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Solid-State Lithium Batteries Using Glass Electrolytes

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AGENDA

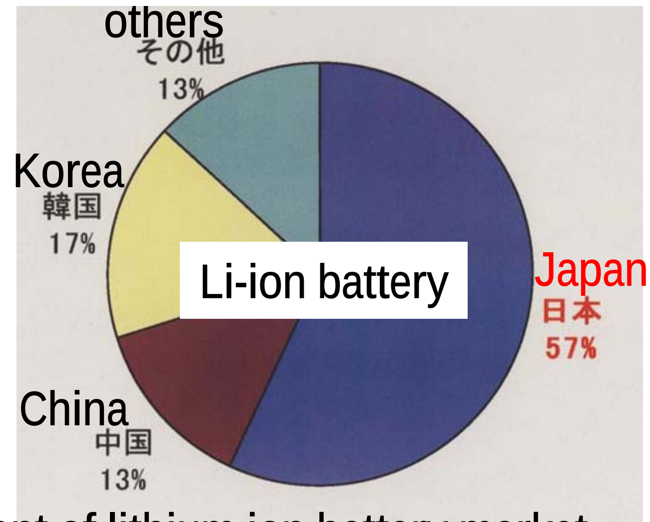
- **Introduction – Why all-solid-state battery?**
  Why glass-based electrolytes?
- **Preparation of lithium ion conducting glasses and glass-ceramics**
- **All-solid-state lithium secondary batteries using Li_2S-based glass-ceramics**
- **Preparation of glassy electrode materials for all-solid-state lithium secondary batteries - A new concept of all-glass-based battery systems**
- **Conclusions**

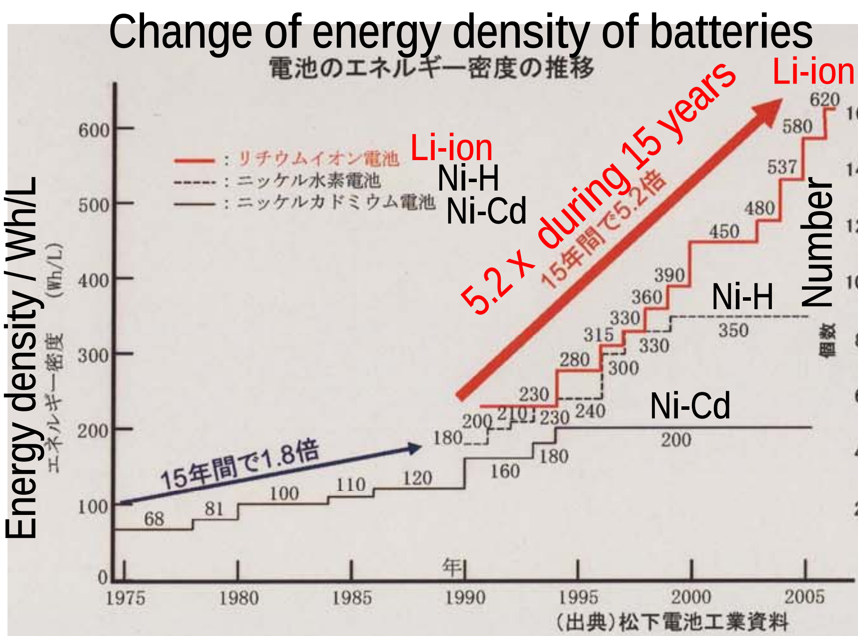
Introduction

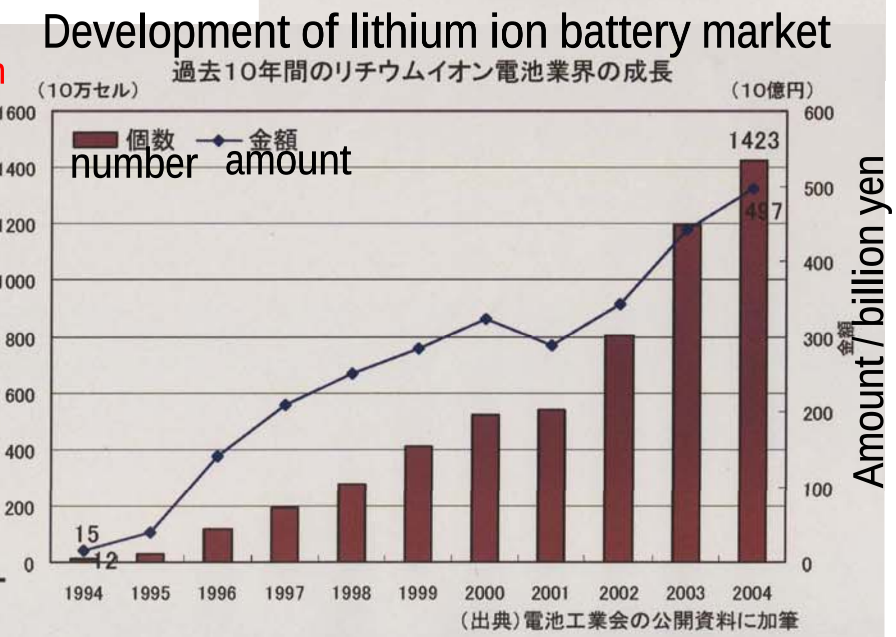
Development of the battery business

Development of miniaturized electric appliances

Share of battery in the world







The lithium ion secondary battery is very promising not only for miniaturized electric appliances but also as a large energy storage device for HEV and EV.

There are serious safety problems present in lithium ion secondary batteries using flammable organic liquid electrolytes.

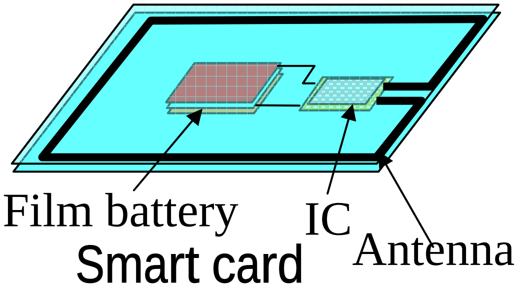
All-solid-state lithium secondary battery system using non-flammable inorganic solid electrolytes

Ultimate goal of rechargeable energy sources

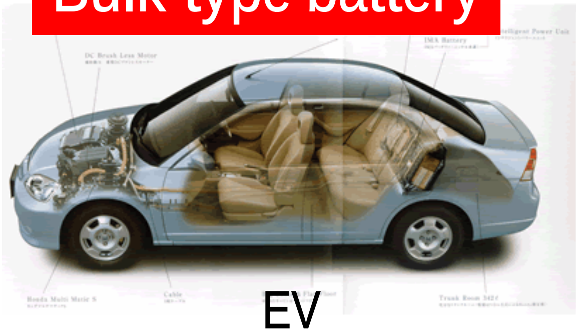
- high safety
- high reliability
- high energy density

Studies on all-solid-state lithium secondary battery

Thin-film battery



Bulk-type battery



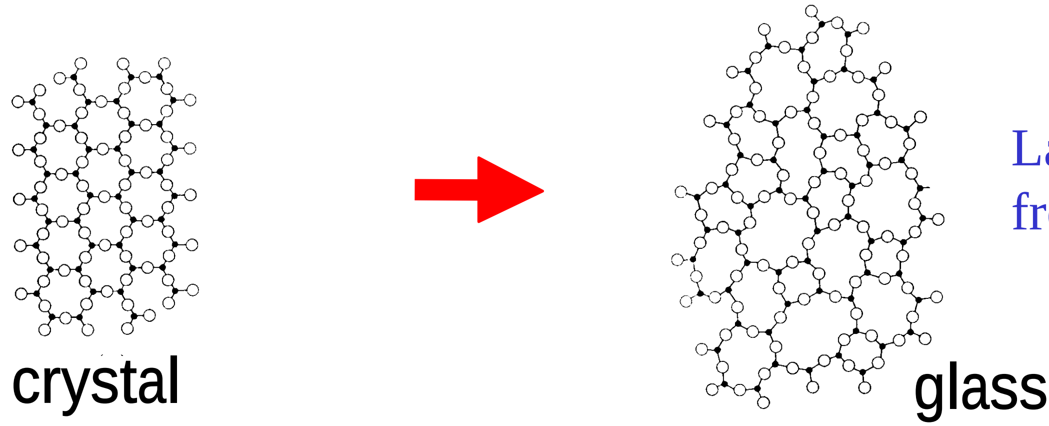
Inorganic glassy solid electrolytes

………. very promising for use in
all-solid-state batteries

- wide selection of compositions
- isotropic properties
- no grain boundaries
- easy film formation
- nonflammability
- etc.

