

All Solid-State Battery Using Inorganic Lithium Super Ion Conductor

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Introduction

All solid lithium battery has been paid much attention, because it will give a fundamental solution for the future power source based on the lithium battery technology. Non-flammable solid electrolyte used in place of organic liquid electrolyte must overcome the safety hazard issue of the conventional "lithium ion" systems which prevents further development toward larger scale and higher energy-density batteries.

Inorganic super lithium ion conductors such as thio-LISICON ($\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$) [1] opened the possibility to fabricate solid systems with large current drain. In this paper, we will present Li-Al/ Mo_6S_8 cell using thio-LISICON as a prototype configuration for the all-solid system. Interface behavior as well as an excellent cycling performance of the cell will be shown.

Experimental

Thio-LISICON, $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$, was synthesized as described previously [1] and was used as the solid electrolyte (SE) after being pulverized into powder with an average grain size of 1 – 5 μm .

Interface study was carried out based on Li/SE/Li and Li-Al/SE/Al-Li symmetrical cells. The impedance data at 25°C were collected at each charge-and-discharge cycle at the current density of 1.3 mA/cm² for 20 min. The DC resistivity of each cell was calculated from the voltage-current relationship.

For the charge-and-discharge test of all solid-state cells, Mo_6S_8 with a Chevrel structure [2] was prepared by reducing $\text{Cu}_2\text{Mo}_6\text{S}_8$ (Nippon Inorganic Colour & Chemical) with conc. HCl. The Mo_6S_8 was mixed with thio-LISICON and acetylene black (Denki Kagaku Kogyo) in the gravimetric ratio of 70:30:3.5 to give a cathode mixture.

Results and Discussion

Fig.1 shows DC resistivity of Li/SE/Li and Li-Al/SE/Al-Li symmetrical cells plotted as a function of cycle number. The total resistivity of the Li-Al/SE/Al-Li cell was constant at a low resistivity-value while that of the Li/SE/Li cell drastically increased with cycling. The Li-Al/SE interface is quite stable and this makes the all solid-state cell possible to operate even under the condition of high current drain.

Further investigations using AC impedance analysis as well as X-ray photoelectron spectroscopy indicated the formation of interfacial phases during the electrochemical reactions. We regard these phases as a solid electrolyte interface (SEI) phases, which are similar to the carbon anodes of lithium ion batteries. The SEI phase that formed at the carbon surface prevents exfoliation of graphene layers and makes the intercalation reaction possible [3].

Although the importance of the SEI phase has not been

indicated for the inorganic all solid-state batteries, the self-assembled SEI at the Li-Al/SE interface played a great role in the charge-and-discharge cycle. This SEI phase would promote a closer contact at the hard electrolyte/electrode interface.

Fig. 2 shows the charge-and-discharge characteristics of Li-Al/ Mo_6S_8 all-solid cell given at a current density of 1.3 mA/cm² in the potential range of 0.5 - 3.0 V at 25°C. For the Li-Al anode system, high capacity was obtained without fading. To confirm the effect of the SEI phase for the Li-Al anode, the cells with the bare Li anode were examined and found to show considerable degradation with cycling.

Dramatic improvement given by the SEI design represents another milestone in the study of the all-solid lithium battery.

References

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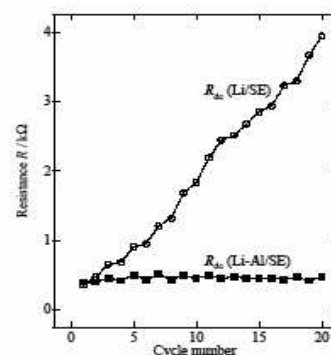


Fig. 1 The DC resistivity of the cells, Li-Al/SE/Al/Li, and Li/SE/Li.

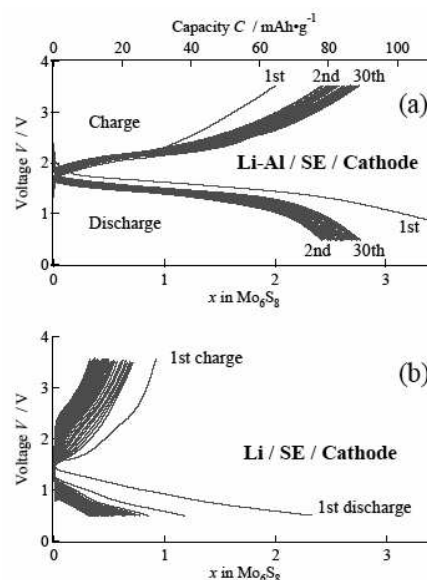


Fig. 2 Typical charge-discharge cycle performance of the Li-Al/SE/cathode cell (a), and the Li/SE/cathode cell (b).