Development of all-solid-state lithium batteries with sulfide solid electrolytes

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Outline

1. Background
   Motivation of all-solid-state rechargeable batteries
2. Sulfide glass solid electrolytes
3. All-solid-state Li batteries with sulfide electrolytes
   Approaches to fabricate favorable electrode-electrolyte interfaces
4. Na⁺ ion conductors for all-solid-state Na batteries
5. Summary
Organic liquid electrolyte

Inorganic solid electrolyte

Lithium-ion battery

all-solid-state battery

Demand for all-solid-state battery

Serious safety problems become obvious and thus improving safety of batteries (especially large-sized batteries) is a big issue to be solved.
Two types of all-solid-state rechargeable lithium batteries

**Thin-film battery**

**Bulk-type battery**

Consisting of powder-compressed layers of electrode and electrolyte

high energy density!

Key points:
1. Solid electrolytes with high conductivity
2. Favorable contact at solid-solid interface

Data from the web site of Excellatron

Li / LiPON / LiCoO₂

Long cycle performance
Why inorganic solid electrolytes?

Merits of inorganic solid electrolytes

- Single cation conduction
- Wide electrochemical window
- Simple electrochemical reactions

- charge-transfer reaction at electrode

M. Chiku et al., Electrochemistry, 80, 740 (2012).
Why sulfide glass solid electrolytes?

**Advantages of sulfide glass electrolytes**
- High ionic conductivity
- Easy reduction of grain-boundary resistances
- Wide selection of compositions
- Superionic crystalline phases are easily precipitated from glass.

Cross-sectional SEM images of compressed powder pellets

Sulfide glass electrolyte

Li₂S-P₂S₅

\[ \sigma_{Li^+} = \sim 10^{-3} \text{ S cm}^{-1} \]

Oxide crystalline electrolyte

Li₇La₃Zr₂O₁₂

\[ \sigma_{Li^+} = \text{too small} (\sim 10^{-7} \text{ S cm}^{-1}) \]

(sintered pellet: \sim 10^{-4} \text{ S cm}^{-1})

Easy deformation of sulfide electrolytes is useful for achieving favorable interface between electrode and electrolyte.
Precipitation of superionic Li\textsubscript{7}P\textsubscript{3}S\textsubscript{11} phase from the 70Li\textsubscript{2}S \cdot 30P\textsubscript{2}S\textsubscript{5} (mol\%) glass

The formation of a superionic metastable phase is responsible for increasing conductivity of glass-based solid electrolytes.

Solid electrolytes with high lithium ion conductivity

\[ \text{Li}_{10}\text{GeP}_2\text{S}_{12} \text{ crystal} \]
\[ \sigma_{25} = 1.2 \times 10^{-2} \text{ Scm}^{-1} \]

\[ \text{Li}_7\text{P}_3\text{S}_{11} \text{ glass-ceramic} \]
\[ \sigma_{25} = 1 \times 10^{-2} \text{ Scm}^{-1} \]

\[ \text{Li}^+ \text{ ion conductivity of the sulfide solid electrolytes is now higher than that of liquid electrolytes!} \]
Chemical stability in air of sulfide electrolytes

Sulfide solid electrolytes with moderate chemical stability in air atmosphere are prepared by selecting compositions.

Main structural unit ($\text{PS}_4^{3-}$) did not change after exposure to air for 1 day. Hydrolysis is suppressed.

Li$_2$S-P$_2$S$_5$ glasses

H$_2$S generation (R.H. 50%)

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Application to bulk-type all-solid-state batteries

Stainless-steel (current collector)

Polycarbonate (insulator)

Working electrode: e.g. Li$_4$Ti$_5$O$_{12}$

Solid electrolyte (SE): Li$_2$S-P$_2$S$_5$ glass-ceramic

Counter electrode: Li-In alloy (reference electrode)

Composite electrode

The formation of Li$^+$ and e$^-$ conduction paths to active material particles is significant.

SE active material conductive additive = 60 : 40 : 4 (wt %)
The cell operated at a high current density of 12.8 mA cm$^{-2}$ and kept the capacity of 130 mAh g$^{-1}$ for 700 cycles.

