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# Unifying Concepts in Electro- and Thermocatalysis toward Hydrogen Peroxide Production

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**ABSTRACT:** We examine relationships between  $H_2O_2$  and  $H_2O$  formation on metal nanoparticles by the electrochemical oxygen reduction reaction (ORR) and the thermochemical direct synthesis of  $H_2O_2$ . The similar mechanisms of such reactions suggest that these catalysts should exhibit similar reaction rates and selectivities at equivalent electrochemical potentials ( $\bar{\mu}_i$ ), determined by reactant activities, electrode potential, and temperature. We quantitatively compare the kinetic parameters for 12 nanoparticle catalysts obtained in a thermocatalytic fixed-bed reactor and a ring—disk electrochemical rate constants and transfer coefficients, which informed mixed-potential models that treat each nanoparticle as a short-circuited electrochemical cell. These models require that the



hydrogen oxidation reaction (HOR) and ORR occur at equal rates to conserve the charge on nanoparticles. These kinetic relationships predict that nanoparticle catalysts operate at potentials that depend on reactant activities (H<sub>2</sub>, O<sub>2</sub>), H<sub>2</sub>O<sub>2</sub> selectivity, and rate constants for the HOR and ORR, as confirmed by measurements of the operating potential during the direct synthesis of H<sub>2</sub>O<sub>2</sub>. The selectivities and rates of H<sub>2</sub>O<sub>2</sub> formation during thermocatalysis and electrocatalysis correlate across all catalysts when operating at equivalent  $\overline{\mu}_i$  values. This analysis provides quantitative relationships that guide the optimization of H<sub>2</sub>O<sub>2</sub> formation rates and selectivities. Catalysts achieve the greatest H<sub>2</sub>O<sub>2</sub> selectivities when they operate at high H atom coverages, low temperatures, and potentials that maximize electron transfer toward stable OOH\* and H<sub>2</sub>O<sub>2</sub>\* while preventing excessive occupation of O–O antibonding states that lead to H<sub>2</sub>O formation. These findings guide the design and operation of catalysts that maximize H<sub>2</sub>O<sub>2</sub> formation, and these concepts may inform other liquid-phase chemistries.

# 1. INTRODUCTION

Interest in H<sub>2</sub>O<sub>2</sub> production has grown in recent years because this oxidant may supersede the use of chlorine in selective oxidations, disinfection, and bleaching applications, which would reduce the formation of environmentally hazardous chlorinated wastes.<sup>1-4</sup> Traditionally, industries manufacture H<sub>2</sub>O<sub>2</sub> through the anthraquinone autoxidation process, but two emerging methods include the thermocatalytic direct synthesis reaction  $(H_2 + O_2 \rightarrow H_2O_2)$  and the electrocatalytic two-electron oxygen reduction reaction  $(2H^+ + 2e^- + O_2 \rightarrow$  $H_2O_2$ ). Metal nanoparticles can catalyze both reactions in aqueous solutions in either neutral or acidic media (pH  $\leq$ 7), but rates for both pathways increase with the activity of protons (i.e., the rates are greater at low pH).<sup>5,6</sup> The electrochemical literature agrees that the oxygen reduction reaction (ORR) occurs through heterolytic proton-coupled electron transfer.<sup>7</sup> Researchers of the direct synthesis of H<sub>2</sub>O<sub>2</sub> have not reached a consensus on the mechanism for thermocatalytic H<sub>2</sub>O<sub>2</sub> formation. Most studies of direct synthesis propose homolytic surface reaction mechanisms that involve chemisorption of H<sub>2</sub> and O<sub>2</sub> to a metal surface and sequential addition of  $H^*$  to  $O_2^*$  (where \* denotes an

adsorbed intermediate).<sup>8–10</sup> Wilson et al. proposed that the solvent mediates the reduction of  $O_2$  into  $H_2O_2$  and  $H_2O$  through proton–electron transfer (PET) steps that resemble the electrochemical ORR.<sup>11</sup> Specifically, that work suggested that  $H_2O$  heterolytically oxidizes H\* to generate protons (H<sup>+</sup>) and electrons (e<sup>-</sup>), which transfer to  $O_2^*$  and  $O_2^*$ -derived intermediates bound to the same nanoparticle. Recent work corroborates the involvement of PET steps in these reactions through a combination of detailed rate measurements and *ab initio* calculations.<sup>12</sup> From an electrochemical perspective, these coupled heterolytic oxidation and reduction reactions resemble a short-circuited hydrogen fuel cell, in which a single metal nanoparticle cocatalyzes the hydrogen oxidation reaction

