



Electrocatalytic activity of electrodeposited cobalt oxide films to produce oxygen gas from water



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ABSTRACT

An electrocatalytic cobalt oxide film for water oxidation was prepared on an indium tin oxide (ITO)-coated substrate by anodic electrodeposition. Atomic force microscopy measurements revealed that numerous particles with a diameter of 100–250 nm were uniformly dispersed on the ITO substrate and the particle size increased when prepared at higher temperature. Cyclic voltammograms of the Co oxide-coated ITO electrodes were measured in alkaline and neutral aqueous solutions to examine their redox characteristics and ability to catalyze water oxidation. When Co oxide was electrodeposited from solutions kept at 10, 25 and 50 °C, the amount of electroactive Co oxide per unit area (Γ_{ea}) was 1.06×10^{-8} , 1.72×10^{-8} , and 2.31×10^{-8} mol cm⁻², respectively. The increase in Γ_{ea} accompanied the increase in particle size observed with rising deposition temperature. Quantitative analyses of O₂ gas produced by water electrolysis were carried out under potentiostatic conditions using these Co oxide-modified electrodes and a bare ITO electrode for comparison. For the Co oxide-coated electrode prepared at 10 °C, the amount of O₂ evolved by electrolysis for 2 h at 1.3 V vs. Ag/AgCl was 1.3×10^{-5} mol cm⁻² in alkaline electrolyte solution and 1.52×10^{-5} mol cm⁻² in neutral electrolyte solution containing phosphate ions. In addition, when the Co oxide-coated electrode treated at 450 °C was used, the amount of O₂ evolved by the electrolysis increased to 2.58×10^{-5} mol cm⁻² in the neutral electrolyte solution containing phosphate ions, resulting from a stable catalytic current.

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1. Introduction

Effective and cheap catalysts for O₂ evolution by water oxidation (Eq.: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$) are needed for the development of industrial electrochemical processes as well as artificial photosynthetic devices to provide a socially acceptable renewable energy source. Converting water to O₂ and H₂ is a major subject for developing energy conversion systems that store renewable resources in the form of chemical fuels. Conductive metal oxides have been used as water oxidation catalysts in electrolyzers for many decades. It is well known that metal oxides such as RuO₂, IrO₂ and Co₃O₄ have catalytic activities for water oxidation [1–4]. In our previous studies, we prepared IrO₂ nanoparticle- and colloid-coated electrodes by electrodeposition and self-assembly which revealed high catalytic-activity for water electrolysis [5–7]. However, although RuO₂ and IrO₂ are the high-active catalyst, their noble metals are rare materials on earth and are not suitable for use on a very large scale. Therefore, it is important to develop

other oxide catalysts using more abundant transition metals. Cobalt (Co) oxide catalysts have been attracting much attention as a promising candidate for photo- [8,9] and electrocatalysis [10–21] of water oxidation. Recently, Kanan and Nocera [22] reported a cobalt–phosphate (Co–Pi) catalyst for water oxidation. Their Co–Pi catalyst not only exhibited high activity but also a self-healing feature that suppressed release of Co²⁺ ions into solution during water-splitting catalysis [23,24]. Herein we report the characterization of Co oxide films prepared from a citrate-cobalt complex by electrodeposition, and determine the electrocatalytic activity of the Co oxide catalysts based on the amount of O₂ evolved. It is found that the catalytic activity decreases with increasing deposition temperature, possibly because of the increased particle size.

2. Experimental section

2.1. Materials

Cobalt chloride hexahydrate (CoCl₂·6H₂O), sodium hydroxide (NaOH), potassium nitrate (KNO₃), sodium dihydrogen phosphate

