Alloying is a powerful tool that can improve the electrocatalytic performance and viability of diverse electrochemical renewable energy technologies. Herein, we enhance the activity of Pd-based electrocatalysts via Ag-Pd alloying while simultaneously lowering precious metal content in a broad-range compositional study focusing on highly comparable Ag-Pd thin films synthesized systematically via electron-beam physical vapor co-deposition. Cyclic voltammetry in 0.1 M KOH shows enhancements across a wide range of alloys; even slight alloying with Ag (e.g. Ag0.1Pd0.9) leads to intrinsic activity enhancements up to 5-fold at 0.9 V vs. RHE compared to pure Pd. Based on density functional theory and x-ray absorption, we hypothesize that these enhancements arise mainly from ligand effects that optimize adsorbate–metal binding energies with enhanced Ag-Pd hybridization. This work shows the versatility of coupled experimental-theoretical methods in designing materials with specific and tunable properties and aids the development of highly active electrocatalysts with decreased precious-metal content.
Large-scale deployment of fuel cells (FCs) and batteries could help lower anthropogenic CO₂ emissions and create a more energy efficient society. Hydrogen FCs (H₂ FCs) are particularly interesting because H₂ is an abundant commodity already produced at a large scale as an industrial chemical feedstock (~60 Mt y⁻¹). Furthermore, H₂ FCs can reduce up to ~50% of net CO₂ emissions (relative to fossil fuel derived power) if hydrogen is produced by traditional methane reforming, and up to ~90% if hydrogen is produced by electrolysis with renewable electricity. H₂ FC vehicles are attractive for both light-duty and heavy-duty transportation as they can be refueled in minutes and provide sufficient energy density to be viable for a broad range of transportation modes including automobiles, trucks, buses, airplanes, and boats. The large overpotential required for the oxygen reduction reaction (ORR) leads to low energy efficiency and is an important factor limiting the implementation of several electrochemical renewable energy technologies such as H₂ FCs, direct methanol FCs, and metal-air batteries. Development of catalysts with improved activity, stability, and selectivity for the ORR will be necessary for the large-scale deployment of these technologies.

Based on guidelines from the U.S. Department of Energy, a large portion of H₂ FC research and development has focused on lowering catalyst cost by decreasing the Pt content in proton exchange membrane FCs. This has been done successfully by alloying and microstructuring. However, owing to the thermodynamic instability of many first and second row transition metals in acidic conditions during the ORR, further alloy-based routes towards precious-metal elimination at low pH are limited. In contrast, anion exchange membrane FCs (AEMFCs) offer a higher pH regime, enabling the stable use of less-expensive materials. Currently, one of the most active known ORR catalysts in alkaline media is Pd. Due to its high price, developing bimetallic Pd catalysts with decreased Pd content and/or higher intrinsic activity could make AEMFCs more economical. Ag shows promise as a secondary species because of its relatively low cost, high abundance, base stability, and high 4e⁻ selectivity. Furthermore, previous experimental studies have demonstrated enhancement both in Ag-based bimetals (e.g., Cu-Ag, Co-Ag, and Sn-Ag) and Ag-Pd nano-configurations and physics-based modeling has predicted enhancement for the ORR based on d-band changes. Understanding the mechanism behind alloy-based enhancement could guide the discovery of structure-activity relationships for more complicated ternary or quaternary systems.

In this work, we use a thin film model system to study the compositional dependence of intrinsic activity for the ORR on Ag-Pd catalysts. Using electrochemical cycling, atomic force microscopy, x-ray diffraction, and x-ray spectroscopies we investigate activity, surface topography, crystal structure, and solid miscibility, and composition and electronic structure, respectively. With our highly comparable layered catalysts, we demonstrate activities greater than that of pure Pd even after lowering Pd content by half. Using density functional theory together with these experimental results we probe the nature of the active site and rationalize the intrinsic activity trends seen for Ag-Pd electrocatalysts. By lowering the catalyst cost by ~50% via non-precious-metal alloying (Pd is currently ~100 times more expensive than Ag), without sacrificing overall performance, this work demonstrates an avenue for making H₂ FCs and other electrochemical devices more economical.

