Electrochemical Oxidation of Polyalcohols in Alkaline Media on Palladium Catalysts Promoted by the Addition of Copper

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Abstract

Pd-Cu catalysts ($Pd_{63}Cu_{37}/C$, $Pd_{46}Cu_{54}/C$, $Pd_{28}Cu_{72}/C$, $Pd_{11}Cu_{89}/C$) and Pd/C were synthesized, characterized, and used to electrochemically oxidize ethylene glycol (EG), propylene glycol (PG), and glycerol (G). The oxidation rate at -0.4 V vs SCE after 3 hours on each $PdCu/C$ catalyst was compared Pd/C . The oxidation rate for every polyalcohol on every $PdCu/C$ catalyst was at least 3 times greater than on the Pd/C catalyst. The greatest promotion for the oxidation of EG was observed on $Pd_{28}Cu_{72}/C$ (7 times faster), for PG was on $Pd_{11}Cu_{89}/C$ (12 times), and for G was on $Pd_{63}Cu_{37}/C$ (14 times). We observe a decrease in density of states near the Fermi level with increasing amount of Cu and a shift of the d-band center away from the Fermi energy. This surface electronic perturbation could be one of the factors affecting the oxidation of the polyalcohols. A second factor could be the bi-functional effect as we also observe an increase in hydroxyl adsorption at lower potentials on all $PdCu/C$ compared to Pd/C . Therefore, we suggest that the combination of both of these effects, electronic and bifunctional, contributes to the promotion of the oxidation of these polyalcohols. Furthermore, the ratio of Cu to Pd appears to play an important role in the oxidation rate.

Keywords: direct liquid fuel cell, direct alcohol fuel cell, $PdCu$ catalyst, bifunctional effect, electronic effect, XPS

1. Introduction

1.1 Electrochemical Oxidation of Polyalcohols

The alkaline anion exchange membrane (AEM) makes it possible to electrochemically oxidize many alcohols in alkaline media that were inefficiently oxidized in acidic media (in the presence of a cation exchange membrane such as Nafion). [1-5] In alkaline media, electrochemical oxidation of alcohols on Pd proceeds with lower overpotential than in acidic media. In a fuel cell operating with an AEM, there is no crossover of fuel since the movement of the ion is toward the anode, where the fuel is located. Finally, a fuel cell operating with an AEM is not limited by cathode water management since water is produced at the anode, where there is already aqueous solution present.

While initial AEM fuel cells were powered by ethanol, presently there is significant interest in using polyalcohols to power AEM fuel cells. [6-19] Numerous alcohols can be electrochemically oxidized on a Pd nanoparticle catalyst, but the efficiency of ethanol oxidation is significantly (10-20x) greater than that of polyalcohols. [20] Three polyalcohols have been the focus of recent works: ethylene glycol (EG), propylene glycol (PG), and glycerol (G). All three can be sourced renewably: EG and PG can be made from cellulosic feedstock, and G is a byproduct of biodiesel production. [21-25] Because these polyalcohols can be made renewably from sources that do not compete with food production as ethanol does, there is a compelling need to develop alternative catalysts that would make polyalcohol oxidation at least as efficient as ethanol so that a greater variety of fuels can be oxidized in AEM fuel cells.

