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All-solid-state Lithium Secondary Batteries Using $Li_2S–P_2S_5$ Solid Electrolytes and $LiFePO_4$ Electrode Particles with Amorphous Surface Layer

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All-solid-state batteries using $Li_2S–P_2S_5$ solid electrolyte and $LiFePO_4$ glass ceramic electrode particles were constructed. The batteries were charged and discharged with reversible capacity of 110 mA h g^{-1}. Amorphous oxide surface layer formed on $LiFePO_4$ glass ceramic particles improved interfacial properties between $LiFePO_4$ electrode and $Li_2S–P_2S_5$ solid electrolytes.

Lithium-ion secondary batteries are widely used as power sources from portable devices to electric vehicles because of their high energy density and long cycle life. Although the lithium ion secondary batteries show excellent performance, the batteries have some problems with respect to use in electric vehicles such as safety and high cost.

Solidification of electrolytes is one of the most effective solutions to resolve the safety issues. By using nonflammable solid electrolyte, safety of batteries is highly improved. All-solid-state lithium secondary batteries using $LiCoO_2$ and indium as electrodes exhibit excellent cycle performance. The batteries are charged and discharged for more than 700 cycles without capacity fading.[1] Among many kinds of solid electrolytes, sulfide-based solid electrolytes such as thio-LiSICON,[2] $Li_{10}GeP_2S_{12}$ crystals,[3] and $Li_2S–P_2S_5$ glasses and glass-ceramics[4,5] are promising because of high lithium-ion conductivities over 10^{-3} S cm^{-1} at room temperature, which is close to the lithium-ion conductivity of organic liquid electrolytes. $LiCoO_2$ is the most popular positive electrode material which shows excellent performance. However, the cost of $LiCoO_2$ is relatively high because of the expensive cobalt. As an alternative, $LiFePO_4$ is the most promising because of low cost and high safety.

So far, $LiFePO_4$ has not been used as an electrode of all-solid-state batteries using sulfide-based solid electrolytes, because of the difficulty of forming an effective electrode–electrolyte interface. Formation of an interface with low side reaction between electrode and solid electrolyte is important to achieve high performance in all-solid-state batteries. Especially, the surface structure of the electrode particles is important in electrochemical performance. We reported the interfacial reaction between charged $LiCoO_2$ and $Li_2S–P_2S_5$ solid electrolytes observed by cross-sectional transmission electron microscopy (TEM).[6] The reaction caused the degradation of the interface. The formation of a buffer layer on $LiCoO_2$ positive electrode particles was effective in suppressing the reaction between charged $LiCoO_2$ and $Li_2S–P_2S_5$ solid electrolytes. As a result, the interfacial resistance between $LiCoO_2$ and $Li_2S–P_2S_5$ was greatly decreased. It has been revealed that lithium-ion conducting oxide materials are effective as the interfacial layer between electrode and electrolyte to decrease interfacial resistance.[6–8]

Highly conducting electrode materials are more suitable than low conducting electrodes because both lithium-ion and electron conducting paths should be effectively formed in the composite electrode of all-solid-state batteries. $LiFePO_4$ generally shows low electronic conductivity. Reportedly the electronic conductivity is improved by carbon coating.[9]

Here, we report all-solid-state lithium secondary batteries using $LiFePO_4$ glass ceramic positive electrode and $Li_2S–P_2S_5$ solid electrolytes. The $LiFePO_4$ glass ceramic particles used in this study have an amorphous surface layer which contains carbon.[10] In this study, both increasing electronic conductivity and improving interfacial properties were achieved by the use of the $LiFePO_4$ glass ceramics. The surface layer is suitable for the improvement of electrochemical performance of all-solid-state batteries.

The $LiFePO_4$ glass ceramic was prepared through the heat treatment of $Li_2O–Fe_2O_3–P_2O_5$ glass powder.[10] The mixture of starting materials was melted at 1200 to 1300 °C and quenched to prepare $LiFePO_4$ glass. The prepared glasses were pulverized by ball milling. The obtained glass particles were mixed with aqueous solution of polyoxyethylene nonyl phenyl ether to obtain slurry, and then the slurry was dried at 100 °C followed by subsequent heat treatment at 700 °C to obtain $LiFePO_4$ glass ceramic. The polyoxyethylene nonyl phenyl ether effectively forms the carbon coating on $LiFePO_4$ glass ceramic and suppresses the increase of particle size by the heat treatment. The reversible capacity of the prepared $LiFePO_4$ measured using the liquid electrolyte cell based on 1 M $LiPF_6$ in EC/DEC was 161 mA h g^{-1}.[10]

All-solid-state cells using an $80Li_2S\cdot20P_2S_5$ (mol %) glass as a solid electrolyte were constructed as follows.[4] The $80Li_2S\cdot20P_2S_5$ glass was prepared from Li_2S (99.9%; Idemitsu) and P_2S_5 (99%; Aldrich) by mechanical milling using a zirconia pot (45 mL) and 160 zirconia balls (5 mm diameter). The $LiFePO_4$ glass ceramic, the $80Li_2S\cdot20P_2S_5$ glass electrolyte, and acetylene black with a weight ratio of 40:60:6 were mixed to prepare positive composite electrodes. Indium foil (99.999%; Furuuchi) was used as a negative electrode. A bilayer pellet consisting of the composite positive electrode (10 mg) and the glass solid electrolyte (80 mg) was obtained by pressing under 360 MPa (ϕ10 mm), and the indium foil was then attached to the bilayer pellet by pressing under 240 MPa. The pellet was pressed using two stainless steel rods. The all-solid-state cell using commercial $LiFePO_4$ with carbon coating was also prepared for comparison. All the processes for preparation of solid electrolytes and fabrication of all-solid-state batteries were performed in a dry Ar-filled glove box ($[H_2O] < 1$ ppm).