Results and discussion

Alloying Ag and Pd as thin films. Ag-Pd alloys have been previously synthesized and are thermodynamically stable and miscible at all compositions. Here, we synthesize a series of Agₓₗ₋ₚₓ (0 ≤ x ≤ 1) thin films (~70 nm thick) via electron-beam physical vapor deposition (PVD) and probe the crystal structure, extent of alloying, electronic structure, and topography of the as-prepared thin films with x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), x-ray absorption spectroscopy (XAS), and atomic force microscopy (AFM). Structurally, grazing incidence XRD (GI-XRD) (Fig. 1a, see full 2θ range for all Agₓₗ₋ₚₓ films in Supplementary Fig. 1a) of the pure Ag and pure Pd thin films shows strong peaks characteristic of a face-centered cubic (fcc) crystal structure with lattice parameters of a = 4.07 Å and a = 3.87 Å, respectively (see lattice data for all Agₓₗ₋ₚₓ films in Supplementary Table 1). Similar to their parent structures, the bimetallic Agₓ₋ₚₓ films have peaks corresponding to a fcc structure. Furthermore, at all compositions, the (111) peak ranges between the Ag(111) (38.30°) and Pd(111) (40.35°) peaks (Fig. 1a). The absence of two distinct (111) peaks in the bimetallic thin film diffractograms suggest that Ag and Pd are present as an alloy. Finally, the center of the (111) peak shifts linearly to higher diffraction angles as a function of increasing Pd composition. This linear shift is consistent with a decreasing lattice parameter as Pd is added to the Ag matrix. Using Vegard’s law (Fig. 1b), atomic alloy-compositions are seen to closely follow the nominal thin film composition (defined by the Ag and Pd masses as measured during evaporation), however slight deviations could suggest the presence of minor Pd-richer phases ~50% nominal Pd loading. In short, XRD analysis highlights that electron-beam PVD produces highly miscible solid solution (alloy) phases of Agₓₗ₋ₚₓ.

To probe the surface and clarify the role that composition plays in the electronic structure of the Agₓₗ₋ₚₓ alloys, we analyzed high resolution XPS (see survey spectra and XPS compositional analysis in Supplementary Figs. 3 and 4) and Pd L₃-edge XAS. As seen in Fig. 1c, the binding energy of the Ag 3d peaks shifts negatively as a function of increasing Pd content, with a maximum shift of ~1.0 eV between Ag and Agₓ₀.₉Pd₀.₁. This negative shift in the Ag 3d doublet, as a function of Pd content, has been seen previously for mixed Ag-Pd systems and has been attributed to increased charge mixing. Specifically, studies have shown that with increasing Pd content, the electron density in the Ag d-band increases, whereas the electron density in the sp-band decreases. The Pd 3d (Fig. 1d) peak positions, however, vary only by a maximum of ~0.3 eV. This small shift is in qualitative agreement with the majority of previously reported Pd 3d BE shifts in Ag-Pd alloys (mostly negative BE shifts); however, owing to instrument energy resolution it is difficult to draw trends as a function of Ag composition.

Although Pd XPS is complicated to interpret, the L₁-edge XAS of Pd has been used effectively in the literature to elucidate the charge density within Ag-Pd alloys. The small deviations from the single-particle-model for 4d metals makes the use of the L₁-edge quantitatively meaningful. Figure 1e, f (see Supplementary Fig. 5 for the full energy range plot) shows the experimental spectra and FEFF simulations of the Pd L₁-edge for several Agₓ₋ₚₓ compositions. Looking at the x-ray absorption near-edge spectra (XANES), we see that the normalized white-line (Pd L₁-edge peak) intensity decreases with increased Ag loading. This clear decrease in white-line intensity is indicative of a net shift in electron density from Ag to Pd producing a decrease of 4d-holes in Pd. Moreover, the extended region features in Fig. 1e, f shift to lower energies with increased Ag loading in agreement with an expanding lattice owing to the addition of Ag (see Supplementary Fig. 5). The observed trends in the XANES of the Pd L₁-edge (Fig. 1e) of Ag-Pd alloy thin films are well reproduced by FEFF simulations (Fig. 1f) of select Agₓ₋ₚₓ compositions (x = 1, 0.9, 0.8, 0.5, 0.2).
Together, the Ag 3d XPS and Pd L$_3$-edge XAS support a model, similar to that seen in previous Ag-Pd alloys,$^{23,22,35}$ in which the Ag and Pd d-bands become more filled as each metal dilutes the other. According to the d-band theory description of metal-adsorbate interactions, this change in d-band electron density has important catalytic implications that will be described further below.

