Structure–Property-Performance Relationship of Ultrathin Pd–Au Alloy Catalyst Layers for Low-Temperature Ethanol Oxidation in Alkaline Media

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Supporting Information

ABSTRACT: Pd-containing alloys are promising materials for catalysis. Yet, the relationship of the structure–property performance strongly depends on their chemical composition, which is currently not fully resolved. Herein, we present a physical vapor deposition methodology for developing PdAu1−x alloys with fine control over the chemical composition. We establish direct correlations between the composition and these materials’ structural and electronic properties with its catalytic activity in an ethanol (EtOH) oxidation reaction. By combining X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements, we validate that the Pd content within both bulk and surface compositions can be finely controlled in an ultrathin-film regime. Catalytic oxidation of EtOH on the PdAu1−x electrodes presents the largest forward-sweeping current density for x = 0.73 at ~135 mA cm−2, with the lowest onset potential and largest peak activity of 639 A g−1 observed for x = 0.58. Density functional theory (DFT) calculations and XPS measurements demonstrate that the valence band of the alloys is completely dominated by Pd particularly near the Fermi level, regardless of its chemical composition. Moreover, DFT provides key insights into the PdAu1−x ligand effect, with relevant chemisorption activity descriptors probed for a large number of surface arrangements. These results demonstrate that alloys can outperform pure metals in catalytic processes, with fine control of the chemical composition being a powerful tuning knob for the electronic properties and, therefore, the catalytic activity of ultrathin PdAu1−x catalysts. Our high-throughput experimental methodology, in connection with DFT calculations, provides a unique foundation for further materials’ discovery, including machine-learning predictions for novel alloys, the development of Pd-alloyed membranes for the purification of reformate gases, binder-free ultrathin electrocatalysts for fuel cells, and room temperature lithography-based development of nanostructures for optically driven processes.

KEYWORDS: metal alloys, Pd, Au, electrocatalysis, band structure, ethanol oxidation, alkaline medium, ultrathin catalyst layer

INTRODUCTION

The discovery of novel materials through rational design can be substantially accelerated by the implementation of experimental high-throughput methods and computational machine-learning (ML) approaches.1,2 The high-throughput experimental development and ML combination can enable the rapid identification of precise figures-of-merit that define ideal candidates for renewable energy-harvesting systems. In the realm of photovoltaics, ML has been implemented to downselect compounds suitable for solar cells based on their band gap and also their device stability.3 Concerning water splitting and catalysis, the extremely large number of materials that can potentially offer high performance has triggered intense research correlating the structure and properties of thin films and nanostructures, encompassing compounds and alloys.4−8 Particularly, ultrathin films and catalyst layers (i.e., 20−500 nm)8 have generated a significant amount of interest in part because of their ability to perform purification of reformate gases9 and optical sensing10,11 and to create alternative catalyst platforms for polymer electrolyte membrane fuel cells9,12,13 as well as cocatalyst or nanostructured arrays derived from lithography-based processes.14 However, achieving an optimal structure–property performance for alloyed materials in the ultrathin-film regime involves the balancing of various design parameters, with fine control over the chemical composition required. Therefore, scalable high-throughput methodologies such as physical vapor deposition

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(PVD) capable of generating a broad range of alloy materials are needed and provide a unique platform for generating data sets utilized in training, for example, ML algorithms.

As an exemplar material platform, Pd-based catalysts have been utilized for various oxidation reactions. This includes benzyl alcohol, formic acid, H₂ and ethanol (EtOH) redox reactions, to name a few. Prior findings show that when Pd is alloyed or doped with other metals/nonmetals, there is an enhancement in the catalytic activity. Additionally, alloying Pd with coinage metals (e.g., Ag, Au, or Cu) that exhibit plasmon-induced resonances under visible illumination has created exciting possibilities. 

Because pure metals have predefined permittivity, the options available for photocatalysis have already been extensively investigated, whereas it has only recently been shown that alloyed metals can deliver optical responses engineered in the UV–near-IR range of the electromagnetic spectrum, providing permittivity values not obtained by any pure metals. For example, metallic mixtures formed by earth-abundant metals (Al and Cu) have delivered near-unity light absorption (>99%) in thin-film configurations. Additionally, Pd–Au alloys can promote remarkable hydrogenation, which can be used to modify the optical behavior of the metallic material. 

Developing Pd-based alloys for the EtOH oxidation reaction (EOR) is particularly interesting because EtOH possesses a high theoretical energy density of ~8.0 kWh kg⁻¹ and is easily contained for transportation and delivery because of an existing infrastructure. However, the EtOH molecule contains a C–C bond that makes the complete oxidation to CO₂ difficult at low temperatures (i.e., ≤80 °C). Pd-based alloys have shown EtOH oxidation enhancements compared to their monometallic counterparts. However, more efforts are needed to bridge the structure–property-performance gap for Pd-based alloys, especially if considered for energy-harvesting applications. This includes cross-correlating optical, physical, and electrochemical properties. Moreover, investigations of ultrathin PdₐAu₁₋ₓ catalysts with finely controlled compositions and corresponding optical dispersion relationships are lacking.

Here we demonstrate the catalytic activity of a series of ultrathin PdₐAu₁₋ₓ alloys as a function of their chemical composition through EtOH oxidation and explain their performance in terms of the alloys’ tailored band structures. We achieve high control on the chemical composition of the alloys, as demonstrated by comparative bulk and surface analyses. Using density functional theory (DFT) calculations, we resolve their band structure, where Pd dominates the valence band of all alloys for x ≥ 0.25. This result indicates that the wavelength of the interband transitions in PdₐAu₁₋ₓ can be engineered by varying x. We unfold the performance of these alloys on the oxidation reaction of EtOH, a model system, and find that the maximum current density is obtained for PdₐAu₁₋ₓ with x ≥ 0.58. Our correlated study of the structure–property performance of PdₐAu₁₋ₓ opens the door for the rational design of alloys for catalysis through band-structure engineering, where their electronic properties can provide control over the electromagnetic spectrum.

