# Preparation of sodium ion conductive $Na_{3-x}SbS_{4-x}Cl_x$ glass-ceramic electrolytes

Fumika Tsuji [a], Naoki Masuzawa [a], So Yubuchi [a], Atsushi Sakuda [a],
Akitoshi Hayashi [a, b], Masahiro Tatsumisago [a]
[a] *Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka, 599-8531, Japan.*
[b] *Elements Strategy Initiative for Catalysts and Batteries, Kyoto University, Yoshidahonmati, Sakyo-ku, Kyoto, 606-8501, Japan.*

E-mail: swb02095@edu.osakafu-u.ac.jp

All-solid-state batteries using non-flammable inorganic solid electrolytes are expected to solve safety issues in commercially available batteries by removing flammable liquid electrolytes. Moreover, rechargeable sodium-ion batteries potentially have lower material costs than lithium-ion batteries due to the abundance of sodium sources. Development of sodium ion conducting solid electrolytes is important for the realization of all-solid-state sodium-ion batteries. We have found that all-solid-state sodium-ion batteries with a $Na_3PS_4$ glass-ceramic electrolyte successfully operated as a rechargeable battery at room temperature[1]. The $Na_3PS_4$ glass-ceramic exhibited a high conductivity of $4.6 \times 10^{-4}$ S cm$^{-1}$ at room temperature.

In recent years, $Na_3SbS_4$ solid electrolyte with high ionic conductivity of exceeding $10^{-3}$ S cm$^{-1}$ at room temperature and high chemical stability has been reported[2,3]. On the other hand, Chu *et al*. have reported the synthesis of a Cl-doped tetragonal $Na_3PS_4$ (t-$Na_{3-x}PS_{4-x}Cl_x$, $x$ = 0.0625) solid electrolyte with $Na^+$ vacancies. The electrolyte shows a high sodium-ion conductivity of $10^{-3}$ S cm$^{-1}$ at 25$^o$C[4], which is higher than the conductivity of tetragonal $Na_3PS_4$. In this study, the $Na_{3-x}SbS_{4-x}Cl_x$ ($x$ = 0, 0.0625) solid electrolytes were firstly synthesized via mechanical milling and consecutive heat treatment, and their conductivity and stability were examined.

Ionic conductivities of the $Na_{3-x}SbS_{4-x}Cl_x$ ($x$ = 0, 0.0625) samples were evaluated by the AC impedance measurements. The measurement was carried out for a compressed powder pellets. In the case of cold-pressed samples, the ionic conductivity of $Na_{2.9375}SbS_{3.9375}Cl_{0.0625}$ glass-ceramic was higher than that of $Na_3SbS_4$ glass-ceramic. The hot-pressed $Na_{2.9375}SbS_{3.9375}Cl_{0.0625}$ glass-ceramic had less pores than the cold-pressed one. The room-temperature conductivity of the hot-pressed one was $5.7 \times 10^{-3}$ S cm$^{-1}$, which is the highest conducutvity among the sulfide-based sodium ion conductive electrolytes reported so far.

In order to evaluate chemical stability of these electrolytes, $Na_{2.9375}SbS_{3.9375}Cl_{0.0625}$ glass-ceramic was exposed to air. The $H_2S$ gas evolution from the $Na_{2.9375}SbS_{3.9375}Cl_{0.0625}$ glass-ceramic was much less than that from the $Na_3PS_4$ glass-ceramic.

The $Na_{2.9375}SbS_{3.9375}Cl_{0.0625}$ glass-ceramic is a promising solid electrolyte with high conductivity and safety for all-solid-state sodium-ion batteries.

**References:**

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