Finally, AFM (Supplementary Fig. 6 and Supplementary Table 2), indicates that the surfaces of the as-prepared Ag$_{1-x}$Pd$_x$ thin films are very flat with roughness factors ≤1.02 at all compositions. This highly uniform surface morphology, regardless of composition, suggests that the geometric surface area is approximately equal to the exposed catalyst surface area for all films. Altogether, this in-depth physical characterization of the as-prepared Ag$_{1-x}$Pd$_x$ bimetallic thin films indicates that these materials have highly comparable, smooth surfaces. Furthermore, the unique electronic and physical properties as a function of Ag alloying with Pd, particularly the increase in d-band electron density and lattice expansion, motivates the investigation of their intrinsic catalytic activity for the ORR.

**Intrinsic ORR activity enhancement with Ag$_{1-x}$Pd$_x$ alloying.**

The development of effective design principles for new materials requires characterizing and understanding the complexities and mechanisms behind activity enhancements. Using cyclic voltammetry (CV), we investigated the ORR activity as a function of alloy composition by cycling (20 mV s$^{-1}$) various Ag$_{1-x}$Pd$_x$ thin films in 0.1 M KOH using a rotating disk electrode (RDE, 1600 rpm) (Fig. 2a and Supplementary Fig. 7). As seen in Fig. 2a and Supplementary Fig. 7, mass transport limited current densities are ~−6 mA cm$^{-2}$, indicating all compositions are selective to the four electron transfer pathway to $\text{OH} \; (< 0.5\% \; \text{H}_2\text{O}_2 \; (\sim 3.98)$ above 0.3 V vs. the reversible hydrogen electrode (RHE) verified by rotating ring disk electrode and Koutecký–Levich (KL) selectivity measurements on Ag$_{1-x}$Pd$_{0.9}$, see Supplementary Figs. 8 and 9, respectively$^{14,16,37}$. The ORR polarization curves for pure Ag and pure Pd thin films are consistent with those of previous studies showing onset potentials at ~−0.1 mA cm$^{-2}$) ~0.83 V and 0.96 V vs. RHE, respectively$^{14,17,38,39}$. Furthermore, CV profiles in N$_2$-purged electrolyte for pure Ag and Pd exhibit the redox features expected based on studies of single crystals and polycrystalline electrodes$^{17,21,40,41}$. The bimetallic Ag$_{1-x}$Pd$_x$ thin films demonstrate a combination of these features (Supplementary Fig. 10). Figure 2a shows representative ORR voltammograms (with O$_2$-saturation) for the Ag$_{1-x}$Pd$_x$ thin films, where $x =$ 0, 90, and 100. From this voltammetry we see that the highest performing composition, Ag$_{0.1}$Pd$_{0.9}$, has a very similar profile to the Pd control, indicating similar selectivity and reaction mechanism. However, this alloy outperforms both parent materials, on average, by a ~20 and ~55 mV lower overpotential,
Fig. 2 Electrochemical ORR evaluation of Ag-Pd thin film alloys. 

