various weight ratios of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$:oxysulfide glass:acetylene-black = $x:50 - x:3$ were used, where $x = 10, 20, 30$ and 40. All the cells were charged and discharged in the potential range from 2 to 3.7 V under a current density of $64 \mu\text{A cm}^{-2}$.

weight ratios of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$:oxysulfide glass:acetylene-black = 20:30: y ($y = 1, 2, 3, 4, 6$). Current density in this measurement was also $64 \mu\text{A cm}^{-2}$. Except for the cell with $y = 1$, the cells are charged and discharged. The cell with $y = 3$ exhibits the largest discharge capacity in those cells.

It was revealed from Figs. 1 and 2 that the most suitable weight ratio of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$:oxysulfide glass:acetylene-black in the composite electrodes in this study was 20:30:3, and the cell using this composite electrode exhibited charge and discharge capacities of 130 and 70 mAh g^{-1} at the 1st cycle, respectively. The cells with $x = 40$ (Fig. 1) and $y = 1$ (Fig. 2) did not work because of large overpotential derived from the lack of conduction paths of lithium ions or electrons in the composite cathode materials.

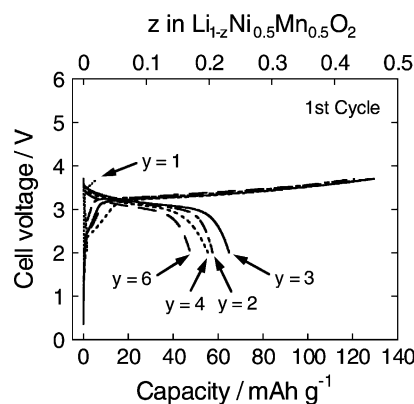


Fig. 2. First charge and discharge curves for all-solid-state cells of $\text{In}/\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ with the 95(0.6 Li_2S :0.4 SiS_2):5 Li_4SiO_4 (mol%) oxysulfide glass as a solid electrolyte. Composite electrodes with various weight ratios of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$:oxysulfide glass:acetylene-black = 20:30: y were used, where $y = 1, 2, 3, 4$ and 6. All the cells were charged and discharged in the potential range from 2 to 3.7 V under a current density of $64 \mu\text{A cm}^{-2}$.

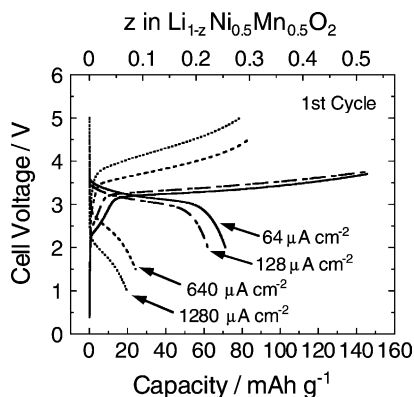


Fig. 3. First charge and discharge curves under various current densities from 64 to 1280 $\mu\text{A cm}^{-2}$ for the cells using the composite electrode with the weight ratio of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$:oxysulfide glass:acetylene-black = 20:30:3. The current densities are 64, 128, 640 and 1280 $\mu\text{A cm}^{-2}$.

Fig. 3 shows the first charge and discharge curves under various current densities from 64 to 1280 $\mu\text{A cm}^{-2}$ for all-solid-state cells using the composite electrode with the weight ratio of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$:oxysulfide glass:acetylene-black = 20:30:3. The discharge capacity over 60 mAh g^{-1} is obtained under a current density of 128 $\mu\text{A cm}^{-2}$. The polarization increases with an increase in current densities and the cell cannot be sufficiently charged and discharged under current densities of 640 and 1280 $\mu\text{A cm}^{-2}$. In our previous work [8], the solid-state cells with LiCoO_2 could be sufficiently discharged even under high current densities such as 1529 $\mu\text{A cm}^{-2}$. SEM observations revealed that LiCoO_2 consisted of primary particles with the size of 2–3 μm which were dispersed with no aggregation, whereas $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ mainly consisted of secondary particles of around 5 μm in size formed by the aggregation of primary particles (0.5–1.0 μm). Thereby, it is suggested that poor rate performances for the cell using $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ are mainly caused by insufficient contacts among the active material, the glass powder and the acetylene-black in the composite electrodes.