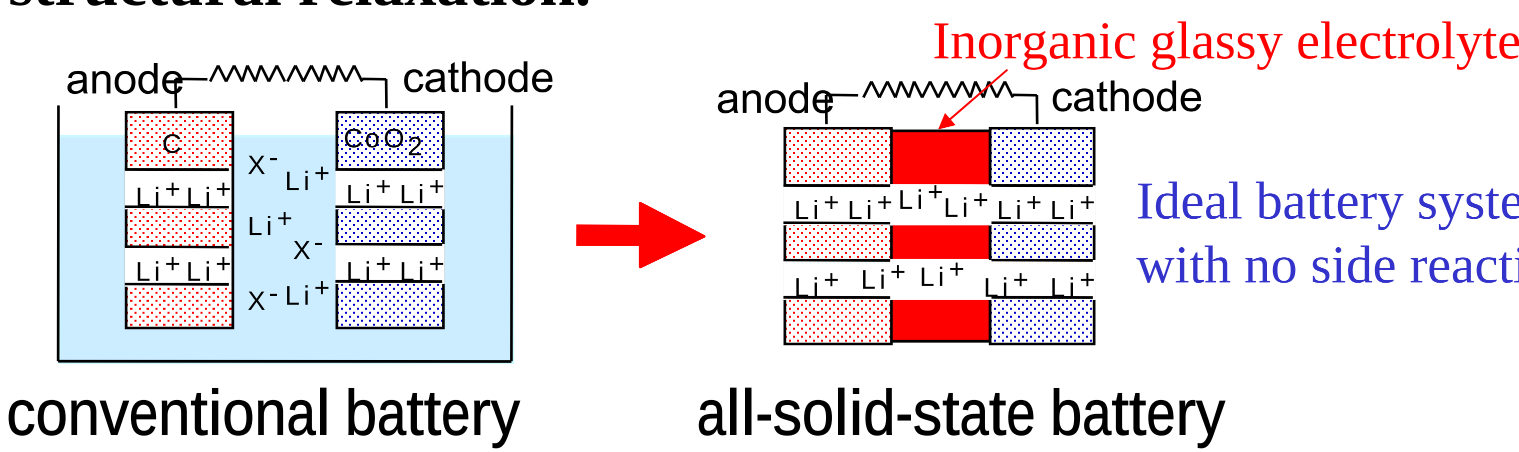
Inorganic glassy solid electrolytes

1. Ion conductivity is generally higher in glass than that in corresponding crystal due to the so-called "open structure."



Large amounts of free volume

2. Single cation conduction is realized because glassy materials belong to the so-called "decoupled systems" in which the mode of ion conduction relaxation is decoupled from the mode of structural relaxation.

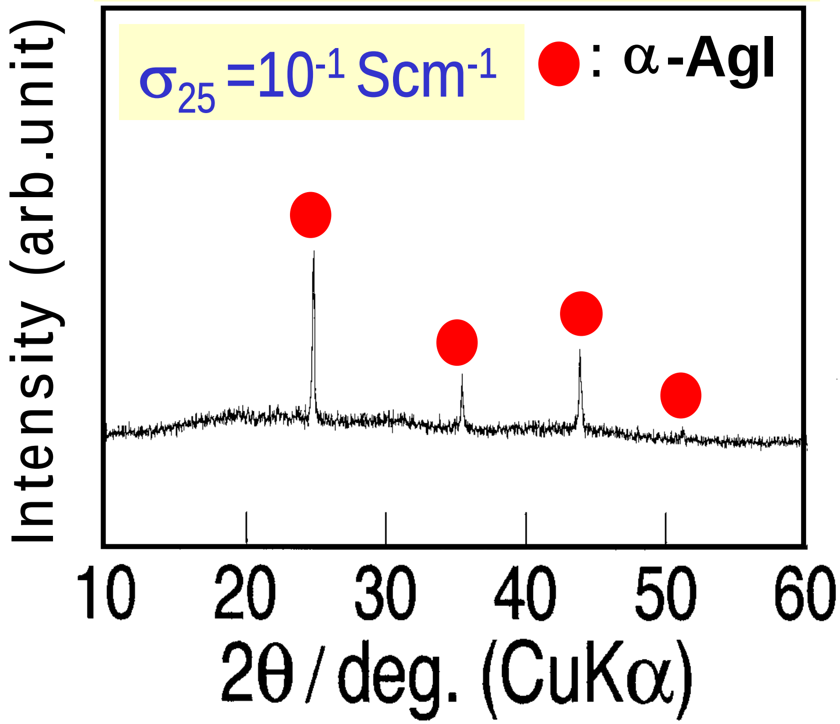


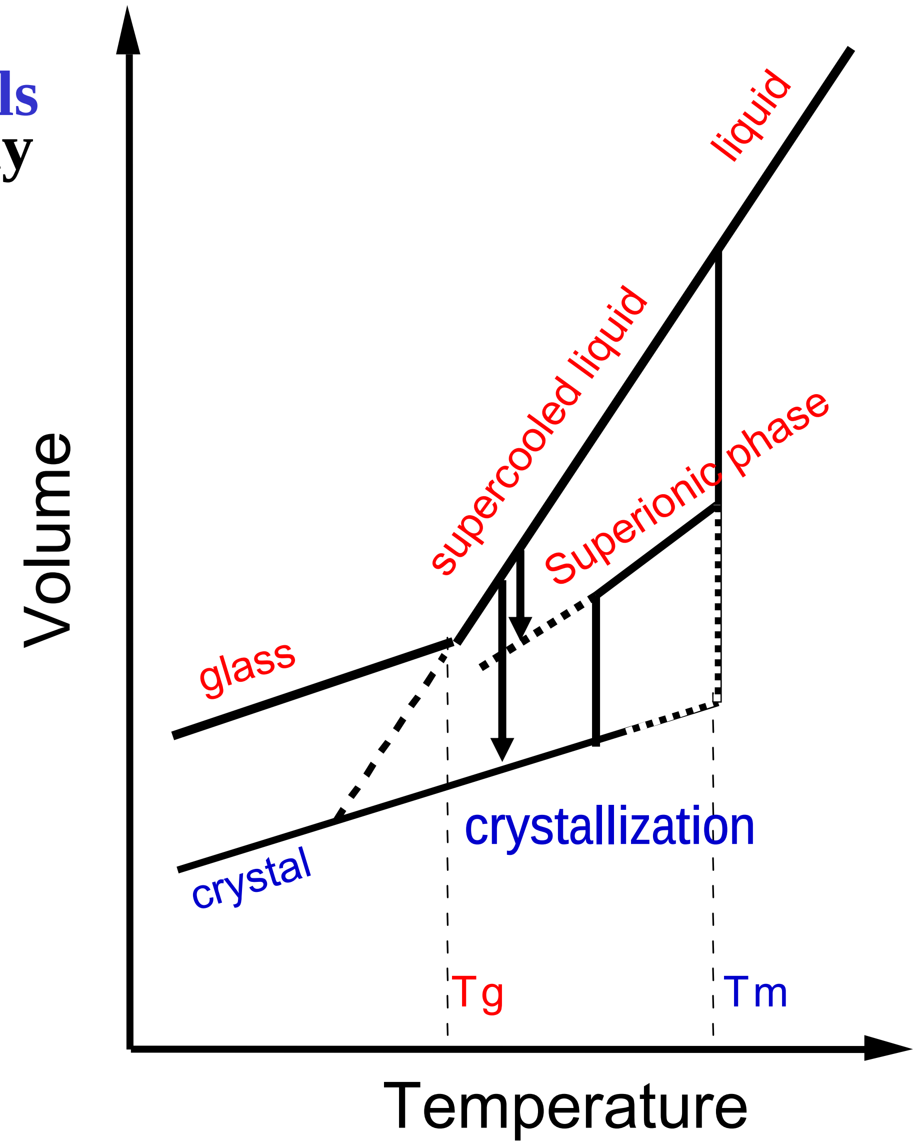
Ideal battery system with no side reactions

Inorganic glassy solid electrolytes

3. Superionic coducting crystals as a metastable phase are easily formed from inorganic glassy electrolytes.

$74AgI \cdot 26(0.33Ag_2O \cdot 0.67MoO_4)$





Tatsumisago et al., *NATURE*, 354 (1991) 217; *Chem. Lett.* (2001) 814.

