Novel Li$_2$RuO$_3$-Li$_2$SO$_4$ positive electrode active material for all-solid-state batteries

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For commercial use of all-solid-state batteries, the development of active materials with high capacity is desired. Recently, Sabi et al., reported the preparation of amorphous lithium transition-metal phosphate (Li$_x$M$_{3-x}$PO$_4$; M = Ni, Co, Mn, etc.) active materials by a sputtering technique\cite{1}. Thin film-type all-solid-state battery using amorphous active materials exhibited the relatively high operation voltage of around 3 V vs. Li and the high capacity of more than 300 mAh g$^{-1}$. We have therefore specifically examined the preparation of amorphous oxide electrode particles suitable for bulk-type all-solid-state batteries with high energy density. Recently, we reported the synthesis of amorphous LiCoO$_2$-Li$_2$SO$_4$ system positive electrode active materials by a mechanochemical technique\cite{2}. A bulk-type all-solid-state cell using the Li$_{1.2}$Co$_{0.8}$O$_{2.4}$ (80LiCoO$_2$-20Li$_2$SO$_4$ (mol%)) active material operated as a secondary battery at 100°C and showed the initial discharge capacity of 163 mAh g$^{-1}$.

To achieve much higher capacity, amorphization of the lithium-rich transition metal oxides such as Li$_2$RuO$_3$\cite{3,4} with Li$_2$SO$_4$ was examined. In this study, the novel amorphous Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ (80Li$_2$RuO$_3$-20Li$_2$SO$_4$ (mol%)) positive electrode material was prepared and the electrochemical performances were investigated. The Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ positive electrode active material was prepared via mechanochemistry from crystalline Li$_2$RuO$_3$ and Li$_2$SO$_4$. XRD pattern indicated that no-diffraction peaks attributable to the starting materials and the broad peaks attributable to cation-disordered rock-salt phase were observed. TEM observation indicated that the Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ was the nanocomposite material; the cation-disordered Li$_2$RuO$_3$ nanocrystals are dispersed in the amorphous Li$_2$RuO$_3$-Li$_2$SO$_4$ matrix. The electronic and lithium ionic conductivities were measured by a direct current polarization method. From the measurement, it is noted that the Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ is the mixed conductor with high electronic and lithium ionic conductivities. The all-solid-state cell (Li-In/Li$_3$PS$_4$/Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$) was fabricated and the charge-discharge properties were investigated at 100°C. The all-solid-state cell operated as a secondary battery with showing the large capacity of about 230 mAh g$^{-1}$. This capacity exceeded the theoretical capacity expected by the charge compensation of Ru$^{4+}$/Ru$^{5+}$ redox (141 mAh g$^{-1}$); the additional capacity was based on the oxygen redox, which was supported by the results of soft X-ray absorption spectroscopy. In addition, the structural change during the charge-discharge process was investigated by XRD measurements and TEM observations. Amorphization of the rock-salt phase proceeded during the charge process, while the phase was re-precipitated during the discharge process. This structural change was similar to that reported in the Li$_2$TiS$_3$ electrode with cation-disordered rock-salt structure\cite{5}.

References: