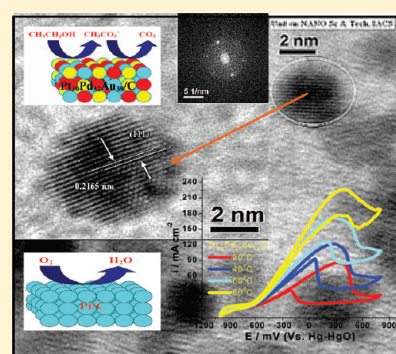


The Beneficial Role of the Cometals Pd and Au in the Carbon-Supported PtPdAu Catalyst Toward Promoting Ethanol Oxidation Kinetics in Alkaline Fuel Cells: Temperature Effect and Reaction Mechanism

Jayati Datta,^{*,†} Abhijit Dutta,[†] and Sanjeev Mukherjee[‡][†]Electrochemistry & Fuel Cell Laboratory, Department of Chemistry, Bengal Engineering and Science University, Shibpur, Howrah—711 103, West Bengal, India[‡]Department of Chemistry and Chemical Biology, 317 Egan Center, Northeastern University, 360 Huntington Avenue, Boston, Massachusetts 02115, United States

Supporting Information

ABSTRACT: Electrochemical investigations have been carried out to study the oxidation kinetics of ethanol in alkaline solution on carbon-supported ternary alloy catalysts Pt–Pd–Au within the temperature range of 20–80 °C. To derive a better understanding of the contribution of each of the metallic components toward the catalytic oxidation of ethanol, some of the investigations were extended to the individual noble metals for comparison, however, at a single temperature (20 °C). The individual metals could barely show their catalytic efficiency toward ethanol oxidations when compared to the alloyed catalyst. The ternary catalyst exhibited much lower values and a larger temperature dependence of onset potential for ethanol oxidation. With the rise of potential, the apparent activation energy ($E_{a(\text{app})}$) for ethanol oxidation on the Pt/C electrode increased, whereas a decreasing trend was observed with the Pt₃₀Pd₃₈Au₃₂/C electrode. It was suggested that the Pt₃₀Pd₃₈Au₃₂/C electrode bears an excellent tolerance toward ethanolic residues, for the temperature range studied. In correlation with the results obtained from the above study, attempts were made to elucidate the oxidation reaction mechanism, and this further evoked interest in extending the work to the estimation of products formed during oxidation of ethanol within the same temperature range through ion chromatographic analysis. The pronounced increase in the quantity of oxidation products, such as acetate and carbonate, obtained over the ternary catalyst as compared to single Pt, substantiates the kinetic enhancement of ethanol oxidation, attributable to the cometal partnership between Pd and Au when incorporated in the Pt matrix. In summary, the multimetallic nanocrystallites can not only show their capability of extracting the best possible number of electrons from the alcohol fuel in alkaline solutions, harnessing more energy, but also, at the same time, bring down the cost of the catalyst material by reducing the Pt content to a considerable extent.



1. INTRODUCTION

The Pt-based alloys and composites are being explored as the alternatives to single Pt for electrocatalysis in fuel cell reactions.^{1–8} Particularly for the anodic reaction in DEFCs operating in acidic environments, several Pt-based alloys have superseded the single Pt with respect to their catalytic activity toward promoting faster kinetics and complete conversion of the alcohol fuel to the end products. The success in electrocatalysis of these alloy materials has been attributed to the bifunctional mechanism⁹ and the electronic effect^{10–12} induced by the electronic interaction of Pt with other metals. However, the search for efficient catalysts for selective oxidation in alkaline solutions is scarce. Therefore, a major thrust may be put to investigate the catalytic activity of the alloy materials in alkaline media for obtaining favorable kinetics and better selectivity toward CO₂ production.^{13–16}

In the present investigation, the carbon-supported single metal catalysts, Pt/C, Au/C, and Pd/C, and the ternary

Pt:Pd:Au/C [~1:1:1] catalysts were synthesized through a borohydride reduction method. The identification of crystal phases, the matrix morphology, and the surface area of the nanoparticles have been studied by X-ray diffraction (XRD), transmission electron microscopy (TEM-EDAX), and the Brunauer–Emmet–Teller (BET) method, respectively. The catalytic activity toward ethanol oxidation in alkaline solutions was investigated with the help of several electrochemical techniques, such as cyclic voltammetry (CV), chronoamperometry (CA), and electrochemical impedance spectroscopy (EIS), and the temperature effect on ethanol oxidation was investigated with Pt/C and PtPdAu/C electrodes in particular. Apparent activation energies ($E_{a(\text{app})}$) for the oxidation reaction were determined at different potentials

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