1.2 Enhancement of Electrochemical Oxidation Rate

The electrochemical oxidation of EG, PG, and G is complex and can result in formation of a variety of products. It has been proposed that the oxidation of these polyalcohols (and ethanol) proceeds via a rate determining step that requires the simultaneous presence of **adsorbed alcohol and hydroxyl** at the catalyst surface. [5, 15] While it is possible to adsorb hydroxyls over a noble Pd metal surface, it would be more thermodynamically favorable to adsorb them over a non-noble metal Cu surface at the potentials used by the anode of a typical AEM fuel cell. [26] Since the Pd surface readily adsorbs the carbon-containing alcohol, it is reasonable to combine these two metals for promoting a reaction that is highly dependent on the simultaneous presence of **surface adsorbed alcohol and hydroxyl** via *bifunctional effect*. [27-30] The electrochemical oxidation of small organic molecules can also be promoted by an *electronic effect*, whereby a mixture of two dissimilar metals (i.e., Cu and Pd) results in unequal sharing of electrons between them. This electronic perturbation influences the nature of chemical bonding of key intermediate species over the catalyst surface during the electrochemical reactions. [31-41] This effect can easily be probed by x-ray photoelectron spectroscopy (XPS). In particular, the valence XPS data can be used to measure the density of states (DOS) near the Fermi level (E_F) and estimate the d-band center energy position. The interaction between the adsorbate and catalyst surface as well as the overall reaction rate can be correlated to the d-band center. Therefore, the option to tune the electronic effect offers one way to efficiently design new catalysts for the electrochemical oxidation of polyalcohols. The ratio of Cu to Pd on the surface of the catalyst could induce various degrees of the bifunctional and electronic effects to promote higher oxidation of a specific polyalcohol.

Improvements to the electrochemical oxidation rates of EG, PG, and G have been studied using other metals such as Sn, Sb, Pb, Bi, Ni, and Zn. [5, 15, 42-49] We have also recently shown that the polyalcohol oxidation rate can be improved by the addition of small amounts of Cu (e.g., Pd₈₇Cu₁₃/C). [50, 51] Recent work also showed that the mass activity for oxidation of EG and G on unsupported PdCu catalyst was faster as measured by voltammetry. [52] The improvements have been attributed to both the electronic and the bifunctional effects, and fuel cell results have been shown in several of studies. However, extended amperometric studies of high concentrations of Cu have not been done, and the efficiency of the oxidation of these polyalcohols is to date less efficient than that of ethanol, the most efficiently oxidized alcohol in alkaline media.

2. Experimental

2.1 Catalyst Synthesis

The catalysts were synthesized using metal salt reduction of palladium chloride (H₂PdCl₄, Aldrich) and copper chloride (CuCl₂, Aldrich). Nominal molar ratios (Pd:Cu) of 10:90, 25:75, 50:50, 63:37, and 100:0 were mixed with activated carbon (Vulcan XC-72, pretreated with HCl) under sonication to form a slurry. The slurry was diluted into a beaker, and reducing agent (NaH₂PO₂, Aldrich) was added drop wise to reduce the salt to nanoparticles under mechanical stirring. After the reaction was complete, NaOH was added, the nanoparticles were allowed to settle, and the mixture was filtered and dried in air.

2.2 Materials Characterization

A Hitachi H7000 transmission electron microscope (TEM) was used to observe the size, shape, and distribution, of the nanoparticles on the carbon support. Carbon analysis was performed at the University of California – Irvine (FlashEA 1112 Carbon Analyzer) in order to quantify the metal loading on the activated carbon support. Elemental analysis was performed by inductively coupled plasma-optical emission spectroscopy (Perkin-Elmer 7300DV ICP-OES).

Powder X-ray diffraction (XRD) was performed on a Rigaku Miniflex equipped with a variable width anti-scattering slit. The samples for XRD were prepared on a miscut silicon zero-background slide secured with petroleum jelly.

X-ray photoelectron spectroscopy (XPS) was performed with a Kratos AXIS-165 with a monochromatized AlK α X-ray anode (1486.6 eV). The spectrometer was calibrated against the Au 4f_{7/2} peak at 84.0 eV and the Ag 3d_{5/2} peak at 368.3 eV. The samples were cleaned using argon sputtering to remove any remaining precursor compounds and air contaminants. The valence band was analyzed using commercial software (CasaXPS). All spectra were smoothed using the Sawitzki-Golay algorithm with a kernel of 5 pts.