**a** Select ORR polarization curves for representative Ag, Pd, and Ag₀.₆Pd₀.₄ thin films. 

**b** Onset potential (bars) (potential at −0.1 mA cm⁻²), Tafel slope (circles), and specific activity (kinetic current density at 0.9 V vs. RHE normalized by surface roughness determined by AFM) on an absolute (black circles) and Pd fraction-normalized (color-mapped triangles) bases for all Ag₁₋ₓPdₓ compositions investigated. Measurements were taken at 1600 rpm in 0.1 M KOH, saturated 0.1 M KOH, have non-ORR current subtracted (from CVs in N₂-purged electrolyte), and are corrected for the uncompensated electrolyte series resistance. All data points are representative of the average value from the cathodic and anodic scan of the third CV cycle and error bars are the standard deviation from measurements with separate samples (see Supplementary Figs. 7, 11, 12 and Supplementary Table 3 for representative ORR CV curves, kinetic current densities at 0.9 and 0.8 V vs. RHE, representative Tafel plots, and tabulated data, respectively). The colors refer to the nominal Pd loading, consistent with the text labels in the figure.

**c** Select ORR polarization curves for representative Ag, Pd, and Ag₀.₆Pd₀.₄ thin films. 

The Tafel slope analysis of kinetic current densities further supports this site enhancement hypothesis (Fig. 2b, circles). Specifically, there is a striking decrease in Tafel slope, commensurate with the appearance of specific activity enhancements, from −90−100 mV dec⁻¹ (Ag-like) to −40−60 mV dec⁻¹ (Pd-like) at Pd compositions of 40 at% or greater. Although the exact mechanistic change(s), leading to the observed differences in Tafel slope are difficult to pinpoint by Tafel analysis alone due to the multi-step nature of the ORR, this suggests intrinsic changes in the structure of the active site, the rate-limiting step, and/or the adsorbates are responsible for the observed enhanced ORR kinetics on the medium-to-high Pd content films. The observed activity enhancements (specific activity at 0.9 V and 0.8 V vs. RHE) are only seen in the electrocatalysts with Tafel slopes similar to that of pure Pd. This could suggest a reaction mechanism similar to that of pure Pd, but in which Pd-based active sites are being enhanced by Ag atoms within the lattice via ligand and/or strain effects.

In contrast to the medium-to-high Pd content catalysts, the films with ≤30 at% Pd show performance greater than that of pure Ag, but specific activities less than the linear combination of
Ag and Pd activities at 0.8 V (or 0.9 V) vs. RHE. This suggests no overall synergistic effect between Ag and Pd at this low-Pd-content regime. Normalizing by Pd loading suggests that at this high-Ag-content compositional regime Pd atoms are playing an important role and are behaving as they do in their pure metal form (following an approximately linear activity-composition relationship). Moreover, Tafel slope analysis suggests that the reaction mechanism on the low-Pd-loading films is similar to that of pure Ag and supports the hypothesis that Ag is involved in the active site at this compositional regime. Despite no enhancement beyond the linear combination of Ag and Pd activities at this low-Pd-content regime, specific activity, and Tafel slope analyses suggest that both Ag and Pd are playing a role in increasing the overall performance above that of Ag. The composition-dependent role of Ag and Pd in modulating the ORR activity of Ag-Pd alloys will be described in the next section.

