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Comparison of Fuel Performance in Novel Palladium Based Electro-catalysts

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Introduction

Palladium catalysts are a relatively new and interesting alternative to platinum for use in fuel cells. Several problems exist for Pt-based catalysts. For instance, Pt is a rare and expensive resource; the use of Pd as a catalyst in fuel cells could greatly reduce the cost of production. Of significantly greater importance is the potential for Pd catalysts to bypass some of the problems associated with oxidation across Pt catalysts. Wang, et al¹ have developed the pathway shown in Figure 1:

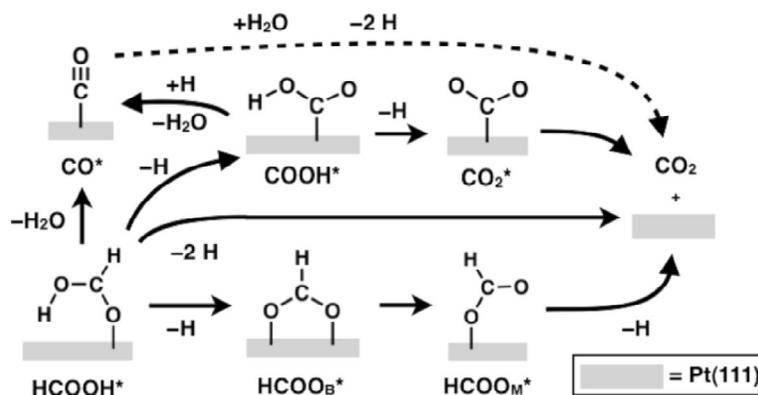
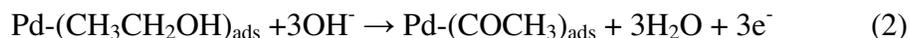


Figure 1: Mechanistic scheme for electrochemical formic acid oxidation (from Wang, et al¹)

The scheme shows three possible pathways for oxidation, each involving different intermediates of varying strength. The indirect H₂O pathway involves a strongly bound CO intermediate; the indirect OH pathway involves a HCOO intermediate; and the direct pathway results in the direct oxidation of formic acid with no intermediate. Extensive studies have shown that Pt catalysts have a tendency to follow the CO intermediate pathway, which results in significant degradation of the catalyst over time. However, Pd-based catalysts may dominantly follow one of the other oxidation pathways, in which case CO poisoning should be significantly reduced². Other benefits of Pd-catalysts include being able to operate the fuel cell in alkaline conditions and ability to be diluted by non-noble metals for use in membrane electrode assemblies³.

Direct Ethanol Fuel Cells (DEFCs) are “electrochemical devices that directly convert the chemical energy stored in liquid ethanol into electricity.”⁴ Pd-based catalysts have been shown to perform well in alkaline DEFCs and Liang, et al have developed the following reaction path for the electro-oxidation of ethanol on a Pd catalyst through cyclic voltammetry:



This mechanism was found to happen rapidly with the rate-determining step being the removal of the adsorbed COCH_3 by the adsorbed hydroxyl on the Pd electrode. These authors demonstrated that the mechanism shown in studies of the methanol oxidation reaction (MOR) using a Pd catalyst in an alkaline media is similar in efficiency and kinetics their developed mechanism for the ethanol oxidation reaction (EOR). A review by these authors found that Pd-based catalysts are more stable and active than Pt-based catalysts, and thus more favorable to the EOR. That study also found that the optimal fuel mixture was 1 mol L^{-1} ethanol + 1 mol L^{-1} potassium hydroxide.

A literature search showed that little information on the kinetics and efficient of ion-formate fuels exists. However, some biochemical applications studies of the interaction of formate salts with a Pd/C catalyst show that potassium formate provides fuel for sufficient hydrogen transfers⁵:



where A is an acceptor. The preferred acceptor in electro-oxidation settings would be the Pd-catalyst, to which the hydrogen would adsorb. The study showed that sodium and ammonium formates also provide a pathway, although neither was as efficient as potassium formate. The shedding of adsorbed hydrogen was studied by Lukaszewski, et al⁶, who developed the following mechanism:



Although this process yields fewer electrons than the electro-oxidation of ethanol, its kinetic merit as a fuel still needs to be investigated.

