Electrochemical properties of layer-structured $H_x(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ for electrochemical capacitors in alkaline aqueous solutions

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ABSTRACT

The electrochemical properties of layer-structured $H_x(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ were examined for the first time to evaluate its use as an electrode for an electrochemical capacitor in alkaline aqueous solutions. The protonated $H_x(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ (HNCM) was prepared by reacting $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ (LNCM) with an HCl aqueous solution. The HNCM exhibited a large capacitance of $720\,F\,g^{-1}$ ($290\,mAh\,g^{-1}$, -1 to $0.45\,V$ vs. Hg/HgO) at a current density of $50\,mA\,g^{-1}$ in 8 M KOH aqueous solution, which is the highest level for the bulk electrodes in aqueous solutions. High power density, that is a capacitance of $560\,F\,g^{-1}$ at a large current density of $1500\,mA\,g^{-1}$, was also confirmed. The HNCM exhibited good cycle stability, especially in 1 M KOH aqueous solution. The HNCM was found to be a promising electrode material for electrochemical capacitors because of its large capacitance, high cycle stability, and high rate capability.

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1. Introduction

There is a great demand for energy storage devices with high power density and high energy density, especially for electric or hybrid vehicles. Electrochemical capacitors have attracted much attentions as such devices because of their high power density, long cycle life and relatively high energy density [1–4]. Electric energy is stored using both capacitive and pseudocapacitive processes in electrochemical capacitors. The pseudocapacitive process is based on Faradaic redox reactions taking place at the surface of the active electrode materials, and the generated charge density is much larger than that of the capacitive process based on charge separation at the electrode/solution interface. To enhance the Faradaic redox reactions, many studies have been conducted to use oxide material electrodes for electrochemical capacitors. Among them, ruthenium oxide is the representative electrode material and has been reported to exhibit a large capacitance up to $1580\,F\,g^{-1}$ in

the case of quite thin films in aqueous electrolyte [5–8]. However, since ruthenium oxide is not naturally abundant, alternative materials are demanded. Many studies have also been done for MnO_2 as a cathode for electrochemical capacitors [9–17]. There are many advantages of using MnO_2 compounds, such as their low toxicity, environmental safety, cost effectiveness and large capacitance. A large reversible capacitance is expected for MnO_2 because Mn ions take various oxidation states between Mn^{2+} and Mn^{4+} within the potential window of aqueous electrolytes. One strategy for taking advantage of the two-electron redox reactions of MnO_2 is to use an alkaline aqueous solution, because Mn^{2+} can exist in a solid form such as $Mn(OH)_2$ in an alkaline system [18,19]. Although good electrode properties can be expected for MnO_2 in an alkaline system, effective usage of the redox reaction between Mn^{4+}/Mn^{2+} has not been achieved because of the low ionic conductivity, low electric conductivity, and rapid capacitance decay caused by the formation of Mn_3O_4 during reduction from MnOOH to $Mn(OH)_2$ [17,20].

Here, we focus on a layer-structured (Ni, Co, Mn) oxide as an electrode material for electrochemical capacitors. Many studies on the electrode properties of the layer-structured (Ni, Co, Mn) oxides as cathodes for Li-ion batteries have been reported [21,29], and excellent electrochemical properties have been reported such as large capacity of approximately $150–190\,mAh\,g^{-1}$ ($284–360\,F\,g^{-1}$, $2.5–4.4\,V$ vs. Li/Li^+) with a high cycle stability and improved electric conductivity by Co-doping [21,22]. On the other hand, there has been no report on the electrode properties or proton storage mechanism of this material in an aqueous solution.

In the present study, we report the electrode properties of layer-structured $H_x(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ for the first time to evaluate its
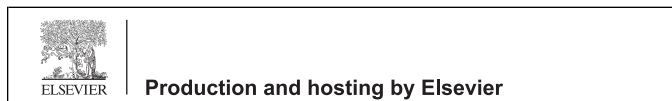
use as an electrode material for electrochemical capacitors in an alkaline system. $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ (LNCM) was prepared using a co-precipitation method, and protonated $H_x(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ (HNCM) was prepared by reacting LNCM with an HCl aqueous solution. Various evaluations of the HNCM were conducted in order to clarify its electrochemical properties and charge/discharge mechanism in alkaline aqueous solutions.

2. Experimental

Layer-structured $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ (LNCM) was synthesized using a co-precipitation method [23]. Aqueous solutions of $NiSO_4$, $CoSO_4$, and $MnSO_4$ (Ni:Co:Mn = 1:1:1) with a total concentration of 2.0 M were added into a continuously stirred reactor under an argon atmosphere. At the same time, an NaOH aqueous solution of 2.0 M as a pH conditioner and an NH_4OH aqueous solution (metal ion:NH_4OH = 1:1) as a chelating agent were also separately added into the reactor. The co-precipitated particles were kept stirring for 80 °C for 12 h. The pH during the co-precipitation reaction was kept to 12. The obtained $(Ni_{1/3}Co_{1/3}Mn_{1/3})(OH)_2$ particles were filtered, washed, and dried at 80 °C in a vacuum for 2 h. Then, the $LiOH \cdot H_2O$ powders were mixed and calcined. The mixture was first heated at 480 °C for 5 h in air and was calcined at 1000 °C for 10 h in air to obtain the LNCM powders. The interlayer lithium was exchanged with protons by stirring the LNCM in a 1 M HCl aqueous solution at room temperature for 5 days, during which the HCl solution was refreshed every day. The powders were filtered, washed with pure water, and dried at 80 °C for 2 h to obtain the $H_x(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ (HNCM).