Post-reaction characterization of composition, structure, and surface smoothness suggests that the catalyst surface does not significantly change due to ORR testing on the timescale of our electrochemical measurements (see Supplementary Figs. 1, 4, 16, 14, and Supplementary Tables 1 and 2)\(^47\). This suggests that the ex situ material properties can be meaningfully related to the activity trends, however, in operando physical characterization would be necessary to confirm the exact state of the catalyst surface during reaction. Most notably, the fact that surface smoothness did not change after ORR testing suggests that there was negligible surface restructuring (within AFM detection limits), an effect often associated with roughening\(^48\). To probe stability, we performed a chronoamperometry (CA) experiment at 0.8 V vs. RHE, for 2 hrs (Supplementary Fig. 14a), for our best-performing composition, Ag\(_{0.1}\)Pd\(_{0.9}\), and observed a decrease in the ORR geometric current density of ~40%. We hypothesize that this decrease in performance, which we find to be recoverable, could be due to carbon uptake from corrosion of the graphite rod counter electrode, as well as possible Pd and/or Ag partial surface oxidation; the latter (oxidation) is in fact one of the main sources of decreased performance in similarly high performing Pt-based ORR catalysts\(^49\). ORR CVs pre- and post-CA testing (Supplementary Fig. 14b) support this hypothesis, as 100% of the initial (pre-CA) performance is recovered by cycling the working electrode down to ~0.2 V vs. RHE to reductively clean off any accumulated carbon and/or surface oxide on the film's surface. Additionally, using angle resolved (AR)-XPS (Supplementary Fig. 14c), to attain increased surface sensitivity, together with depth profiling (Ar\(^+\) sputtering, Supplementary Fig. 14d), we find that the composition of the film did not change significantly as a function of depth after stability testing\(^47,50\). Altogether, our stability testing and post-ORR in-depth characterization indicate that there is no irreversible intrinsic material or performance degradation on the timescale of our experiments, supporting the hypothesis that any trends in activity are related to intrinsic differences in material surface electronic structure rather than differences in catalyst morphology or any instabilities. Possible enhancement mechanisms for tuning the oxygen adsorbates binding energies correlated with these enhancements will be discussed in the next section.

Pure Pd catalysts have been noted among the most active materials for the ORR in alkaline media\(^12,13\). Here, we have shown that by alloying Ag with Pd we can both decrease the Pd content by 50% without activity loss and enhance the intrinsic activity of Pd five-fold, yielding high performing state-of-the-art ORR electrocatalysts. Supplementary Table 4 compares the specific activity (normalized by a physically representative exposed catalyst surface area) at 0.9 V vs. RHE of our best-performing thin films to representative state-of-the-art electrocatalysts for the ORR in 0.1 M KOH (or similar) using a RDE setup. Notably, our Ag\(_{0.1}\)Pd\(_{0.9}\) alloy thin film electrocatalyst is among the most intrinsically active catalysts for the ORR in alkaline media yet reported when normalizing by exposed catalyst surface area. Although out of scope from this work, the high performance of the medium-to-high Pd content Ag-Pd alloys motivates future studies of this ideal catalyst system within FC systems.

**Electronic effects on ORR activity from alloying Ag and Pd.** Based on the d-band model, which describes metal-adsorbate orbital hybridization, it is largely understood that there is an optimal \(*\text{OH}^*/\text{OOH}^*\) binding energy for ideal ORR catalysts\(^51-54\). Ag binds oxygen adsorbates too weakly, while Pd binds them too strongly\(^54,55\). Hence, the alloying of Ag and Pd might lead to more optimal catalysts, with stronger Ag- or weaker Pd-adsorbate binding\(^24,53-55\). Using density functional theory (DFT) we can investigate the theoretical activity for the ORR as a function of Ag-Pd structure and composition. Therefore, a complementary theoretical study was undertaken to gain a fundamental understanding of the nature of the active sites and trends in activity to rationalize the experimental observations, namely the physical and electronic properties and the enhanced ORR activity on Ag-Pd alloys compared with their pure components. First, we identify the composition of the most active sites and then determine the role of strain (tensile or compressive) and ligand (hybridization) effects, both of which can arise from alloying, in modulating the electronic structure within these active sites. We consider a variety of Ag-Pd (111) configurations representative of the synthesized materials (Fig. 3a), as well as all possible active sites, to deconvolute strain from ligand effects. We evaluate activity based on the calculated thermodynamic limiting potential for the ORR (U\(_{\text{L}}\))\(^56\), which is dependent on the surface binding energies of reacting oxygen adsorbates (Fig. 3b).

