

# Effects of complex agents on the anodic deposition and electrochemical characteristics of cobalt oxides

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## Abstract

The anodic deposition rate of cobalt oxide from  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  is strongly affected by the type of complex agents (acetate ion ( $\text{AcO}^-$ ), citrate ion, EDTA) added into the deposition solutions. The oxidation potential of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , examined by linear sweep voltammetry (LSV), is negatively shifted from ca. 1.1 V to about 0.8, 0.5, and 0.2 V by adding  $\text{AcO}^-$ , citrate ion, and EDTA, respectively. The deposition rate of cobalt oxide is found to depend not only on the coordinating strength between Co and ligands but also on the conversion rate of the Co–L complexes (L: ligand) into the oxy-hydroxyl-Co species after electron transfer. The textural and electrochemical characteristics of resultant Co oxides, examined by X-ray photoelectron spectroscopic (XPS), scanning electron microscopic (SEM), open-circuit potential versus time, and cyclic voltammetric analyses, are also influenced by varying the complex agents. The deposition rate is the highest when the Co oxide is deposited from the precursor solution containing  $\text{AcO}^-$ , which also exhibits the highest specific capacitance of ca.  $230 \text{ F g}^{-1}$  among all Co oxide deposits (as the oxide loading  $\geq 0.05 \text{ mg cm}^{-2}$ ), demonstrating its most promising applicability in the electrochemical supercapacitors.

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## 1. Introduction

Cobalt oxides and their mixtures have been widely used as electrode materials for various applications such as oxygen evolution [1–3] and reduction [4], electrochromic devices [5,6], lithium ion batteries [7,8], supercapacitors [9–11], and the protection film of cathodes in molten carbonate fuel cells [12–14]. For the above applications, hydrous Co oxides are usually the preferred material in aqueous systems because of the excellent electrochemical activity and/or reversibility. Hence, several methods, such as spray pyrolysis [15], sputtering [16], thermal decomposition [1–3], sol–gel [17–19], and electrochemical deposition [9,20–22] were developed to synthesize Co oxides.

Among these methods, Co oxides prepared via the spray pyrolysis, thermal decomposition, and sputtering processes are usually of the anhydrous nature, which are not suitable for most

energy storage/conversion systems with the exception of Li-ion batteries and molten carbonate fuel cells [12–14]. On the other hand, the fabrication of powdered Co oxides through the sol–gel process shows an additional disadvantage because the electrochemical and hydrophilic properties as well as the electronic conductivity of the resultant oxide-coated electrodes may be significantly affected by introducing binders and other additives in the electrode fabrication process. Based on these viewpoints, electrochemical deposition, meeting the above requirements, is an attractive method for hydrous Co oxide preparation without considering its simplicity, reliability, low cost, large-area preparation, one-step, and versatility for electrode preparation.

For electrochemical deposition, hydrous Co oxides were prepared by cathodic precipitation [11,23], anodic deposition [9,12–14,20–22], or potentiodynamic method [22,24]. Among these deposition modes, complex agents such as acetate, tartrate, citrate, and glycine are usually employed to stabilize the Co(II) species in basic media [14,21,22]. In addition, the textural and electrochemical characteristics of these electrochemically deposited Co oxides were reported to depend on the deposition variables such as deposition modes,

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temperatures, pH, or complex agents. Unfortunately, there is lack of a systematic comparison for these factors. Based on this consideration and the potential application in supercapacitors, hydrous Co oxide is deposited under the anodic, galvanostatic mode from a 10 mM  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  solution without/with the addition of various complex agents, including the acetate ion, citrate ion, and EDTA. The textural and capacitive properties of these deposits are also compared for the supercapacitor application.

## 2. Experimental

Cobalt oxide (denoted as  $\text{CoO}_x \cdot n\text{H}_2\text{O}$ ) was deposited anodically onto the  $10 \text{ mm} \times 10 \text{ mm} \times 3 \text{ mm}$  graphite substrates (Nippon Carbon EG-NPL,  $\text{N} > \text{C.K.}$ , Japan). These substrates were first abraded with ultrafine SiC paper, degreased with acetone and water, etched in a 0.1 M HCl solution at room temperature (ca.  $26^\circ\text{C}$ ) for 10 min, and finally degreased with water in an ultrasonic bath. The exposed geometric area of these pre-treated 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 10 mM  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  with/without the addition of complex agents at pH of 6.3 adjusted with HCl or NaOH. The total concentration of ligands including carboxyl, hydroxyl, and amine groups, not otherwise specified in this work, is fixed to be 20 mM. The anodic deposition was performed at a constant current density of  $120 \mu\text{A cm}^{-2}$  with the total passed charges reaching the specified values. After deposition, the PTFE films were removed from the electrode which was doubly cleaned with pure water. The loading of hydrous oxide-coated electrode is the weight difference of the electrode without PTFE coating before and after the application of oxide growth measured by a microbalance with an accuracy of  $10 \mu\text{g}$  (Sartorius BP 211D, Germany). The electrode before and after oxide deposition was dried in a cool airflow.