Preparation of lithium ion conducting glasses and glass-ceramics

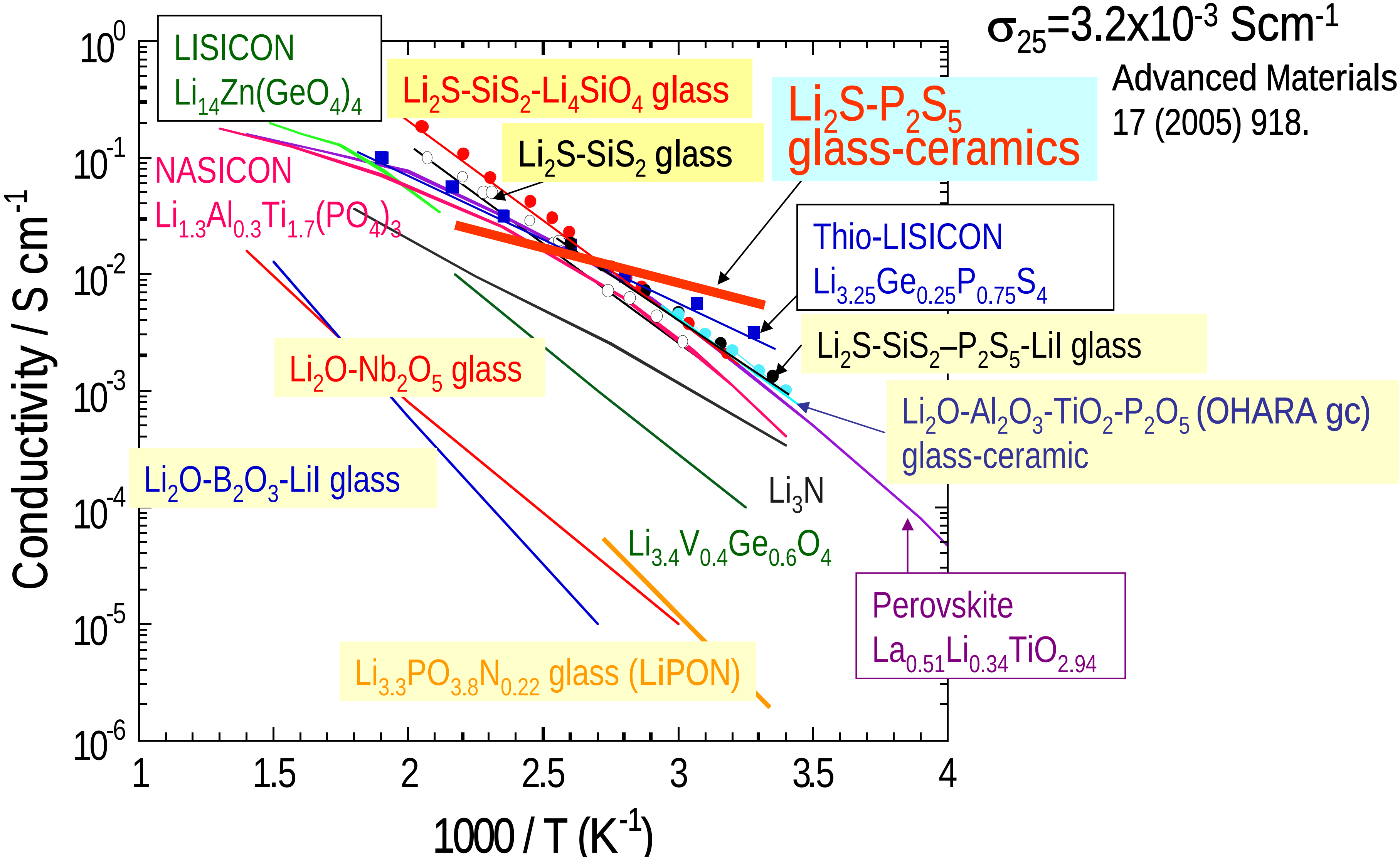
Lithium Ion conducting glassy systems

System	σ_{25} / Scm^{-1}	Procedure	Researcher
Li_2O-Nb_2O_5	10^{-6}	Twin-roller quenching	Nassau
Li_4SiO_4-Li_3BO_3	10^{-6}	Twin-roller quenching	Tatsumisago
Li-P-O-N	10^{-6}	Sputtering	Bates
Li_2S-GeS_2	10^{-5}	Melt quenching	Souquet
Li_2S-P_2S_5	10^{-4}	Melt quenching	Malugani
Li_2S-B_2S_3	10^{-4}	Melt quenching	Levasseur
Li_2S-SiS_2	10^{-4}	Twin-roller quenching	Ribes
Li_2S-SiS_2-LiI	10^{-3}	Melt quenching	Kennedy
Li_2S-P_2S_5-LiI	10^{-3}	Melt quenching	Malugani
Li_2S-SiS_2-Li_3PO_4	10^{-3}	Melt quenching	Kondo
Li_2S-SiS_2-Li_4SiO_4	10^{-3}	Twin-roller quenching	Tatsumisago

High Li^+ ion conduction in glass

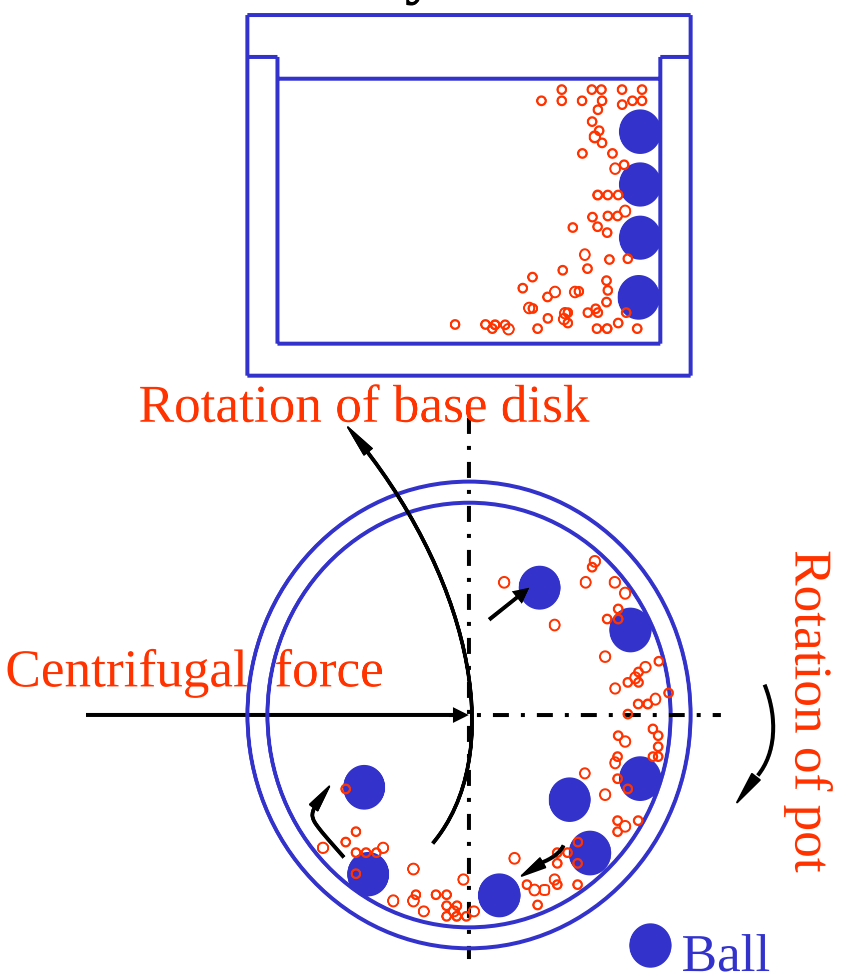
- Increase in Li^+ ion concentration as much as possible
- Use of counter anions with high polarizability