In Ag-Pd alloys, the absolute strain, seen by changes in bond lengths, on each atom (Ag or Pd) changes as a function of the Ag-Pd ratio. This is because, as seen by XRD (Fig. 1a), Pd has a smaller lattice constant than Ag. As a function of this difference in lattice parameter, Pd and Ag atoms will be under increased tensile or compressive strain that strengthens or weakens the adsorption energy of reaction intermediates as a function of Pd content, respectively. Therefore, strain would only lower the activity of pure Ag- or Pd-like active sites (we show a quantitative example of this in Supplementary Fig. 15a). Based on this traditional understanding of strain effects, we would expect no enhancement in activity for the Ag-Pd system. However, there are additional electronic effects to consider for active sites that share electrons locally. To model the activity of Ag-Pd alloys resembling the experimental Ag-Pd thin films, the ORR \(U_{\text{L}}\) was calculated for the Ag\(_{0.1}\)Pd\(_{0.9}\), Ag\(_{0.3}\)Pd\(_{0.7}\), and Ag\(_{0.5}\)Pd\(_{0.5}\) structures (structures (iv)–(vi) in Fig. 3a). Our calculations suggest that the most active (lowest energy) sites for the Ag\(_{0.3}\)Pd\(_{0.7}\) and Ag\(_{0.5}\)Pd\(_{0.5}\) surfaces are Pd–Pd bridge sites, whereas the active site for Ag\(_{0.1}\)Pd\(_{0.9}\) is the Pd–Ag bridge site. The theoretical activity results for these alloy structures, as well as for Pt(111), Pd(111), and Ag(111) are shown in Fig. 3b. The limiting potentials for Pt(111) and Pd(111) are 0.80 V and 0.79 V, respectively. The limiting potentials for Ag\(_{0.1}\)Pd\(_{0.9}\) and Ag\(_{0.3}\)Pd\(_{0.7}\) are 0.83 V and 0.82 V, respectively, and are slightly higher than for pure Pd(111) indicating enhancement of the Pd–Pd bridge sites in medium-to-high Pd content Ag-Pd alloys. The \(d\)-projected density of states analysis (see Supplementary Fig. 16) for the structures in Fig. 3a illustrates that the slightly lower d-band edge relative to the Fermi level observed for Ag\(_{0.3}\)Pd\(_{0.7}\) and Ag\(_{0.5}\)Pd\(_{0.5}\) compared with Pd(111) results in a weaker oxygen adsorption on Pd atoms and consequently an
increase in activity. As illustrated by the Pd L$_3$-edge XANES measurements (Fig. 1e) discussed earlier and the calculated Pd effective Bader charge (Supplementary Table 6), this change in Pd d-band arises from the increased filling of Pd 4$d$-holes upon charge hybridization between Ag and Pd. Therefore, we hypothesize activity enhancements on medium-to-high Pd content electrocatalysts are likely due to ligand effects, specifically optimal charge redistribution between Ag and Pd. Furthermore, the presence of an increased number of active Pd−Pd bridge sites may explain why the experimental activity increases with Pd content despite Ag$_3$Pd$_1$(111) being slightly more theoretically active than Ag$_3$Pd$_1$(111).