### Ultrathin PdₐAu₁₋ₓ Alloy Films

The ultrathin PdₐAu₁₋ₓ alloy films are fabricated by PVD cosputtering of both Au and Pd metals onto different substrates. This includes deposition on Si wafers and glass substrates with a 1.0 in. × 1.0 in. area and Ti disks with a 0.196 cm⁻² cross-sectional area (see Methods in the Supporting Information). A constant rotation was used to attain high control of the chemical composition with precise uniformity, which was confirmed by energy-dispersive X-ray spectroscopy (EDS) measurements, as presented in Figure 1. Seven PdₐAu₁₋ₓ films with a uniform chemical composition were obtained, where x = 1, 0.73, 0.58, 0.5, 0.35, 0.14, and 0. The photographs of the samples show that the Pd₁₄Au₈₆ sample has a unique hue, while all other alloys (with x ≥ 0.35) present approximately the same color. The distinct color of this alloy indicates that the optical behavior (permittivity) of this sample is likely different from that of all other alloys investigated here in the visible range of the electromagnetic spectrum. Furthermore, we obtained a series of smooth films (i.e., low roughness) with gradual variation in the chemical composition, as shown in the scanning electron microscopy (SEM) images in Figure S1, with complementary atomic force microscopy (AFM) images shown in Figure S2. We determined the PdₐAu₁₋ₓ composition by analyzing different locations on each sample with EDS. Representative SEM images and select EDS spots are shown in Figure S1. Table 1 lists the compositions with standard deviations for at least four different measurements as well as the surface roughness determined from AFM measurements. We further investigate the degree of alloying and the tunability of the bulk chemical composition of PdₐAu₁₋ₓ alloys by X-ray diffraction (XRD). As shown by the XRD pattern in Figure 2a, all films are composed primarily by polycrystalline grains and adopt the face-centered-cubic (fcc) crystal structure with strong (111) diffraction peaks. The literature values for the lattice constant of pure Au and Pd are 4.078 and 3.891 Å, respectively, with the (111) peak gradually shifting to larger values of 2θ as the content of Pd increases, following Bragg’s Law. The change in the position of the diffraction condition for the (111) peak confirms the formation of PdₐAu₁₋ₓ alloys, consistent with Vegard’s Law, as displayed in Figure 2b. A similar peak shift is observed for PdₐAu₁₋ₓ nanoparticles, as previously reported with the relative Au/Pd composition proportional to that of the feeding solution.
To corroborate the EDS and XRD results, we performed X-ray photoelectron spectroscopy (XPS) measurements. As expected, the general shapes for both the pure Pd and Au curves agree with those previously reported.\textsuperscript{37} Survey and high-resolution scans were collected for the Au 4f, Pd 3d, and valence-band-spectral (VBS) regions. Figure S3 shows the normalized intensity of the Au 4f and Pd 3d spectra for the different Pd$_x$Au$_{1-x}$ compositions. A negative shift in the Au 4f and Pd 3d binding energy peak locations was observed, consistent with previous reports.\textsuperscript{16} In addition, a decreased doublet intensity for Au 4f with a concomitant increase in the Pd 3d doublet intensity is observed with increasing Pd composition. The negative shift in the binding energies suggest a d-band modification due to charge transfer between the Au and Pd atoms upon alloying. In addition to Au 4f and Pd 3d scans, Figure 3 shows the VBS for different Pd$_x$Au$_{1-x}$ electrodes. To better understand the band structure of the Pd$_x$Au$_{1-x}$ alloyed electrodes, we determined the centroid of the integrated VBS area ($\bar{E}_{\text{d}}(\text{Pd}_{x}\text{Au}_{1-x})$) from the experimental VBS as follows:

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{(a) XRD measurements of Pd$_x$Au$_{1-x}$ electrodes. The orange markers indicate the positions of the different crystallographic peaks. (b) Linear dependence of the (111) peak position as a function of the Pd composition following Vegard’s Law. The error bars refer to deviation of the peak position for at least three different depositions (values of the intercept and slope are displayed as insets showing a strong linear dependence). The color palette refers to the chemical composition of the alloys analyzed.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{VBS of the Pd$_x$Au$_{1-x}$ alloy thin films obtained by XPS. The centroid of the integrated VBS (i.e., from 2 eV up to 10 eV) is used to evaluate the d-band center. The color palette refers to the Pd content x (atom %).}
\end{figure}

Table 1. Pd$_x$Au$_{1-x}$ Compositions Determined by EDS, with the Surface Roughness Evaluated Using AFM$^a$

<table>
<thead>
<tr>
<th>Pd$<em>x$Au$</em>{1-x}$ alloys</th>
<th>EDS composition (Pd atom %)</th>
<th>AFM surface roughness (nm)</th>
<th>coverage ($\Gamma_{\text{Pd}}$ mol cm$^{-2}$)</th>
<th>active Pd$_{\text{active}}$ (%)</th>
<th>onset potential (mV vs RHE)$^b$</th>
<th>peak activity (A g$_{\text{Pd}}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>100</td>
<td>5.12</td>
<td>$5.3 \times 10^{-7} \pm 2.1 \times 10^{-7}$</td>
<td>16.3 ± 0.65</td>
<td>427</td>
<td>260.55</td>
</tr>
<tr>
<td>Pd$<em>{0.73}$Au$</em>{0.27}$</td>
<td>73.0 ± 0.45</td>
<td>5.16</td>
<td>$4.3 \times 10^{-7} \pm 3.1 \times 10^{-7}$</td>
<td>18.49 ± 1.36</td>
<td>399</td>
<td>544.42</td>
</tr>
<tr>
<td>Pd$<em>{0.62}$Au$</em>{0.38}$</td>
<td>58.4 ± 0.38</td>
<td>4.63</td>
<td>$2.8 \times 10^{-7} \pm 3.3 \times 10^{-7}$</td>
<td>14.45 ± 1.67</td>
<td>379</td>
<td>639.25</td>
</tr>
<tr>
<td>Pd$<em>{0.5}$Au$</em>{0.5}$</td>
<td>50.3 ± 0.22</td>
<td>5.01</td>
<td>$2.0 \times 10^{-7} \pm 2.9 \times 10^{-7}$</td>
<td>11.35 ± 1.60</td>
<td>395</td>
<td>547.22</td>
</tr>
<tr>
<td>Pd$<em>{0.37}$Au$</em>{0.63}$</td>
<td>55.6 ± 0.39</td>
<td>3.13</td>
<td>$9.0 \times 10^{-7} \pm 1.4 \times 10^{-7}$</td>
<td>6.5 ± 0.98</td>
<td>461</td>
<td>331.07</td>
</tr>
<tr>
<td>Pd$<em>{0.14}$Au$</em>{0.86}$</td>
<td>35.6 ± 1.33</td>
<td>2.56</td>
<td>$7.1 \times 10^{-7} \pm 1.7 \times 10^{-7}$</td>
<td>11.32 ± 2.76</td>
<td>719</td>
<td>18.99</td>
</tr>
</tbody>
</table>

$^a$The coverage ($\Gamma_{\text{Pd}}$) and active Pd$_{\text{active}}$ (%) were evaluated in 1 M KOH. The lowest onset potential and peak activity in 1 M KOH + 0.5M EtOH were evaluated from the anodic sweep at 5 and 20 mV s$^{-1}$, respectively. All measurements were performed at 22 °C with the potential versus RHE.  
$^b$The onset potential was determined at 500 μA cm$^{-2}$.
\[ E_{d(Pd_{x}Au_{1-x})} = \frac{\int_{-\infty}^{E_F} E_d(E - E_F)\, dE}{\int_{-\infty}^{E_F} D_d(E - E_F)\, dE} \]  

