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## *Structural Basis for Emergence of Superionic Conductivity by an Ion Exchange*

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Various superionic conductors have been examined in terms of the application to electrolytes for solid fuel cells [1]. Recently we demonstrated by impedance measurements that a simple two-step chemical reaction transformed an electronic conductor $Na_xCoO_2$ into a superionic one. In the present study, we performed in situ synchrotron X-ray diffraction experiments to investigate a structural mechanism for the superionic conductivity driven by the chemical treatment of the layered oxide $Na_xCoO_2$. We developed a temperature- and humidity-controllable capillary cell under hydrogen and helium gas flow to install in the Debye-Scherrer camera at BL44B2 of SPring-8. This cell allows us to explore a structural transformation process by reduction and humidification treatments. Structural identifications and refinements with in situ diffraction data proved that Co vacancies formed by a CoO separation suppressed the electronic conductivity. Meanwhile it turned out from charge estimation in the Na layers that the superionic conductor transition originated from an ion exchange of $H_3O^+$ for $Na^+$, which was confirmed by Raman spectroscopy measurements. In addition, charge densities clearly visualized the $H_3O^+$ ions disordering around the Na original sites, suggesting that the $H_3O^+$ behave as a carrier source. Finally it was found from electrostatic potentials that the disordering $H_3O^+$ sites were coupled through shallow potential barriers to trace a honeycomb-like ion pathway. In the presentation, I will discuss what a carrier is for the superionic-conductive phase from different viewpoints such as activation energies, concentration cell tests, and molecular dynamics simulations using the experimental structure information.

***[1]*** *R. Makiura, T. Yonemura, T. Yamada, et al., Nature Mater. 8, 476 (2009).*

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