All-solid-state Li battery using a light-weight solid electrolyte

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Contents

- Introduction
- LiBH$_4$ as an ionic conductor
- Fabrication & properties of all-solid-state Li battery using LiBH$_4$
  - Bulk type
  - Thin-film type with an intermediate layer
- Li precipitation behavior in a LiBH$_4$-Cu composites
## All-solid-state Li secondary battery

### Advantages:
- Low risk of fire
- No liq. leakage
- Wide operating Temp.
- No Li dendrite growth
- \( t_{\text{Li}} \approx 1 \)
- Flexibility of cell design

### Drawbacks:
- Large G.B. resistance
- Low power density
- Interfacial resistance between electrolytes and Li

New Li-ion conductor: \( \text{LiBH}_4 \)

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### Table: Li-ion conductors to be used for all-solid-state LIB

<table>
<thead>
<tr>
<th>Type</th>
<th>Group</th>
<th>Material</th>
<th>( \sigma_{\text{bulk}} ) @ RT / S cm(^{-1} )</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxide</td>
<td>LISICON</td>
<td>( \text{Li}<em>3.6\text{Ge}</em>{0.6}\text{V}_{0.4}\text{O}_4 )</td>
<td>( 4 \times 10^{-5} )</td>
<td>1980</td>
</tr>
<tr>
<td></td>
<td>NASICON</td>
<td>( \text{Li}<em>{1.3}\text{Al}</em>{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3 )</td>
<td>( 3 \times 10^{-3} )</td>
<td>1989</td>
</tr>
<tr>
<td></td>
<td>NASICON</td>
<td>( \text{Li}<em>{1.6}\text{Al}</em>{0.6}\text{Ge}<em>{0.8}\text{Ti}</em>{0.6}(\text{PO}_4)_3 )</td>
<td>( 7 \times 10^{-4} )</td>
<td>2003</td>
</tr>
<tr>
<td>Perovskite</td>
<td></td>
<td>( \text{La}<em>{0.55}\text{Li}</em>{0.36}\text{TiO}_{2.94} )</td>
<td>( 1.5 \times 10^{-3} )</td>
<td>1998</td>
</tr>
<tr>
<td>Garnet</td>
<td></td>
<td>( \text{Li}_7\text{La}_3\text{Zr}<em>2\text{O}</em>{12} )</td>
<td>( 2.4 \times 10^{-4} )</td>
<td>2011</td>
</tr>
<tr>
<td>Nitride</td>
<td></td>
<td>( \text{Li}_3\text{N} )</td>
<td>( 6.6 \times 10^{-4} )</td>
<td>1982</td>
</tr>
<tr>
<td>Oxynitride</td>
<td>LiPON</td>
<td>( \text{Li}<em>{2.88}\text{PO}</em>{3.73}\text{N}_{0.14} )</td>
<td>( 3.3 \times 10^{-6} )</td>
<td>2006</td>
</tr>
<tr>
<td>Sulfide</td>
<td></td>
<td>( \text{Li}_{10}\text{GeP}<em>2\text{S}</em>{12} )</td>
<td>( 1.2 \times 10^{-2} )</td>
<td>2011</td>
</tr>
<tr>
<td>Thio-LISICON</td>
<td>( \text{Li}<em>{3.2}\text{Ge}</em>{0.2}\text{P}_{0.75}\text{S}_4 )</td>
<td>( 2.2 \times 10^{-3} )</td>
<td>2001</td>
<td></td>
</tr>
<tr>
<td>Thio-LISICON</td>
<td>( \text{Li}<em>{3.4}\text{Si}</em>{0.4}\text{P}_{0.6}\text{S}_4 )</td>
<td>( 6.4 \times 10^{-4} )</td>
<td>2002</td>
<td></td>
</tr>
<tr>
<td>Thio-LISICON</td>
<td>( \text{Li}<em>{3.3}\text{Si}</em>{0.3}\text{P}_{0.9}\text{S}_4 )</td>
<td>( 1.5 \times 10^{-4} )</td>
<td>2004</td>
<td></td>
</tr>
<tr>
<td>Sulfide glass</td>
<td>( \text{Li}<em>{0.67}\text{S}</em>{0.33}\text{P}_{2}\text{S}_5 )</td>
<td>( 1.0 \times 10^{-4} )</td>
<td>1981</td>
<td></td>
</tr>
<tr>
<td>Sulfide glass</td>
<td>( \text{Li}<em>{0.6}\text{S}</em>{0.4}\text{Si}_{2} )</td>
<td>( 5.3 \times 10^{-4} )</td>
<td>1987</td>
<td></td>
</tr>
<tr>
<td>Sulfide glass</td>
<td>( (0.55\text{Li}<em>{0.67}\text{S}</em>{0.33}\text{P}_{2}\text{S}_5)-0.45\text{LiI} )</td>
<td>( 1.0 \times 10^{-3} )</td>
<td>1981</td>
<td></td>
</tr>
<tr>
<td>Sulfide glass</td>
<td>( (0.6\text{Li}<em>{0.6}\text{S}</em>{0.4}\text{Si}_{2})-0.4\text{LiI} )</td>
<td>( 1.8 \times 10^{-3} )</td>
<td>1987</td>
<td></td>
</tr>
<tr>
<td>Glass ceramics</td>
<td>( \text{70Li}<em>{2}\text{S}-30\text{P}</em>{2}\text{S}_5 )</td>
<td>( 3.2 \times 10^{-3} )</td>
<td>2006</td>
<td></td>
</tr>
<tr>
<td>Glass ceramics</td>
<td>( \text{75Li}<em>{2}\text{S}-25\text{P}</em>{2}\text{S}_5 )</td>
<td>( 4.5 \times 10^{-4} )</td>
<td>2006</td>
<td></td>
</tr>
<tr>
<td>Glass ceramics</td>
<td>( \text{80Li}<em>{2}\text{S}-20\text{P}</em>{2}\text{S}_5 )</td>
<td>( 1.3 \times 10^{-3} )</td>
<td>2006</td>
<td></td>
</tr>
<tr>
<td>Organic electrolyte</td>
<td>( 1\text{M LiPF}_6/\text{EC-DMC} )</td>
<td>( 1.15 \times 10^{-2} )</td>
<td>1999</td>
<td></td>
</tr>
</tbody>
</table>
Solid electrolyte: LiBH₄