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Figure 1. (a) The proposed series of elementary steps for  $H_2O_2$  and  $H_2O$  formation during direct synthesis on metal nanoparticles, which decouples the electrochemical hydrogen oxidation and oxygen reduction reactions proposed in the electrocatalytic literature. (b) A visual representation of the proposed mechanism for the simultaneous occurrence of the HOR and ORR on a single catalytic nanoparticle.

(HOR) at rates that balance the quantity of  $H^+$  and  $e^-$  required for the ORR.

Figure 1 shows the series of elementary steps for the thermocatalytic reduction of  $O_2$ , which includes adsorption, desorption, and heterolytic processes, also found in the electrocatalytic HOR (steps 1–3) and ORR (steps 4–13).<sup>13</sup> This scheme predicts a fundamental connection between the direct synthesis reaction and the HOR and ORR. Further, the similarities between these mechanisms imply that a given catalyst (e.g., carbon-supported metal nanoparticles) should provide identical rates and selectivities in thermocatalytic and electrocatalytic reactors at equivalent electrochemical potentials ( $\overline{\mu}_i$ ). In other words, the rates and selectivities of H<sub>2</sub>O<sub>2</sub> formation are controlled by either adjusting the chemical potential ( $\mu_j$ ) of the reactant species (j) or applying an electrical potential ( $\phi$ ) from an electrode to achieve a given value for  $\overline{\mu}_i$ :<sup>14</sup>

$$\overline{\mu}_{j} = \mu_{j} + z_{j} F \phi \tag{1}$$

Here,  $z_j$  is the charge of species j and F is Faraday's constant. In comparison, the chemical potential  $(\mu_j)$  takes the functional form<sup>14</sup>

$$\mu_{j} = \left(\frac{\partial G}{\partial n_{j}}\right)_{T,P,n_{j}} = \mu_{j}^{0} + \text{RT} \ln\left[j\right]$$
(2)

where G represents the Gibbs free energy of the system,  $n_j$  is the total number of species j,  $\mu_j^0$  is the standard state chemical potential of species j, R is the universal gas constant, T is the temperature (K), and [j] is the thermodynamic activity of species j.

In both thermocatalytic and electrocatalytic systems, values of  $\overline{\mu}_j$  provide one method to control reaction rates. For the ORR, investigators have deposited catalytic materials onto an electrode surface and characterized the electrode potential ( $\phi$ ) required to drive the reaction. Here, the measured currents reflect the rate of reaction on the catalyst. As the value of  $\phi$  decreases (i.e., is made more negative), the electrode provides a greater driving force to provide electrons to the catalyst for Faradaic reactions, which lowers the apparent activation barriers to reduce oxygen.<sup>15</sup> For direct synthesis, however, investigators have manipulated reaction rates by changing the temperature (*T*) or chemical potential ( $\mu_i$ ), adjusted by hydrogen and oxygen pressures ([H<sub>2</sub>], [O<sub>2</sub>]).<sup>11,13,16</sup>

Therefore, researchers can control the electrochemical potential  $(\overline{\mu}_i)$  through an infinite number of combinations of  $\phi$ , T, and [j]. This understanding provides opportunities to examine the processes depicted in Figure 1 through established methods and analyses used within the thermocatalysis and electrocatalysis communities and, in doing so, connect these disciplines. Oxygen reduction and hydrogen oxidation reactions provide an excellent foundation to examine these concepts, because the reaction network involves only two reactants  $(H_2, O_2)$  and two products  $(H_2O, H_2O_2)$ , and their reaction rates are readily measured. If these reactions are inherently linked, as is hypothesized, then the vast literature on the ORR and HOR would inform catalyst design and reaction engineering principles for the direct synthesis of H<sub>2</sub>O<sub>2</sub>. These insights would also enable the translation of high-throughput catalyst synthesis and screening methods developed within the electrochemical community to develop high-performance materials for thermocatalytic  $H_2O_2$  formation.