where \( D_d \) is the density of states (DOS) at a given binding energy \( (E) \) and \( E_F \) is the Fermi energy of the system. The DOS is largely made-up of d-band contributions around the Fermi energy. Thus, one may interpret the centroid of the integrated VBS area as the d-band center, as we will further discuss in the next section. It should be mentioned that the sp character is relatively less for a given energy level \( E_F \) compared to the d-band contribution. Therefore, for simplicity, we include both sp- and d-band contributions by integrating over a range of binding energies \( i.e., \) from \(-2.3\) eV up to \(+4.3\) eV), and throughout the text, we refer to the centroid of the integrated VBS area as that related to the d-band center because this is the largest fraction of the projected DOS. On the basis of concepts derived from chemisorption theory, contributions from the d band of the surface metal atoms correlate well with shifts in various adsorbate binding energies. The upper limit of the energy range \( (y) \) used for integration varies based on the Pd\(_{x}\)Au\(_{1-x}\) composition, with all of the VBS background-subtracted and normalized to account for experimental differences. Furthermore, the binding energy range considered takes into account only experimentally relevant energy levels \( (e.g.,\) avoiding inelastic electrons), consistent with previous observations for Au. The \( E_{d(Pd_{x}Au_{1-x})} \) values of the Pd and Au films are found to be \(-2.3\) and \(+4.3\) \pm 0.2 eV, which are close to the previously reported values of \(-2.0\) and \(+4.3\) eV, respectively, based on XPS VBS. It should be noted that our experimental d-band centers deviate slightly from theoretical calculations because we shift all spectra relative to the adventitious C 1s line located at 284.8 eV. Regardless, our VBS d-band-center findings agree well with previous measurements. Figure S4 shows the Pd composition (atom %) determined by EDS and XPS surface analysis as a function of \( E_{d(Pd_{x}Au_{1-x})} \). The strongly correlated linear trends suggest that both XPS and EDS measurements are well described and utilized as methods for evaluating the Pd\(_{x}\)Au\(_{1-x}\) composition and the experimental d-band center for Pd\(_{x}\)Au\(_{1-x}\) catalysts. For consistency, we refer to our samples throughout the remainder of the text in terms of the bulk Pd compositions determined by EDS for the Pd\(_{x}\)Au\(_{1-x}\) samples with \( x = 0, 0.14, 0.35, 0.5, 0.58, 0.73, \) and 1.0 compositions. The bulk characterization results \( (i.e.,\) XRD, EDS) corroborated by the surface-sensitive techniques \( (i.e.,\) XPS) indicate that the high-throughput PVD co-sputtering method reported herein has the versatility and reproducibility to synthesize alloy compositions across the full compositional range in the ultrathin-film regime.

### CHEMICAL COMPOSITION AND BAND STRUCTURE ENGINEERING

We use DFT to determine the electronic band structure of the Pd—Au alloys, as displayed in Figure 4, where the color scale corresponds to the weighted contributions of Pd \( (\text{dijon}) \) and Au \( (\text{navy}) \). Because of the fcc symmetry of both metals, the \( \Gamma \)–R direction corresponds to the diagonal of the Brillouin zone of the crystalline cell \([\{111\} \text{ direction}]\). Therefore, we focus our analysis on the d bands below the Fermi level and the empty states above it. Four atoms are sufficient to simulate the crystalline unit cells of the Pd\(_{x}\)Au\(_{1-x}\) alloys with \( x = 0, 0.25, 0.5, 0.75, \) and 1.0, where one atom occupies the vertex of the cell and the other three atoms are positioned on each side of the cube. Note that calculation of the band structure of some experimentally fabricated \( x \) values would require simulation of the unit cells containing more than four atoms because of the lack of full symmetry \( (e.g.,\) to resolve the band structure of Pd\(_{x}\)Au\(_{0.88}\), one needs to use 32 atoms for the unit cell). Nevertheless, the symmetric cells presented in Figure 4 demonstrate the overall effect of Pd on the electronic behavior of the alloys. These symmetric structures provide highly degenerate bands even for the binary mixtures. Overall, there is a steep and nonmonotonic rise of the energy level of the valence band with an increase of the Pd content at the \( \Gamma \) point. This is consistent with recent findings for the measured optical properties of Pd\(_{x}\)Au\(_{1-x}\) nanodisks. The addition of 25\% Pd to the mixture results in a strong hybridization close to the Fermi level \( (E_F) \); see Figure 4b. Pd dominates the values and profiles of the additional d energy bands created by alloying of the two metals near the Fermi level \( (\sim -2.0 \text{ to } +0.3 \text{ eV}) \) for \( x \geq 0.25 \), as indicated by their colors \( (\text{blue hues}) \). For Pd\(_{0.4}\)Au\(_{0.6}\), the Pd character also dominates the valence band. This result is in contrast with previous work with AuAg alloys, where the dominant states around the Fermi level belong to Au even at low concentrations.

The band structure analysis provides important insight into the Pd\(_{x}\)Au\(_{1-x}\) alloys not previously reported. In addition, the analysis provides a self-consistent methodology connecting the VBS and DOS contributions with \( E_{d(Pd_{x}Au_{1-x})} \). It is also worth noting, although not the main point of this particular study, that the band structure analysis provides additional insight into the optical properties. For example, the overall decrease in the energy gap between the d band and the first empty state \( (>1.0 \text{ eV}) \) suggests that interband transitions for the Pd\(_{x}\)Au\(_{1-x}\) alloys should occur at longer wavelengths as the Pd content increases. In turn, the alloying of Pd and Au can indeed be used to tailor the wavelength in which light absorption is maximum, very relevant for photoelectrocatalysis. In fact, DFT is a powerful tool for the design of Pd\(_{x}\)Au\(_{1-x}\) with well-defined chemical compositions that lead to interband transitions at a priori selected wavelengths and will be the subject of future studies. Here, we demonstrate the utility of the facile PVD methodology to tune the chemical composition of ultrathin Pd\(_{x}\)Au\(_{1-x}\) alloy films for control over the materials’ electronic and catalytic properties. Moreover, we utilize the experimental VBS and theoretical calculations to determine the d-band contributions, as well as gain insight into the chemisorption descriptors from DFT surface simulations.
Figure 5. (a) CVs of Pd$_{1-x}$Au$_x$ electrodes in 1 M KOH at a stationary electrode and a scan rate of 50 mV s$^{-1}$. Plots shown for the potential versus RHE for $x = 1, 0.73, 0.58, 0.5, 0.35, 0.14,$ and 0 atom %. (b) Charge versus time (20 mV s$^{-1}$ cathodic scan direction) for different Pd-containing electrodes and the Au$_{1-x}$Pd$_x$-O and Pd-O reduction regions. (c) Comparison of the Pd (navy) and Pd$_{0.58}$Au$_{0.42}$ (light blue) catalysts in 1.0 M KOH with and without 0.5 M EtOH. (d) Slow scan anodic sweeps (5 mV s$^{-1}$) of the different Pd$_{1-x}$Au$_x$ electrodes in 1.0 M KOH with 0.5 M EtOH. The solution temperature was maintained at 22 °C via a circulating water bath. For EtOH oxidation experiments, the rotation rate was set to $\omega = 900$ rpm to provide a constant resupply of EtOH reactant to the Pd$_{1-x}$Au$_x$ electrode surface.