Temperature dependence of conductivity of a variety of high lithium ion conducting materials



Mechanochemical preparation of 95(0.6Li_2S・ 0.4SiS_2)・ 5Li_4SiO_4 glass

Planetary ball mill

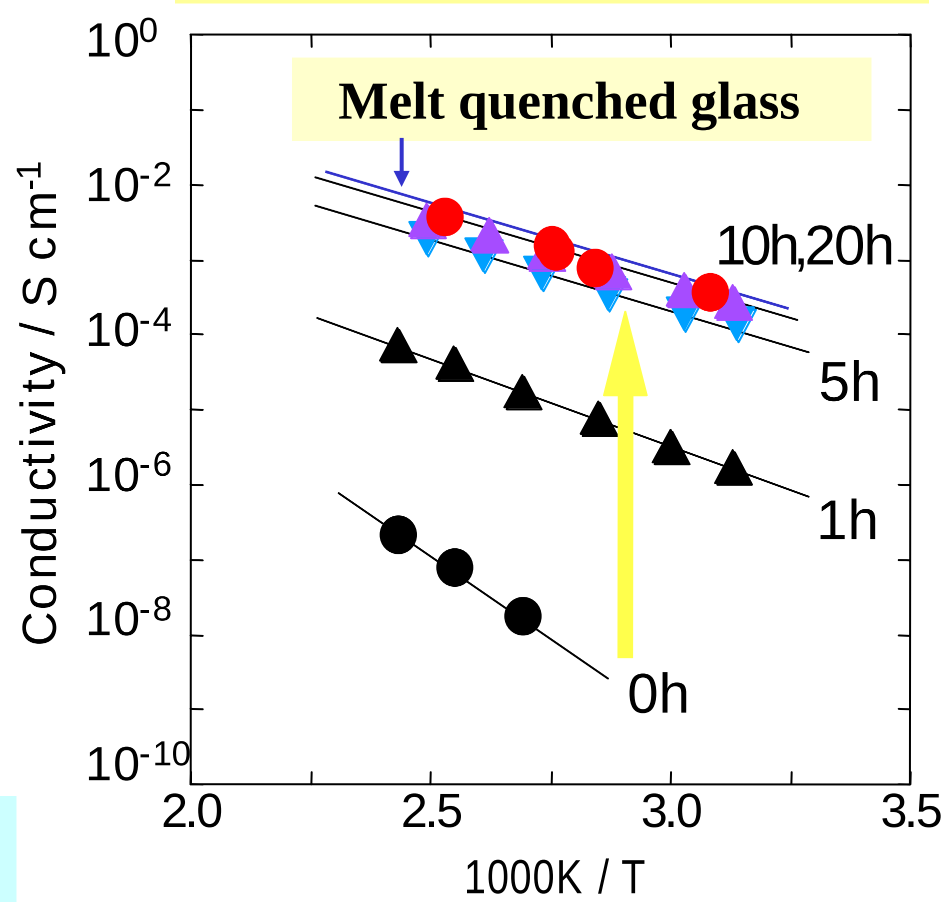


Mechanical energy → pulverization chemical reaction

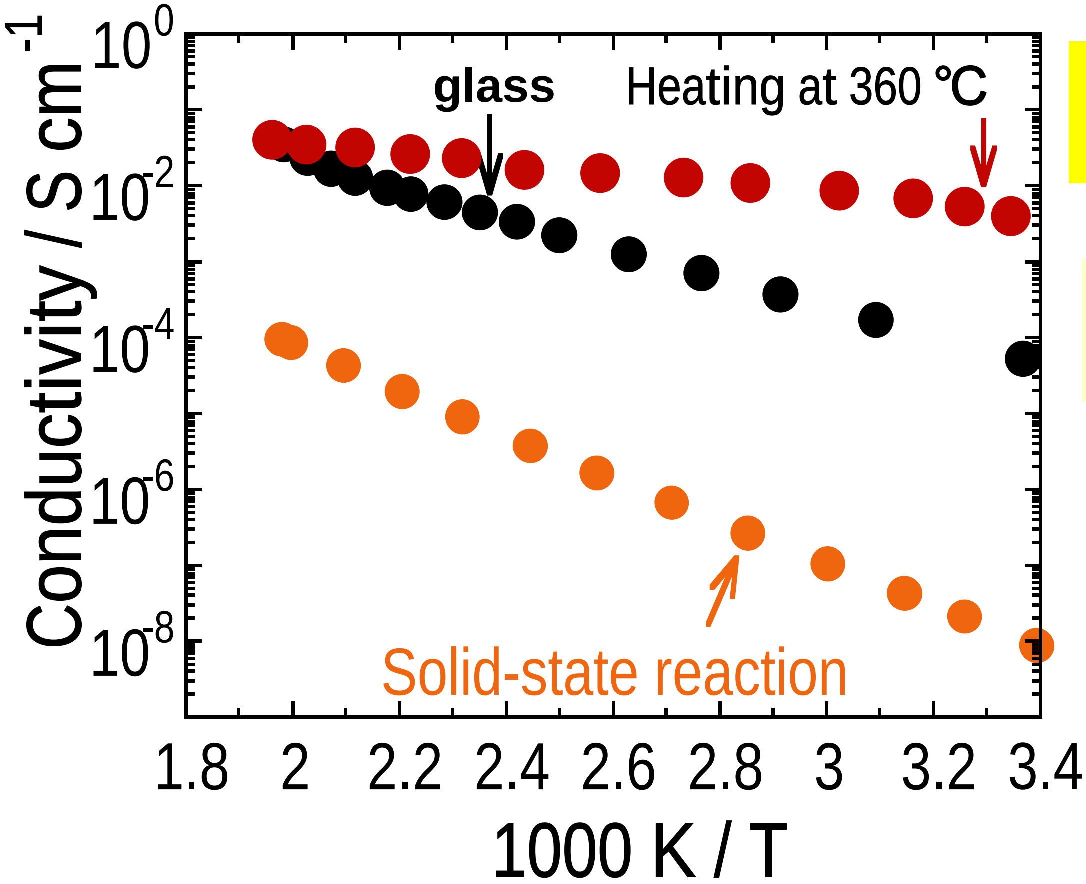
Mechanochemical synthesis

- Room temperature process
- Obtaining fine powders directly

95(0.6Li_2S・ 0.4SiS_2)・ 5Li_4SiO_4

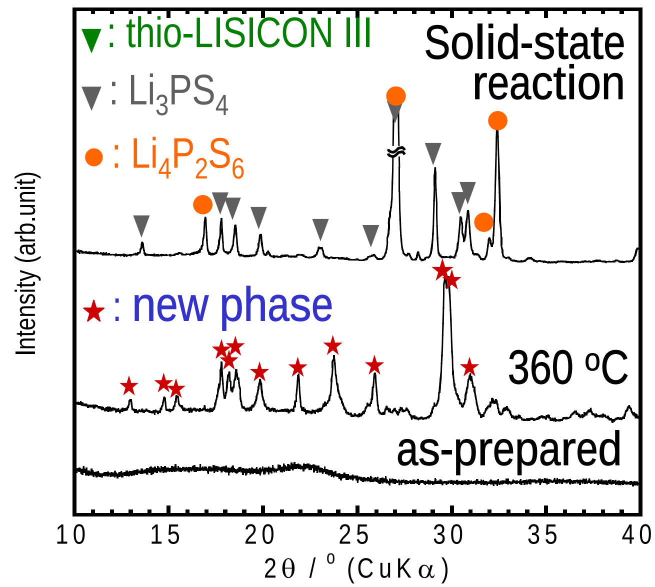


Temperature dependence of conductivity for the $70Li_2S \cdot 30P_2S_5$ glass and glass-ceramic