Here, we explore the similarities and differences between electrocatalysis and thermocatalysis through the reduction of O<sub>2</sub> and the oxidation of H<sub>2</sub>. First, Koutecky–Levich and Butler–Volmer analyses were used to extract intrinsic rate constants ( $k^0$ ) and transfer coefficients ( $\alpha$ ) for the ORR and HOR across a library of 12 Pd- and Pt-based bimetallic catalysts. Two models, each with distinct assumptions and inequivalent levels of molecular detail, were evaluated using measured kinetic parameters ( $k^0$  and  $\alpha$ ). These models predict the steady-state operating potential of catalytic nanoparticles (treated as electrode surfaces) during the ostensibly thermocatalytic production of H<sub>2</sub>O<sub>2</sub>. The first model builds upon the Butler-Volmer equation and assumes that each catalytic nanoparticle simultaneously performs the HOR and the ORR at equal potentials and with reaction rates constrained by mass and charge conservation. The second model expresses steady-state rates for O<sub>2</sub> reduction and H<sub>2</sub> oxidation, which depend on the rate constants of elementary reactions and the coverages of reactive species on the nanoparticle surface (Figure 1). Overall, the coupled heterolytic reactions between hydrogen and oxygen-derived intermediates lead to differences in operating potentials that reflect differences between the charge transfer coefficients and barriers for their respective kinetically relevant steps. Insight from these models reveals the parameters that affect O<sub>2</sub> reduction rates and selectivities (e.g., toward H<sub>2</sub>O<sub>2</sub>) in both thermal and electrocatalytic reactors. Notably, this analysis shows that the different hydrogen and oxygen activities can lead to the formation of selective surface structures (e.g.,  $\beta$ -PdH<sub>x</sub>) that do not form under typical electrochemical ORR measurements. Similarly, each catalyst displays potentialdependent H<sub>2</sub>O<sub>2</sub> selectivities in electrochemical measurements, for which their maxima are often inaccessible at the  $H_2$  and  $O_2$ pressures used during thermocatalytic measurements.

Electrode measurements of Au, PdAu, and PtAu materials show similar ORR kinetic parameters, while the Pt and Pd materials show much greater HOR rates (PtAu > PdAu ≫ Au). Analogous thermocatalytic measurements show similar  $H_2O_2$  selectivities at equivalent values of  $\phi$ , but the presence of Pt or Pd results in significantly greater steady-state reaction rates (PtAu > PdAu  $\gg$  Au). These observations suggest that heterolytic hydrogen oxidation rates determine the rate of electron transfer within the thermochemical system. From these observations, it is not surprising that H<sub>2</sub>O<sub>2</sub> selectivities measured under thermochemical and electrochemical conditions agree closely when catalyst nanoparticles operate at identical electrode potentials ( $\phi$ ) and similar coverages of reactive species. Overall, these findings establish tangible connections between principles common within the heterogeneous catalysis and electrocatalysis communities, provide reaction engineering strategies to maximize selectivities toward H<sub>2</sub>O<sub>2</sub>, and suggest that electrochemical techniques may enable the screening of catalysts for thermocatalytic reactions.

#### 2. EXPERIMENTAL METHODS

2.1. Catalyst Preparation. Catalytic nanoparticles were formed upon activated carbon (Vulcan XC-72, pellets, Cabot Corporation) by strong electrostatic adsorption (Pd, PdNi, PdZn, PdCu, PdCo, Pt, PtCo, or PdPt),<sup>11</sup> incipient wetness impregnation (Au),<sup>1</sup> and electroless deposition methodologies (PdAu<sub>60</sub>, PtAu<sub>60</sub>, PtAu<sub>15</sub>, PtAu<sub>5</sub>). Strong electrostatic adsorption involved the addition of Vulcan XC-72 (5 g) to 270 cm<sup>3</sup> of deionized (DI) water (17.8 M $\Omega$ cm), to which 30 cm3 of 14.5 M NH4OH (Macron, 30 wt %) was added to increase the pH to a value of  $\sim$ 11. The metal nitrate precursors were dissolved in 30 cm<sup>3</sup> of DI water and then added to the catalyst slurry. The Vulcan XC-72 was added to a mass of metal nitrate that would provide a 1 wt % loading of metal on the support (details are provided in Section S1 of SI). These mixtures were stirred intermittently for 12 h and then decanted, after which the solids were filtered and then dried at 333 K in a vacuum oven for 12 h. The dried materials were later heated to 973 K at 10 K min<sup>-1</sup> and then held at 973 K for 4 h in a flowing mixture of 20 kPa of H<sub>2</sub> and 81 kPa of He (100 cm<sup>3</sup> min<sup>-1</sup>; Airgas, 99.999%) with the intent to reduce the adsorbed metal precursors and form metallic nanoparticles. After reduction, each sample was cooled to ambient temperature and

