

Novel $\text{Li}_2\text{RuO}_3\text{-Li}_2\text{SO}_4$ 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 ($\text{Li}_x\text{M}_y\text{PO}_z$; M = Ni, Co, Mn, *etc.*) active materials by a sputtering technique^[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 $\text{LiCoO}_2\text{-Li}_2\text{SO}_4$ system positive electrode active materials by a mechanochemical technique^[2]. A bulk-type all-solid-state cell using the $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$ (80LiCoO₂-20Li₂SO₄ (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_2RuO_3 ^[3,4] with Li_2SO_4 was examined. In this study, the novel amorphous $\text{Li}_2\text{Ru}_{0.8}\text{S}_{0.2}\text{O}_{3.2}$ (80Li₂RuO₃-20Li₂SO₄ (mol%)) positive electrode material was prepared and the electrochemical performances were investigated. The $\text{Li}_2\text{Ru}_{0.8}\text{S}_{0.2}\text{O}_{3.2}$ positive electrode active material was prepared via mechanochemistry from crystalline Li_2RuO_3 and Li_2SO_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 $\text{Li}_2\text{Ru}_{0.8}\text{S}_{0.2}\text{O}_{3.2}$ was the nanocomposite material; the cation-disordered Li_2RuO_3 nanocrystals are dispersed in the amorphous $\text{Li}_2\text{RuO}_3\text{-Li}_2\text{SO}_4$ matrix. The electronic and lithium ionic conductivities were measured by a direct current polarization method. From the measurement, it is noted that the $\text{Li}_2\text{Ru}_{0.8}\text{S}_{0.2}\text{O}_{3.2}$ is the mixed conductor with high electronic and lithium ionic conductivities. The all-solid-state cell (Li-In/Li₃PS₄/Li₂Ru_{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 Ru⁴⁺/Ru⁵⁺ 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_2TiS_3 electrode with cation-disordered rock-salt structure^[5].

References:

- [1] Y. Sabi *et al.*, *J. Power Sources*, **258** (2014) 54-60. [2] K. Nagao *et al.*, *J. Power Sources*, **348** (2017) 1.
- [3] A. C. W. P. James and J. B. Goodenough, *J. Solid State Chem.*, **74** (1988) 287.
- [4] M. Sathiya *et al.*, *Nature Mater.*, **12** (2013) 827. [5] A. Sakuda *et al.*, *Sci. Rep.*, **4** (2014) 4883.