

The Promotion Effect of an Oxide Phase on Pd Electro-catalysts for the Oxidation of Ethanol: *in situ* IRRAS studies in an alkaline environment

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Direct ethanol fuel cells (DEFCs) are promising alternatives to conventional H₂-based PEMFCs for applications ranging from portable devices to vehicles due to the advantages of handling, storage, and transportation of ethanol. Further, ethanol is a renewable fuel source that can be obtained from biomass conversion. Nevertheless, the commercialization of DEFCs has been limited by the use of expensive and scarce Pt-based electrocatalysts. Recent studies have shown that Pd electrocatalysts, which are less costly, offer better performances than Pt electrocatalysts when employed in an alkaline environment¹. Additionally, preliminary reports have shown the promotion effect on the electrocatalytic activity of Pd by an oxide phase for the electrooxidation of alcohols².

The study presented here develops further understanding of the promotion effect of an oxide phase by performing fundamental mechanistic studies of the oxidation of ethanol using an *in situ* spectroelectrochemical technique, IRRAS, to complement conventional electrochemical techniques such as cyclic voltammetry and chronoamperometry. Three different highly active electrocatalytic systems: Pd-SnO₂, Pd-CuO, and Pd-In₂O₃ were investigated.

Synthesis of electrocatalysts was accomplished through a combination of spray pyrolysis (SP), sacrificial support (SSM), and chemical reduction synthesis methods. The use of spray pyrolysis for the synthesis of materials produces spherical particles with homogeneous compositions with particle sizes ranging in the hundreds of nanometers. Conversely, the sacrificial support method produces highly porous oxides particles (~50 m²/g) with sizes of a few microns. Physical characterization of the synthesized electrocatalysts was obtained via SEM, HRTEM, and XRD. Figures 1 and 2 display SEM micrographs of Pd-SnO₂ electrocatalysts in which the oxide phase was synthesized via SSM (Figure 1) and SP (Figure 2). Pd was chemically reduced onto the formed oxides at a ratio of 3:1.

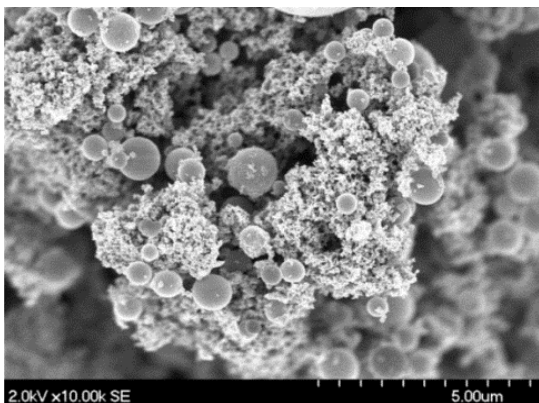


Figure 1. SEM micrograph of Pd-SnO₂ electrocatalyst. SnO₂ synthesized via spray pyrolysis.

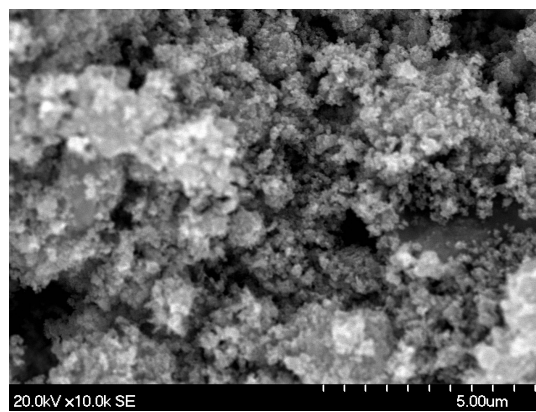


Figure 2. SEM micrograph of Pd-SnO₂ electrocatalyst. SnO₂ synthesized via sacrificial support method.

Rotating disc electrode experiments were performed to assess the electrochemical activity of the synthesized electrocatalysts for the oxidation of ethanol. Improved performance was observed from all tested catalytic systems confirming previous reports. Furthermore, understanding of the role of the oxide was achieved through *in situ* IRRAS studies performed at two different electrolyte concentrations, 1 M KOH (Figure 3) and 0.1 M KOH (Figure 4).

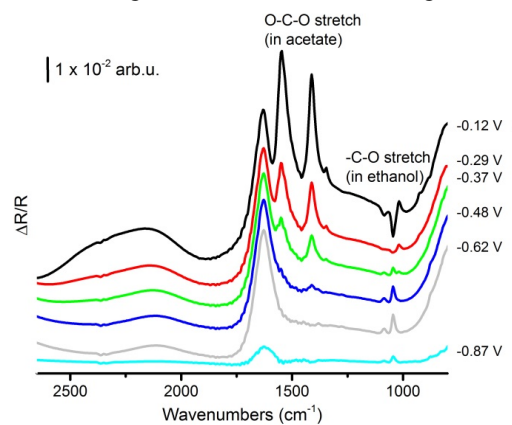


Figure 3. IRRAS spectra of the oxidation of ethanol by Pd-SnO₂ (SP) in a 1 M KOH electrolyte.

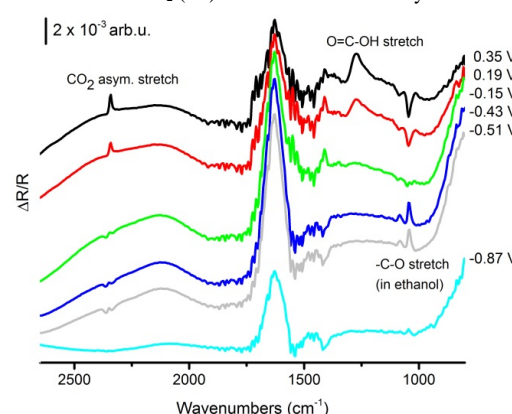


Figure 3. IRRAS spectra of the oxidation of ethanol by Pd-SnO₂ (SP) in a 0.1 M KOH electrolyte.

Not surprisingly, the final product for the oxidation of ethanol in 1 M KOH electrolyte is acetate as a result of a 4-electron process (Figure 3). A thorough mechanistic study was performed to identify the role of the oxide phase, which was determined to be the provider of hydroxide ions to reaction surface at the onset potential preventing the adsorbed species to proceed to complete oxidation. Moreover, a decrease in the pH of the electrolyte results in the complete oxidation of ethanol producing CO₂ (Figure 4) although at the expense of higher overpotentials and an order of magnitude lower reaction rate. Further *in situ* IRRAS experiments using more oxophilic In and Cu oxide phases were studied to decrease the overpotentials for ethanol oxidation.

References:

- (1) Antolini, E. *Energ Environ Sci* **2009**, 2, 915.
- (2) Xu, C.; Tian, Z.; Shen, P.; Jiang, S. P. *Electrochimica Acta* **2008**, 53, 2610.