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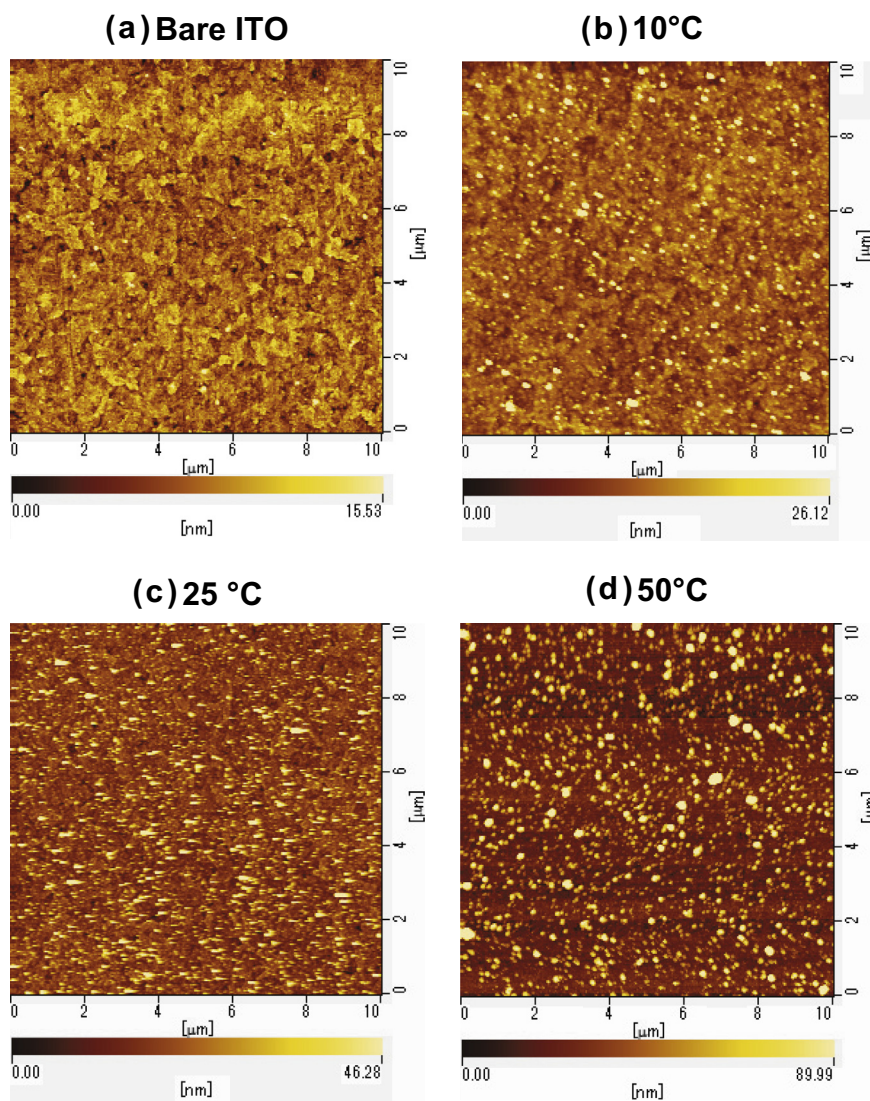


Fig. 1. Surface AFM images of (a) bare ITO and Co oxide-modified electrodes deposited at temperatures of (b) 10 °C, (c) 25 °C, and (d) 50 °C.

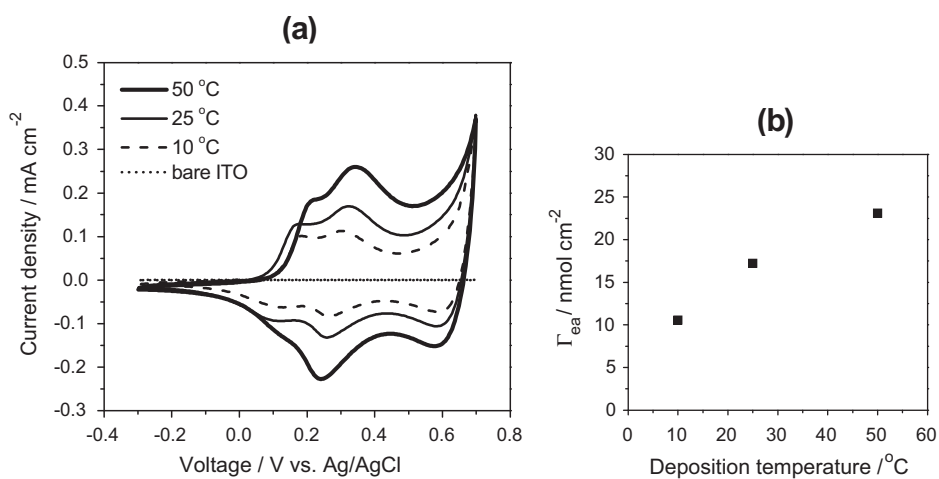


Fig. 2. (a) Cyclic voltammograms of Co oxide-modified electrodes prepared at various temperatures in 0.1 M KNO₃ aqueous solution at pH 11.6 and a scan rate of 20 mV s⁻¹. The potential range was from -0.3 to 0.7 V vs. Ag/AgCl. (b) Dependence of the amount of electroactive Co oxide (Γ_{ea}) on electrodeposition temperature.

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