

## Structure-controlled Ternary Electrocatalysts for Selective Ethanol Oxidation to CO<sub>2</sub>

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### Introduction

Direct ethanol fuel cells are attractive as alternative power sources for mobile and portable applications. However, for practical use, the anode catalysts which have high catalytic activity for complete oxidation reaction of ethanol to CO<sub>2</sub> are required. Many studies have proved that binary PtSn catalysts were the best anode catalysts. But the main product was not CO<sub>2</sub> but acetic acid. In contrast, PtRh catalysts were effective for C-C bond splitting in an ethanol molecule, but the EOR activity was low. Previously, we prepared cumulated Pt/Rh, Pt/SnO<sub>x</sub> and Pt/Rh/SnO<sub>x</sub> catalysts by depositing Rh and/or SnO<sub>x</sub> monolayers on a Pt substrate by using underpotential deposition and then galvanic replacement, and the role of each constituent and its appropriate arrangement were analyzed from in-situ infrared reflect absorption spectroscopy (IRRAS). Consequently, it was expected that the Pt-Rh-SnO<sub>x</sub> arrangement in which Pt and SnO<sub>x</sub> were not adjacent was important for the complete oxidation of ethanol to CO<sub>2</sub>. In this study, in order to realize the complete oxidation reaction of ethanol to CO<sub>2</sub>, structure-controlled Pt/Rh/SnO<sub>x</sub> electrocatalysts in which SnO<sub>x</sub> was deposited only on Rh were prepared, and their EOR activity and stability of catalysts were evaluated. In addition, mechanism of EOR for the electrocatalysts was discussed on the basis of in-situ IRRAS.

### Experimental

The Pt/Rh was prepared by galvanic replacement between electrochemically adsorbed atomic hydrogen on Pt and Rh<sup>3+</sup> ions. A tandem-type Pt/Rh/SnO<sub>x</sub> electrocatalyst was prepared by deposition of SnO<sub>x</sub> only on Rh sites of Pt/Rh whose Pt sites were protected by preadsorption of CO, while a random-type Pt/Rh/SnO<sub>x</sub> electrocatalyst was prepared by depositing SnO<sub>x</sub> without preadsorption of CO on Pt. In the latter SnO<sub>x</sub> can be deposited on Pt and Rh surface. Electrocatalytic activity for EOR was evaluated in an Ar-saturated 0.1 M HClO<sub>4</sub> aqueous solution containing 1 M ethanol. Products in EOR were identified by in-situ IRRAS.

### Results and Discussion

Figure 1 shows IR-RAS spectra at 0.5 or 0.6 V vs. RHE for various electrodes. A peak assigned to CO<sub>2</sub> is observed at 2343 cm<sup>-1</sup>, while peaks assigned to acetic acid are observed at 1391 and 1271 cm<sup>-1</sup>. For the Pt/SnO<sub>x</sub> (θ=0.35), acetic acid was mainly produced at 0.5 V. For the random-type Pt/Rh/SnO<sub>x</sub>, the production of acetic acid was suppressed, and CO<sub>2</sub> was the main product. For the tandem-type Pt/Rh/SnO<sub>x</sub>, peaks assigned to acetic acid were not observed at all, while CO<sub>2</sub> was produced actively with higher potentials. Thus the tandem-type Pt/Rh/SnO<sub>x</sub> in which SnO<sub>x</sub> was deposited only on Rh surface realized selective oxidation of ethanol to CO<sub>2</sub>.

Figure 2 shows linear sweep voltammograms of various electrodes in the Ar-saturated 0.1 M HClO<sub>4</sub>

aqueous solution containing 1 M ethanol. The ethanol oxidation current density for the tandem-type Pt/Rh/SnO<sub>x</sub> was about five times as large as that for the Pt electrode.

Potentiostatic electrolyses of various electrodes at 0.5 V vs. RHE in the Ar-saturated 0.1 M HClO<sub>4</sub> aqueous solution containing 1 M ethanol were performed. The oxidation current density after 90 min for the tandem-type Pt/Rh/SnO<sub>x</sub> was larger than that for the Pt electrode.

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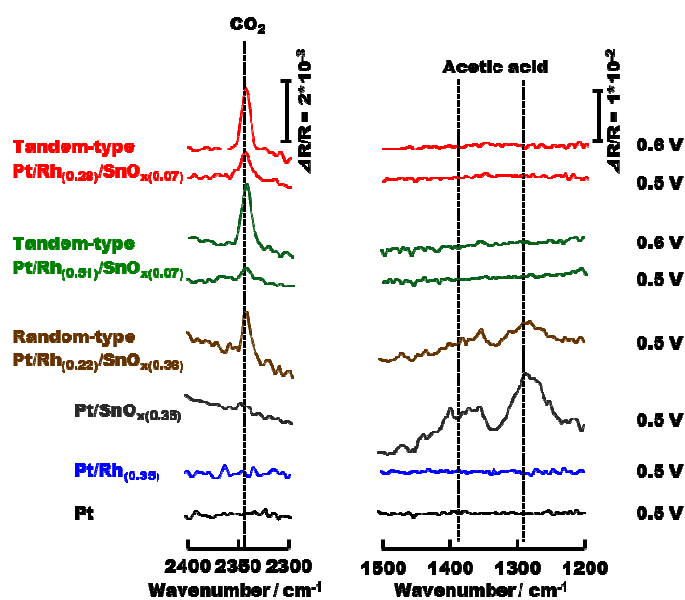


Fig. 1 IR-RAS spectra at 0.5 or 0.6 V vs. RHE for various electrodes.

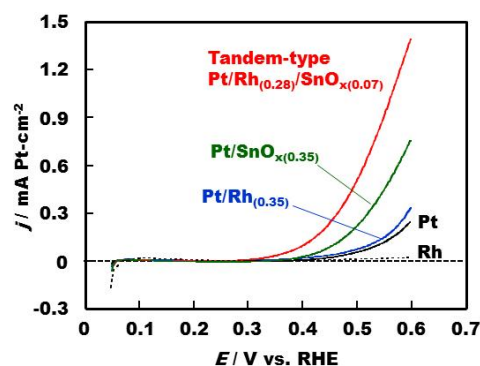


Fig. 2 Linear sweep voltammograms of various electrodes in (1 M ethanol + 0.1 M HClO<sub>4</sub>) solution.