

Synthesis and Electrochemical Characterization of Spinel-type Mg Complex Oxides as Positive Electrode Active Materials for Mg Batteries

Yuya Ichikawa^a, Shunsuke Yagi^{a,*}, Tetsu Ichitubo^b, and Eiichiro Matsubara^b

^aNanoscience and Nanotechnology Research Center, Osaka Prefecture University, Osaka 599-8570, Japan

^bDepartment of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan

*Email: s-yagi@21c.osakafu-u.ac.jp

Mg batteries have been attracting significant interest as low-cost batteries with high electromotive force, high capacity, and safety, because Mg has the lowest standard electrode potential among the air-stable metals, and Mg resources are abundant and widely spread in the world compared to Li resources. However, the difficulties of diffusion and desolvation of divalent Mg²⁺ ions limit the choice of positive electrode (cathode) active materials. Factually, only Chevrel compounds are the workable positive electrode active materials with a relatively high charge/discharge rate and high reversibility at this time.¹ Their redox potentials are about 1.2 V vs. Mg, which are far below the anodic stability limit of electrolytes being developed recently (around 3 V vs. Mg).² Thus, the discovery of positive electrode active materials with higher redox potentials immediately leads to the enhancement of the electromotive force.

In the present work, we synthesized spinel-type Mg complex oxides, MgM₂O₄ (M: transition metal, e.g. Cr, Mn, Fe, and Co) via inverse coprecipitation.³ First, metallic salt solutions were prepared by dissolving 0.080 M Mg(NO₃)₂·6H₂O; 0.160 M M(NO₃)₂·6H₂O (M: Co, Mn) or M(NO₃)₃·9H₂O (M: Cr, Fe) in deionized water. A sodium carbonate solution was then prepared as a precipitation solution for pH control. The metallic salt solutions were added dropwise to the precipitation solution. The resulted suspensions were vigorously stirred at 70–80 °C for 30 min and then filtered. The filtered precipitates (precursors) were rinsed with deionized water at 80 °C, followed by drying at 80 °C for 24 h. The precursors were pulverized by planetary ball milling at 500 rpm for 8 x 15 min at intervals of 5 min. The pulverized precursors were calcined at 500 or 750 °C for 24 h. The structure parameters of the obtained spinel-type oxide powders, specifically the occupancies of atomic sites were analyzed on the basis of the synchrotron XRD data using the Rietveld program RIETAN-FP.⁴

Fig. 1 shows the crystal structure of a spinel type oxide AB₂O₄. In normal spinel oxides AB₂O₄, all the divalent cations, A, occupy the tetrahedral sites (8a sites) and all the trivalent cations, B, occupy the octahedral sites (16d sites). In inverse spinel oxides, all the A cations and half the B cations occupy octahedral sites (16d sites) and the remaining half of the B cations occupy tetrahedral sites (8a sites). There are also disordered intermediate states with random A and B cation distributions. In this abstract, we show the result of MgCo₂O₄ as an example. **Fig. 2** presents the synchrotron XRD profile of the spinel-type MgCo₂O₄ powder calcined at 500 °C. Rietveld refinement revealed that the synthesized MgCo₂O₄ was a disordered spinel, (Mg_{0.53}Co_{0.47})(Mg_{0.24}Co_{0.76})₂O₄. The expected charge and discharge reactions of MgCo₂O₄ are as follows:

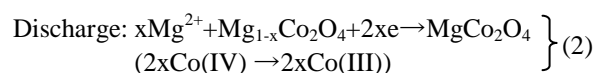
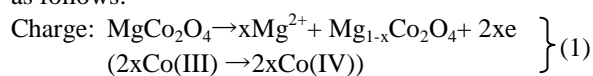


Fig. 3 shows the cyclic voltammogram measured at 0.1 mV s⁻¹ with 3-electrode setup using MgCo₂O₄ as the working electrode (WE) and Mg ribbons as the counter electrode (CE) and reference electrode (RE). Two characteristic redox peak couples (Red₁/Ox₁ and Red₂/Ox₂) are observed at around 3 and 2 V vs. Mg, respectively. It should be noted that the electrolyte was oxidatively decomposed above 2.7 V vs. Mg,⁵ and there is an offset of anodic current density above 2.7 V. Although further detailed investigation is required to determine which redox peak couple corresponds to Eqs.1-2, it is expected that the valence change of Co(III)/Co(IV) occurs at higher potentials. Considering this fact, the redox peak couple around 2 V vs. Mg (Red₂/Ox₂) would correspond to the valence change of Co(II)/Co(III), implying the existence of the oxygen vacancies in the structure of MgCo₂O₄ because of charge compensation.

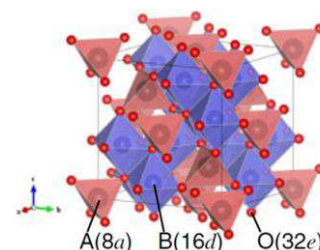


Fig. 1 Crystal structure of a spinel type oxide AB₂O₄.

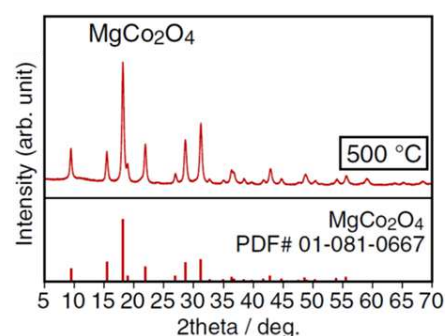


Fig. 2 Synchrotron XRD profile of MgCo₂O₄ powder calcined at 500 °C for 24 h.

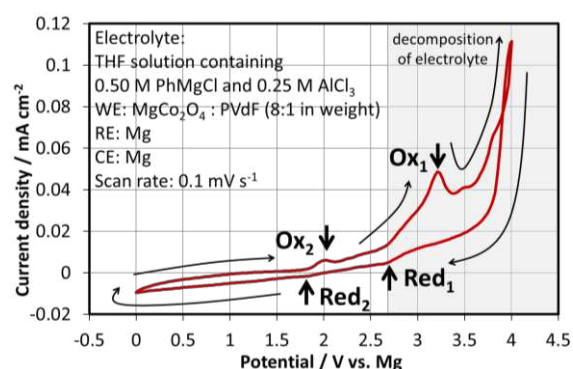


Fig. 3 Cyclic voltammogram measured at 0.1 mV s⁻¹ using MgCo₂O₄ as the working electrode in THF solution containing 0.50 M PhMgCl and 0.25 M AlCl₃.

References

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