σ_{25} = 3.2 x 10^{-3} S/cm
Ea = 12 kJ/mol

σ_{25} = 5.4 x 10^{-5} S/cm
Ea = 38 kJ/mol

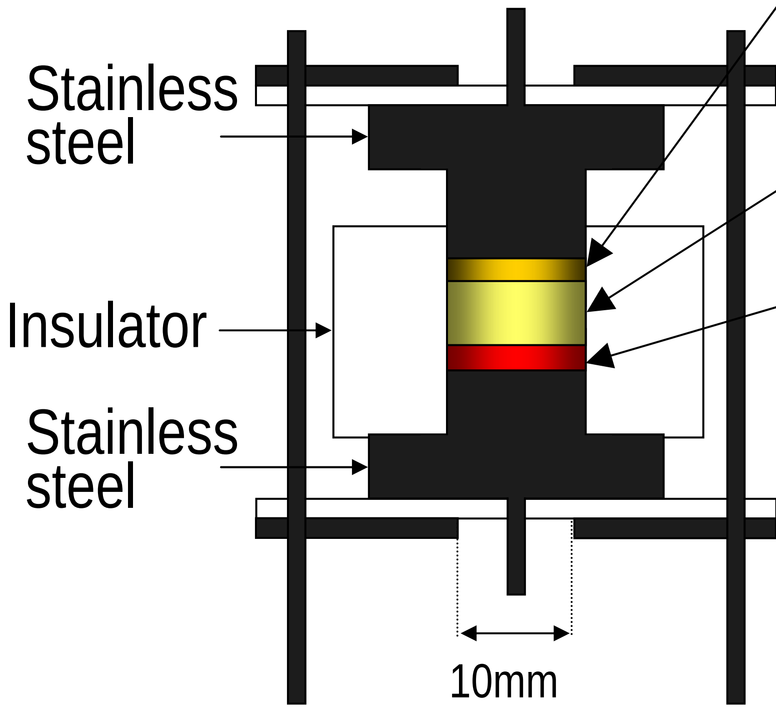


The formation of superionic metastable phase is the most remarkable advantage of glass-based solid electrolytes.

All-solid-state lithium secondary batteries using Li_2S-P_2S_5 glass-ceramics

All-solid-state batteries (In / Li_2S-P_2S_5 glass-ceramic / $LiCoO_2$)

Laboratory-scale all-solid-state cell



Negative electrode

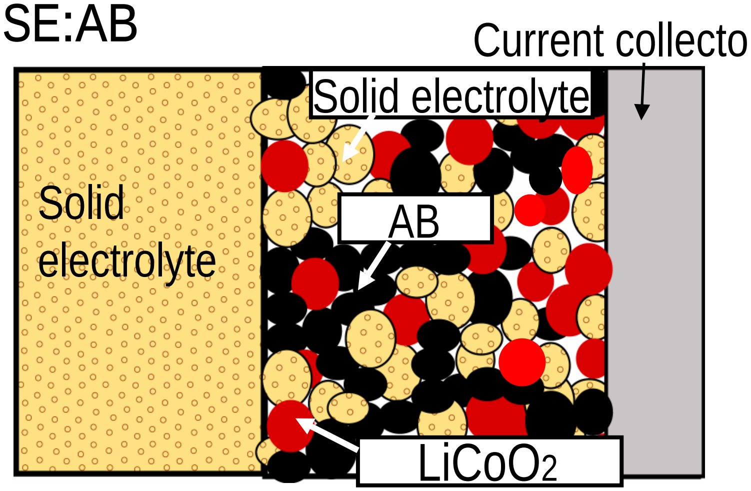
In or
SnS-P_2S_5 glass: SE:AB

Solid electrolyte (SE)