Experimental

Preparation of catalysts

Catalysts were prepared in a multi-step process: 6.0 +/- .5 mg of Pd-black (Aldrich Chemistry) were weighed out in a vial on an analytical balance (Sartorius Analytic). 1.0 +/- .1 g of E-Pure water (Barnstead, 18 MΩ-cm) was then added to the vial while still on the balance. After removal from the balance, three drops of Nafion (Ion Power, Inc. DE520 Nafion Solution) were added to the vial. The catalyst solution was then sonicated for one minute in a Branson 1510 sonicator. 30 uL of this solution was pipetted onto a gold rotating disk electrode (AFCPRB, Pine Instrument Company) using a 10-100 uL Thermo-Scientific Finnipipette. The electrode was placed in a 350 °C oven (CencoR) for 5-10 minutes to allow the catalyst to dry smoothly on the gold surface. Once the catalyst was sufficiently dry, it was cooled to room temperature before use.

Preparation of fuels

Each fuel was a mixture of 1 mol L^{-1} fuel solution + 1 mol L^{-1} KOH. Formate fuels were made by dissolving appropriate amounts of either ammonium formate (Alfa Aesar), sodium formate (Fluka Analytical), or potassium (Alfa Aesar) and

KOH (BDH) in 250 mL of E-Pure water. Alcohol fuels were made by dissolving the appropriate amount of ethanol (Pharmco-Aaper) or isopropyl alcohol (BDH) and the appropriate amount of KOH in 250 mL of E-Pure water. 1 mol L⁻¹ sulfuric acid was made by adding and dissolving stock H₂SO₄ (GFS) with E-Pure water in a 500 mL volumetric flask.

Procedure

Experiments were run on EG&G Princeton Applied Research Potentiostat/Glavanostat (Model 263 A) using CorrWare Version 32 (Scribner Associates). In addition to the gold RDE, a Pt coil/foil counter electrode and a leakless Ag/AgCl reference (eDAQ) electrode were used in all experiments. Prior to experiments, nitrogen gas was pumped through the solution for fifteen to thirty minutes, and then across the solution for five minutes. Solutions were gassed across for the duration of all experiments. A ten-cycle cyclic voltammetry in 1 mol L⁻¹ H₂SO₄ was run for each new catalyst before experimentation to establish a surface area. The general parameters for this experiment were: initial potential: 0 V vs. reference, Vertex 1: 0.8 V vs. reference, Vertex 2: -0.3 V vs. reference, final potential: 0 V vs. reference, and a scan rate of 30 mV/s. Next, a five-cycle CV was run in the fuel with these parameters: initial potential: 0 V vs. open circuit, Vertex 1: 0.4 V vs. reference, Vertex 2: -0.3 V vs. open circuit, final potential: 0 V vs. open circuit, with a scan rate of 30 mV/s. This was followed by a twenty or thirty minute or twenty-four hour chronoamperometry. Different experimental parameters were used for each type of fuel during CA experiments. For example, formate fuels were set at a potential of 200 mV versus open circuit (-0.8 versus reference), while alcohol fuels were set at an initial potential of 500 mV versus open circuit (-0.5 versus reference). To minimize the formation of air bubbles on the catalyst surface, all twenty-four hour experiments required the electrode to be spun at 2000 revolutions per minute on an AFCPRB Rotator (Pine Instrument Company). To monitor CO poisoning and surface area changes over the course of the oxidation-reduction process, a 10-cycle CV in H₂SO₄ was run after experimentation with the same parameters as the “CV before.”

Methods of data analysis

Results of the experiments were analyzed using CorrView Version 32 (Scribner Associates) and Microsoft Excel 2010. Surface area calculations were done in CorrView using the Integration tool. For consistency, the oxidation region of the hydrogen UPD for every other cycle was analyzed. At least three scans were used to then calculate the average area under the curve. This value was then divided by the accepted value of 0.000210 C/cm² to obtain the surface area of the catalyst. Data from CorrWare were imported to Excel for further analysis. The calculated surface areas were used to adjust CA and CV values, which were plotted in charts for analysis.

Results

Initial experimentation provided a general open circuit potential (OCP) of -1000 mV for chronoamperometry. Graphical results showed that 1 mol L⁻¹ potassium formate + 1 mol L⁻¹ KOH was the best of all formate fuels, and that 1 mol L⁻¹ ethanol + 1 mol L⁻¹ was the best alcohol. Figure 2 shows that the formate and ethanol fuels behave differently in chronoamperometry.