Fig. 4 shows the cycling behavior of charge–discharge capacities and its efficiencies for the cell using the composite electrode with the weight ratio of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$:oxysulfide glass:acetylene-black = 20:30:3. Current density in this measurement was 64 $\mu\text{A cm}^{-2}$. Filled and open circles, respectively, denote the charge and discharge capacities and the solid line denotes the charge–discharge efficiency. Although the cell has relatively large irreversible capacity at the 1st cycle, both charge and discharge capacities keep a constant value around 70 mAh g^{-1} and charge–discharge efficiency is almost 100% from 2nd to 50th cycle. The cell using $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ exhibits an excellent cycling performance in the low rate operation with 64 $\mu\text{A cm}^{-2}$, as compared with the one using LiCoO_2 ; the discharge capacity for the cell with LiCoO_2 gradually decreased from 90 mAh g^{-1} at the 1st cycle to 60 mAh g^{-1} at the 50th cycle [7]. This implies that the charge–discharge reaction to the

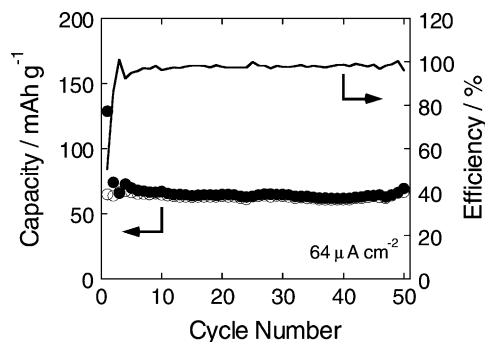


Fig. 4. Cycling dependence on charge–discharge capacities and its efficiencies for the cell using the composite electrode with the weight ratio of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$:oxysulfide glass:acetylene-black = 20:30:3. Filled and open circles, respectively, denote the charge and discharge capacities and the solid line denotes the charge–discharge efficiency.

cell with $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ occurs more smoothly in the interface between solid electrolytes and solid electrodes than that to the cell with LiCoO_2 . The very small volumetric change of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ [10] during charge–discharge reaction must be one of the reasons.

Here, we discuss the origin of the irreversible capacity at the 1st cycle. Ohzuku and Makimura [9] have reported that the reversible capacity of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ is approximately 150 mAh g^{-1} when the cell using a conventional liquid electrolyte is charged and discharged in the potential range from 2.5 to 4.2 V (versus Li^+/Li) under a current density of 100 $\mu\text{A cm}^{-2}$. This reversible capacity is much larger than that of 70 mAh g^{-1} in the all-solid-state cell. Since an effective interface area between an active material and an electrolyte or an electron conducting material in an all-solid-state system is probably much smaller than that in a system using a liquid electrolyte, the electrochemical reactions in the positive electrode would not occur smoothly in the former system. This suggests that lithium ions intercalating to positive electrode on the 1st discharge process would be limited in the solid electrolyte system. Furthermore, in the charge process, lithium ions migrate from $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ positive electrode to Indium negative electrode and then immediately form Li–In alloy on the surface of negative electrode. Another possible reason of irreversible capacity at the 1st cycle is the fact that all of lithium would not be extracted from the alloy on the discharge process. Although all lithium ions deintercalating from $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ at the 1st charge process cannot be exploited in the present stage, the lithium ions intercalating into the positive electrode at the 1st discharge process probably provide reversible paths, which lead the good cycle performance of the all-solid-state cell after the 2nd cycle.

4. Conclusion

All-solid-state cells of $\text{In}/\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ using the 95(0.6 Li_2S ·0.4 SiS_2)·5 Li_4SiO_4 oxysulfide glass as a solid

electrolyte worked as lithium secondary batteries. The cell kept the reversible capacity around 70 mAh g^{-1} under a current density of $64 \mu\text{A cm}^{-2}$ after the 2nd cycle and exhibited superior cycling performance with no capacity loss up to the cycle number of 50.

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