【Grant-in-Aid for Scientific Research (S)】

Materials development of ionic conductors based on local Ion dynamics

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Project Information	Project Number : 24H00042　Project Period (FY) : 2024-2028 Keywords : Superionic conductor, Solid state ionics, energy conversion/storage, Synchrotron X-ray·neuton·muon

Purpose and Background of the Research

●Outline of the Research

Ionic conductors are key materials that determine the performance of electrochemical devices such as storage batteries and fuel cells. Recently, we have found that the local atomic arrangement is key to lowering the ionic diffusion barrier and achieving a superionic conductivity. We aim to systematize the connection between the local structure and ionic conduction based on actual measurements. We synthesize solid electrolytes and active materials with small amounts of elemental substitution, and investigate their local structures and diffusion coefficients and carrier densities to clarify their local ion dynamics. The purpose of this project is to develop new ionic conductors by expanding the material exploration area from average structural information to local ion dynamics.

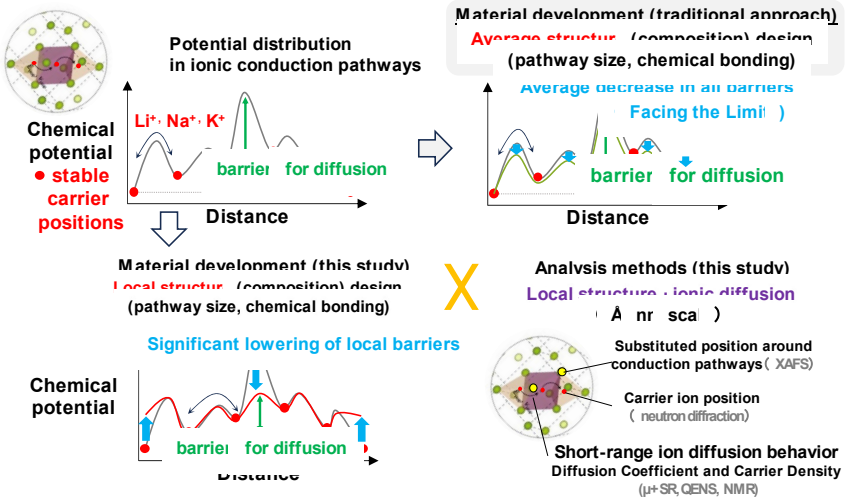

Figure 1. Research strategy for the development of highly conductive ionics materials.

●Why ion dynamics research is necessary

Ionic conductors have been explored through repeated synthetic experiments based on the known requirements of an average structure that exhibits ionic conductivity. In the recently discovered solid electrolyte $Li_{9.54}[Si_{0.6}Ge_{0.4}]_{1.74}P_{1.44}S_{11.1}Br_{0.3}O_{0.6}$ with the highest lithium-ion conductivity, S^{2-} around the lithium position with locally high diffusion barrier is replaced by other anions, and the low diffusion barrier The local structure and the conductive pathway of the low diffusion barrier are suggested to be formed continuously. The key to the development of next-generation materials is to deepen the understanding of ion dynamics based on the correlation between the local structure and conductivity, which has not yet been explored.

●How to Measure Ionic Transport in Solid

Measurements of the local structure and ionic diffusion are essential for understanding local ion dynamics. We clarify the rate-determining process of ionic diffusion without the influence of material morphology by measuring the crystal and electronic structures around substituted elements using synchrotron X-ray and neutron analyses, and the material-specific diffusion coefficient and carrier density from neutron quasi-elastic scattering, muon spin rotation relaxation, and nuclear magnetic resonance. Researchers in the fields of synthesis and advanced analysis will work together with the common goal of elucidating the ionic diffusion mechanism and exploring new materials.

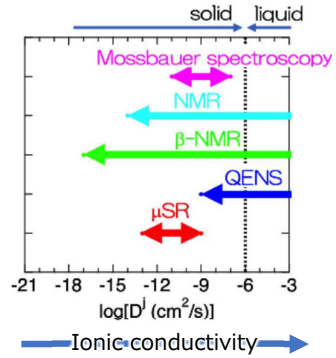

Figure 2. Scale of ionic diffusion measurable by each method

Expected Research Achievements

●Exploring superionic conductors

The basic strategy is to reduce the energy barrier in the conduction pathway by substituting small amounts of the elements. In the case of lithium solid electrolytes, we aim to develop all-solid-state batteries that can be recharged in a very short time. We will expand our research to sodium-based electrolytes to achieve superionic conductivity and to electrode active materials (lithium, sodium, and potassium) to explore materials with excellent electronic and ionic conductivities.

●Deepening of ion dynamics

We will clarify the rate-determining process of ion diffusion in superionic conductors by correlating the local structures around the substituted elements with the diffusion coefficients and carrier densities. By incorporating the findings our original material search know-how, we will construct a scientific theory of ion dynamics that is more directly related to material design.

●Acceleration of materials development

To accelerate the ionic diffusion measurement, which is the rate-limiting step in material exploration based on local ion dynamics, we will establish a new system for quantum beam measurements. A spectrometer will be installed in the existing μ+SR channel at J-PARC to enable operando μ+SR measurements of the various samples. For the synchrotron radiation and QENS experiments, we will utilize existing equipment and install several dedicated cells.

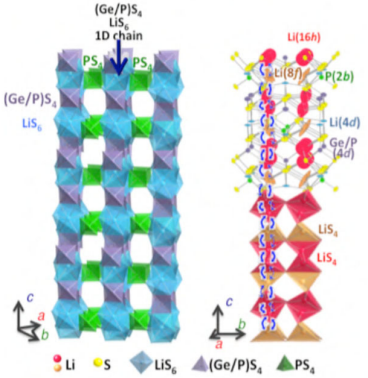

Figure 3. Crystal structure of LGPS-type ionic conductors that are the main target of this study. (Science, 381, 50-53, 2023)

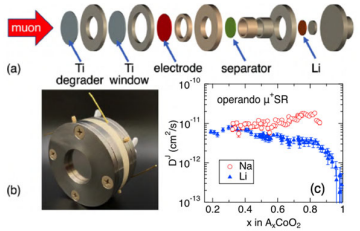

Figure 4. (a,b) Configurations of the cell for operando μ⁺SR measurement and (c) variations of self-diffusion coefficients of Li and Na in Li_xCoO_2 and Na_xCoO_2. (ACS Appl. Energy Mater., 5, 12538-12544, 2022)

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