Li_2S-P_2S_5 glass ceramics

Positive electrode

$LiCoO_2$:SE:AB=20:30:3 (wt%) or
(S+CuS):SE:AB

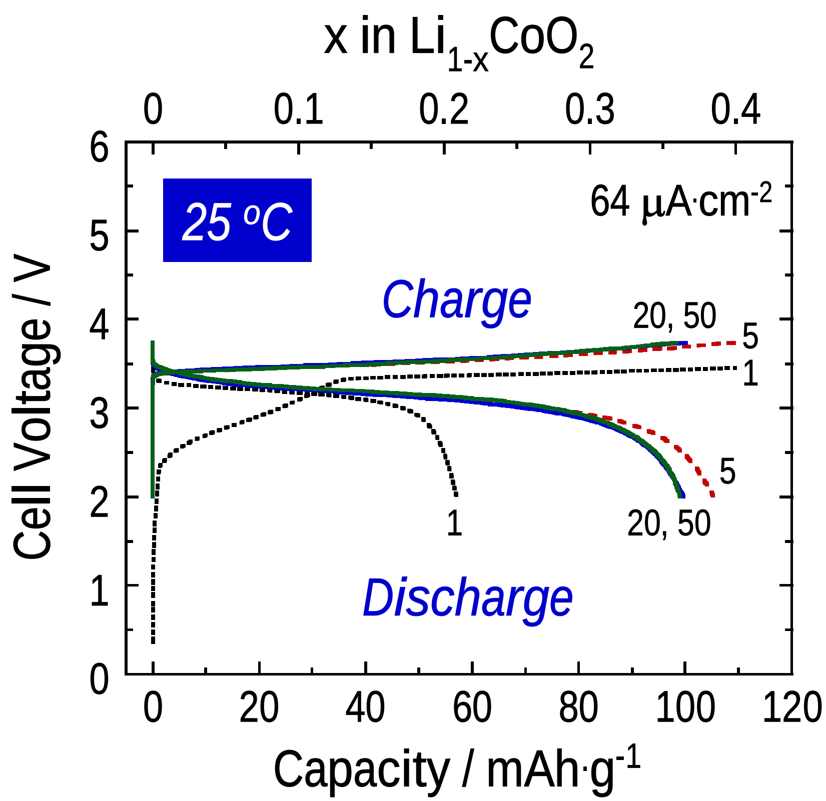


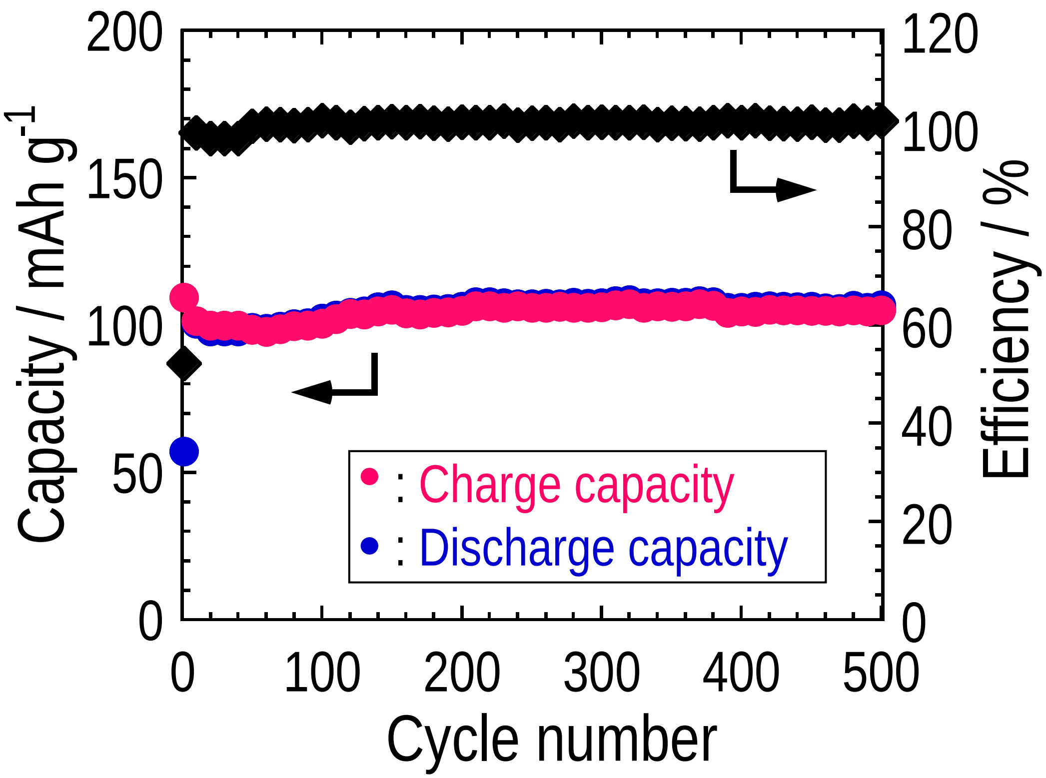
Composite electrode is a mixture of three kinds of fine powders

Ionic and electronic conduction paths through SE and conducting additives to active materials

Cell performance of the all-solid-state battery

In / $80Li_2S \cdot 20P_2S_5$ glass-ceramic / $LiCoO_2$



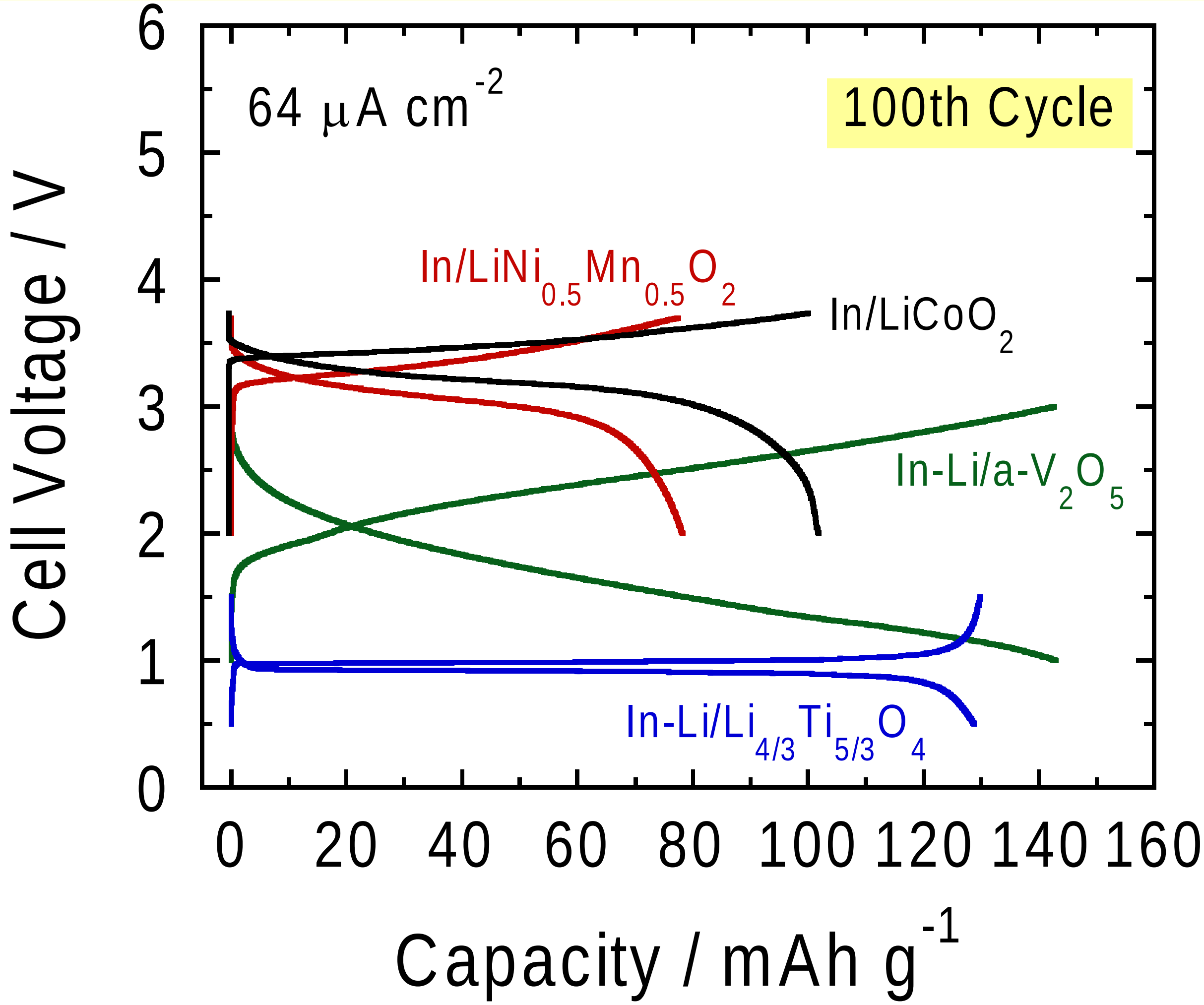


Excellent cycle performance with no loss of capacity up to the cycle number of 500

The advantage of the glass-ceramics with their high conductivity and dense microstructure would promote smooth charge-discharge reaction in the solid / solid interface between electrolyte and electrode.

All-solid-state cell performance using a variety of electrode active materials

In or In-Li / $80Li_2S \cdot 20P_2S_5$ glass-ceramic / Cathode



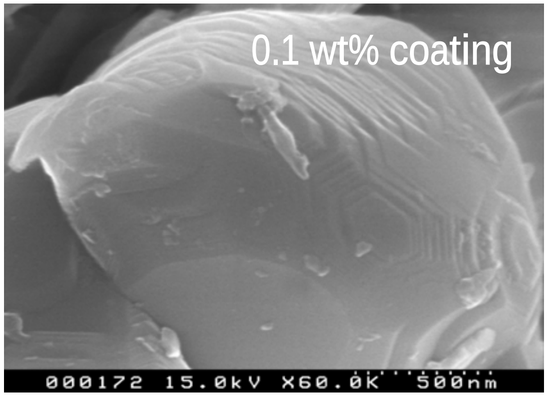
All-solid-state batteries with high reversibility and high cycle performance

For high rate performance

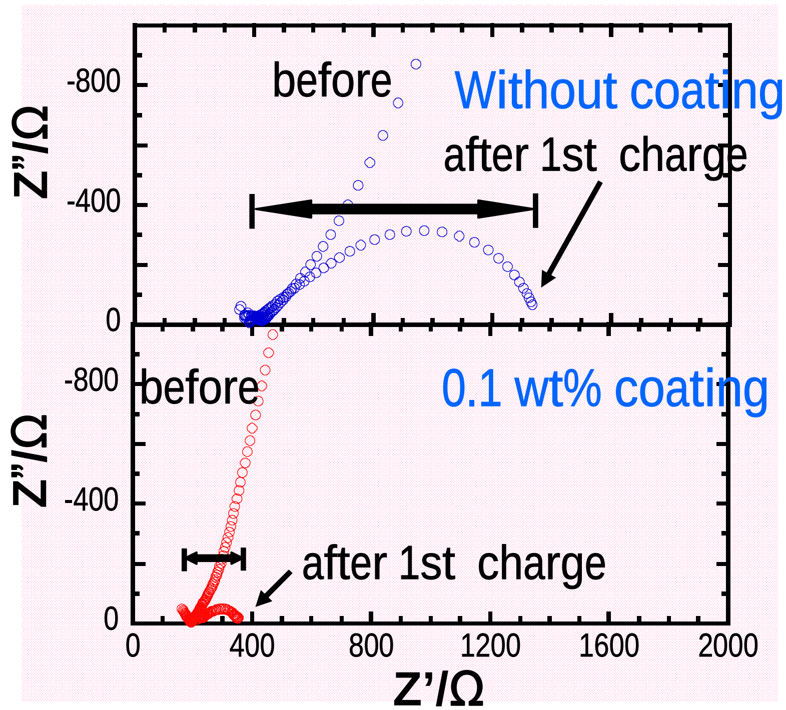
・ Coating on active materials with cobalt sulfide