passivated for 1 h by exposure to a flowing mixture of 2 kPa of  $O_2$ , 10 kPa of  $N_2$ , and 89 kPa of He (100 cm<sup>3</sup> min<sup>-1</sup>; Airgas, 99.999%).

The incipient wetness impregnation involved the addition of 15 cm<sup>3</sup> of a 5–60 mM HAuCl<sub>4</sub> solution in DI water, which was added dropwise to 10 g of the Vulcan XC-72 support. Specifically, HAuCl<sub>4</sub> was added to the Vulcan XC-72 to yield 0.25%, 0.75%, and 3 wt % loadings of metal on the support. The incipiently wet support was first washed with 300 cm<sup>3</sup> of a 30 wt % aqueous NH<sub>4</sub>OH solution with the intent to precipitate Au(OH)<sub>3</sub> in the pores of the support. The material was then washed with 300 cm<sup>3</sup> of deionized water to remove trace ions and vacuum-filtered overnight at 298 K. The precursor material was later heated to 393 at 10 K min<sup>-1</sup> and held at 393 K for 4 h in a flowing mixture of 20 of kPa H<sub>2</sub> and 81 kPa of He (100 cm<sup>3</sup> min<sup>-1</sup>; Airgas, 99.999%) to produce metallic nanoparticles.

The electroless deposition involved the addition of Pt and Pd salts onto the Au materials discussed above. The PdAu<sub>60</sub> and PtAu<sub>60</sub> materials were synthesized from the 3 wt % Au material, whereas the PtAu15 and PtAu5 catalysts were prepared from the 0.75 and 0.25 wt % Au materials, respectively. Here, 4 g of the carbon-supported Au was added to 140 mL of deionized H<sub>2</sub>O and stirred at 500 rpm in a flask under a flowing mixture of 20 kPa of  $H_2$  and 81 kPa of  $H_2$  (100 cm<sup>3</sup> min<sup>-1</sup>; Airgas, 99.999%). For the PdAu<sub>60</sub> and PtAu<sub>60</sub> materials, the solution was initially heated to 343 K, while the  $PtAu_{15}$  and  $PtAu_5$ materials were stirred at 298 K. After stirring for 30 min, 10 cm<sup>3</sup> of aqueous 1 mM Pd  $(NO_3)_2$  or  $(NH_3)_4$ Pt $(NO_3)_2$  was added dropwise to the solution to form the PdAu and PtAu alloys. The PdAu<sub>60</sub> and PtAu<sub>60</sub> materials were maintained at 343 K for 3 h, while the PtAu<sub>15</sub> and  $\tilde{Pt}Au_5$  materials were heated from room temperature to 343 K and held at that temperature for 3 h. The resulting catalyst slurries were then cooled to ambient temperature and vacuum-filtered at 298 K overnight.

**2.2.** Catalyst Characterization. The average diameters of carbon-supported nanoparticles were estimated from the particle size distributions obtained by transmission electron microscopy (TEM). The distribution of nanoparticle diameters was measured by bright-field TEM imaging (JEOL, 2010 LaB<sub>6</sub>) of more than 100 particles. Each sample was prepared by grinding the catalyst to a fine powder (<200 mesh), which was dusted onto a Cu holey-carbon TEM grid (200 mesh, Ted Pella Inc.). The surface area normalized average cluster diameter ( $\langle d_{\text{TEM}} \rangle$ ) for each catalyst was calculated using eq 3

$$\langle d_{\rm TEM} \rangle = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2} \tag{3}$$

where  $n_i$  is the number of nanoparticles with the diameter  $d_i$ . Figure 2 shows a representative TEM image of the 9 nm Pd nanoparticles on Vulcan XC-72. This image includes an inset histogram of the particle size distribution, and TEM images for the other nanoparticle catalysts are shown in Figure S1 and discussed in section S1 in the Supporting Information. The metal content of each sample was measured by inductively coupled plasma optical emission spectroscopy (PerkinElmer, Optima 2000DV) and energy dispersive X-ray fluorescence (Shimadzu, EDX-7000). The characterization results for all prepared catalysts are shown in Table S1.