2.3 Electrochemical Analysis

Electrochemical analysis was performed using a PAR263A potentiostat in a custom-designed, three-electrode electrochemical glass cell. The working electrode consisted of a smooth, gold rotating disk electrode covered with a 30 μ L drop of dried catalyst ink. The ink was prepared by sonication of a mixture of the carbon-supported nanoparticles, a few drops of AS-4 binder (Tokuyama), and water. The disk was rotated at 2000 rpm to remove any gas bubbles formed during the electrochemical oxidation reaction. Gold electrode was used for

better adherence of the catalyst ink containing AS-4; the low surface area gold electrode contributed less than 1% to the overall oxidation of the high surface area catalysts at various potentials. The counter electrode was Pt mesh (Alfa Aesar), and the reference electrode was a saturated calomel electrode (SCE, CH instruments). Chronoamperometry experiments were performed by holding the potential at -0.4 V for 3 hours in each polyalcohol on each catalyst formulation. The polyalcohol solution was 1 M polyalcohol + 1 M KOH to maintain a constant, alkaline pH with support electrolyte. Cyclic voltammetry (CV) at 30 mV s^{-1} was performed in the same solutions to determine the transient behavior of the alcohols on the catalyst. CV in 1 M H_2SO_4 was also performed on each catalyst following completion of chronoamperometry so that the electrochemical surface area could be determined for each catalyst ink application.

3. Results and Discussion

3.1 Materials Characterization

Catalysts for the electrochemical oxidation of the polyalcohols EG, PG, and G were synthesized so that various concentrations of Pd:Cu nanoparticles were obtained. Previous work on the electrochemical oxidation of the polyalcohols on $\text{Pd}_{87}\text{Cu}_{13}/\text{C}$ showed that the presence of Cu increased the oxidation rate 3 (G) and 4 (EG, PG) times compared to the oxidation rate on Pd/C. The maximum power density of a direct alcohol fuel cell increased by 61, 54, and 14% for PG, G, and EG, respectively, when the anode catalyst was $\text{Pd}_{87}\text{Cu}_{13}/\text{C}$ compared to Pd/C. The strong promotion of the oxidation rate was the motivation for this work: the exploration of other ratios of Pd:Cu with increased Cu. The nominally targeted ratios of Pd:Cu were 63:37, 50:50, 25:75, and 10:90, in order to complement the previous work on 87:13. The actual ratios of Pd:Cu were 63:37, 46:54, 28:72, and 11:89, respectively, as determined by ICP-OES. Thus, it is

confirmed that our actual metal ratios are quite close to the nominal ratios, indicating that the metal reduction proceeds at the same pace for both Pd and Cu. Carbon analysis showed that the metal loading was 54, 52, 44, 42, and 38%, respectively, for decreasing Pd concentration from 100 to 11%. High metal loading was targeted to provide a means for better estimation of the electrochemical surface area. At low metal loadings, which are desirable for fuel cell assembly, the carbon support induces a large double layer charging region in the voltammogram that interferes with analysis of the metal catalyst surface area. The catalyst activity is not significantly altered by the small range of metal loadings that we observed.

TEM was used to image the nanoparticles in order to confirm that the particle size and distribution were similar among all catalysts and matched that of our previous work. In our previous work we found particle sizes of 4.7 ± 0.9 and 5.0 ± 1.2 nm, and in this work we find that the average particle size is 4.8 ± 1.0 nm. **Figure 1** shows typical Pd₁₁Cu₈₉/C nanoparticles representative of all the catalysts synthesized for this work and that are similar to the ones in previous work.[50] We observe an even distribution of the metal catalyst on the carbon support with size much less than 10 nm which excludes any electronic contributions due to the particle size effect that would lead to the misinterpretation of our results.

Powder XRD patterns of each catalyst are shown together in **Figure 2**. The Pd/C catalyst shows the pattern that would be expected for pure Pd, with strong peaks for the (111), (200), (220), (311), and (222) planes. All PdCu/C catalysts show a slight shift to lower *d*-spacing of all of the main peaks, and the Pd₄₆Cu₅₄/C and Pd₂₈Cu₇₂/C show a second peak shifted to higher 2θ values next to each of the primary peaks indicating some heterogeneity. In Pd₆₃Cu₃₇/C the