Considering the Ag-rich compositional regime, the calculated limiting potential for the ORR on Ag$_3$Pd$_1$(111) (0.72 V) improved relative to Ag(111) but does not reach the enhancement observed in the Ag$_2$Pd$_2$(111) and Ag$_3$Pd$_3$(111) surfaces. To consider strain effects on the predicted mixed-metal active site for structures with <50 at% Pd, we calculated the $U_l$ of Ag$_3$Pd$_1$(111) surface with a trapped single Pd atom (Pd$_{atom}$−Ag) (structure (ii) in Fig. 3a). The calculated $U_l$ of Pd$_{atom}$−Ag is 0.63 V, indicating a slight increase in activity compared to pure Ag (111) with a $U_l$ of 0.61 V. For this system, the ORR $U_l$ increases with compressive strain (lattice contraction weakens adsorbate binding), indicating that the Pd$_{atom}$−Ag site lies on the strong binding side of the ORR volcano, as shown in Fig. 3b. With a compressive strain of 5%, Pd$_{atom}$−Ag (−5%) shows a calculated $U_l$ of 0.80 V (see Supplementary Figs. 15b and 17a); tensile strain (lattice expansion), on the other hand, leads to a significant decrease in $U_l$. Ag$_3$Pd$_1$(111), specifically, has an active site similar to Pd$_{atom}$−Ag(−2%) ($U_l$ of 0.66 V), and compressive strain (relative to Ag(111)) arising from the addition of Pd could partly lead to a higher $U_l$, but strain alone does not explain the higher $U_l$ for Ag$_3$Pd$_1$(111) compared with Pd$_{atom}$−Ag(−2%). Therefore, ligand effects are likely also playing a role in increasing the $U_l$ of Ag$_3$Pd$_1$(111). Consequently, we conclude that the increased $U_l$ for the Ag$_3$Pd$_1$(111) structure is due to the intrinsic electronic interactions between Ag and Pd at such Ag-rich compositions, as well as strain on the Ag−Pd site. However, as suggested by the specific activity of the low-Pd-loading thin films not reaching the linear combination of their parent materials’ activity, the charge hybridization of Ag and Pd, as well as compressive strain, have a suboptimal effect at this compositional regime. Altogether, the DFT calculations on Ag-Pd structures of different composition agree well with the activity enhancement observed in Ag-Pd thin films with medium-to-high Pd-loading, and the lack of synergistic enhancement (but still higher activity than pure Ag) at lower Pd loadings.

Overall, DFT results on mixed-metal structures along with the experimentally observed specific activities for the ORR suggest that the most likely mechanism for activity enhancement is the electronic structure tuning of Pd−Pd active site induced by the surrounding bonding environment (ligand effects) in medium-to-high Pd content Ag-Pd alloys. For the thin films with low-Pd loading, there is still an increase in limiting potential and onset potential for the ORR relative to pure Ag, but the specific activity is less than the expected linear combination of Ag and Pd activities. Therefore, we can conclude that the Ag-Pd electronic interactions at this low-Pd-loading regime do not enhance ORR activity. Correlating the DFT, XPS, and Pd L$_3$-edge XANES results for the Ag-Pd alloy thin films, the observed activity enhancements for films with ≥40 at% Pd are attributed to electronically enhanced active Pd−Pd sites, which we hypothesize have optimized Pd and Ag d-band filling and center.

In conclusion, Ag$_1$Pd$_{40}$ thin films, with 0 ≤ x ≤ 1, were synthesized by electron-beam PVD. XRD and XPS measurements indicate that the metals alloyed, and the films were created with the intended nominal composition, which remained approximately constant after electrochemical testing. In alkaline conditions, the ORR activity of the thin films with ≥40 at% Pd loading surpassed the linear combination of Ag and Pd activities. In addition to very high activity, Ag$_3$Pd$_{80}$ exhibited the most enhanced ORR intrinsic specific activity, on both an exposed catalyst surface area and Pd content bases. Overall enhancements over pure Pd were found down to 50 at% Pd loading, with the intrinsic activity of these films (50–100 at% Pd) among the highest recorded. Based on experimental results and DFT