$$NaS_2CN(C_2H_5)_2 + CoCl_2 \rightarrow Co[S_2CN(C_2H_5)_2]_2$$

$$Co[S_2CN(C_2H_5)_2]_2 \xrightarrow{\triangle} CoS$$

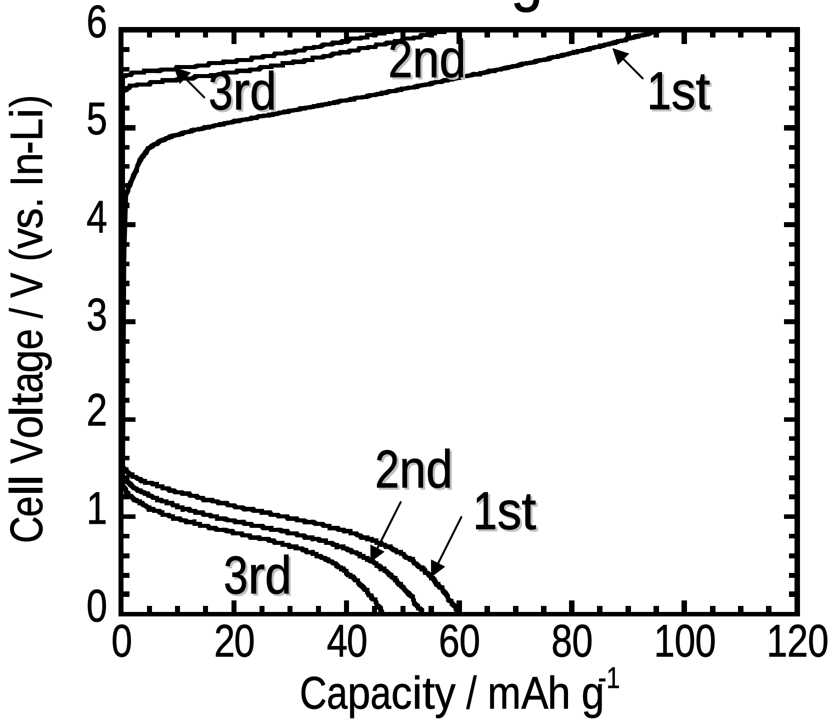


In / $80Li_2S$-20 P_2S_5 / $LiCoO_2$ -xCoS



I = 10 mA cm^{-2} (10C)

0.1 wt% coating



Preparation of glassy electrode materials for all-solid-state lithium secondary batteries
- A new concept of all-glass-based battery systems -

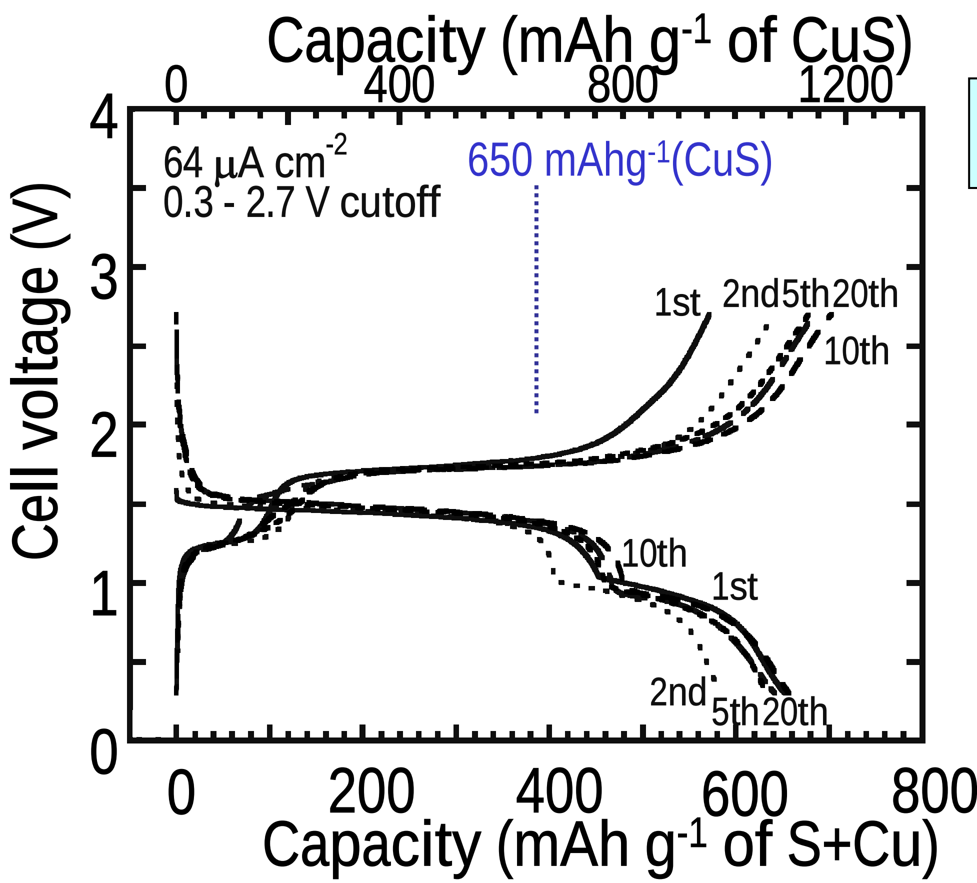
Cell performance of all-solid-state Li / S battery using Cu-S composites prepared by MM as a cathode material

Sulfur

Theoretical capacity : 1672 mAh g^{-1} → Candidate of cathode materials for next-generation secondary batteries
Cheep, Non-toxic

•Polysulfides formed in the discharge process are soluble in liquid electrolytes.

In-Li / $80Li_2S \cdot 20P_2S_5$ glass-ceramic / Cu-S composite



$3S + Cu \xrightarrow{MM} S, CuS$ composite

After Machida (2002)

Sulfur is utilized as active materials

Sulfur cathode materials, which could not be used with liquid electrolytes, can be used in all-solid-state batteries using the sulfide glass-ceramic electrolytes.

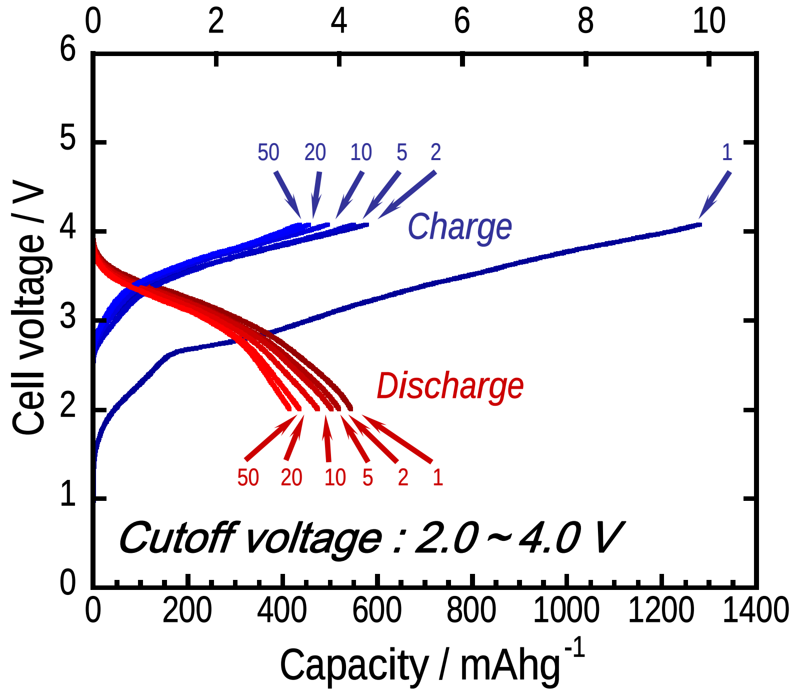
Cell performance using $SnS-P_2S_5$ glasses as an anode material