increase in 2θ is a result of the smaller Cu substituting in the Pd lattice and is expected for this Cu dopant range according to the Pd-Cu bulk phase diagram.[53, 54] The bulk phase diagram predicts the presence of a PdCu_3 phase adopting the prototypical AuCu_3 structure at Pd composition less than ~20% which was observed for the $\text{Pd}_{11}\text{Cu}_{89}/\text{C}$ catalysts. Differentiating the PdCu_3 structure can be difficult due to the overlap of the strongest peaks with that of the Pd structure, however the presence of an additional peak at $\sim 24^\circ 2\theta$ is indicative of the (100) peak of the AuCu_3 structure type which is absent in the Pd FCC pattern. The heterogeneous mixtures established in the $\text{Pd}_{46}\text{Cu}_{54}/\text{C}$ and $\text{Pd}_{28}\text{Cu}_{72}/\text{C}$ samples are mixtures of the same PdCu solid solution observed in the $\text{Pd}_{63}\text{Cu}_{37}/\text{C}$ sample and a tetragonally distorted PdCu_3 structure. The distorted structure is marked by a larger $a = 3.67 \text{ \AA}$ corresponding with the shift of the (111) peak relative to the cubic PdCu_3 structure observed in the $\text{Pd}_{11}\text{Cu}_{89}/\text{C}$ sample. The presence of the heterogeneous mixtures does not agree with the bulk phase diagram, which indicates that the thermodynamic minimum has not been reached and the formation of the nano-catalysts at room temperature is diffusion limited. While there is some variety in the structures, the emphasis of this present work is demonstration of the electrochemical behavior of these four ratios of PdCu/C nanoparticles.

XPS valence band is a good representation of the density of states (DOS) of materials. Here, we measure the DOS of all synthesized catalysts and calculate their d-band centers. **Figure 3a** displays the XPS valence band of Cu and Pd nanoparticles supported on carbon. The dashed lines display the d-band center for both Pd/C and Cu/C at values of 2.45 eV and 3.18 eV, respectively. A **change** from pure Pd or Cu results in a change in the density of states and a shift in the d-band center energy as seen in **Figure 3b**. A shape change in DOS near the Fermi level

(E_F) is measured as more Cu atoms are added to the mixtures PdCu/C. The density of states near E_F decreases with increasing amount of Cu atoms and the calculated d-band center upshifts away from the E_F from 2.67 eV for Pd₆₃Cu₃₇/C to 3.24 eV for Pd₁₁Cu₈₉/C. We observe a narrowing of the valence band for the catalyst with more Cu and a broadening of the valence band for the catalyst with more Pd. A broad band (smaller d-center energy) indicates weaker adsorption of undesirable species during the surface oxidation reaction while a narrow band (larger d-band energy) promotes adsorption of these species on the catalyst [35, 55]. The change of DOS near the Fermi level shifts the d-band center away or towards the E_F impacting the electrochemical behavior of the catalysts towards the oxidation of the polyalcohols studied in this work.

3.2 Electrochemistry

Chronoamperometry was performed to determine the activity of each catalyst for the electrochemical oxidation of each polyalcohol. **Figure 4** shows one amperogram of each catalyst oxidizing one of the polyalcohols compared to the oxidation of the same polyalcohol on Pd/C. In each case, the electrochemical oxidation rate for the PdCu/C catalyst is significantly greater than for the Pd/C catalyst. For oxidation of each polyalcohol on Pd/C, there is a steady decay in current for the first 90 minutes, followed by a stabilization of the oxidation rate through 3 hours. However, the oxidation rate of PG on the Pd₆₃Cu₃₇/C catalyst *increases* for the first hour before stabilizing and slowly decaying. The oxidation rate of EG on the Pd₄₆Cu₅₄/C catalyst sharply *increases* for the first 30 minutes, followed by slow decay and then stabilization near 3 hours. The oxidation rate of G on the Pd₂₈Cu₇₂/C and Pd₁₁Cu₈₉/C catalysts also sharply *increases* for the first 30 minutes, followed by decay to 3 hours. The shape of these amperograms is consistent for all 3 polyalcohols oxidized on all four PdCu/C catalysts; however, it was not observed on the

lower Cu loadings from our previous work on Pd₈₇Cu₁₃/C.[50] This behavior, in which the oxidation rate *increases* for the first 30-90 minutes is unusual behavior for chronoamperometry, where current typically decays as a function of $t^{-1/2}$ due to diffusion limitations near the electrode surface.[56]