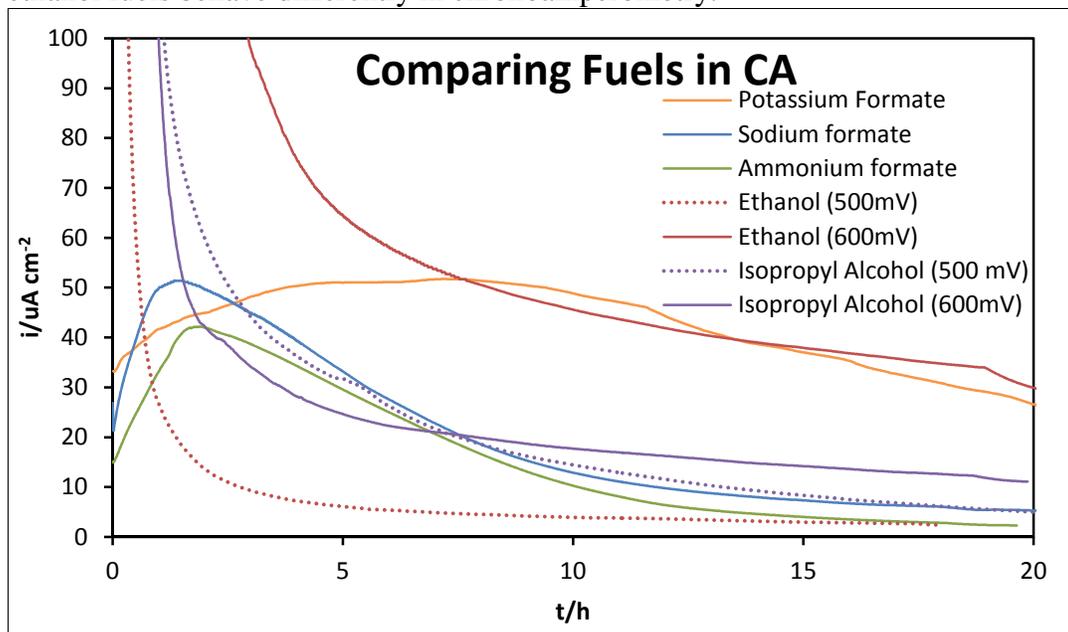


Figure 2: Chronoamperometry in different fuels using Pd-Black on gold RDE. Ethanol and potassium formate perform the best over the duration of the experiment. Values are corrected for surface area of catalyst.

The different potentials for the alcohol fuels are versus OCP. Each formate showed an initial increase in current density, followed by a steady decline over the duration of the experiment. Of these, 1 mol L⁻¹ potassium formate + 1 mol L⁻¹ KOH sustained current the longest. Both alcohols showed a marked initial decrease in current density, followed by a slow, asymptotic decline. 1 mol L⁻¹ ethanol 1 mol L⁻¹ KOH, when run at a potential of 600 mV, sustained a higher current density than the same fuel run at 500 mV and 1 mol L⁻¹ isopropyl alcohol + 1 mol L⁻¹ KOH at both either potential. The terminal current densities from Figure 3 are shown in Table 1.

Table 1: Current densities after 18 hours in fuel. Values are adjusted for surface area.

Fuel	Current Density ($\mu\text{A}/\text{cm}^2$)
Ethanol (600 mV)	35.2
Potassium Formate	30.8
Isopropyl (600 mV)	12.6
Isopropyl (500 mV)	6.20
Sodium Formate	6.05
Ammonium Formate	2.87
Ethanol (500 mV)	2.53

1 mol L^{-1} ethanol + 1 mol L^{-1} KOH at 600 mV and 1 mol L^{-1} potassium formate + 1 mol L^{-1} KOH performed significantly better than the other fuels. Figure 3 shows the same fuels' performance in cyclic voltammetry.