### DEMONSTRATION OF THE CATALYTIC ACTIVITY OF Pd–Au ALLOYS

We demonstrate the catalytic activity of ultrathin Pd$_{1-x}$Au$_x$ alloy films for the EOR. Figure 5a shows current–voltage cyclic voltammograms (CVs) of the Pd$_{1-x}$Au$_x$ thin-film-coated Ti electrodes in N$_2$-saturated 1 M KOH without EtOH or dissolved O$_2$. At potentials of less than ~0.6 V versus reference hydrogen electrode (RHE), redox peaks associated with the adsorption/desorption of H bound to Pd$_{1-x}$Au$_x$ sites (Au$_{1-x}$Pd$_x$-H$_{ads}$) are observed based on the following equation:

$$\text{Au}_{1-x}\text{Pd}_x + \text{H}_2\text{O} + e^- \leftrightarrow \text{Au}_{1-x}\text{Pd}_x\text{-H}_{ads} + \text{OH}^-$$ (2)

The initially bound H species is a result of cycling of the Pd$_{1-x}$Au$_x$ electrodes in the range from 0.12 V up to approximately 1.55 V. H adsorption is observed in Figure 5a in the negative sweep direction from 0.45 to 0.12 V, followed by H desorption in the positive sweep direction from 0.12 V to approximately 0.6 V. The H desorption current changes in the anodic scan direction after the addition of Au, resulting in a current density decrease with decreasing Pd content especially for alloys with $x < 0.73$. After a sufficient quantity of Au has been added, the Au$_{1-x}$Pd$_x$-H$_{ads}$ current density eventually approaches the Au electrode limit; essentially no appreciable H desorption features or capacity is observed. Figure 5a shows that scanning to increasingly more positive electrode potentials causes the adsorption of OH$^-$ ions onto the Pd$_{1-x}$Au$_x$ catalyst, forming Au$_{1-x}$Pd$_x$-OH$_{ads}$ species. Further anodic scanning generates higher valence oxides (Au$_{1-x}$Pd$_x$-O) according to

$$\text{Au}_{1-x}\text{Pd}_x + \text{OH}^- \rightarrow \text{Au}_{1-x}\text{Pd}_x\text{-OH}_{ads} + e^-$$

$$\rightarrow \text{Au}_{1-x}\text{Pd}_x\text{-O} + \text{H}_2\text{O} + e^-$$ (3)

The upper-limit switching potential for these catalysts is ~1.5 V, followed by cathodic scanning. Sweeping to more negative potentials yields three different peak reduction regions. We assign the first region at ~1.1 V to gold oxide (Au-O) reduction, the second region at ~0.82 V to Pd$_{1-x}$Au$_x$ alloy oxide (Au$_{1-x}$Pd$_x$-O) reduction, and the third region at ~0.64 V to Pd-O reduction. The reduction of Pd$_{1-x}$Au$_x$ is as follows:

$$\text{(Au}_{1-x}\text{Pd}_x)\text{-O} + \text{H}_2\text{O} + 2e^- \rightarrow (\text{Au}_{1-x}\text{Pd}_x) + 2\text{OH}^-$$ (4)

Interestingly, the peak potential positions (i.e., associated with the reduction of the Au$_{1-x}$Pd$_x$-O region) at the current density maximum shift in approximately a linear manner for samples containing Pd. A linear shift of the peak potential with the reduction of the Au$_{1-x}$Pd$_x$ composition has been previously observed for measurements in 0.1 M H$_2$SO$_4$ solutions for five different Pd$_{1-x}$Au$_x$ compositions. Similarly, we observe pure Pd and Au peak oxide reduction potentials comparable to those reported after iR correction. If we draw a tie line (i.e.,
connect the Au and Pd peaks with a line), then for \( x = 0.14 \) and 0.35, there is a slight deviation from linearity. This is possibly due to the PVD cosputtering method, which for dilute Pd samples could alter the topmost surface structure, creating variations in the local Pd\(_{\text{Au-x}}\) ordering. In addition, cycling the electrode in 1 M KOH is expected to marginally alter the outermost Pd\(_{\text{Au-x}}\) layers based on surface energy considerations. These electrochemical results are relevant because it was previously measured (by low-energy ion-scattering measurements) that the composition of the topmost layer of the sample deviates from the bulk composition by up to 30 atom %.37

To better understand the active Pd within each alloy composition, we investigate the magnitude of the oxide reduction current density for the Au\(_{1-x}\)Pd\(_x\)-O catalysts in the cathodic regions. A prior report has shown that this reduction region (i.e., cathodic region from 0.37 to 0.97 vs RHE) is largely associated with the concentration of electroactive Pd sites for EtOH oxidation, yielding the accumulated charge for a largely associated with the concentration of electroactive Pd region (i.e., cathodic region from 0.37 to 0.97 vs RHE) is determined from the XPS/EDS measurements and the measured bulk composition from XPS and EDS. The measured bulk composition is associated with the various Pd\(_x\)loading (g cm\(^{-2}\)) of each catalyst. The decreased electroactive Pd coverage (\( \% \)) for each catalyst is determined from the XPS/EDS measurements and the coverage (\( \% \)) and percentage of electroactive Pd (Pd\(_{\text{active}}\)) are derived from C\(_{\text{Pd,Au-x}}\) and calculated as follows:

\[
\Gamma_{\text{Pd}} = \frac{10^{-3}C_{\text{Pd,Au-x}}}{M_{\text{Pd}}} \tag{5}
\]

\[
Pd_{\text{active}}\% = \frac{10 \Gamma_{\text{Pd}}M_{\text{Pd}}}{M_{\text{Pd}}} \tag{6}
\]

whereby \( F \) is the Faradaic constant (96500 C mol\(^{-1}\)), \( M_{\text{Pd}} \) is the atomic mass of Pd (g mol\(^{-1}\)), and \( M_{\text{Pd}} \) is the total net Pd loading (g cm\(^{-2}\)) on the electrode. The total net Pd loading is determined from the XPS/EDS measurements and the deposited loading for a given Pd\(_{\text{Au-x}}\) electrode. Table 1 lists both the coverage of electroactive Pd and electroactive Pd\(_{\text{active}}\)\% for each catalyst. The decreased electroactive Pd atom percent relative to the total Pd deposited is indicative of the catalyst layer utilization. The electroactive Pd\(_{\text{active}}\)\% of the catalyst is associated with the various Pd\(_{\text{Au-x}}\) compositions, the lattice parameter, the electronic band structure, and the charge-transfer properties (e.g., strain, ligand, and ensemble effects) for each Pd\(_{\text{Au-x}}\). As expected, the C\(_{\text{Pd,Au-x}}\) is linear with the Pd atom percent with a Pearson’s \( r \) of 0.97, which confirms that the surface composition correlates strongly with the measured bulk composition from XPS and EDS. The fraction of active Pd at the surface is less than the total deposited Pd because of the inaccessibility of the underlying layers, an expected result indicating a densely packed ultrathin Pd\(_{\text{Au-x}}\) layer deposited by the PVD cosputtering method. Despite the densely packed ultrathin film, Pd\(_{\text{active}}\)\% is still comparable to the previously reported results for Pd–Ni–P nanocatalysts.48,51

The EOR is measured after the addition of 0.5 M EtOH to the 1 M KOH solution in a rotating-disk-electrode hydrodynamic setup. A rotation rate of 900 rpm is set to maintain a consistent hydrodynamic boundary layer with fresh EtOH reactant supplied to the Pd\(_{\text{Au-x}}\) electrode surface throughout the measurement. All samples measured for the EOR are temperature-controlled at 22 °C with a circulating water bath. The hydrodynamic flow of reactant species to and from the electrode is an important aspect of the EOR and has been discussed at length in previous reports related to the convective transport for ex situ and in situ device applications utilizing ultrathin films (i.e., 50–500 nm).8,52–54 Similarly, our ultrathin films require balancing of the stationary and convective removal of EOR byproducts. For clarity, we report only the 900 rpm results because they have a large EOR enhancement relative to increased rotation rates that yield a lower activity.27 The electrocatalytic oxidation of EtOH requires multiple electron-transfer steps and may result in different final products. In alkaline media (pH = 14), the desired EtOH electrooxygenation pathway is as follows:

\[
\text{CH}_3\text{CH}_2\text{OH} + 16\text{OH}^- \rightarrow 2\text{CO}_3^{2-} + 11\text{H}_2\text{O} + 12e^- \tag{7}
\]