The electrochemical oxidation rate for each polyalcohol on each catalyst is reported in [Table 1](#). The greatest increase in oxidation rate is observed for the oxidation of G on Pd₆₃Cu₃₇/C (0.332 mA cm⁻²), which is 14 times faster than the oxidation rate of G on Pd/C (0.023 mA cm⁻²). The least increase in oxidation rate is for the oxidation of G on Pd₂₈Cu₇₂/C (0.077 mA cm⁻²), which is 3 times faster than on Pd/C. The oxidation rate of EG ranges from 5 to 8 times faster on PdCu/C than Pd/C, and the oxidation rate of PG ranges from 8 to 12 times faster. Polyol alcohol oxidation on each Cu-containing catalyst is *significantly higher* than on the pure Pd/C catalyst without exception.

Cyclic voltammetry was performed, and 3 voltammograms are overlaid in [Figure 5](#), showing the voltammetric behavior of the lowest loading of Cu (Pd₆₃Cu₃₇/C), highest loading of Cu (Pd₁₁Cu₈₉/C), and Pd/C, for the electrochemical oxidation of PG. These voltammograms are representative of each polyalcohol oxidized on each catalyst. When the potential is increased in the positive direction, polyalcohol oxidation is observed above -0.6 V. The oxidation rate increases until a maximum is reached immediately prior to surface deactivation by oxide formation. At 0.3 V, a small peak is observed due to oxidation of the small amount of Au surface exposed from the rotating disk electrode. In the reverse direction, the surface reactivates near -0.3 V, following oxide reduction; thus an increase in electrochemical oxidation of the

polyalcohol is observed. The general shape of the voltammograms is consistent with previous work on the Pd₈₇Cu₁₃/C catalyst. However, it is important to note that the peak oxidation current (in the positive direction) shifts to higher current density and lower potentials with increased Cu concentrations. The higher peak current density is due to the higher activity of the Cu-containing catalyst, although the magnitude of the increase in oxidation rate is much smaller than after 3 hours of oxidation at -0.4 V. The lower peak potential is observed because the surfaces with higher Cu concentration activate for alcohol oxidation at lower potentials than the surfaces with higher Pd concentration: hydroxyl adsorption on (i.e., oxidation of) the less noble Cu is more thermodynamically favorable than hydroxyl adsorption on the more noble Pd.[26]

Cyclic voltammetry was also performed in 1 M KOH in the absence of the polyalcohols to observe the electrochemical activity of the catalysts in aqueous solutions (Figure 6). The same three catalysts were compared, and the Pd/C catalyst exhibits standard behavior. In the positive scan, the surface oxidizes above 0 V, and the oxides reduce in the reverse scan at -0.4 V. Hydrogen adsorption/desorption are also observed between -1.1 and -0.7 V, although the peaks are not intense due to the alkaline medium. Increasing the Cu concentration in the catalyst results in a larger surface oxidation peak and a negative shift in the onset of the surface oxidation. This is again due to the thermodynamic favorability of the oxidation of the less noble Cu and supports the observation in Figure 5 that the peak current density is higher and occurs at lower potential as the amount of Cu in the catalyst is increased.

