

Anti-site mixing governs electrochemical performances of olivine type MgMnSiO₄ for magnesium ion battery cathode

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Introduction

Mg battery is expected as high energy density, safe and low cost battery because of its divalent features, relatively low redox potential (Mg²⁺/Mg (-2.37 V vs. NHE)), high melting point, and abundant mineral. The development of Mg batteries, however, has been hindered by several reasons. The main problem is the limitation in the choice of cathode material due to the difficulty in achieving reversible Mg²⁺ insertion and extraction in a host material. This difficulty is caused by the strong polarization character of the small and divalent Mg²⁺ [1]. To overcome this problem, we focused on polyanion compound because of its high structural stability. Recently Mg olivine silicates were reported to have high capacity and good reversibility for Mg battery cathode [2]. For improvement the performances of these materials, we focused on the diffusion path in the crystal structure. In the case of Olivine phosphate, Li⁺ ion diffuse through one dimensional channels oriented along the [010] direction of the orthorhombic crystal structure [3]. The diffusivity of the Li⁺ ion in olivine structure were hindered by point defect [4]. On the Mg battery case, it is so easily occurred because of the Mg²⁺ and TM²⁺ have same valence and similar ionic radius. Then we focused on Mg manganese olivine silicates. It can be controlled the crystallographic site by synthesis temperature [5].

In this work, the effect of the anti-site mixing for the electrochemical performance of MgMnSiO₄ was investigated. We controlled concentrations of the anti-site mixing in the crystal structure by controlling synthesis temperature, and performed the galvanostatic charge-discharge measurements. We also performed X-ray absorption spectroscopy (XAS) measurements and X-Ray diffraction (XRD) in order to clarify the reaction mechanisms of MgMnSiO₄ from the point of crystal structural change and electronic structures.

Experimental

MgMnSiO₄ was prepared by flux methods. To change synthesis temperature, we used KCl for 900 and 1000°C, NaCl-KCl for 700°C and LiCl-KCl for 450 and 500°C respectively. Prepared samples were characterized by XRD, and SEM. Site occupancies were analyzed by Rietveld analysis. Galvanostatic charge - discharge measurements were conducted with three-electrode cells. The working electrode comprised a composite mixture of the active material, Acetylene Black (AB), and PTFE binder (55:45:5) pressed between two Pt mesh current collectors. Mg rod and double junction-type Ag⁺/Ag were used as the counter and reference electrode respectively. 0.5 M Mg[N(CF₃SO₂)₂]₂ / acetonitrile (AN) was used as electrolyte.

XAS spectra at Mn K-edge of MgMnSiO₄ electrodes were measured in a transmission mode at the beam line BL01B1 at SPring-8 (Japan). XRD measurements were carried out at the beam line BL02B2 at SPring-8 (Japan). All samples are sealed into Ar filled glass capillary.

Results & Discussions

Figure 1 shows the projection of olivine-type MgMnSiO₄. M1 and M2 sites are occupied by Mg and Mn ions. The ratio of site occupancy is changed by synthesis temperature. Figure 2 shows the temperature dependences of the site occupancy of the Mg in M1 site which is the site of the diffusion path, and the crystallite sizes. By synthesizing the samples at lower temperature, the site occupancy of the magnesium in M1 site is so high and the crystallite size is decreased. MgMnSiO₄ positive electrode which synthesized at 450°C shows about 110 mA h g⁻¹, however one synthesized at 700°C shows about 20 mA h g⁻¹. The dominant factor of electrochemical performance is anti-site mixing in the structure, because their site occupancies of the Mg in M1 site are more difference than their crystallite sizes.

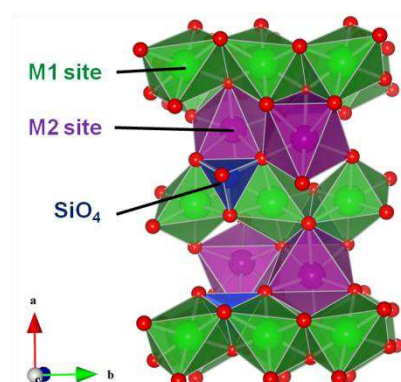


Fig. 1 Projection of olivine-type MgMnSiO₄

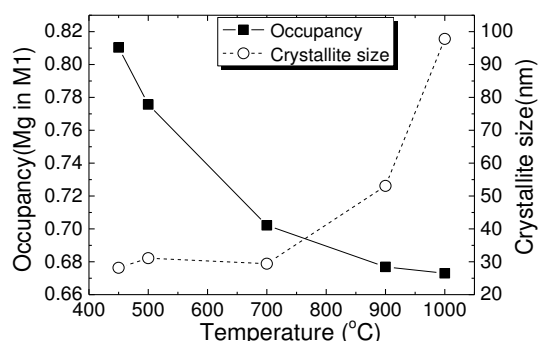


Fig. 2 Synthesis temperature dependence of the site occupancy and crystallite sizes.

ACKNOWLEDGMENTS

This work was supported in part by Core Research for Evolutional Science and Technology (CREST) program of Japan Science and Technology Agency(JST) in Japan.

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