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Preparation of perovskite type oxide thin-films as oxygen electrodes by pulsed laser deposition method and their electrochemical properties

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Introduction

There has been increasing interest in batteries using alkaline electrolytes, for example, metal-air secondary batteries and anion-exchange membrane fuel cells. These batteries have a wide range of selectivity about electrocatalysts. Among them, much attention has been paid to oxide catalysts because their costs are much lower than those of noble metals. So far, many researchers have tried to find catalysts with high activities towards oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) since the exchange current densities of ORR and OER are very low.

Most oxides have inadequate electron conductivity to proceed the electrocatalytic reactions. Therefore, almost of all the experiments in the literature employed the oxides mixed with conductive additives as electrode catalysts (composite electrode) [1-3]. Perovskite type oxides with considerably high ORR and OER activities have been also studied together with electron conductive additives.

In order to study the intrinsic electrochemical properties of the above oxides, the use of a thin-film electrode without any binders and conductive additives is desirable. In particular, pulsed laser deposition (PLD) is one of the attractive method to fabricate thin-films because dense, thin, flat and pinhole-free films can be obtained. In this research, we report the preparation of perovskite type oxide thin-film electrodes by PLD method and evaluate their electrocatalytic behavior.

Experimental

Perovskite type oxide thin-films were prepared by PLD method. Various types of lanthanum-based perovskite type oxides were used as targets. Pt tip was used as a substrate. Resultant perovskite thin-films were characterized by X-ray diffraction (XRD) measurement and inductively coupled plasma – atomic emission spectrometry (ICP-AES).

A three-electrode electrochemical cell was used as electrochemical measurements. Preparing rotating disk electrode for working electrode was done by mounting Pt tip on a rotating disk electrode (RDE) rod. Pt wire and reversible hydrogen electrode (RHE) were used as counter and reference electrodes, respectively. For catalytic activity measurements of perovskite thin-films, a solution of 1.0 mol dm^{-3} KOH (saturated by O_2) was used as an electrolyte. Linear sweep voltammetry (LSV) was carried out at the sweep range from 1.0 V to 0.5 V vs. RHE (as ORR measurements) or from 1.3 to 1.8 V vs. RHE (as OER measurements). For electron conductivity measurements of them, a solution of deaerated 1 mol dm^{-3} KOH + 20 mmol dm^{-3} $K_3[Fe(CN)_6]$ solution was used. Sweep range of LSV was from 0.1 to –0.4 V vs. $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$.

Results and discussion

XRD patterns of resultant perovskite type oxide thin-films were in good agreement with ICDD diffraction patterns. Linear sweep voltammogram of $La_{0.8}Sr_{0.2}CoO_3$ thin-film as an ORR activity measurement was shown in Fig. 1. We observed rotation independent currents. This result was obviously different from that of Pt-RDE. The result of electron conductivity measurement for $La_{0.8}Sr_{0.2}CoO_3$ thin-film was shown in Fig. 2. It indicates that above thin-film has enough electron conductivity for electrocatalytic reactions.

Based on the results of Figs. 1 and 2, it was found that intrinsic catalytic activity of perovskites for oxygen electrode was different from those of composite electrode [1,2]. Details will be discussed in the conference.

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Reference

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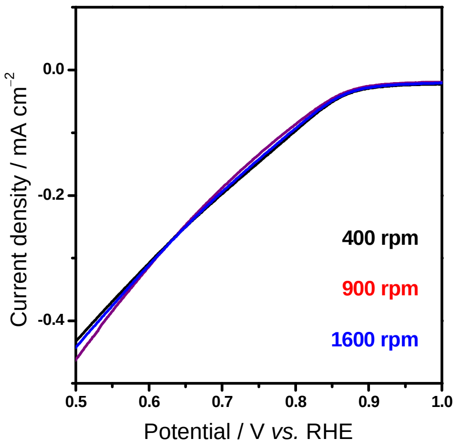

Fig. 1. Linear sweep voltammogram of $La_{0.8}Sr_{0.2}CoO_3$ thin-film rotating disk electrode electrode in O_2 sat'd 1 mol dm^{-3} KOH solution.

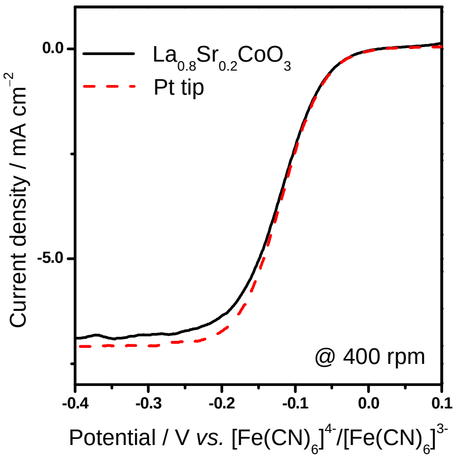

Fig. 2. Linear sweep voltammogram of $La_{0.8}Sr_{0.2}CoO_3$ thin-film rotating disk electrode electrode in deaerated 1 mol dm^{-3} KOH + 20 mmol dm^{-3} $K_3[Fe(CN)_6]$ solution.