Figure 1 shows scanning electron microscopy (SEM) images of (a) $LiFePO_4$ glass ceramic and (b) commercial

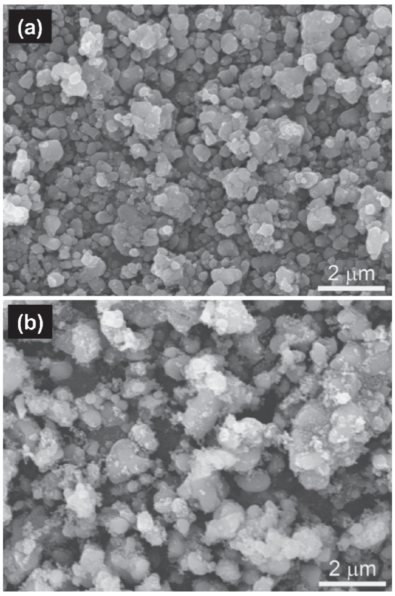

Figure 1. SEM images of (a) $LiFePO_4$ glass ceramic and (b) commercial $LiFePO_4$ particles.

$LiFePO_4$ particles. The average particle sizes of $LiFePO_4$ glass ceramic and commercial $LiFePO_4$ were ca. 0.4 and 0.6 µm, respectively. The particle size of $LiFePO_4$ glass ceramic was similar to that before heat treatment. The amorphous layer was observed at the surface area of $LiFePO_4$ glass ceramic particles by transmission electron spectroscopy (TEM) observation (not shown here). The amorphous surface layer was composed of Li, Fe, Nb, P, O, and C elements with a thickness of several nanometers. The electronic conductivity of the pellet of the $LiFePO_4$ glass ceramic was $4.2 \times 10^{-3}\,S\,cm^{-1}$ and that of the commercial $LiFePO_4$ was $1.6 \times 10^{-1}\,S\,cm^{-1}$. The electronic conductivity of the $LiFePO_4$ glass ceramic was 1/40 of that of commercial $LiFePO_4$.

Figure 2 shows the charge–discharge curves of all-solid-state cells using the $LiFePO_4$ glass ceramic and the commercial $LiFePO_4$ particles at 50 °C. The current densities used were $13\,\mu A\,cm^{-2}$ for $LiFePO_4$ glass ceramic and $6.4\,\mu A\,cm^{-2}$ for commercial $LiFePO_4$. The all-solid-state cells using $LiFePO_4$ were charged and discharged. The cell using $LiFePO_4$ glass ceramic shows a capacity of $110\,mA\,h\,g^{-1}$, which is 65% of the theoretical capacity for $LiFePO_4$. The cell retained a capacity of ca. $100\,mA\,h\,g^{-1}$ after 10 cycles (Figure S1).[12] The cell using commercial $LiFePO_4$ shows the reversible capacity of 40 $mA\,h\,g^{-1}$. The reversible capacity of the cell using $LiFePO_4$ glass ceramic is larger than that using the commercial $LiFePO_4$.

The reason of the larger capacity in $LiFePO_4$ glass ceramic is discussed here. The larger capacity is not explained by electronic conductivity because the commercial $LiFePO_4$ had much higher conductivity than the $LiFePO_4$ glass ceramic. Moreover, the current density used for the $LiFePO_4$ glass ceramic was higher than that for the commercial material. Therefore, the difference in surface structure of the $LiFePO_4$ particles was focused on. The surface layer formed on $LiFePO_4$ glass ceramic is amorphous lithium phosphate containing iron and carbon. The surface layer should act as a favorable interfacial layer between $LiFePO_4$ electrodes and Li_2S–P_2S_5 solid electrolytes to increase charge-transfer reaction. Kang et al. reported that the surface transfer was important for the rate performance in the liquid electrolyte system. Amorphous surface layer formed on $LiFePO_4$ increases the surface transfer.[11] Similarly, the amorphous layer of $LiFePO_4$ glass ceramic in this study should improve surface transfer. Additionally, the surface layer contains carbon, which increases electronic conductivity of $LiFePO_4$ particles. As a result, the cell using $LiFePO_4$ glass ceramic showed higher capacity than that using commercial $LiFePO_4$.

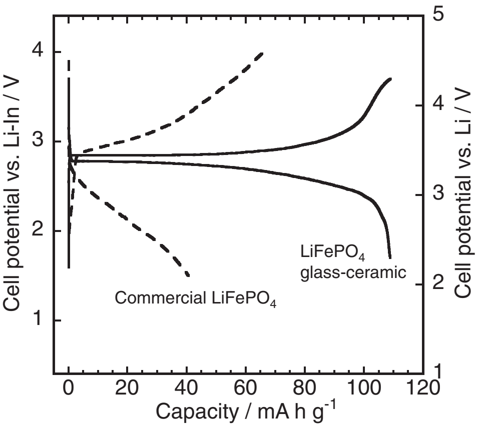

Figure 2. Charge–discharge curves of all-solid-state cell In/$80Li_2S\cdot20P_2S_5$/$LiFePO_4$ measured at 50 °C.

In conclusion, all-solid-state batteries using $LiFePO_4$ glass ceramic as a positive electrode operated with a reversible capacity of $110\,mA\,h\,g^{-1}$. The performance was supported by the amorphous surface layer on $LiFePO_4$ glass ceramic particles. The $LiFePO_4$ glass ceramic is a promising positive electrode material for all-solid-state batteries using sulfide-based solid electrolytes.

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