The generation of \( \text{CO}_3^{2-} \) results from the conversion of \( \text{CO}_2 \) to carbonate in alkaline media.52,53 However, a complete 12e⁻ transfer is difficult, and various products such as acetaldehyde (\( \text{CH}_3\text{CHO} \), \( n = 2e^- \)) and acetic acid (\( \text{CH}_3\text{COOH} \), \( n = 4e^- \)) are commonly observed based on the following equations:

\[
\text{CH}_3\text{CH}_2\text{OH} + 2\text{OH}^- \rightarrow \text{CH}_3\text{CHO} + 2\text{H}_2\text{O} + 2e^- \tag{8}
\]

\[
\text{CH}_3\text{CH}_2\text{OH} + 5\text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + 4\text{H}_2\text{O} + 4e^- \tag{9}
\]

Ratios of the experimentally measured and theoretical selectivity for the \( \text{CH}_3\text{CHO} \), \( \text{CH}_3\text{COO}^- \), and \( \text{CO}_2 \) products yield values of 16, 33, and 100% for the electronic efficiencies (i.e., taking only the selectivity into consideration), respectively. It is desirable to achieve >4e⁻ per EtOH molecule; otherwise, the overall device operating efficiency would be significantly decreased. Our previous efforts investigated different EtOH electrooxygenation pathways with acetaldehyde formed at a commercially available Pd-black-coated electrode.48 The acetic acid product is not for Pd-black-coated electrodes, indicating that electronic structural changes are needed to affect a change in the selectivity. The low selectivity previously led to the creation of Pd–Ni alloy electrocatalysts, different alloys with advantageous metal charge-transfer characteristics. Therefore, improvement in the EOR performance relative to a pure Pd electrode is a benchmark for understanding the efficacy beyond the 2e⁻ transfer route. Figure 5c shows EOR CVs (20 mV s⁻¹) for Pd and Pd\(_{0.35}\)Au\(_{0.65}\) compared to 1 M KOH only solutions. The onset potential associated with EtOH oxidation coincides with H desorption (as expressed in eq 2), which could suggest that the bound H species marginally competes with the EOR, effecting a change in the takeoff current at low overpotentials. This is further highlighted in Figure 5d after a comparison of the different Pd\(_{\text{Au-x}}\) electrocatalysts scanned at a slow 5 mV s⁻¹ rate. The slow scan rate is essentially a steady-state potentiodynamic condition that considerably decreases the electrode double-layer capacitance background. The onset potentials (i.e., defined in this study as the potential at which a 500 \( \mu \)A cm⁻² EOR current density is achieved) for the different Pd\(_{\text{Au-x}}\) alloys are listed in Table 1 and increase in the following order: Pd\(_{0.35}\)Au\(_{0.65}\) < Pd\(_{0.5}\)Au\(_{0.5}\) < Pd\(_{0.27}\)Au\(_{0.73}\) < Pd < Pd\(_{0.14}\)Au\(_{0.86}\) < Au. It is worth mentioning...
that the same trend in the onset potential is observed when recorded for the alloys at a current density of $1 \, \text{mA cm}^{-2}$. The lower onset potential for the Pd−Au alloys relative to the Pd electrode suggests substantial kinetic improvements.

Figure 6 shows full EOR CVs ($20 \, \text{mV s}^{-1}$) for the different alloyed electrodes. Anodically scanning from $\sim 0.1 \, \text{to} \, 1.5 \, \text{V}$ results in a large EtOH oxidation current with a broad forward sweep oxidation current observed over a wide potential range. The cathodic scan similarly results in an oxidation current increase albeit with a less broad oxidation peak and a smaller full width at half-maximum. The qualitative differences in the CV curves in the cathodic/anodic scanning direction are a result of the surface composition of each Pd$_x$Au$_{1-x}$ alloy catalyst surface, with Au-rich electrodes possessing a higher current density at more positive potentials in the forward sweeping direction. The addition of Pd to Au generally enhances the EtOH oxidation current density.\(^{39,56,57}\) However, the maximum current density drops from $\sim 50$ to $<5 \, \text{mA cm}^{-2}$ (i.e., from $x = 0.35$ to 0.14), indicating a threshold for the EOR performance. Figure 6a highlights the forward and backward peak current density maximum ($I_F$ and $I_B$, respectively). In the forward direction, the oxidation of EtOH occurs simultaneously with the production of an oxide layer according to eq 3. The Pd$_{0.1-x}$Au$_{1-x}$ catalyst reaches a peak current density followed by a drop in the current due to excessive coverage of the active sites and competition with O-forming species. This is also observed in the cathodic direction, whereby at more negative potentials a ramp to the current density peak maximum is observed compared to the anodic sweep. The measured current density in the cathodic sweep is attributed to oxidation at the freshly exposed catalyst surface as a result of oxide layer removal (per eq 4). This is clearly seen in Figure

**Figure 6.** Hydrodynamic rotating-disk-electrode EOR CVs of the different Pd$_x$Au$_{1-x}$ alloys. (a–f) Current density versus iR-corrected potential for $x = 1, 0.73, 0.58, 0.5, 0.35,$ and 0.14 performed at a scan rate of 20 mV s$^{-1}$. (e and f) Plotted on different current density scales for clarity. All measurements shown for 1 M KOH + 0.5 M EtOH with potentials reported versus RHE. The solution temperature was maintained at 22 °C with a circulating water bath. The rotation rate was set to $\omega = 900 \, \text{rpm}$ to provide a fresh resupply of EtOH reactant to the Pd$_x$Au$_{1-x}$ electrode.
could be compared. For example, samples with different potentials were chosen so that all electrodes are typically not desired in device applications. In addition, the potentials were selected to ensure that the d-band center (\(E_d\)) was determined from the centroid of the VBS on the right axis. The mass activity versus Pd composition (atom %) is shown at 0.5 V (diagonal stripe) and 0.6 V (filled) versus RHE. The MA versus \(E_d(Pd, Au)\) is shown at 0.6 V (open circles) and 0.5 V (open squares) versus RHE. The color palette refers to the Pd content \(x\) (atom %).

5c, where the cathodic sweep shows a takeoff current coinciding with a reduction in the Au(1−Pd)O species. Parts a–f of Figure 6 show that the magnitude of the current density, from largest to smallest, in the positive scanning direction is as follows: \(Pd_{0.75}Au_{0.25} > Pd_{0.55}Au_{0.42} > Pd_{0.35}Au_{0.65} > Pd > Pd_{0.35}Au_{0.65} > Pd_{0.15}Au_{0.86} > Au\), with the \(Pd_{0.75}Au_{0.25}\) alloy yielding the largest current density of \(\sim 135\) mA cm\(^{-2}\). In addition, the current density in the negative scanning direction is \(Pd_{0.75}Au_{0.25} > Pd_{0.55}Au_{0.42} > Pd > Pd_{0.35}Au_{0.65} > Pd_{0.35}Au_{0.65} > Au\), with the \(Pd_{0.75}Au_{0.25}\) alloy also exhibiting the largest peak current density of \(\sim 141\) mA cm\(^{-2}\). This behavior results in observed peak activities for \(Pd_{0.55}Au_{0.42}\), \(Pd_{0.35}Au_{0.5}\), and \(Pd_{0.75}Au_{0.25}\) of approximately 639, 547, and 544 A g\(^{-1}\), respectively. The peak activities are comparable to a recently reported 622 A g\(^{-1}\) activity measured for carbon- and binder-free Ni@Pd-Ni nanowire arrays. The results indicate that the PVD method for generating binder-free ultrathin Pd(1−x)Ni films is a suitable high-throughput room temperature platform for future alloy catalyst development.