- Enhancement of Li-ion conductivity at 115°C accompanied by phase transition
- The H.T. phase can be stabilized by partial substitution of BH₄⁻ by halides.

Solid electrolyte: LiBH$_4$

**Chemical compatibility with Li**

- Thermodynamically stable with Li metal → No SEI
- Negligible Electrode & G.B resistance

![Graph showing chemical compatibility with Li](image)
Solid electrolyte: LiBH₄

Advantages

• Light weight < 0.7 g/cm³
• Good compatibility with Li metal
• Plasticity
  • High density
  • Lower interfacial resistance

Drawbacks

• Easy to oxidize
  • It may cause a redox reaction with cathode materials, e.g. LiCoO₂
• Unstable in air
  • Difficult to handle
  • Reaction with water

\[
\text{LiBH}_4 + 2\text{H}_2\text{O} \rightarrow \text{LiBO}_2 + 4\text{H}_2
\]
Key issues to use LiBH₄ in ASS Li batteries

- To manage interface between the LiBH₄ electrolyte and LiCoO₂ cathode.

- To use LiBH₄ for anode side to realize a high-capacity anode.
Result 1

Electrochemical properties of a simple cell

Li | LiBH$_4$ | LiCoO$_2$
Rapid capacity fade
Large overvoltage
The large interfacial resistance (350 Ω) at 1st cycle further increases with charge-discharge cycles.
Interface of LiBH$_4$ and LiCoO$_2$

- Black area corresponds to LiBH$_4$.
- Some holes were observed in LiBH$_4$ after charge-discharge.

Gas (H$_2$) evolution
Raman spectra of the LiCoO$_2$ cathode

\[ Li_{0.5}CoO_2 + \frac{1}{8}LiBH_4 \rightarrow \frac{1}{4}Co_3O_4 + \frac{1}{4}CoO(OH) + \frac{1}{8}LiBO_2 + \frac{1}{4}Li_2O + \frac{1}{8}H_2 \]

Decomposition reaction

Charged state

Not identified
Suppression of the interfacial resistance by use of an intermediate layer
Intermediate layer

- As for the high interfacial resistance between LiCoO$_2$ cathode and electrolyte, that is also an issue to overcome in sulfide and oxide electrolytes.
  - It is considered to be due to space charge layer or mutual diffusion.
- An intermediate layer deposited on LiCoO$_2$ surface is reportedly effective to suppress the interfacial resistance.

