

# Degradation Analysis of Sulfide-based All-solid-state Batteries via Cycle Testing

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Through industry-academia collaboration, a project to develop an all-solid-state lithium ion battery for electric vehicles (NEDO “Development of Fundamental technologies for All Solid State Battery applied to Electric Vehicles (SOLiD-EV)”) is now underway. All the participants are working on the development of elemental technologies to solve the project’s issues. In this study, we conducted a standard life test specified in IEC 62660-1, a high-temperature cycle test, and a high-temperature storage test on a SOLiD-EV prototype cell (an Argyrodite-type sulfide-based all-solid-state LIB) to better understand the durability and degradation mechanism of the sulfide-based all-solid-state LIB. Each test reduced the capacity of the SOLiD-EV prototype cell, and the loss in capacity retention tested at high temperatures was faster than the decrease in capacity retention tested at low temperatures. Increases in the internal resistance were also confirmed, and the temperature dependence was almost the same as the capacity tendency. Disassembly analyses of the SOLiD-EV prototype cell before and after the standard life test and the high-temperature cycle test were used to explore the degradation mechanism of the sulfide-based all-solid-state LIB. The X-ray photoelectron spectroscopy (XPS) spectra of each electrode and the compositions of the solid electrolyte (SE), which were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) of a degraded cell through the high-temperature cycle test, were used to discuss the respective degradation mechanisms of SE in the positive and negative electrodes. Fig. 1 illustrates the proposed degradation scheme for the SOLiD-EV prototype cells. First, the substitution of a part of  $\text{PS}_4^{3-}$  in  $\text{Li}_{7-x}\text{PS}_{6-x}\text{Cl}_x$  with P-S-P, -S-S-, and sulfur (S) components in XPS and the decrease of Li/P ratio in ICP-AES indicate that SE ( $\text{Li}_{7-x}\text{PS}_{6-x}\text{Cl}_x$ ) in the positive electrode has been oxidatively decomposed as a result of the positive electrode’s potential (noble potential). Sulfur (S), an oxidative decomposition product, has been shown to be a poor conductor of  $\text{Li}^+$  ions and is considered to increase charge transfer resistance and pathway resistance in the positive electrode. Second, the substitution of  $\text{PS}_4^{3-}$  in  $\text{Li}_{7-x}\text{PS}_{6-x}\text{Cl}_x$  with  $\text{Li}_3\text{P}$  and  $\text{Li}_2\text{S}$  components as well as the increase in Li/P ratio indicate that SE ( $\text{Li}_{7-x}\text{PS}_{6-x}\text{Cl}_x$ ) in the negative electrode has been reductively dissolved due to the negative electrode’s potential (low potential). The capacity fade of the cell is due to the loss of active  $\text{Li}^+$  ions caused by the reduction of the sulfide electrolyte in the negative electrode. Furthermore, the results of the high-temperature storage tests suggest that all or part of these degradation reactions adhere to the Arrhenius law.

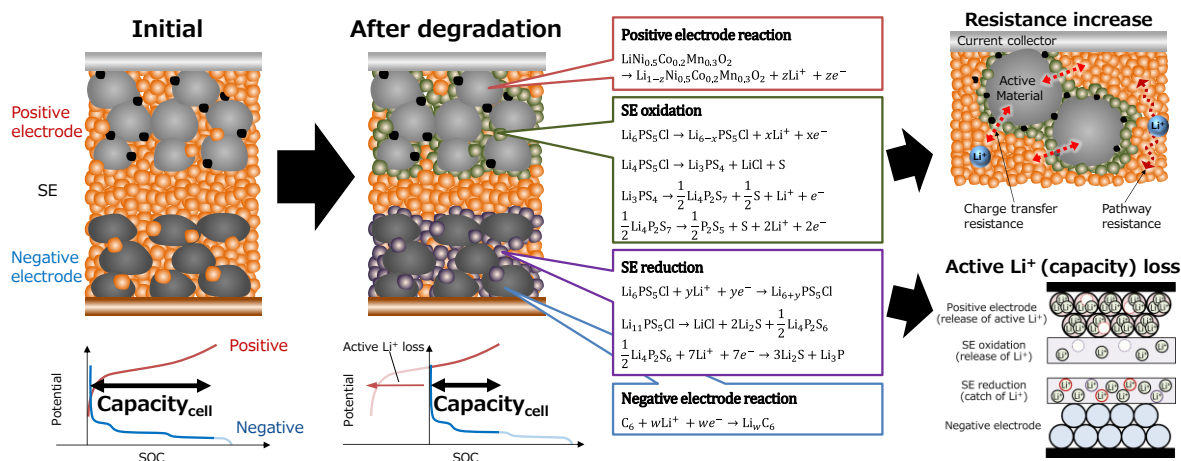


Fig. 1 Proposed degradation scheme of the SOLiD-EV prototype cell with sulfide solid electrolyte.