Figure 7a shows the difference in the peak potential for the forward (\(E_F\)) and backward (\(E_B\)) scans evaluated at the current density maximum (\(\Delta\text{Peak Max}\)). We observe the lowest \(\Delta\text{Peak Max}\) for the \(Pd_{0.75}Au_{0.25}\) and \(Pd_{0.35}Au_{0.65}\) electrodes. In addition, \(I_F/I_B\) reveals a similar trend that tracks with the \(Pd_{0.35}Au_{0.65}\) alloy with a ratio of approximately 2.0 mV cm\(^{-1}\) for \(Pd_{0.35}Au_{0.65}\) and \(Pd_{0.35}Au_{0.65}\) alloyed catalysts. The smaller \(\Delta\text{Peak Max}\) and larger \(I_F/I_B\) peak ratio indicate that the oxide formation/reduction species affects the EOR to a lesser degree for anodic/cathodic scanning conditions than that observed for compositions with \(x > 0.58\) or \(x < 0.35\). This indicates that a trade-off exists between the O and C species forming during the electrooxidation scan. To better understand this phenomenon, we evaluated the mass activity at two different potentials (0.5 and 0.6 V vs RHE). This chosen range is preferred for kinetic considerations because larger overpotentials are typically not desired in device applications. Additionally, the potentials were chosen so that all electrodes could be compared. For example, samples with \(x \leq 0.14\) exhibit larger overpotentials compared to samples with higher Pd content. It is worth noting that similar trends are observed for currents of less than 1 mA cm\(^{-2}\) (not shown), with little difference in the forward/reverse scans especially for \(x > 0.14\).

**Figure 7.** (a) Difference in the peak potential determined at the current density maximum (\(\Delta\text{Peak Max}\)), where \(E_F\) and \(E_B\) refer to the potentials in the forward and backward scans, respectively. (b) Stacked histogram of the mass activity (mA mg\(^{-1}\)) as a function of the Pd composition (atom %) on the left axis, as well as the mass activity as a function of the d-band center (\(E_d(Pd, Au)\)) determined from the first moment of the centroid in the VBS on the right axis. The mass activity versus Pd composition (atom %) is shown at 0.5 V (diagonal stripe) and 0.6 V (filled) versus RHE. The MA versus \(E_d(Pd, Au)\) is shown at 0.6 V (open circles) and 0.5 V (open squares) versus RHE. The color palette refers to the Pd content \(x\) (atom %).
earlier findings, we focus our DFT calculations on the initial stages of the \textit{inner-sphere} EOR oxidation mechanism and leave other mechanisms as a subject of future studies. The DFT calculations are performed following the method of Norskov et al.\textsuperscript{41,60} \textit{Pd}_{\text{ Au(x)}}(111) slabs are generated based on the experimental results shown in Figure 2. The slab is then “cleaved” along the (111) plane to expose the same surface for \textit{H}, \textit{EtOH}, or \textit{CO} adsorption, where \textit{H} desorption (eq 2) and \textit{EtOH} (eq 7) adsorption was previously discussed, and the oxidation of bound \textit{CO} proceeds as follows in alkaline media:

\[
\text{Au}_{x}\text{Pd}_{y}−\text{CO} + \text{Au}_{x}\text{Pd}_{y}−\text{OH} + \text{OH}^− \rightarrow \text{CO}_2 + \text{H}_2\text{O} + e^−
\]

A typical four-layer cell is utilized, with the top two layers allowed to relax and the bottom two layers fixed to the experimentally determined lattice parameter.\textsuperscript{22,23} The \textit{H}, \textit{EtOH}, and \textit{CO} molecules are considered and placed at the center site (\textit{Pd}*) or \textit{Au}*) of the 5 atom × 5 atom cell with a 15 Å vacuum placed above the surface. The binding energy (\text{BE}_{\text{adsorbate}}) of the \textit{H}, \textit{EtOH}, and \textit{CO} molecules is then calculated in the gas phase using the following formula:

\[
\text{BE}_{\text{adsorbate}} = E_{\text{Bound}} - (E_{\text{Pd}_{x}\text{Au}_{y}−} + E_{\text{Isolated}})
\]

where the subscript absorbate represents \textit{H}, \textit{EtOH}, or \textit{CO} to yield the \text{BE}_{\text{H}}, \text{BE}_{\text{EtOH}}, and \text{BE}_{\text{CO}} energies, respectively. \text{E}_{\text{Pd}_{x}\text{Au}_{y}−} refers to the different alloyed surfaces considered, with ~70–75 configurations evaluated for each absorbate. \text{E}_{\text{Isolated}} and \text{E}_{\text{Bound}} correspond to the energies of the isolated \text{H}, \text{EtOH}, or \text{CO} molecules in a periodic cell and the \text{Au}_{x}\text{Pd}_{y}−\text{bound} species. Figures S5 shows representative surfaces for \textit{EtOH} calculations. Different top, bridge, and hollow-site configurations were considered for \textit{H}, whereas \textit{EtOH} and \text{CO} were evaluated in top configurations only because of the massive amount of simulations required to fully explore \text{Pd}_{x}\text{Au}_{y}− surfaces. Note that the high-throughput PVD method in combination with the DFT activity descriptor calculations could significantly accelerate characterization of the other candidate alloyed surfaces. However, this is beyond the scope of this work and will be the subject of a future investigation.

\text{Parts a and b of Figure S6} show \text{BE}_{\text{EtOH}} and \text{BE}_{\text{CO}} as functions of the \text{Pd} composition, respectively. \text{BE}_{\text{EtOH}} is indicative of the first step in the EOR and may bind in a number of arrangements to a \text{Pd}_{x}\text{Au}_{y}− surface. In general, an increase in the adsorption strength with an increase in the \text{Pd} composition is observed compared to that of \text{Au}(111). In certain cases, \text{BE}_{\text{EtOH}} on \text{Pd}_{x}\text{Au}_{y}− surfaces is greater than that calculated on the \text{Pd}(111) surface. This is readily apparent because several of the \text{EtOH} binding energies for different alloyed compositions are below the pure \text{Au}(111)–\text{Pd}(111) tie line (i.e., as indicated by the dashed black line). It should be noted that \text{Au}(111) does show slight binding for the \text{Pd}–\text{Burke}–\text{Emmerhof} (PBE) functional. However, the overall trend is similar to the revised PBE (RPBE) functional that we report. Herein, and for consistency, we only show simulations for RPBE because it was previously reported to improve chemisorption energetics for the \text{Pd}(111) surfaces.\textsuperscript{61}

Interestingly, even small quantities of \text{Pd} show significantly enhanced binding energies, which are consistent with previous reports for pseudomorphic overlayers, adlayers, and monatomic high steps of \text{Pd} for a variety of different reactions.\textsuperscript{9,41,62} In addition, Figure S6a shows essentially no adsorption of \text{EtOH} on \text{Au} via the \text{O} atom in the alcohol group, suggesting that \text{Pd} is the predominate \textit{inner-sphere} adsorption site. It is worth noting that \text{Au} has been previously reported to be more active in alkaline media because of base catalysis; however, the relative magnitude of the \text{Au} activity is significantly lower than that observed on \text{Pd} or \text{Pd}_{x}\text{Au}_{y}− surfaces.\textsuperscript{83}

Figure 8a shows the average \text{BE}_{\text{EtOH}} for the different \text{Pd}_{x}\text{Au}_{y}− compositions, with error bars included for the \text{Pd}*) sites (left axis). For comparison, the onset potential (mV vs RHE) is shown (right axis) for the experimentally determined \text{Pd}_{x}\text{Au}_{y}− compositions, indicating very agreeable experimental and theoretical trends, with the lowest onset potential observed for approximately 0.50 < x < 0.80 (\text{Pd} atom %).