The LNCM and HNCM electrodes were prepared by mixing the active material (LNCM or HNCM), acetylene black, and PTFE with a weight ratio of 5:5:1 and pressing the mixture onto a Ti mesh with a loading of 5 mg cm^{-2}. The electrochemical measurements were performed using a three-electrode cell with an Hg/HgO electrode as the reference electrode and a Pt mesh as the counter electrode. KOH aqueous solutions with concentrations of 1 or 8 M were used as electrolytes.

The crystal structures of the samples were confirmed by performing X-ray diffraction (XRD) analysis using a Bruker D8 ADVANCE. The morphologies of samples were observed by performing scanning electron microscopy (SEM) with a Hitachi S-4500 and a Hitachi SU 8000. The chemical compositions of the LNCM and HNCM were determined by performing inductively coupled plasma (ICP) atomic emission spectrometry with a Hitachi High-Tech Science SPS3100. The galvanostatic charge and discharge tests and cyclic voltammetry tests were carried out using a Solartron 1470E Cell-Test system, a Hokuto Denko HZ-3000 system, and a BioLogic VMP3.

3. Results and discussion

Microstructures of the obtained powders were confirmed by XRD measurements, ICP analyses, and SEM observations. Fig. 1 shows the XRD patterns for (a) $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ (LNCM) and (b) proton-exchanged $H_x(Ni_{1/3}Co_{1/3}Mn_{1/3})$ (HNCM) along with (c) the ICSD data for $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$. The chemical compositions listed in the figure were obtained form the ICP analysis. The amount of interlayer lithium ions was successfully decreased after the ion-exchange reaction. The LNCM and HNCM patterns showed good agreement with the ICSD data. Single-phase LNCM was successfully obtained, and no phase change was observed for the HNCM. Fig. 2 shows SEM images of (a) LNCM and (b) proton-exchanged HNCM. Both the LNCM and HNCM were made up of polygonal particles with sizes of 500 nm to 2 μm. No major
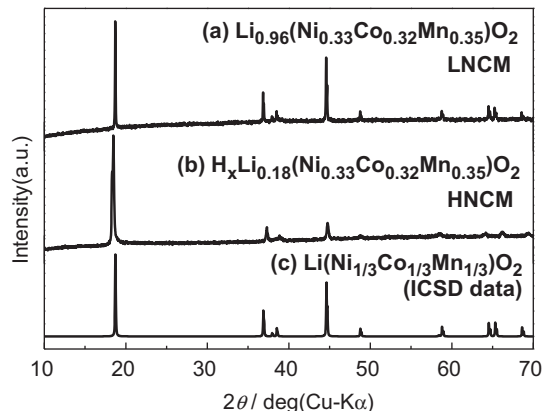
Fig. 1. X-ray diffraction (XRD) patterns for (a) LNCM and (b) HNCM along with (c) ICSD data for $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$.

morphological change was observed after the ion-exchange reaction. These results confirm that the ion-exchange reaction did not cause any changes in phase or morphology.

A total energy stored in electrodes for electrochemical capacitors can be separated into (1) a non-Faradaic contribution from the surface double layer capacitance, (2) a Faradaic contribution from the surface charge transfer process, and (3) a Faradaic contribution from the insertion reaction into the bulk of the active material [15,16,30]. The first non-Faradaic process uses fast charge storage through an electric double layer at the surface of the electrode and the charge density is as small as 16–50 μC cm^{-2} using. The second surface Faradaic contribution is based on the adsorption of alkali metal cations in the electrolyte on the surface of the active material. The first two surface contributions cannot be separated, of which the specific capacitance in cyclic voltammetry tests is independent of scanning rate or reaction potential. On the other hand, the third bulk reaction is based on an insertion reaction of protons (H$^+$) or alkali metal cations into the lattice of the materials, which usually has a specific reaction potential and large current peak in a cyclic voltammogram (CV).

In an alkaline solution system, the following proton insertion process into metal oxides, MeO_2, has been proposed [31–33]. In the first step, an electron from the external circuit is inserted into MeO_2 to reduce Me^{4+} to Me^{3+}. In the next step, in order to maintain the charge balance, a water molecule present at the MeO_2/electrolyte interface is decomposed into a proton, which is inserted into the lattice of the MeO_2, and an OH$^-$ ion, which diffuses from the interface to the electrolyte. The reduction of Me^{3+} to Me^{2+} occurs in the same way.

The electrochemical properties of the LNCM and HNCM were examined using cyclic voltammetry tests and constant current charge/discharge tests. Fig. 3 shows CVs of the LNCM and HNCM in 8 M KOH aqueous solutions taken at a sweep rate of 0.1 mV s^{-1}. The redox peaks were observed at the same potentials for both LNCM and HNCM, although the HNCM exhibited a much larger redox current than the LNCM. This suggests that the interlayer protons play an important role in the redox reaction. The redox potentials suggested that the Ni^{3+}/Ni^{2+}, Co^{3+}/Co^{2+}, and Mn^{4+}/Mn^{2+} redox reactions took place at the same potentials as Ni, Co, and Mn oxides/hydroxides [20,34,35]. Nearly no current for the reduction of Co^{3+} to Co^{2+} was observed. This suggests that Co^{3+} was reduced at the reduction potential of the Mn^{4+}/Mn^{2+}. Only the Ni^{4+}/Ni^{2+}, and Co^{4+}/Co^{3+} redox reactions have been reported in previous investigations of the Li insertion/extraction reactions occurring in LNCM in organic electrolyte systems [24–26], and there has been no report of these Co^{3+}/Co^{2+} and Mn^{4+}/Mn^{2+} redox reactions observed in the