Approaches to fabricate favorable electrode-electrolyte interfaces

Sulfide electrolyte coating on LiCoO$_2$ electrode by PLD

**Deposition conditions**

- **Target**: Pellet of mixture of Li$_2$S and P$_2$S$_5$ crystalline powder (80Li$_2$S・20P$_2$S$_5$ mol%)
- **Ambient gas**: Ar gas (5 Pa)
- **Temperature**: Room temperature
- **Frequency**: 10 Hz
- **Laser fluence**: 2 J cm$^{-2}$
- **Target-substrate distance**: 7 cm

Cross-sectional SEM image

Lithium-ion conducting paths are formed with small amounts of solid electrolytes.

In / Li$_2$S-P$_2$S$_5$ / LiCoO$_2$

0.13 mA cm$^{-2}$

With SE particles

With SE coatings

With SE particles (30 wt% SE particles were mixed)

With SE coatings (10 wt% SE films were coated)

Sulfur active material

- abundant element
- large theoretical capacity (1672 mAh g⁻¹)

Li-In / 80Li₂S·20P₂S₅ (SE) / 25S·25AB·50SE (wt%)

Sulfur positive electrode in all-solid-state cells shows a good cycle performance.

Increase of the sulfur content in a positive electrode

Li-In / SE / 50S・20AB・30SE (wt%)

Ball-milling the S-AB composite at 155°C (the lowest viscosity coefficient of sulfur)

- Energy density based on the weight of the total positive electrode is increased (1007 Wh kg⁻¹).
- Sulfur with the size less than 200 nm and AB particles are homogeneously dispersed in the SE matrix. ▶️ Large capacity & good cyclability

M. Nagao et al., Energy Technology, in press.
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Why Na batteries?

**Na⁺ ion batteries**

Next-generation batteries with high energy density using abundant sodium sources

**Sodium-sulfur (NAS) batteries**

- Large energy density (760 Wh kg⁻¹)
- High-temperature operation (>300 °C)
- Strict security apparatus

Limitation of usage environment

All-solid-state Na/s batteries operating at room temperature are strongly desirable from safety point of view.

New solid electrolytes suitable for solid-state batteries

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*Sodium-sulfur (NAS) batteries*

<table>
<thead>
<tr>
<th>Metal</th>
<th>Atomic weight [g mol⁻¹]</th>
<th>Valency change</th>
<th>Specific charge [Ah kg⁻¹]</th>
<th>Electrode potential [V]</th>
<th>Terrestrial abundance [%]</th>
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<tr>
<td>Li</td>
<td>6.94</td>
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<tr>
<td>Pb</td>
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</tbody>
</table>

[a] Versus normal hydrogen electrode.

New Na⁺ ion conducting sulfide electrolytes

\[ 75\text{Na}_2\text{S} \cdot 25\text{P}_2\text{S}_5 \text{ (mol%) } = \text{Na}_3\text{PS}_4 \]

Conductivity increases by crystallization of the Na₃PS₄ glass.

\[ \sigma_{25} = 2 \times 10^{-4} \text{ S cm}^{-1} \]

A cubic Na₃PS₄ phase, which has not been reported, is precipitated in the glass-ceramic electrolyte.

The all-solid-state sodium battery with the Na$_3$PS$_4$ electrolyte is charged and discharged for 10 cycles and shows a good cycleability at room temperature.
**Summary**

1. Sulfide glass-based materials have favorable properties as solid electrolyte for bulk-type all-solid-state batteries. Especially, the glass-ceramics in the system Li$_2$S-P$_2$S$_5$ show high Li$^+$ ion conductivities of $10^{-3}$ to $10^{-2}$ S cm$^{-1}$, which are higher than those of liquid electrolytes.  

2. Electrochemical performance of all-solid-state Li batteries has been developed by the modification of the electrode-electrolyte interface.

3. Cubic-Na$_3$PS$_4$ glass-ceramic electrolyte with the conductivity of $10^{-4}$ S cm$^{-1}$ is prepared and all-solid-state Na batteries with the electrolyte operate at room temperature.

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