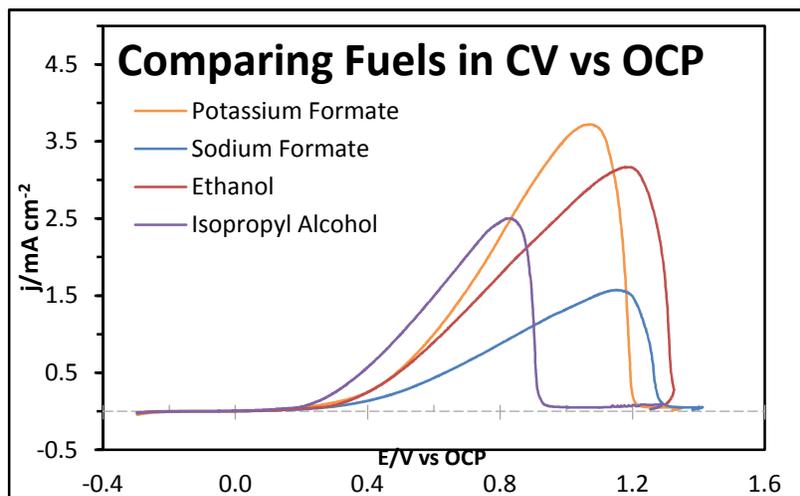


Figure 3: Cyclic voltammetry for different fuels using Pd-Black on gold RDE. OCP: Potassium formate: -1.013 V, Sodium formate: -1.013 V, Ethanol: -0.927 V, Isopropyl alcohol: -0.892 V. Ethanol and potassium formate show the highest peak current densities. Values are adjusted for both OCP and surface area of the catalyst.

Again, 1 mol L^{-1} ethanol + 1 mol L^{-1} KOH and 1 mol L^{-1} potassium formate + 1 mol L^{-1} KOH demonstrate significantly better peak current densities. 1 mol L^{-1} ammonium formate + 1 mol L^{-1} KOH was not included in this chart due to its extremely poor and uncharacteristic performance.

Figure 5 uses the same data presented in Figure 4, but is plotted against a standard hydrogen potential.

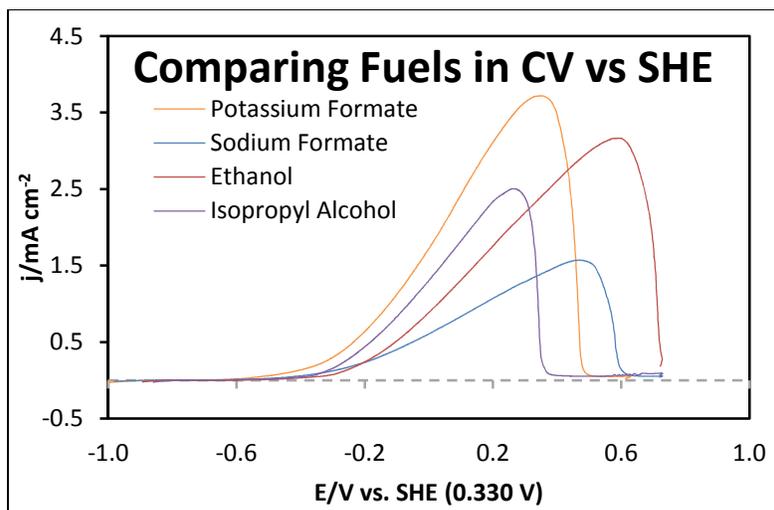


Figure 4: Cyclic voltammetry adjusted for SHE for different fuels using Pd-Black on gold RDE. Potassium Formate and Ethanol show the highest peak current densities. Values also adjusted for the surface area of the catalyst.

Peak current densities observed in Figure 4 are presented in Table 2.

Table 2: Peak current densities and corresponding potentials of fuels during second cycle of CV in fuel. Values are adjusted for surface area of catalyst

Fuel	Current Density (mA/cm ²) OCP	Potential (V)
Potassium Formate	3.71	1.05
Ethanol	3.16	1.18
Isopropyl alcohol	2.47	0.87
Sodium Formate	1.65	1.13

Table 2 shows that 1 mol L⁻¹ ethanol + 1 mol L⁻¹ KOH and 1 mol L⁻¹ potassium formate + 1 mol L⁻¹ KOH demonstrate the highest peak current densities. The potential at which the peak current density was observed was similar in all fuels, and is largely a product of similar experimental setup. The same pattern is observed in CVs run against SHE, and for that reason, a table of peak current densities and corresponding potentials is not included.

