

Ir-Sn Nanoparticles for the Ethanol Oxidation Reaction

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Ethanol is a promising fuel for low-temperature direct fuel cell reactions. Compared to hydrogen and methanol, ethanol is a promising fuel in the so-called direct ethanol fuel cell (DEFC) reaction for several reasons. First, ethanol is less toxic; Second, ethanol is easy to store and transport due to its relatively higher boiling point; Third, ethanol has higher energy density due to the nature of twelve-electron transfer upon complete oxidation; Fourth, ethanol has been qualified as a substantial energy source since it can be produced in large quantities from sugar- and cellulose-containing raw materials. However, the implementation of the DEFC technology has been hindered by the sluggish ethanol oxidation reaction (EOR) at the anode, due to the lack of an active anode catalyst. Due to its low toxicity, ease of storage and transportation, high energy density, and availability from biomass. However, the implementation of ethanol fuel cell technology has been hindered by the lack of low-cost, highly active anode catalysts.

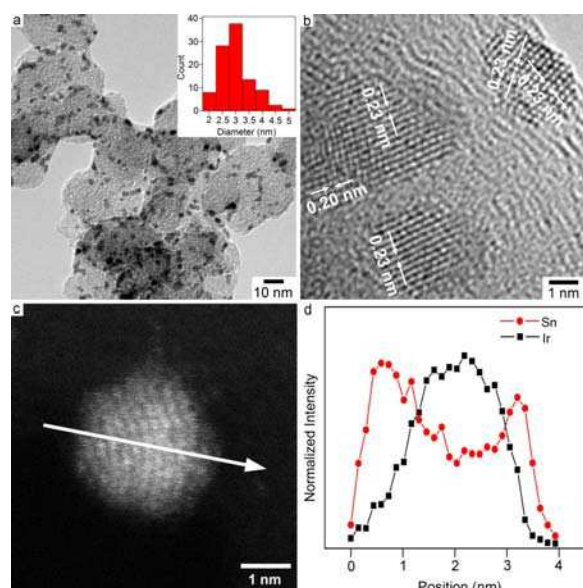


Figure 1. (a) TEM, (b) HRTEM, and (c) HAADF images of the carbon-supported $\text{Ir}_{71}\text{Sn}_{29}$ catalyst after reduction in H_2/Ar flow. (d) EELS line scans across individual the $\text{Ir}_{71}\text{Sn}_{29}$ nanoparticle as indicated by white arrows in (c). The inset in (a) shows particle size distribution

In this paper, we have studied Iridium (Ir) based binary catalysts as alternative electrocatalysts replacing Pt-based catalysts for the direct ethanol fuel cell (DEFC) reaction. We report the synthesis of carbon supported $\text{Ir}_{71}\text{Sn}_{29}$ catalysts with an average diameter of 2.7 ± 0.6 nm through a “surfactant-free” wet chemistry approach. The complementary characterization techniques, including aberration-corrected scanning transmission electron microscopy (STEM) equipped with electron energy loss spectroscopy (EELS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and X-ray absorption spectroscopy (XAS), are used to identify the “real” heterogeneous structure of $\text{Ir}_{71}\text{Sn}_{29}/\text{C}$ particles as Ir/Ir-

Sn/SnO_2 , which consist of an Ir-rich core, and an Ir-Sn alloy shell with SnO_2 present on the surface (**Fig. 1**).

The $\text{Ir}_{71}\text{Sn}_{29}/\text{C}$ heterogeneous catalyst exhibited high electrochemical activity towards the ethanol oxidation reaction compared to the commercial Pt/C (Etek), PtRu/C (Johnson Matthey) as well as PtSn/C catalysts. And alloying effect between Ir and Sn may be responsible for the enhanced electroactivities found in this study (**Fig. 2**). Electrochemical measurements and density functional theory (DFT) calculations demonstrate that the superior electro-activity is directly related to the high degree of Ir-Sn alloy formation, as well as the existence of non-alloyed SnO_2 on surface.

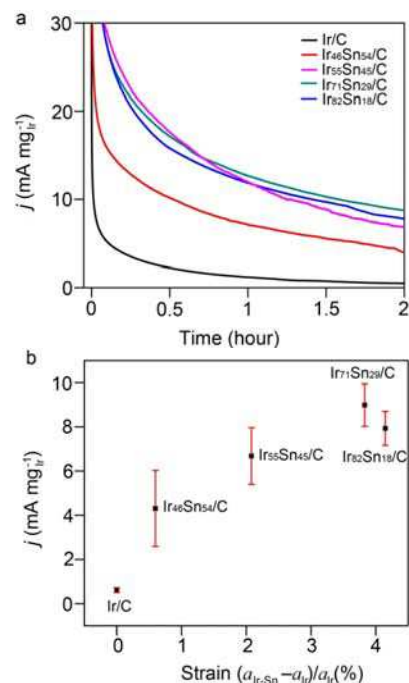


Figure 2. (a) Chronoamperometric measurements of Ir/C, $\text{Ir}_{46}\text{Sn}_{54}/\text{C}$, $\text{Ir}_{55}\text{Sn}_{45}/\text{C}$, $\text{Ir}_{71}\text{Sn}_{29}/\text{C}$ and $\text{Ir}_{82}\text{Sn}_{18}/\text{C}$ at 0.10 V in 0.5 M H_2SO_4 / 0.5 M ethanol electrolyte, and (b) plot of IT activity vs. strain $(a_{\text{Ir-Sn}} - a_{\text{Ir}})/a_{\text{Ir}}$ (%). Specifically, ‘ $a_{\text{Ir-Sn}}$ ’ is denoted as the lattice constant of each individual electrocatalyst while ‘ a_{Ir} ’ represents the lattice constant of home-made carbon-supported Ir nanoparticles.

In summary, our cross-disciplinary work, from novel “surfactant-free” synthesis of Ir-Sn catalysts, theoretical simulations, catalytic measurements, to the characterizations of “real” heterogeneous nanostructures, will not only highlight the intriguing structure-property correlations in nanosized catalysts, but also have a transformative impact on the commercialization of DEFC technology by replacing Pt with low cost, highly active Ir-based catalysts.

Reference:

1. Du, W. X.; Wang, Q.; Saxner, D.; Deskins, N. A.; Su, D.; Krzanowski, J. E.; Frenkel, A. I.; Teng, X. W., *Highly Active Iridium/Iridium-Tin/Tin Oxide Heterogeneous Nanoparticles as Alternative Electrocatalysts for the Ethanol Oxidation Reaction*. **Journal of the American Chemical Society** 2011, 133, (38), 15172-15183