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論文 / 著書情報
Article / Book Information

題目(和文)	固体高分子電解質を用いたエタノール水溶液の純水素への電極触媒によるリフォーミングにおけるPt, Ru, Snの三元相乗効果
Title(English)	The Three-way Synergy of Pt, Ru, and Sn in the Electrocatalytic Reforming of Aqueous Ethanol Solutions to Pure Hydrogen Using Solid Polymer Electrolyte Electrolysis
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種別(和文)	要約
Type(English)	Outline

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Doctoral Thesis Outline

Thesis Title

The Three-way Synergy of Pt, Ru, and Sn in the Electrocatalytic Reforming of Aqueous Ethanol Solutions to Pure Hydrogen Using Solid Polymer Electrolyte Electrolysis

Thesis Summary

This work was carried out to utilize bioethanol as a feedstock for the efficient production of hydrogen. The objective of this thesis is to develop an anode for the SPE electrolysis of EtOH (aq) (Figure 1) with high ethanol utilization efficiency ($mol_{H2}\ mol_{EtOH}^{-1}$) and catalytic activity for high energy efficiency ($mol_{H2}\ mol_{kWh}^{-1}$) and clarify the reaction mechanism of EOR on the developed catalysts.

This paper consists of 6 chapters and is structured as below:

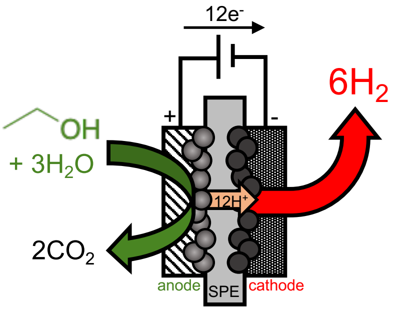

Figure 1. Electrocatalytic reforming of EtOH (aq) in an SPE electrolysis cell

Chapter 1. Introduction to electrocatalytic reforming of aqueous ethanol solutions

Renewable production of hydrogen is essential to mitigate climate change. The electrocatalytic reforming of biomass-derived bioethanol to hydrogen is a promising renewable method of hydrogen production using a solid polymer electrolyte (SPE) electrolysis cell. The objective of this work is to develop an anode with for the SPE electrolysis of aqueous ethanol solutions.

Chapter 2. SPE Electrolysis of Ethanol (aq) over Ketjenblack-supported precious metal anodes.

Experimental conditions for the evaluation of anodes for ethanol (aq) electrolysis were established. EtOH(aq) electrolysis over Ketjenblack-supported precious metals (M/KB, M = Pt, Ir, Ru, Pd, Rh) at 10 wt% loading were investigated. Ru was found to be able to maintain the lowest overvoltage at a current density of 10 mA cm^{-1}.

Chapter 3. Synergy of Pt and Ru in Pt–Ru/KB anodes ethanol (aq) electro-oxidation

Ethanol oxidation over a Pt–Ru/KB anode results in synergistic enhancement of catalytic activity. Enhanced current density over Pt(10)Ru(5)/KB anode compared to 50 wt% Pt/KB even at a much was lower metal loading was observed. This was accompanied by an enhanced rate of oxidation to acetic acid at a terminal voltage of around 0.6 V.

Chapter 4. Structure of Pt–Ru/KB anodes and mechanism of ethanol (aq) electrolysis

Various characterization techniques were performed to reveal the structure of the Pt–Ru/KB electrocatalyst. An Ru core with Pt-rich PtRu surface was proposed. In-situ XANES studies were also performed to further elucidate the reaction mechanism of ethanol (aq) electro-oxidation. Based on the in-situ studies, together with the CV studies from Chapter 3, a reaction A reaction mechanism is proposed where ethanol is initially electrochemically dehydrogenated through the Ru–O interface to form hydroxyl on the oxide sites ($(O)H_{ads}$) and Pt on the surface allow for the reverse hydrogen spillover mechanism to enhance $(O)H_{ads}$ migration for successive oxidation of intermediates.

Chapter 5. Three-way synergy of Pt, Ru, and Sn in Pt–Ru–Sn/KB anodes for ethanol (aq) electro-oxidation

A three-way synergy between Pt, Ru, and Sn was observed in the electro-oxidation of ethanol (aq) over Pt(10)Ru(5)Sn(5)/KB anodes. Current densities were almost two times higher than that of Pt(10)Ru（5)/KB. A reaction mechanism for this synergy was proposed based on the characterization and CV studies wherein the observed dehydrogenation of EtOH by Ru in the previous chapters was enhanced by Sn (Figure 2). The low metal-metal coordination and high metal-oxygen coordination of the three metals then indicated that the synergy was facilitated through interactions through a proposed oxide network in the surface where reverse hydrogen spillover for mobile (O)H_{ads} migration resulted into enhanced activity.

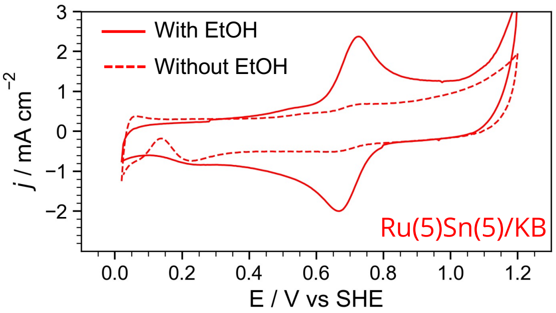

Figure 2. Cyclic voltammogram of Ru(5)Sn(5)/KB in 0.5 M H_2SO_4 (+ 1 M EtOH)

Chapter 6. Summary and conclusions

The results obtained from Chapters 2 to 3 thesis are summarized and the conclusion is presented. The performance of electrocatalytic reforming of EtOH (aq) over Pt(10)Ru(5)Sn(5)/KB at 0.6 V was studied quantitatively and EtOH utilization and energy efficiencies were determined to be 1.43 $\mathrm{mol_{H2} \cdot mol_{EtOH}^{-1}}$ and 16.1 kWh ・ $\mathrm{kg_{H2}^{-1}}$ showing that carbon-neutral H_2 production with much less energy consumption that water electrolysis was achieved.