**2.3. Steady-State Thermocatalytic Reaction Rate Measurements.** All steady-state  $H_2O_2$  and  $H_2O$  formation rates were measured in a continuous-flow trickle-bed reactor (48 cm length, 1 cm inner diameter) housed within a stainless-steel cooling jacket (Figure S2 and Section S2 in the Supporting Information). The reactor was loaded with 0.15–1 g of catalyst, which was held between plugs of glass wool (~10 mg), each supported by borosilicate glass rods (8 mm diameter). These rods were secured between silvercoated fritted VCR gaskets (Swagelok, SS-4-VCR-2-60M), which were also used to seal the reactor. The temperature was controlled across the reactor by flowing aqueous ethylene glycol (50% volume; Fisher Scientific E178, 99.8%) through the cooling jacket from a recirculating temperature bath (Cole-Parmer Polystat). The temperature of the catalyst bed was monitored directly using a K-type thermocouple contained within the cooling jacket and in firm contact



**Figure 2.** Representative TEM image of 37 nm Pd nanoparticles supported on Vulcan XC-72 with an inset histogram of the particle size distribution. More than 100 particles were measured to calculate the value of  $\langle d_{\text{TEM}} \rangle$ , which is the surface-area-averaged diameter. Figure S1a–1 shows similar images and histograms for the other materials studied.

with the stainless-steel wall surrounding the catalyst bed. H<sub>2</sub> and O<sub>2</sub> compositions in the reactor were controlled by flowing certified gas mixtures (25% H<sub>2</sub>/N<sub>2</sub> and 5% O<sub>2</sub>/N<sub>2</sub>, Airgas, 99.999%) through digital mass-flow controllers (Bronkhorst, F-211CV). Warning: pressurized mixtures of H<sub>2</sub> and O<sub>2</sub> are explosive when the two components exceed a mole fraction of 0.05. Before it contacted the catalyst, the gaseous reactant stream contacted the DI water (>17.8 M $\Omega$  cm) that served as the solvent and was delivered by an HPLC pump (SSI, LS class). The pressure of the resultant gas–liquid mixture was maintained by a back-pressure regulator (Equilibar, LF) and controlled by an electronic pressure regulator (Equilibar, GP1). The upstream pressure of the reactor was monitored using a digital pressure transducer (Omega, PXM409-USBH).

Sampling and analysis of the liquid and gaseous effluent streams were automated and operated continuously. The reactor effluent entered a gas-liquid separator (GLS), from which the gas stream flowed to a gas chromatograph (Agilent, 7890B) equipped with a capillary column (Vici, Molecular Sieve 5 Å, 30 m × 0.53 mm × 20  $\mu$ m) and a thermal conductivity detector that used Ar gas (Airgas, 99.999%) as a reference. The liquid fraction was drained from the GLS at 10 min intervals by an electronic valve (ALSCO Inc., LEV025PL) and flowed into an electronic two-position valve (Vici Valco, 10 port EPC10W), which injected 1 cm<sup>3</sup> of the liquid effluent and 1 cm<sup>3</sup> of a colorimetric titrant (12 mM neocuproine (Sigma-Aldrich, > 99%), 8.3 mM CuSO<sub>4</sub> (Fisher Scientific, > 98.6%), 25/75 (v/v) ethanol/deionized water mixture (Decon Laboratories, > 99.9%)) into test tubes held in an automated fraction collector (Biorad, 2110). Each tube was analyzed by a UV-vis spectrophotometer (Spectronic, 20 Genesys) at a wavelength of 454 nm to measure the H<sub>2</sub>O<sub>2</sub> concentration using a corresponding calibration curve. All experiments were conducted at a liquid flow rate of 35 cm<sup>3</sup> min<sup>-1</sup> to avoid external mass transfer limitations.<sup>16</sup>

Measured formation rates are normalized by the total moles of either Pd or Pt within each sample. The number of reactive surface atoms (or active sites) was not estimated because the structure and dispersion of the nanoparticles were uncertain. Similarly, the distribution of elements within individual bimetallic nanoparticles was unclear. Moreover, these factors likely change across the range of reaction conditions examined. For pressure dependence and activation enthalpy measurements, reported rates were corrected by accounting for deactivation, assuming that these changes arise from an exponential reduction in the number of active sites with time.<sup>19</sup> These corrections were determined by returning to the initial conditions for each reaction to more accurately assess the rate of deactivation.

