

Electrochemical Formate Oxidation on a Pd₃Ni/C Nanoparticle Catalyst

Sai Mamidala

Abstract — This study examines the kinetics and mechanistic progression of the electrochemical oxidation of formate. Due to its high energy density, formate shows promise as both an electrochemical fuel for portable applications and a means of storing energy from renewable sources. We show that an electrocatalyst composed of carbon supported palladium-nickel alloy nanoparticles is both active and CO poisoning tolerant. Potentially due to a potential shift in rate determining step, Pd₃Ni/C exhibits high peak current densities with more reversible behavior than other catalysts including Pt and Pd.

I. INTRODUCTION

Rising global temperatures are being attributed to excess greenhouse gases in the Earth's atmosphere, generated by the use of nonrenewable energy sources such as coal and natural gas. Because of the large disparity between humanity's energy demand and peak energy production by renewable sources, reliable methods/devices to generate and store power easily are becoming increasingly necessary. The formate oxidation reaction is especially interesting because it holds potential for renewable energy conversion and storage in the form of a reversible fuel cell. Current technological challenges, however, include the development of a novel catalyst architecture that can efficiently and selectively drive both the cathodic and anodic reactions.

II. MATERIALS & METHODS

The Pt/C control catalyst (20 wt.% Pt/C) was purchased from E-TEK. The Pd/C and Pd₃Ni/C catalysts were synthesized through a solvothermal reduction process using organic precursor salts. Following formation, the size selected nanoparticles were supported on high surface area carbon supports (XC-72R) [1]. Catalytic electrodes were prepared from catalyst inks which were dried on glassy carbon supports. The activity was tested in a standard three-electrode electrochemical cell.

III. RESULTS & DISCUSSION

Figure 1 includes the cyclic voltammetric response of three catalysts in a bicarbonate electrolyte containing a small concentration of formate ion. Of merit in this figure are the high peak current densities for Pd₃Ni/C as well as the ratio of forward and reverse potential sweep peak current densities in comparison to Pt/C and Pd/C. Both of these metrics indicate a significant increase in activity and poisoning tolerance for Pd₃Ni/C. In Figure 2 the rate of current density decay at a fixed overpotential is plotted for Pd₃Ni/C and Pd/C to compare capacity for operational durability in a fuel cell, an intended application of this technology. It is clear that the rate of decay is significantly slower for Pd₃Ni/C; and at the end of the testing period, while Pd/C activity has reached zero, Pd₃Ni/C activity is still well above it. Both the increased activity and CO tolerance as indicated by the extended electrolysis performance is hypothesized to be due to the electronic and geometric effects imparted by the presence of an alloying component (Ni) in the atomic layers below the catalyst surface [2]. These properties are proven here to have a positive impact on the formate oxidation reaction by optimizing the binding strength of key reaction intermediates

while reducing the negative effects of strongly adsorbed poisons such as CO. Additionally, this electronic modification of the catalytically active atoms potentially results in a shift in the formate oxidation reaction mechanism, changing the rate determining step and thereafter propagating the reaction through a more favorable progression.

In summary, this study determined that certain advantageous properties of Pd₃Ni/C, including its higher intrinsic activity and an altered mechanism, allow it to display more favorable performance metrics than its peer catalysts, the Pt group metals.

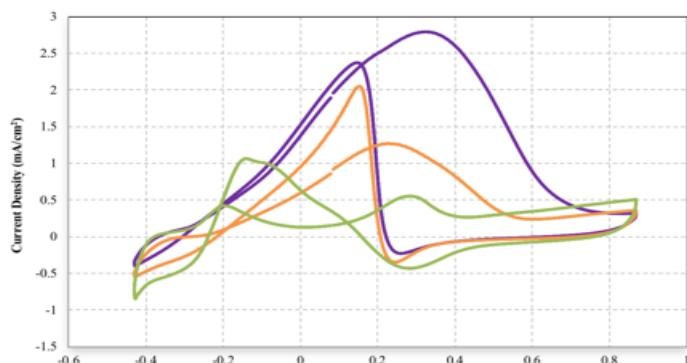


Figure 1: Testing for peak current density, which is indicative of intrinsic activity of the catalysts. Graphs are cyclic voltammograms of Pt/C (green), Pd/C (orange), Pd₃Ni/C (purple) nanoparticle catalyst recorded in a 0.1 M KHC₃O₄/0.01 M NaHCOO electrolyte purged with argon.

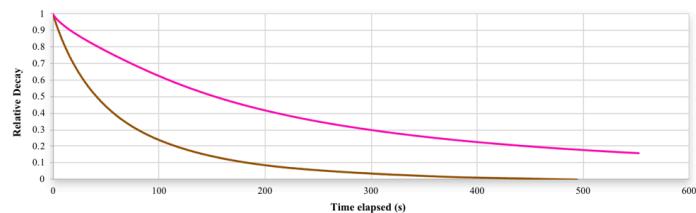


Figure 2: Potential hold experiment to observe potential operational viability and durability in future fuel cell. Graphs compare decay behavior for Pd/C (brown) and Pd₃Ni/C (pink) nanoparticle catalysts recorded in a 0.1 M KHC₃O₄/0.01 M NaHCOO electrolyte purged with argon.

IV. ACKNOWLEDGEMENTS

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V. REFERENCES

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