The morphologies of  $\text{CoO}_x \cdot n\text{H}_2\text{O}$  were observed using a field emission scanning electron microscope (FE-SEM, Hitachi S4800 type I). The X-ray photoelectron spectroscopic (XPS) measurements were performed with an ESCA210 spectrometer (Fison, VG) with Al  $\text{K}\alpha$  ( $h\nu = 1486.6 \text{ eV}$ ) irradiation as the photosource. Electrochemical measurements were performed with an electrochemical analyzer system, CHI 633A (CH Instruments, USA). All experiments were carried out in a three-compartment cell. An Ag/AgCl electrode (Argenthal, 3 M KCl, 0.207 V versus a standard hydrogen electrode (SHE) at  $25^\circ\text{C}$ ) 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 counter electrode. A Luggin capillary, whose tip was set at a distance of 1–2 mm from the surface of substrate, was used to minimize errors from the surface due to  $iR$  drop in the electrolytes.

All solutions used in this work were prepared with  $18 \text{ M}\Omega$  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 precursor solutions for anodic deposition and the electrolytes for electrochemical characterization of  $\text{CoO}_x \cdot n\text{H}_2\text{O}$  were degassed with purified nitrogen gas before measurements and nitrogen was passed over the solution during the measure-

ments. The solution temperature was maintained at  $25^\circ\text{C}$  by a water thermostat (Haake DC3 and K20).

## 3. Results and discussion

### 3.1. Deposition of $\text{CoO}_x \cdot n\text{H}_2\text{O}$

In order to gain a basic understanding on the anodic deposition of  $\text{CoO}_x \cdot n\text{H}_2\text{O}$  with the presence of complex agents, linear sweep voltammetry (LSV) was used to identify the influences of complex agents and the suitable conditions for the anodic deposition of  $\text{CoO}_x \cdot n\text{H}_2\text{O}$ . Typical LSV curves measured at  $5 \text{ mV s}^{-1}$  in 10 mM  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  with pH of 6.3 and those with the addition of 20 mM NaAcO, 5 mM sodium citrate (constant concentration of ligands, including OH and carboxyl groups), and 3.3 mM  $\text{Na}_2\text{EDTA}$  (amine and carboxyl groups) are shown in Fig. 1a. Note that the onset for the oxidation of Co(II) complex species commences at ca. 0.5, 0.75, 0.2 V for curves 2–4, respectively while the anodic deposition of  $\text{CoO}_x \cdot n\text{H}_2\text{O}$  from the pure chloride precursor occurs significantly at about 1.0 V. This result reveals the fact that coordination between Co and ligands significantly reduces the oxidation potential of Co complexes which will be converted into  $\text{CoO}_x \cdot n\text{H}_2\text{O}$  after electron transfer. Similar results have been found for the anodic deposition

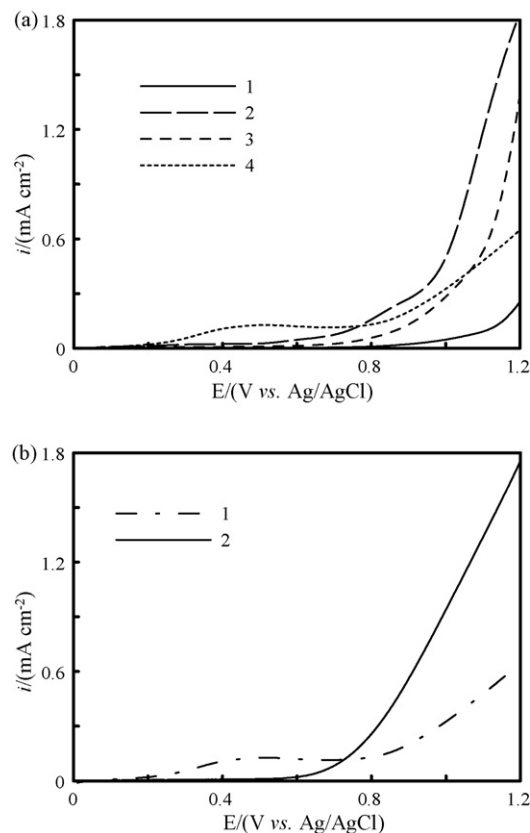


Fig. 1. (a) Linear sweep voltammograms measured at  $5 \text{ mV s}^{-1}$  from (1) 10 mM  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  with the addition of 20 mM ligands: (2) sodium citrate (5 mM), (3)  $\text{CH}_3\text{COONa}$  (20 mM), and (4) EDTA (3.3 mM) with pH of 6.3. (b) Linear sweep voltammograms measured at  $5 \text{ mV s}^{-1}$  from a solution consisting of (1) 10 mM  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  + 3.3 mM EDTA and (2) 3.3 mM EDTA with pH of 6.3.

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