To further evaluate the interaction of nearest neighbors on the \text{Pd}*) or \text{Au}*) site of interest, we show the \text{EtOH} binding energy as a fraction of the surrounding atoms (i.e., ligand fraction). The fraction of surrounding neighbors is calculated as follows:

\[
\text{Ligand Fraction} = \frac{\text{no. of P atoms}}{7 \text{ atoms}}
\]

where the number of \text{Pd} atoms potentially includes the site (*) of interest as well. Figure 9a shows a linear trend of \text{BE}_{\text{EtOH}} versus ligand fraction. Interestingly, for x > 0.36, \text{BE}_{\text{EtOH}} increases more toward higher ligand fractions, whereas for x < 0.36, a wide range of binding energies over a wide range of ligand fractions are observed. This indicates that, although it is possible to achieve strong binding at low \text{Pd} atomic percentages, it is less likely. Moreover, the increase in the \text{Pd} composition increases the likelihood of strong \text{EtOH} binding and subsequent C=C bond activation. Figure 9b illustrates different ligand fractions (outlined with hexagons) for three different \text{Pd}_{x}\text{Au}_{y}− compositions. In addition to \text{EtOH} binding, we investigate the \text{H} and \text{CO} adsorption (eqs 2 and 10, 11, 12).
respectively), which are observed prior to EtOH binding, as well as the intermediate following C–C bond cleavage of the acetic acid molecule, as shown in eq 9. Figure S7 shows the average BEH and BECO for different PdAu1−x surfaces. Both the BEH and BECO quickly reach near-asymptotic values of approximately −0.6 and −1.2 eV, respectively, for x > 0.4. This is unlike EtOH binding because the Au* site starts to marginally favor CO binding with increasing Pd in the ligand fraction. Figure 9c shows CO binding energy versus ligand fraction, with a trend similar to that observed for BEH. The largest BECO values are observed for ligand fractions ≥0.5. However, the spread of BEH around ligand fractions of ~0.6 is larger than the spread of BECO. This result suggests that CO binding is less sensitive to the nearest neighbors for a given ligand fraction. Figure 9d shows that plotting BEH and BECO versus BEEtOH yields a linear relationship for Pd* sites as follows:

\[
BE_{H} (eV) = -0.18 + 2.7BE_{EtOH} (eV)
\]

\[
BE_{CO} (eV) = -0.54 + 4.27BE_{EtOH} (eV)
\]

The linearity of both H and CO with respect to the EtOH adsorption provides activity descriptors for evaluating potential catalysts for the EOR. For example, according to Figure 8, the lowest onset potential occurs for x ≈ 0.6, whereas the BEH increases with increasing Pd content. Tailoring the PdAu1−x surface to effectively bind EtOH while not overbinding CO is critical for the complete oxidation of small organic molecules. Therefore, the d-band center obtained from experiments provides a first approximation for activity in electrocatalysis.

The H- and CO-bound chemisorption descriptors provide an invaluable method for predicting EtOH binding energies, as well as a connection to the onset potential of activation. In addition, the removal of bound CO species with nearby adsorbed OH according to eq 10 is essential to complete the EOR 12e−-transfer process. This should be further explored and is the subject of a future study, with the inclusion of implicit/explicit solvation and activation barriers for the various electron-transfer steps. Combining the experimental and theoretical results with the band-structure analysis presented here will likely provide key insights into the structure–property-performance relationships underlying PdAu1−x electrodes for light-driven chemical reactions. This, in turn, could reveal and inform on other structure–property-performance relationships in these alloys, including how its optical behavior can affect the photocatalytic enhancements.

**CONCLUSIONS**

In summary, we deconvoluted the effects of the chemical composition on the structural and electronic properties of PdAu1−x alloyed films. By performing a series of systematic experiments and simulations, we determined the band structure of PdAu1−x with a range of different Pd contents (x) and identified its influence on the catalytic EOR. Our DFT calculations revealed that Pd absolutely dominates the valence-band structure of all alloys, including those that are Au-rich (where x = 0.25). In addition, the band-structure analysis provided insight into the sp and d states of the system, thereby establishing an experimental–theoretical relationship to the d-band center. The d-band center was specifically correlated with
the VBS obtained by our XPS measurements. Further, XPS and EDS measurements provided bulk and surface compositions that were compared to the coverage and electroactive Pd content derived from electrochemical measurements. The EOR was measured in alkaline media (pH = 14) using a rotating-disk-electrode hydrodynamic apparatus. The lowest onset potential was observed for Pd₈Au₋₀.₄₂, followed closely by PdₓₐAu₀.₄₋ₓ and PdₓₐAu₀.₅₇, suggesting that alloying boosted the overall reaction performance compared to the pure Pd and Au samples. The PdₓₐAu₀.₃₇ alloy yielded the largest forward-sweeping current density of ∼135 mA cm⁻² yet, the mass activity reached a maximum at ∼3.0 eV for the PdₓₐAu₀.₄₂ catalyst (i.e., a peak current activity of 639.25 A g⁻¹) because the balance between Pd and Au enhanced the activity of the Pd site(s). DFT modeling of different PdₓₐAu₋ₓ surfaces derived from XRD experiments provided insight into the role of the topmost layer’s structure—property relationship and nearest surrounding neighboring atoms. The experimentally determined onset potential trends for the different PdₓₐAu₋ₓ compositions agreed very well with the theoretically determined ETOH binding energy trends, with the lowest onset potential observed for approximately 50 < x < 85 Pd atom %. In addition, for x > 36 Pd atom %, the ETOH binding energy clusters toward higher ligand fractions, whereas for x < 36 Pd atom %, a wide range of binding energies were observed over a large portion of ligand fractions. The clustering suggested an increased probability of ETOH conversion with an increase in the Pd content; however, a balance of H and CO adsorption must be considered. The initial desorption of H could be implemented as a quick evaluation tool for determining the relative EOR activity of metallic alloys (beyond Pd–Au). Our combined experimental and theoretical work indicates that a number of activity descriptors may be utilized for future alloyed catalyst development. This, in turn, may lead to ML algorithms based on trained data sets as we outlined, with implications for further multicomponent (ternary and quaternary) alloy development.

