

Electrocatalysis in Direct Ethanol Fuel Cells

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Ethanol as an alternative fuel offers several advantages for polymer electrolyte fuel cells, especially in portable-power applications. Ethanol is a non-toxic liquid that can be produced from renewable sources and is easy to store and transport using existing infrastructure and technologies. Thanks to, among other reasons, a large number of electrons transferred upon complete oxidation of an ethanol molecule to CO₂ (12), the energy content of ethanol is higher than that of methanol (8.0 vs. 6.1 kWh/kg). However, due to the presence of a C-C bond, the ethanol oxidation reaction (EOR) is kinetically handicapped and incomplete, even at the best electrocatalysts developed in the past (PtRu and/or PtSn binary catalysts). Low CO₂ yields indicate that the C-C bond is not broken at practical potentials, i.e., close to the reversible EOR potential of ~0.08 V.¹ Although mechanistic details of ethanol oxidation remain unknown, the prevailing view is that acetaldehyde (CH₃CHO) and acetic acid (CH₃COOH) are the main products of ethanol oxidation in acidic solutions, with carbon dioxide (CO₂) generated mostly at very positive, and thus not necessarily practical potentials. As a consequence, the effective scission of the C-C bond in the ethanol molecule at low overpotentials continues to be the main challenge of ethanol electrocatalysis.

In response to that challenge we successfully synthesized ternary PtRhSnO₂/C and PtIrSnO₂ electrocatalysts, capable of splitting of the C-C bond in ethanol at a room temperature and generating CO₂, as evidenced by in situ infrared reflection-absorption spectroscopy (IRRAS).² In those ternary catalysts, Pt facilitates ethanol dehydrogenation, Rh and Ir aid in the splitting of the C-C bond and SnO₂ activates H₂O to provide OH, the surface oxidant of CO chemisorbed at Pt and Rh sites.

More recently, we also developed electrocatalysts consisting of one Pt monolayer (one atom thick layer) placed on extended or nanoparticle surfaces. Those catalysts show enhanced activity and selectivity for ethanol oxidation, controlled by platinum-support interactions.³ Expanded Pt monolayers exhibit enhanced activity in both ethanol and methanol oxidation. Furthermore, a correlation between substrate-induced lateral strain in a Pt monolayer and its activity/selectivity can be demonstrated by experimental and theoretical studies.

In spite of the progress in ethanol electrocatalysis the performance gap between fuel cells operating on ethanol and methanol remains significant,⁴ indicating that further successful development of not only active and selective but also stable ethanol oxidation electrocatalysts is needed for the commercialization of the direct ethanol fuel cell (DEFC). Besides anode catalysts for the EOR, the DEFC cathode is yet to be studied to a greater extent. The requirements for the DEFC cathode catalyst are a high activity for the oxygen reduction reaction and enhanced ethanol tolerance.

In this lecture, we will present an overview of ethanol oxidation catalysts under development at Brookhaven National Laboratory for the DEFC anode. We will concentrate on the approaches used to enhance both the activity and selectivity for the 12-electron oxidation of methanol to carbon dioxide.

The results of ethanol oxidation catalyst testing at Los Alamos National Laboratory will also be presented, with focus on the reasons for the observed disparity between very high OER activity of the anode catalysts (in full agreement with the electrochemical-cell data) and relatively low performance of the fuel cell itself. In that testing, the onset potential of EtOH oxidation measured at 80°C with the PtRhSnO₂/C and PtIrSnO₂ catalysts was found to be very close to the thermodynamic value of ca. 0.04 V (**Figure 1**). However, the DEFC performance was significantly below that expected based on the catalyst EOR activity. Possible reasons of the DEFC performance losses and mitigation strategies will be discussed.

Finally, we will address the role of the cathode in DEFCs operating with new-generation ethanol oxidation catalysts. We will discuss possible impact of crossover anode species on the ORR activity of the Pt catalyst and its ethanol tolerance.

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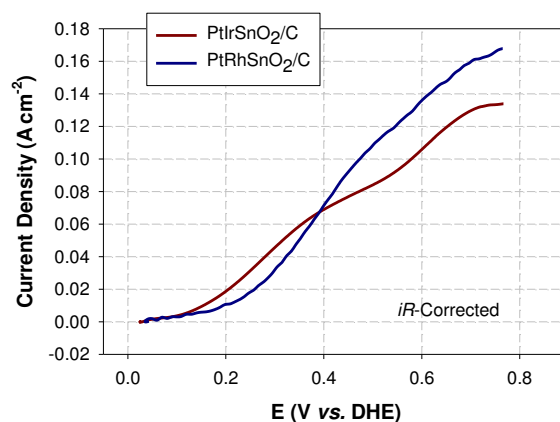


Figure 1. DEFC anode polarization plots recorded with two carbon-supported ternary catalysts, PtIrSnO₂/C and PtRhSnO₂/C at 80°C. Anode: 1.0 mg/cm_{metal}² 12 wt% PtIrSnO₂/C or 13% PtRhSnO₂/C, 0.5 M ethanol, 1.8 ml/min; cathode: 4.0 mg/cm² Pt black, 200 sccm H₂; membrane: a triple Nafion[®] 212 sandwich.

References

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