Discussion

The results of CA experiments showed that ethanol and potassium formate allowed the catalyst to sustain current over extended periods of time. The terminal current density of the catalyst in 1 mol L⁻¹ ethanol + 1 mol L⁻¹ KOH at 600 mV was 35.2 uA/cm², and the same value for the catalyst run in 1 mol L⁻¹ potassium formate + 1 mol L⁻¹ KOH was 30.8 uA/cm². These values are significantly higher than the terminal current densities for all other fuels; the next highest current density was 12.6 uA/cm² (observed in 1 mol L⁻¹ isopropyl alcohol + 1 mol L⁻¹ KOH at 600 mV). An extensive literature search produced no accepted value of

terminal current densities for the fuels used in this experiment. The CV experiments confirm the results of CA; both 1 mol L⁻¹ ethanol + 1 mol L⁻¹ KOH and 1 mol L⁻¹ potassium formate + 1 mol L⁻¹ KOH have higher peak current densities than their counterparts: 3.16 mA/cm² and 3.71 mA/cm², respectively. Theoretically this shows that the electro-oxidation developed in equations (1) – (3) for 1 mol L⁻¹ ethanol + 1 mol L⁻¹ KOH and (4) – (5) for 1 mol L⁻¹ potassium formate + 1 mol L⁻¹ KOH occurs continuously throughout this process, and that the catalyst does not degrade or poison sufficiently. Further analysis of the terminal and peak current densities obtained through CA and CV, respectively, shows that although 1 mol L⁻¹ ethanol + 1 mol L⁻¹ KOH showed the highest terminal current density, 1 mol L⁻¹ potassium formate + 1 mol L⁻¹ KOH shows the highest peak current density. Because 1 mol L⁻¹ ethanol + 1 mol L⁻¹ KOH only performed well at its higher potential (600 mV), these results suggest that 1 mol L⁻¹ potassium formate + 1 mol L⁻¹ KOH may be the most efficient fuel. This is also evidenced by the fact that 1 mol L⁻¹ ethanol + 1 mol L⁻¹ KOH run at 500 mV performed the worst in CA (terminal current density of 2.53 uA/cm²). However, the development of a specific electro-oxidation mechanism for potassium formate, like that of ethanol presented in Equations (1) – (3), needs to be developed before making any conclusions regarding this fuel. While no widely accepted value for peak current density was found in the literature, a useful comparison is the potential at which the current density reached its maximum. However, this value existed only for 1 mol L⁻¹ ethanol + 1 mol L⁻¹ KOH which reached a peak current density of 6.5 mA cm⁻² at -0.12 V.⁴ This experiment found that the same fuel reached 3.16 mA cm⁻² at 1.18 V. But without a comparison of the parameters of each experiment, the differences in values are strictly nominal.

Comparing the alcohol and formate fuels accurately is limited by a variety of factors. Most important of these is the differences in test parameters. To obtain meaningful data from CA and CV experiments, the alcohol fuels required different initial, vertex, and final potentials than formate fuels. Additionally, differences in catalyst surface area may have decreased the compatibility of the results. The surface area calculations themselves contain several contributing sources of error: the integration tool used in CorrView involved subjective placing of cursors on the hydrogen UPD, so variation within and between trials was unavoidable, and different counter electrodes were used in the H₂SO₄ than in the fuel solutions. As such, these nominal differences need to be further investigated under similar parameters to better compare their merits as fuels for electro-oxidation via Pd-based catalysts. It should be noted that these initial results were used as a basis for further electro-oxidation studies. The effectiveness of 1 mol L⁻¹ ethanol + 1 mol L⁻¹ KOH and 1 mol L⁻¹ potassium formate + 1 mol L⁻¹ KOH were such that they were the sole fuels used in studies of Tafel slopes, carbon-paper experiments, additions of transition metals to the catalyst surface,

and the effects of Pd particle-size. Any results of these studies should acknowledge the outcomes and limitations of this study.

Conclusion

Among the various formate fuels, 1 mol L⁻¹ potassium formate + 1 mol L⁻¹ KOH clearly performed the best. 1 mol L⁻¹ ethanol + 1 mol L⁻¹ KOH run at a potential of 600 mV performed the best out of all the tested alcohols. Comparing potassium formate and ethanol, though made difficult by parametric differences, showed that 1 mol L⁻¹ potassium formate + 1 mol L⁻¹ KOH performed best in initial CA and CV studies, especially when considering that ethanol required a greater voltage to sustain current over an extended period of time. Based on these novel results, further studies of electro-oxidation on a Pd-based catalyst in these fuels are needed.

References

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