<table>
<thead>
<tr>
<th>Materials, thickness</th>
<th>Electrolyte</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_4$Ti$<em>5$O$</em>{12}$ 5 - 10 nm</td>
<td>Li$<em>{3.25}$Ge$</em>{0.25}$P$_{0.75}$S$_4$</td>
<td>$R_{\text{interface}}$ 1000 $\Omega \rightarrow$ 40 $\Omega$ [1]</td>
</tr>
<tr>
<td>LiTaO$_3$ 5 - 10 nm</td>
<td>Li$<em>{3.25}$Ge$</em>{0.25}$P$_{0.75}$S$_4$</td>
<td>$R_{\text{interface}}$ 1000 $\Omega \rightarrow$ 12 $\Omega$ [1]</td>
</tr>
<tr>
<td>LiNbO$_3$</td>
<td>Li$_{10}$GeP$<em>2$S$</em>{12}$</td>
<td>Suppression of $R_{\text{interface}}$ [2]</td>
</tr>
<tr>
<td>SiO$_2$ 2 nm</td>
<td>Li$_2$S – P$_2$S$_5$ glass-ceramics</td>
<td>$R_{\text{interface}}$ 270 $\Omega \rightarrow$ 220 $\Omega$ [3]</td>
</tr>
<tr>
<td>Li$_2$SiO$_3$ 2 nm</td>
<td>Li$_2$S – P$_2$S$_5$ glass-ceramics</td>
<td>$R_{\text{interface}}$ 270 $\Omega \rightarrow$ 130 $\Omega$ [3]</td>
</tr>
<tr>
<td>Li-Nb-O</td>
<td>Li$_7$La$_3$Zr$<em>2$O$</em>{12}$</td>
<td>$R_{\text{interface}}$ 2700 $\Omega \rightarrow$ 150 $\Omega$ [4]</td>
</tr>
<tr>
<td>ZrO$_2$ &lt; 10 nm</td>
<td>Organic liquid</td>
<td>Cycle performance [5]</td>
</tr>
</tbody>
</table>

Cross-sectional SEM image of the thin-film

25 nm Li₃PO₄-coated LiCoO₂

EDX analysis

- 25 nm-thick Li₃PO₄ intermediate layer was grown on the columnar LiCoO₂ thin-film.
97% of the initial capacity was retained after 30 cycles.

The value of the interfacial resistance (21 Ω) was 1/1000 of that in a cell without the intermediate layer.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>$R_{\text{interface}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO$_2$ bulk</td>
<td>350 Ω</td>
</tr>
<tr>
<td>LiCoO$_2$ film</td>
<td>15 kΩ</td>
</tr>
<tr>
<td>Li$_3$PO$_4$/LiCoO$_2$ film</td>
<td>21 Ω</td>
</tr>
</tbody>
</table>

Co$_3$O$_4$ in the thin-film was formed in the PLD deposition.

The Li$_3$PO$_4$ intermediate layer suppressed the chemical reaction between LiBH$_4$ and LiCoO$_2$. 

Other intermediate layers

- Uncoated LiCoO$_2$ thin-film
- 25 nm Li$_3$PO$_4$-coated
- 15 nm LiNbO$_3$-coated
- 25 nm Al$_2$O$_3$-coated

Smooth surface was obtained for LiNbO$_3$ and Al$_2$O$_3$.

Several Islands ($t \approx 100$ nm) was observed for Li$_3$PO$_4$.

Optimization of the intermediate layer

Summary

All-solid-state lithium battery using LiBH$_4$ as an electrolyte was fabricated:

- LiBH$_4$ having excellent Li-ion conductivity, chemical stability and plasticity works as a novel solid electrolyte for all-solid-state Li battery.

- Intermediate layer is effective to suppress the interfacial reaction and to improve the capacity retention up to 97% after 30 cycles.

- A concept of composite anode using LiBH$_4$ and Cu was examined; the connection of plating Li inside the electrolyte seems to cause the degradation. The mixture of comparable size of electrolyte and electrode is preferred to improve coulomb efficiency.