

# The electrochemical characteristics of binary manganese–cobalt oxides prepared by anodic deposition

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## Abstract

Hydrous manganese–cobalt oxides (denoted as  $(\text{Mn} + \text{Co})\text{O}_x \cdot n\text{H}_2\text{O}$ ) were anodically deposited onto graphite substrates from 0.01 M  $\text{MnCl}_2 + 0.09$  M  $\text{CoCl}_2$  solutions with various pH values. The electrochemical characteristics of these oxide deposits were examined by cyclic voltammetry (CV) in 0.1 M  $\text{Na}_2\text{SO}_4$  with changing pH values. The voltammetric behavior of  $(\text{Mn} + \text{Co})\text{O}_x \cdot n\text{H}_2\text{O}$  was not significantly influenced by changing the pH value of  $\text{Na}_2\text{SO}_4$  from 4 to 10. The surface morphology and composition of  $(\text{Mn} + \text{Co})\text{O}_x \cdot n\text{H}_2\text{O}$  deposits were obtained from scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX), respectively, which were affected by changing the pH values of deposition solutions. The number of cracks on the deposit surface was found to increase with the Co content in the Mn oxide matrixes. When deposits were subjected to anodic polarization at potentials positive than 1.2 V, these binary  $(\text{Mn} + \text{Co})\text{O}_x \cdot n\text{H}_2\text{O}$  exhibited capacitive-like behavior with specific capacitance approximately equal to  $125 \text{ F g}^{-1}$  (measured at  $25 \text{ mV s}^{-1}$ ) for supercapacitors. © 2005 Elsevier B.V. All rights reserved.

**Keywords:** Manganese–cobalt oxide; Anodic deposition; Cyclic voltammetry; Supercapacitors

## 1. Introduction

The development of power systems with a combination of high-energy and high-power densities becomes one of the urgent issues for several important applications, especially for electric vehicles, digital cameras, cellular phones, etc. Since the energy density and cycle life of conventional primary energy storage units (e.g., rechargeable batteries) were found to decrease with increasing power density [1], an integration of high-energy density units and high-power density devices (i.e., capacitors) becomes an unavoidable subject. Since the capacity of conventional capacitors is too low to deliver enough electricity in an acceptable time interval, supercapacitors become the promising device in this field [1,2].

The electrode materials employed in supercapacitors are generally highly porous activated carbon (denoted as AC) for

electric double-layer capacitors (EDLCs) [1–4] or hydrous transition metal oxides for electrochemical pseudocapacitors or capteries [1,2,5–7]. In addition, the performance of supercapacitors is generally determined by the equivalent series resistance (ESR) which is a function of electrode materials and electrolytes employed. In general, the decomposition potential window of organic electrolytes (e.g., 2.5 V or above) is wider than that of aqueous media (i.e., 1.229 V at 25 °C) [1,2,8,9]. A capacitor with a wider working potential region shows a higher energy density if the charge capacity is the same. However, the mobility of ions in the former media is much slower than that in the latter. This phenomenon results in a lower ionic conductivity and a significant increase in the ESR, reducing the power density of EDLCs employing organic electrolytes. Moreover, the theoretical double-layer capacitance of highly porous AC is high while its capacitive performance is usually limited by its poor conductivity and microporous nature [1–4,8,9]. Hence, hydrous transition metal oxides have been proposed to be promising electrode materials for supercapacitors because their specific capacitance is usually very high [6,10–12]. Since high-power

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performance is an intrinsic requirement for supercapacitors, which comes from a proper utilization of the electroactive materials with the fast charge/discharge characteristics of redox couples [11], the electrochemical reversibility of redox transitions is one of the major concerns in developing new electrode materials. In addition, the electrochemical kinetics of electroactive species has to be characterized in suitable electrolytes before practical applications.

Recently,  $\text{MnO}_2$  thin films prepared by sol-gel or electrochemical deposition methods were found to exhibit excellent capacitive properties in  $\text{KCl}$  and  $\text{Na}_2\text{SO}_4$  [13–17], which generally have the specific capacitance of  $50\text{--}250\text{ F g}^{-1}$ . In addition, a very thin  $\text{MnO}_2$  film prepared by a sol-gel-derived method was found to show a very high specific capacitance of ca.  $700\text{ F g}^{-1}$  (based on the loading of  $\text{MnO}_2$ ) [10] while this ultrathin-film electrode exhibited an unacceptable capacity under a fair current density of discharge for a very short time interval (only 1–4 s). In our previous work [15,18–21], hydrous manganese oxides in the amorphous form (denoted as  $\text{a-MnO}_x\cdot\text{H}_2\text{O}$ ) prepared by electrochemical deposition showed the ideally capacitive characteristics for supercapacitors. In addition, the capacitive performance of  $\text{a-MnO}_x\cdot\text{H}_2\text{O}$  was influenced by the introduction of Ni oxide into the  $\text{a-MnO}_x\cdot\text{H}_2\text{O}$  matrix [22]. Since the electrochemical reversibility of  $\text{NiOOH}/\text{Ni}(\text{OH})_2$  was found to enhance by introducing Co oxide [12,23], the capacitive performance of  $\text{a-MnO}_x\cdot\text{H}_2\text{O}$  is expected to enhance by adding suitable amount of Co oxide. The purpose of this work is to investigate the electrochemical characteristics of binary  $(\text{Mn} + \text{Co})\text{O}_x\cdot n\text{H}_2\text{O}$ . The influences of pH in the deposition solutions and in the test electrolytes on their capacitive behavior are also discussed. The effects of pH in the deposition solution on the composition and morphology of  $(\text{Mn} + \text{Co})\text{O}_x\cdot n\text{H}_2\text{O}$  were shown in this work.