3.3 Electronic and Bifunctional Effects

In this study of the electrochemical oxidation of polyalcohols on various PdCu/C catalysts, we have observed that the oxidation rate on any PdCu/C is *significantly greater* than the oxidation rate on Pd/C. We expected that the electronic effect would play a primary role in this promotion, since it did so for Pd₈₇Cu₁₃/C catalyst previously studied. XPS data confirms that there is a change in DOS near the Fermi level that shifts the d-band center away from E_F indicating that less charge is available for bonding of undesirable species during the surface oxidation reaction. As a result, the electrochemical oxidation rate of the polyalcohols increases. This suggests that some of the promotion is due to an electronic effect. However, if the promotion was due to the electronic effect alone, we would expect to see a “volcano plot” when comparing the Pd:Cu ratios to the electrochemical oxidation rate. [57] In other words, the electronic effect will result in a maximum oxidation rate, at which the electronic perturbation of the alloyed catalysts is optimal, followed by decay in the promotion of oxidation rate at higher concentrations of Cu. For the oxidation of EG, we observe a slight indication that a maximum exists, but the oxidation rate is significantly higher for *all ratios of Pd:Cu* and the differences between different ratios of Pd:Cu is much less than the difference between any Pd:Cu/C and the pure Pd/C. For the oxidation of PG, the oxidation rate actually decreases as the Cu concentration increases from 37 to 54%, but the oxidation rate then increases again at higher Cu concentrations. For the oxidation of G, the oxidation rate decreases sharply as the Cu increases from 54 to 72%: the trend that would be expected if the 54% was the maximum and higher Cu percentages were less optimal. However, when the Cu concentration is further increased to 89%, the oxidation rate sharply increases again, indicating there is no single maximum. The increasing oxidation rates of PG and G at the highest concentrations of Cu strongly suggest the

presence of more than simply an electronic effect which would result in one maximum. Therefore, a second effect needs to be considered. A bifunctional effect will also promote the oxidation rate of the polyalcohols, particularly for PG and G, where there is a clear increase in oxidation rate as the Cu concentration is increased. The presence of a higher Cu concentration at the catalyst surface could promote the adsorption of hydroxyl, which is required for oxidation of the polyalcohols. Thus, increasing the number of Cu atoms at the surface also contributes to a faster electrochemical oxidation rate of the polyalcohols.

In support of the hypothesis of a combination of the electronic and bifunctional effects, we observe three important features in the electrochemical measurements. First, [Figure 6](#) shows that the oxidation of the PdCu surface begins at a lower potential with the presence of more Cu. For the Pd₁₁Cu₈₉/C, the oxidation begins at -0.5 V vs SCE, and for the Pd₆₃Cu₃₇/C, it begins at -0.3 V; in contrast, surface oxidation does not begin on the Pd/C until approximately 0 V, and the start of surface oxidation is more gradual. Oxidation of the surface at lower potential is indicative of easier adsorption of hydroxyls that are required to electrochemically oxidize the polyalcohols; hence, the polyalcohol oxidation rate will be promoted by easier oxidation of the catalyst surface. Second, [Figure 5](#) shows that the surface deactivates at a lower potential when a higher concentration of Cu is present: deactivation (i.e., excessive coverage of hydroxyls) begins at -0.1 V for Pd₁₁Cu₈₉/C, 0.1 V for Pd₆₃Cu₃₇/C, and 0.2 V for Pd/C. This deactivation supports the results from [Figure 6](#) which indicate that the surface coverage of adsorbed hydroxyls occurs at lower potentials. Low to medium surface coverage promotes the reaction, while high coverage deactivates the reaction by blocking the Pd sites from adsorption of the polyalcohols. Third, the voltammetry experiments in [Figure 5](#) show much less promotion than the

amperometry experiments in **Figure 4**, suggesting that the full extent of promotion is not instantaneous but takes time (approximately 30 minutes) to develop at -0.4 V. This is supported by the shape of the amperometry curves, where the oxidation rate *increases* for the first 30 minutes on every PdCu/C catalyst, and the shape of this increase is sharper for the higher concentrations of Cu. In contrast, the Pd₈₇Cu₁₃/C from previous work did not show increasing initial oxidation rate due to the lower Cu concentrations. Therefore, it is possible that the adsorption of hydroxyls at the catalyst surface is promoted by the presence of Cu and builds up over the first 30 minutes of applied potential; this buildup would result in an increased oxidation rate and a strong enhancement of the electrochemical oxidation of the polyalcohols.

