

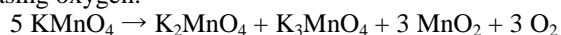
High Temperature Synthesis of Birnessite Type Manganese Dioxides Doped with Cobalt for Rechargeable Li Batteries

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Cathode materials for rechargeable Li batteries have been the focus of intense research for a number of years. Among the candidates for cathodic materials, manganese oxides are particularly attractive due to the low cost of raw materials and the fact that Mn is considered more environmentally friendly than other transition metal oxide systems, such as cobalt and nickel. Much research is focusing currently on the application of the spinel LiMn_2O_4 and $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ to Li ion batteries. The host structures are based on assemblies of MnO_6 octahedra, which can be distinguished on the basis of the connectivity and the pathway available for the electrochemically reversible intercalation of lithium. Among various manganese dioxide frameworks [1], birnessite type manganese dioxides ($\square\text{-MnO}_2$) are believed to provide the most favorable pathways for Li diffusion. Several efforts on application of $\square\text{-MnO}_2$ were made for the application to lithium secondary batteries [2-5]. Furthermore, we reported the unique synthetic method for $\square\text{-MnO}_2$ by thermal decomposition of KMnO_4 [5]. Recently, Tsuda et al. described the precipitation synthesis of layered MnO_2 doped with Co resulting in enhancement of reversibility of lithium intercalation [6]. In this report, we present high temperature synthesis of $\square\text{-MnO}_2$ doped with Co and its application to secondary lithium batteries.

For the synthesis of Co doped $\square\text{-MnO}_2$ powder, potassium permanganate and cobalt nitrate were mixed in a crucible and then heat-treated at constant temperatures (600°C) in air for five hours. The products obtained were treated ultrasonically in water or HCl solution and ground in an agate mortar. The characterization of the products was carried out by powder X-ray diffractometry (XRD) using $\text{Cu K}\alpha$ radiation. The composition of K, Mn and Co in the products was determined by atomic absorption spectrometry after dissolving the products. The morphology of the birnessite type MnO_2 was observed with transmission electron microscopy. For electrochemical measurements, the positive electrode mixtures consisted of manganese oxide, graphite, acetylene black as conductive agent and PVDF as a binder, in a weight ratio of 7:1:1:1. Lithium foil was used for counter electrodes. The electrolyte used were 1 mol dm^{-3} LiClO_4 -propylene carbonate (PC) or 1 mol dm^{-3} LiPF_6 -EC:DEC = 1:1. Discharge-recharge tests as a positive electrode were carried out between 2.0 and 4.3 V vs. Li/Li^+ at 20 mA g^{-1} .

It is known generally that KMnO_4 is decomposed into potassium manganate and MnO_2 above 200°C in air, releasing oxygen:



$\square\text{-MnO}_2$ powders were obtained via the thermal decomposition of KMnO_4 [5]. For partially substituting cobalt for manganese, a mixture of KMnO_4 and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was calcined at 600°C in air. As a result, we obtained a single phase product of $\square\text{-MnO}_2$ powder from XRD pattern. It was confirmed from elemental analysis that this product contained a definite amount of cobalt ($x = 0 - 0.2$ in $\text{Mn}_{1-x}\text{Co}_x\text{O}_2$). This synthesized Co

doped $\square\text{-MnO}_2$ had interlayer spacing about 7.2 \AA which was similar to that of Co-free $\square\text{-MnO}_2$. As comparing Co-doped and Co-free $\square\text{-MnO}_2$ s, the discharge capacity during 20 cycles increased by cobalt doping as shown in Fig. 1. We believe that this improvement of discharge capacity is due to more stable Co^{3+} substitution in $\square\text{-MnO}_2$ [6] and enhanced electronic conductivity [7]. The presence of residual potassium and water in the host is certainly associated with stability of the layered-structure, electrochemical properties and cyclability, because interlayer water molecules and cationic species acting as pillar species are important for stabilizing the layer structure as described by Bach *et al.* [2]. Although the manganese ions are reduced and oxidized during discharge and charge, respectively, we believe that the cobalt ions are always in the Co^{3+} state, thus fixing the potassium ions in the interlayer and stabilizing the layer structure as suggested by Tsuda et al. [6]. It was thought that the sufficient property was due to not only the favorable pathways for lithium but also the Co substitution in MnO_2 framework. Furthermore, because the electrochemical behavior of manganese dioxides is known to be influenced by chemical composition, the presence of impurities, defect structure, particle size and so on, further investigations proceeding now in our laboratory are expected to enhance the performance in the lithium battery system.

In summary, it was found that Co-doped $\square\text{-MnO}_2$ was successfully synthesized by the thermal decomposition of KMnO_4 and cobalt nitrate and showed better performance as a Li battery cathode, that is, it demonstrated a higher reversible capacity as a cathode for lithium secondary batteries.

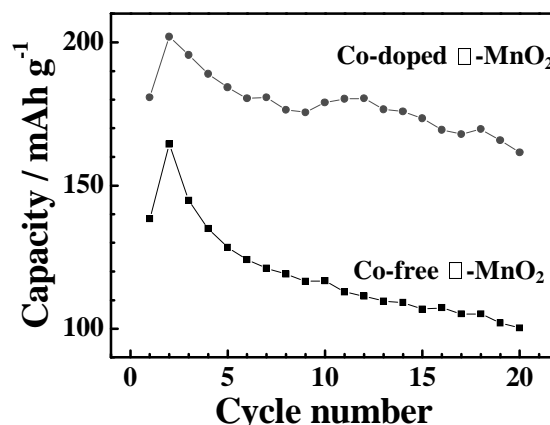


Fig. 1. Variation in discharge capacities of the Co-free and Co-doped $\square\text{-MnO}_2$ s in Li cell.

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