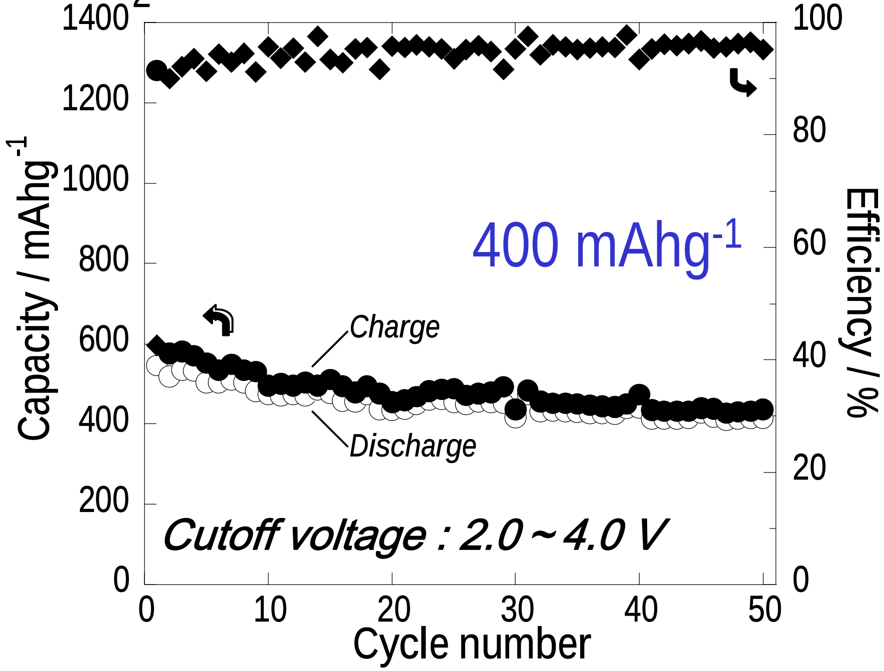
Glassy materials contining Sn

→ anode active material

$SnS + P_2S_5 \xrightarrow{MM} SnS\text{-}P_2S_5$ glasses

$80SnS \cdot 20P_2S_5$ glass / $80Li_2S \cdot 20P_2S_5$ glass-ceramic / $LiCoO_2$



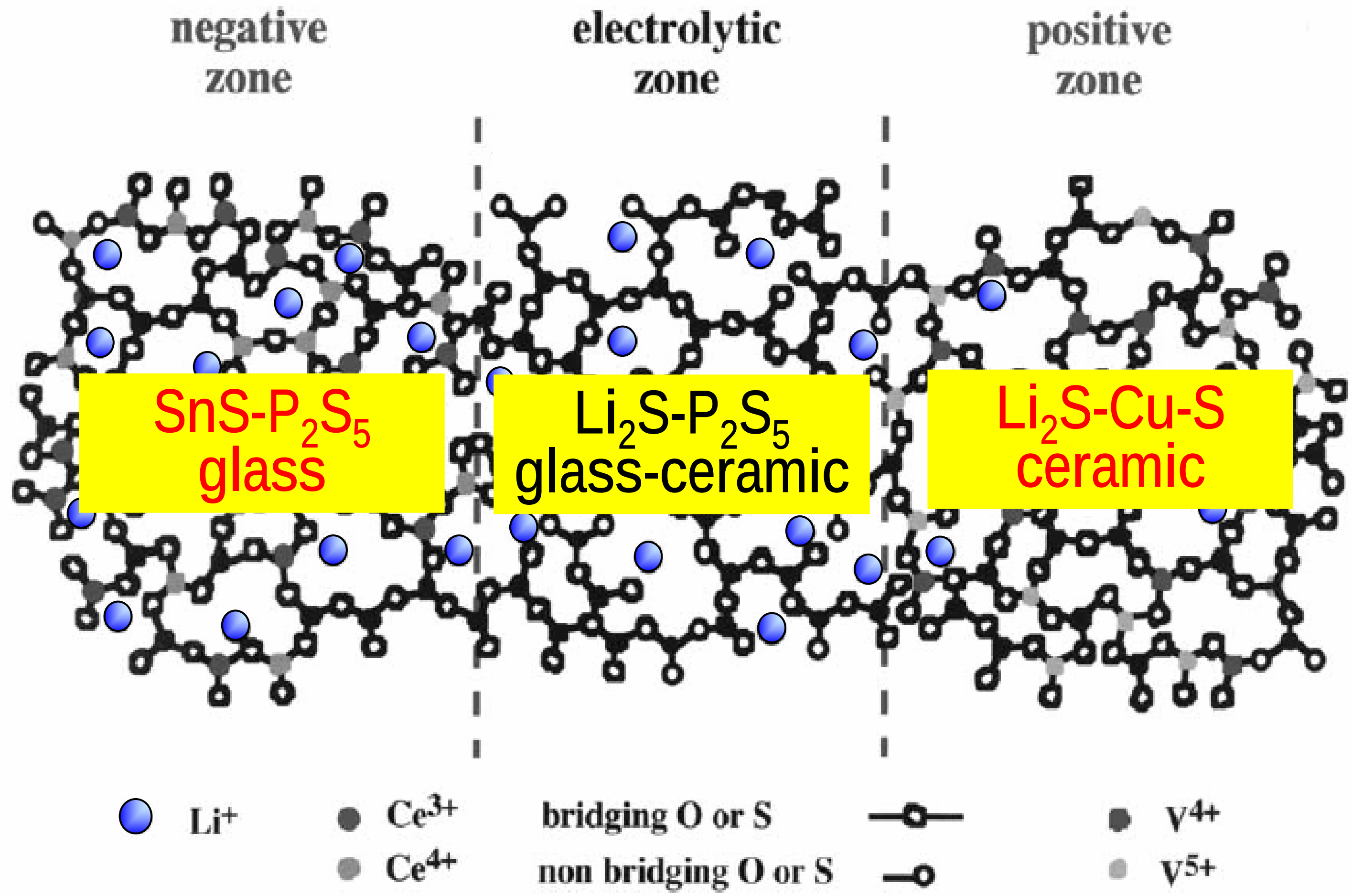


$SnS\text{-}P_2S_5 + Li^+ + e^- \xrightarrow{\text{charge}} Sn^0 + Li_2S\text{-}P_2S_5$ → Self-formation of high conductive solid electrolytes surrounding the anode active materials

$Sn^0 + Li^+ + e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Li_{4.4}Sn$

Glassy monolithic cell

A common network former is used for the electrolyte and electrode materials.



J.L. Souquet et al., *Solid State Ionics*, 148 (2002) 375.

The glassy monolithic cell is expected to facilitate smooth solid-solid contact between electrolyte and electrode, and very promising as a future all-solid-state battery.

Conclusions

CONCLUSIONS

- Sulfide glass-based solid electrolytes are suitable to be used in all-solid-state lithium secondary batteries.
- The all-solid-state batteries showed excellent cycle performance.
- In order to obtain high rate performance, electrons and ions should be smoothly supplied to the active materials through the interface between electrode and electrolyte .
- All-solid-state batteries, in which a common sulfide glass network is used as electrodes and electrolytes, are successfully constructed.

CONCLUSIONS

In order to approach the ultimate goal of all-solid-state lithium secondary battery, the charge transfer at the solid/solid interface between electrolyte and electrode should be analyzed and optimized to obtain much higher performances.