Conclusion

Carbon supported Pd-Cu catalysts (Pd₆₃Cu₃₇/C, Pd₄₆Cu₅₄/C, Pd₂₈Cu₇₂/C, and Pd₁₁Cu₈₉/C) were synthesized, characterized, and used to electrochemically oxidize the polyalcohols EG, PG, and G. The oxidation rate at -0.4 V after 3 hours on each catalyst was compared to the oxidation rate on Pd/C without any Cu present in the catalyst. The oxidation rate for every polyalcohol on every PdCu/C catalyst was at least 3 times greater than on the Pd/C catalyst. The greatest promotion for the oxidation of each polyalcohol was: EG 7 times faster, PG 12 times faster, and G 14 times faster on Pd_{x-1}Cu_x/C alloys than on Pd/C. The shape change in DOS near the Fermi energy with increasing Cu and increasing hydroxyl adsorption at lower potentials evidence the contribution of both an electronic effect and a bifunctional effect for the promotion of the electrochemical oxidation of the polyalcohols, EG, PG, G, on PdCu/C catalysts.

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Figure Captions

Figure 1. Transmission electron microscopy of the Pd₁₁Cu₈₉/C catalyst shows well-distributed nanoparticles of 4.8 nm on activated carbon support. This image is representative of all catalysts used in this work, and it matches the images from previous work on different Pd:Cu ratios synthesized by the same route.[50]

Figure 2. Powder X-ray diffraction patterns for all catalysts used in this work offset for visual clarity. Vertical lines represent the peak positions from the Pd/C catalyst to emphasize deviations from the Pd structure upon introduction of Cu. An asterisk (*) marks an impurity that is present in all samples that most likely results from the phosphate from synthesis with varying composition resulting in a shift between samples.

Figure 3. XPS valence bands for pure Pd and Cu carbon supported nanoparticles (a) and for four Pd_{x-1}Cu_x/C catalysts (b). The shape of the DOS near E_F and the d-band center positions with respect to the Fermi level change as the amount of Cu atoms is changed in the catalyst formulation.

Figure 4. Chronoamperometry for each PdCu/C catalyst and each of the three polyalcohols was performed for 3 hours at -0.4 V vs SCE. Representative amperograms are shown: (a) PG on Pd₆₃Cu₃₇/C, (b) EG on Pd₄₆Cu₅₄/C, (c) G on Pd₂₈Cu₇₂/C, and (d) G on Pd₁₁Cu₈₉/C. All current density results after 3 hours are shown in [Table 1](#).

Figure 5. Cyclic voltammograms at 30 mV s^{-1} for the oxidation of PG on 3 different ratios of Pd:Cu are shown as representative of the voltammograms on each catalyst in each polyalcohol. The solution contained 1 M PG + 1 M KOH.

Figure 6. Cyclic voltammograms at 30 mV s^{-1} in 1 M KOH for 3 different ratios of Pd:Cu are shown as representative of the voltammograms on each catalyst in each polyalcohol; these are the same catalysts shown in **Figure 5**.

Table

Catalyst	Current Density (mA cm^{-2})		
	EG	PG	G
Pd/C	0.029	0.013	0.023
Pd ₆₃ Cu ₃₇ /C	0.146	0.138	0.333
Pd ₄₆ Cu ₅₄ /C	0.154	0.107	0.263
Pd ₂₈ Cu ₇₂ /C	0.217	0.086	0.136
Pd ₁₁ Cu ₈₉ /C	0.142	0.155	0.267

Table Caption

Table 1. The oxidation rate of each polyalcohol on each catalyst is shown. The oxidation rate was determined by holding a potential of -0.4 V vs SCE for 3 hours and the current at 3 hours was reported. The presence of Cu increases the oxidation rate for all polyalcohols with an enhancement of 3 to 14 times, depending on the Pd:Cu ratio and the polyalcohol.

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Figure 1

Figure 2

Figure 3a

Figure 3b

Figure 4a

Figure 4b

Figure 4c

Figure 4d

Figure 5

Figure 6