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**Fig. 3 DFT-calculated ORR activity on Ag-Pd active site motifs.** a Ag-Pd active site models investigated by DFT for their effect on ORR activity: (i) Ag, (ii) Pd$_{atom}$−Ag, (iii) Pd, (iv) Ag$_2$Pd$_1$, (v) Ag$_3$Pd$_2$, and (vi) Ag$_3$Pd$_3$. All the considered surfaces are (111) facets. The identified most active sites are: (i) Ag$_{top}$, (ii) Ag-Pd, (iii) Pd-Pd, (iv) Ag-Pd, (v) Pd-Pd, and (vi) Pd$_{atom}$ Pd. b Oxygen reduction reaction (ORR) activity map showing overpotentials (vs. the computational hydrogen electrode) for various Ag−Pd structures calculated by DFT. $\eta = 1.23 \text{ V} − U_l$. (The ORR $U_l$ is defined as the highest potential at which all the reaction steps become downhill in energy. Lower $\eta$ or higher $U_l$ indicate improved theoretical ORR activity). See Supplementary Figs. 15–17 and Supplementary Tables 5 and 6 for more details about strain effects, projected density of states, and the tabulated data.
calculations, the observed activity enhancements are mainly attributed to electronically enhanced Pd–Pd active sites leading to improved oxygen binding energies. In this study, we leverage the interplay between alloying, electronic structure, and catalytic activity and provide a platform to tune the local active site using a 224 eV pass energy, and high-resolution spectra were obtained using a 55 eV pass energy equipped with Al Kα radiation (1486 eV). Survey spectra were collected employing a 224 eV pass energy, and high-resolution spectra were obtained using a 55 eV pass energy, and the projector-augmented wave method as implemented in the Vienna Ab-initio Simulation Package (VASP version 5.4.4)95. Pure Ag and Pd surfaces were modeled as five–layer (3 × 3) (111) fcc slabs with RPBE optimized lattice constants of 4.219 Å and 3.989 Å, respectively. The Brillouin zone was sampled with a (3 × 3 × 1) Monkhorst–Pack grid.72 Ag-Pd systems were modeled as five–layer (2 × 2) (111) fcc slabs with optimized lattice constants of Ag-Pdδ (4.161 Å), Ag-Pdγ (4.104 Å), and Ag-Pdα (4.047 Å) and the Brillouin zone was sampled with a (4 × 4 × 1) Monkhorst–Pack grid. In all of the slabs, the bottom three layers were constrained at the bulk positions, whereas the top two layers and the adsorbed species were fully relaxed. The slabs were separated in the perpendicular z direction by 15 Å of vacuum, and a dipole correction was applied. The electronic convergence criterion was 10−5 eV, whereas the force criterion for geometry relaxation was 0.05 eV Å−1 for all forces.

Catalytic activities of the different surface structures were evaluated based on the thermodynamic limiting potential for ORR (Uo), versus the computational hydrogen electrode (CHE), defined as the highest potential at which all the reaction steps become exergonic by assuming an association reaction mechanism with •OOH, •O, and •OH as reaction intermediates.94,95 The adsorption free energies, ΔEads, of the adsorbates are calculated as ΔEads = ΔE + ΔZPE − TΔS, where ΔE is the difference in zero-point energies, and ΔZPE is the difference in zero-point energies, and ΔS is the change in entropy of the adsorbed species with respect to the catalyst surface, H2(g), and H2O(g). The (ΔZPE − TΔS) value was taken from an earlier publication96 and subsequently added to all the adsorption calculations. The difference between the equilibrium potential of U = 1.23 V and the limiting potential is referred as the theoretical overpotential (η), i.e., η = 1.23 V − U. (See Supplementary DFT Methodology Notes for further details about our DFT methods).

FEFF XANES simulations. Pd L2-edge XANES simulations were obtained by FEFF 9.86 using the RPA screening approximation and Hedin–Lundqvist exchange-correlation potential for an SCF calculation with a cluster of 7 Å, whereas the size of the cluster for the FMS calculation was 9 Å.43 Conversion was checked both for SCF (from 5 Å to 8 Å) and for FMS (from 6 Å to 10 Å) and a total broadening of 3 eV was used. In order to take into account both the crystal structure expansion and the Ag:Pd atomic ratio, the model for the simulation consists of 1 × 1 × 5 supercells built from the experimental fcc structures for Pd (a = 3.872 Å; ICSD-64918), Ag, and Pdδ (a = 3.911 Å; ICSD-605664), Ag, and Pdδ (a = 3.933 Å; ICSD-197455), Ag, and Pdδ (a = 4.029 Å; ICSD-181301), and Ag, and Pdδ (a = 4.038 Å; ICSD-197458) where the Ag:Pd atomic ratio was adjusted accordingly.

Data availability
All raw data plotted in this work can be accessed on figshare.com through DOI https://doi.org/10.6084/m9.figshare.13049321. Source data are provided with this paper.

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Competing interests

The authors declare no competing interests.

Additional information

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