## 2. Experimental

The binary  $(\text{Mn} + \text{Co})\text{O}_x\cdot n\text{H}_2\text{O}$  deposits were anodically electroplated onto the  $10\text{ mm} \times 10\text{ mm} \times 3\text{ mm}$  graphite substrates (Nippon Carbon EG-NPL, N.C.K., Japan) directly. These substrates were first abraded with ultrafine SiC paper, degreased with acetone and water, etched in a 0.1-M  $\text{HCl}$  solution at room temperature (ca.  $26\text{ }^\circ\text{C}$ ) for 10 min, and finally degreased with water in an ultrasonic bath. The exposed geometric area of these pretreated graphite supports is equal to  $1\text{ cm}^2$  while the other surface areas were insulated with polytetrafluorene ethylene (PTFE) films. The plating solutions consist of 0.01 M  $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$  and 0.09 M  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$  at various pH values (7, 6, 5, 4, 3, and 2.5) adjusted with 0.1 M  $\text{HCl}$  or 0.1 M  $\text{NaOH}$ . The anodic deposition was performed at 1.0 V until the total passed charge reaches  $0.3\text{ C cm}^{-2}$ . After deposition, the PTFE films were removed from the electrode and the electrode was doubly cleaned with pure water. The oxide loading of hydrous oxide-coated electrode is the weight difference of the electrode without PTFE coating before and

after the application of oxide growth (ca.  $230\text{ }\mu\text{g cm}^{-2}$ ) observed by a microbalance with an accuracy of  $10\text{ }\mu\text{g}$  (Sartorius BP 211D, Germany). The electrode before and after oxide growth was dried by a cool airflow.

The average composition of  $(\text{Mn} + \text{Co})\text{O}_x\cdot n\text{H}_2\text{O}$  deposits was measured by an energy-dispersive X-ray (EDX) spectroscope with standards coupled with a scanning electron microscope (SEM, JEOL JSM 35). Electrochemical measurements were performed by an electrochemical analyzer system, CHI 633A (CH Instruments, USA). All experiments were carried out in a three-compartment cell. An  $\text{Ag}/\text{AgCl}$  electrode (Argenthal, 3 M  $\text{KCl}$ , 0.207 V versus a standard hydrogen electrode (SHE) at  $25\text{ }^\circ\text{C}$ ) was utilized as the reference electrode and a piece of platinum gauze with an exposed area equal to  $4\text{ cm}^2$  served as the counterelectrode. A Luggin capillary, whose tip was set at a distance of 1–2 mm from the surface of electrodes, was used to minimize errors from the surface due to  $iR$  drop in the electrolytes.

All solutions used in this work were prepared with  $18\text{ M}\Omega\text{ cm}$  water produced by a reagent water system (Milli-Q SP, Japan), and all reagents not otherwise specified in this work were Merck, GR. The plating solutions for the anodic deposition and the electrolytes used for electrochemical characterization of  $(\text{Mn} + \text{Co})\text{O}_x\cdot n\text{H}_2\text{O}$  were degassed with purified nitrogen gas before measurements and nitrogen was passed over the solution during the measurements. The solution temperature was maintained at  $25\text{ }^\circ\text{C}$  by a water thermostat (Haake DC3 and K20).

## 3. Results and discussion

Typical cyclic voltammograms (CVs) of  $(\text{Mn} + \text{Co})\text{O}_x\cdot n\text{H}_2\text{O}$  prepared from the plating solutions with pH values of 7, 6, 5, 4, 3, and 2.5 are shown in Fig. 1 as curves 1–6, respectively. On the negative sweeps of all curves, there is a shoulder at ca. 0.5 V while no obvious redox peak is found, showing the typical rectangular and symmetric  $i\text{--}E$  responses. Note that the voltammetric currents between  $-0.1$  and 1 V are

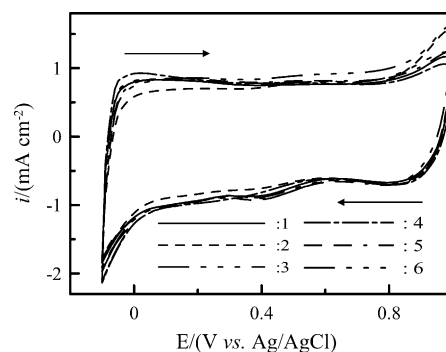


Fig. 1. Cyclic voltammograms of  $(\text{Mn} + \text{Co})\text{O}_x\cdot n\text{H}_2\text{O}$  deposits prepared from 0.01 M  $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$  + 0.09 M  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$  with pH (1) 7, (2) 6, (3) 5, (4) 4, (5) 3, and (6) 2.5. CV curves were measured at  $25\text{ mV s}^{-1}$  in 0.1 M  $\text{Na}_2\text{SO}_4$  with pH 4.

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