

Cathode Performances of Ultrasmall Mg-Mn Binary Oxides for Magnesium-ion Batteries Operated at Room Temperature

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With the widespread use of portable electric devices, electric vehicles, and various future applications, rechargeable batteries are required to provide substantially greater energy densities compared with that of conventional batteries. Rechargeable Mg-ion batteries have much attention as promising alternatives to current Li-ion batteries due to the high natural abundance of Mg and its safety, and high volumetric energy density. However, Mg-ion batteries have problems at cathodes and electrolytes for utilization. One of the problems is very low rate capability at cathodes due to much slower diffusion of Mg^{2+} ions in solids than Li^+ ions, therefore Mg-ion batteries work only at low current densities or at high temperature. Reducing particle size of cathode material is effective to improve the rate capability of Mg-ion batteries. In this study, we aimed at synthesizing ultrasmall Mg-Mn binary oxides via alcohol reduction process, and applying it to the cathodes for Mg-ion batteries operated at room temperature.

Samples were synthesized by alcohol reduction method. $n\text{-Bu}_4\text{NMnO}_4$ was added to a MgCl_2 solution in ethanol and stirred for 3 h. The precipitates were collected by membrane filtration, washed with water and ethanol, and dried at 120°C . Thus obtained sample was mixed with acetylene black and PTFE at the weight ratio of 60/30/10 and pressed on a Pt mesh current collector to serve as a cathode. Charge/discharge test between $-1.0\sim 1.0$ V vs. Ag^+/Ag was carried out in a CC mode using a three-electrode cell with an activated carbon anode and 0.5 M $\text{Mg}(\text{ClO}_4)_2/\text{CH}_3\text{CN}$ as an electrolyte solution.

According to the XRD patterns and ICP-AES analysis, an empirical formula for the obtained sample was estimated to be $\text{Mg}_{0.76}\text{Mn}_2\text{O}_4$. XRD patterns and TEM images suggested that the sample had a distorted spinel-type structure due to defects of Mg^{2+} ion's site, and that the particle size was ca. 3 nm. However, the particle was aggregated to form secondary particles with ca. $1\ \mu\text{m}$. During discharge-charge, gentle slopes were observed, which was attributable to intercalation/deintercalation reactions of Mg^{2+} ions near surface of the sample with widely distributed site-energies, since near surface/bulk ratio was quite large due to its small particle size [1]. The discharge capacity was $80\ \text{mAh g}^{-1}$, which was much smaller than the theoretical capacity ($270\ \text{mAh g}^{-1}$) due to the aggregation. Suppression of the aggregation is important for improving its cathode performance.

References:

- [1] M. Okubo Y, Mizuno, H. Yamada, J Kim, E. Hosono, H. Zhou, T. Kudo, I. Honma, ACS Nano 4 (2010) 741–752.