**METHODS**

Ultrathin Pd–Au Layer Fabrication. Thin PdₓₐAu₋ₓ films were deposited on Ti disks, glass slides, and Si wafers using an AJA ATC VersaProbe III X-ray photoelectron spectrometer. Monochromated Al Kα X-rays were focused on the sample with a 100-μm-diameter spot size at a power of 25 W. A low-voltage (100 V) Ar-ion beam and a BaO electron neutralizer (1.3 V, and 20 μA) were used in tandem to compensate for surface charging, and all spectra were additionally shifted to match the adventitious C 1s peak with 284.8 eV. Elemental transitions were collected with an analyzer pass energy of 55 eV and a takeoff angle of 45°. Signals were averaged over two scans, except for the VBS, which were averaged over four scans each. The operating pressure was <5 × 10⁻⁶ Pa. The system was calibrated to Ag and Au surfaces freshly sputtered by the system’s Ar-ion gun. All spectra were analyzed and fit using MultiPak version 9.6.0.15 made by Physical Electronics Inc. Shirley background spectra of the elemental transitions were subtracted from the raw signal except for the VBS, which was maintained with any background intact.

DFT Calculations. The band-structure calculations were carried out using DFT, as implemented in the SIESTA code in a four-atom cubic supercell for PdₓₐAu₋ₓ with x = 0.0, 0.25, 0.5, 0.75, and 1.0. For all calculations, the generalized gradient approximation (GGA) of PBE was used for the exchange and correlation potentials. Norm-conserving relativistic pseudopotentials with an energy cutoff of 400 Ry and a real space mesh of 30 × 30 × 30 k points within the Monkhorst-Pack scheme were employed throughout. The positions of the atoms and unit cell were fully optimized to their equilibrium positions with a target pressure of 0 kbar, and a threshold of 0.01 eV Å⁻¹, for the forces on the atoms.

The binding energies of H, ETOH, and CO molecules on PdₓₐAu₋ₓ(111) surfaces were determined using CASTEP. The electron correlation was evaluated in the GGA with the RPBE functional. Ultrasoft pseudopotentials were chosen with a plane-wave basis set to an energy cutoff of 360 eV. The BFGS minimizer was utilized, with all geometries considered optimized when the energy per atom fell below 5.0 × 10⁻⁶ eV and the maximum force fell below 0.01 eV Å⁻¹. The binding energies were determined on 5 × 5 unit cells consisting of a variety of different PdₓₐAu₋ₓ(111) surface configurations. The 5 × 5 unit cells allowed for a thorough comparison of the different experimentally determined Pd compositions. The (111) slabs consisted of four layers with a 15 Å vacuum placed above the PdₓₐAu₋ₓ surface. The top two layers of the slab were allowed to relax during optimization, and the bottom two layers and their fractional coordinates were fixed.

Electrochemical Analysis. Electrochemical measurements were performed in a three-electrode custom-made quartz cell. Three electrodes utilized were an Ag/AgCl reference electrode, a Pt coil. The deposition rate was independently verified by measuring the step profile on Si wafer controls. Therefore, the total deposited mass was approximately 75 ± 10 μg for all PdₓₐAu₋ₓ ultrathin films on Ti electrodes with a layer thickness of ∼300 nm. The total deposited mass and layer thickness was approximately the same as those for all electrochemical studies. For spectroscopy measurements, the sample thickness was approximately 100 nm for all samples, which was independently determined to be optically thick with zero light transmission.

**EES Measurements.** The morphology of the PdₓₐAu₋ₓ thin films was imaged using a Tescan G113.3 field-emission scanning electron microscope on control Si wafer substrates. The chemical composition of the PdₓₐAu₋ₓ samples was verified by EDS and analysis of at least four different spots, with the average measured composition reported throughout.

**XRD Measurements.** High-resolution powder XRD was collected on a Rigaku Miniflex 600 diffractometer using Cu Kα (λ = 1.540598 Å) radiation from a sealed-tube X-ray source (40 kV and 15 mA) equipped with a D/teX Ultra detector. The crystalline phase identification and quantification, lattice parameter refinement, and Rietveld refinement were determined from the S–100° range scanned at 5° min⁻¹ (0.02° resolution) for ultrathin alloy metal films deposited on glass with a thickness similar to that reported for deposition on Ti substrates in the Ultrathin Pd–Au Layer Fabrication section.

**XPS Measurements.** Atomic compositions and valence-band structures were measured using a Physical Electronics Inc. VersaProbe III X-ray photoelectron spectrometer. Monochromated Al Kα X-rays were focused on the sample with a 100-μm-diameter spot size at a power of 25 W. A low-voltage (100 V) Ar-ion beam and a BaO electron neutralizer (1.3 V, and 20 μA) were used in tandem to compensate for surface charging, and all spectra were additionally shifted to match the adventitious C 1s peak with 284.8 eV. Elemental transitions were collected with an analyzer pass energy of 55 eV and a takeoff angle of 45°. Signals were averaged over two scans, except for the VBS, which were averaged over four scans each. The operating pressure was <5 × 10⁻⁶ Pa. The system was calibrated to Ag and Au surfaces freshly sputtered by the system’s Ar-ion gun. All spectra were analyzed and fit using MultiPak version 9.6.0.15 made by Physical Electronics Inc. Shirley background spectra of the elemental transitions were subtracted from the raw signal except for the VBS, which was maintained with any background intact.
counter electrode, and the different Pd$_{x}$Au$_{1-x}$ working electrodes fabricated using the PVD process previously described. The fabricated Pd$_{x}$Au$_{1-x}$ working electrode disk inserted were embedded in a poly(ether ether ketone) (PEEK) shroud to control the geometric area in contact with the solution (i.e., 0.196 cm$^2$). The embedded disks were then mounted to a PEEK shaft for stationary and rotating-disk-electrode hydrodynamic measurements. All measurements were temperature-controlled at 22 °C with water circulated through the outer jacket of the quartz cell. Prior to electrochemical measurements, N$_2$ was bubbled in solution for 20 min and then placed in the headspace to maintain the sparged solution. A sequential cycling method was developed to measure the Pd$_{x}$Au$_{1-x}$ electrodes. First, the Pd$_{x}$Au$_{1-x}$ electrodes were cycled in 1 M KOH at 200, 100, 50, 20, and 5 mV s$^{-1}$. For the 200, 100, and 50 mV s$^{-1}$ scan rates, the Pd$_{x}$Au$_{1-x}$ electrodes were cycled 25 times each, whereas for the 20 and 5 mV s$^{-1}$ scan rates, the electrodes were cycled 10 and 6 times each, respectively. The Pd$_{x}$Au$_{1-x}$ electrodes were removed from the 1 M KOH solution and placed in a N$_2$-sparged 1 M KOH with 0.5 M EtOH. The Pd$_{x}$Au$_{1-x}$ electrodes were then subjected to sequential cycling at 50, 20, and 5 mV s$^{-1}$ under stationary and rotating conditions ($\omega = 900$ rpm). For the 50, 20, and 5 mV s$^{-1}$ scan rates, the electrodes were cycled 25, 12, and 10 times each, respectively, to achieve reproducible CVs. A repeat was performed for each Pd$_{x}$Au$_{1-x}$ electrode to ensure reproducibility. In addition, both the 1 M KOH and 1 M KOH + 0.5 M EtOH solutions were refreshed after each Pd$_{x}$Au$_{1-x}$ CV to avoid possible byproduct cross-contamination. Prior to electrochemical measurements, the uncompensated solution resistance ($R_s$) was determined using electrochemical impedance spectroscopy and a circuit-fit extraction of the high-frequency real-value intercept. $R_s$ was corrected using a positive feedback compensation method. All potentials are reported versus the RHE.

**REFERENCES**


