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Ternary Pt/Rh/SnO₂ Electrocatalysts for Oxidizing Ethanol to CO₂

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Introduction

The direct ethanol-oxidation fuel cell (DEFC) could afford an excellent alternative solution to energy-generation problems, and entail major improvements in the prospects for a renewable energy economy. [1] However, the development of DEFC has been impeded by its slow and incomplete oxidation kinetics even on the best electrocatalysts. [2,3] Thus far, the best binary catalysts for ethanol oxidation in acid environments are Pt–Sn alloys. In situ spectroscopic studies have shown that acetaldehyde and acetic acid are the main products of the oxidation of ethanol in acid solution, with carbon dioxide appearing at very high positive potentials. Although it is inconsequential for DEFC, adding Sn to Pt inhibits the splitting of C–C bonds. Indications are that adding Rh to Pt may aid this reaction above 0.6 V, [4] but the overall activity of these electrocatalysts is lower than that of Pt–Sn. [5,6]

Here we describe an efficient electrocatalyst capable of splitting the C–C bond, by designing a ternary electrocatalyst such that each of the constituents performs certain function in the catalytic reaction. Pt was selected because its bare surface is essential for ethanol adsorption, and the abstraction and oxidation of H atoms; SnO₂ was chosen to provide OH to oxidize strongly bound intermediates, such as CO; finally, Rh was selected to help in splitting C–C bond. Our results showed that PtRhSnO₂ electrocatalyst has unprecedented activity for oxidizing ethanol to CO₂, with the onset of the reaction occurring at low potentials.

Materials and Methods

To synthesize this ternary PtRhSnO₂ electrocatalyst we developed a specific cation-adsorption-reduction-galvanic-displacement synthetic method that facilitates the controllable deposition of metal atoms on oxide surfaces. Thus, by placing Pt and Rh atoms on SnO₂, we synthesized the ternary PtRhSnO₂ electrocatalyst. A combination of electrochemical-, *in situ* x-ray absorption spectroscopies, transmission electron microscopy, and density functional theory (DFT) calculations was employed to characterize the geometries and activities of catalysts as well as understand the reaction mechanism.

Results and Discussion

We synthesized the ternary PtRhSnO₂/C electrocatalyst, effective in splitting the C–C bond of ethanol at room temperature, whose predominant oxidation pathway leads to carbon dioxide at low potentials (Figure 1). The generation of carbon dioxide was verified using *in situ* infrared spectroscopy. Our analysis using both experimental and theoretical techniques reveal that its catalytic activity rests on the synergy between the three constituents of the electrocatalyst. Thus, SnO₂ provides a strong interaction to the Pt and Rh deposited on its surface and, by strongly adsorbing water at the interface, precludes the Rh and Pt sites from reacting with H₂O to form M–OH, so making them available for ethanol oxidation. The high activity of SnO₂ with H₂O provides OH species to oxidize the dissociated CO at Rh sites,

while Pt contributes to ethanol dehydrogenation. It also modifies the electronic structure of Rh to afford moderate bondings to ethanol, intermediates, and products, which facilitates C–C bond breaking and, therefore, ethanol oxidation.

Significance

Our synthesized PtRhSnO₂ electrocatalyst effectively splits the C–C bond in ethanol at room temperature in acid solutions. These findings open new possibilities for studies of C–C bond splitting in variety of important reactions, while this electrocatalyst holds great promise for resolving the major impediment to developing direct ethanol fuel cells.

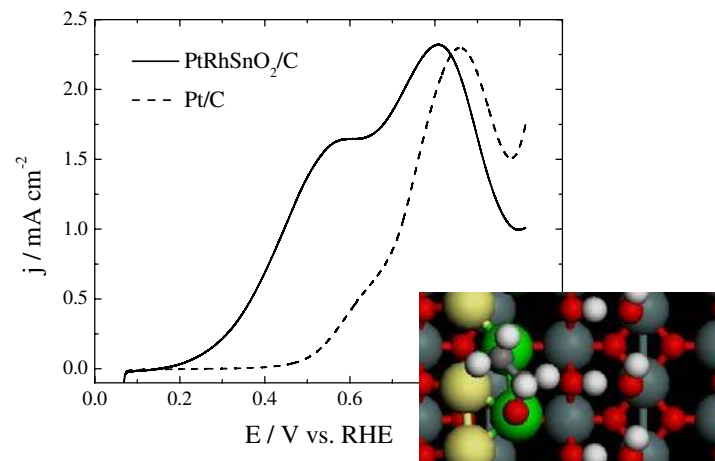


Figure 1. Polarization curves for the oxidation of ethanol on PtRhSnO₂/C- and Pt/C- (20% Pt on C E-TEK Co.) thin-film electrocatalysts deposited on a glassy carbon electrode. Electrocatalysts compositions: PtRhSnO₂/C - 25nmol Pt, 25nmol Rh and 25nmol SnO₂; Pt/C - 25nmol Pt; electrode surface area is 0.2cm²; 0.1MHClO₄; 0.5M ethanol; sweep rate is 1mV/s. Inset: optimized geometry of CH₂CH₂O adsorption on a Rh,Pt/SnO₂(110) surface using DFT. (Sn: large grey; Pt: large yellow; Rh: large green; C: small grey; O: small red; H: small white)

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