2.4. Electrocatalytic Reaction Rate Measurements. All electrochemical parameters for the ORR and HOR (i.e., H2O2 formation rates and hydrogen oxidation rates) were measured using a CHI 760 bipotentiostat (CH Instruments). Rotating ring-disk electrode (RRDE) measurements were performed using a Pine ASR electrode rotator (Pine Research) using a 5.0 mm glassy-carbon disk insert to support the catalyst and a Pt-ring assembly (OD = 7.50 mm, ID = 6.50 mm, Pine Research) for  $H_2O_2$  disk-generation/ringcollection experiments. This setup is schematically shown in Figure S3. The carbon-supported catalysts were suspended in a solution of 5.0 mg of catalyst, 1.0 mL of of DI water (Elga, 18 M $\Omega$  cm), and 0.6 mL of ethanol. A 10.0  $\mu$ L portion of this slurry was drop-cast onto the 5.0 mm glassy-carbon disk and dried with an infrared lamp for  $\sim 1$  h. Once the disk was dry, 5.0  $\mu$ L of a 1 wt % Nafion solution  $(C_7HF_{13}O_5S \cdot C_2F_4$  in a mixture of lower aliphatic alcohols and water, Sigma-Aldrich) was drop-cast onto the modified electrode to prevent detachment of the catalyst during measurements.

Past studies on the impact of Nafion on ORR electrocatalysis on Pt have shown mixed results, ranging from no effect on the Tafel slope or exchange current<sup>20</sup> to a ~2× enhancement in the specific and mass activities of Pt after removing Nafion from the formulation.<sup>21</sup> High loadings of Nafion likely affect the rates of mass transfer and ohmic resistance;<sup>20</sup> however, such effects should not convolute the results presented here, as all materials were prepared using the same loading of Nafion and the rates are corrected for mass transfer effects using a Koutecky–Levich analysis (*vide infra*). Thus, the Nafion may present some experimental error in comparison to the Nafion-free samples used in the thermochemical rate determination (section 2.3). Still, the use of Nafion is common in the electrochemical literature and is necessary to preserve the mechanical integrity of the samples across the breadth of compositions and rotation rates explored herein.

All RRDE experiments were carried out in 0.1 M sodium perchlorate (NaClO<sub>4</sub>, Sigma-Aldrich, 98+%) as the supporting electrolyte with a carbon counter electrode (Alfa Aesar, 99.9995% purity). This medium was chosen to replicate the neutral unbuffered solution used in thermocatalytic experiments as closely as possible (see above). An Ag/AgCl reference electrode (3.5 M KCl, CH Instruments) was used in all measurements, with the electrode placed in contact with the solution via a 0.1 M sodium perchlorate agar/agar salt bridge used to prevent chloride contamination to the solution. Unless otherwise stated, all electrode potentials were corrected relative to a normal hydrogen electrode (NHE) with a unit activity of hydronium  $([H_3O^+] = 1)$  and are reported hereafter as V vs NHE. Experimentally acquired voltammograms and open-circuit potentiometry measurements were adjusted by 205 mV to correct the Ag/ AgCl (KCl 3.5 M) scale and adjusted by an additional 414 mV to correct between a pH of 7 to a pH of 0.

Measurements of the ORR were conducted in 0.1 M sodium perchlorate aqueous solutions sparged with O<sub>2</sub> gas (101 kPa, Airgas, 99.999%). For disk-generation and ring-collection experiments, the disk potential was scanned over the range +0.7 to -0.6 V vs NHE, while the ring was held constant at 1.2 V vs NHE to carry out the mass-transfer-limited oxidation of H2O2. The collection efficiency (CE) of the ring-disk was determined to be ~25%, and this value determined the yield of H<sub>2</sub>O<sub>2</sub> using equation S5.8 (section S5 in the Supporting Information). Measurements of the HOR were conducted in 0.1 M sodium perchlorate aqueous solutions sparged with H<sub>2</sub> gas (101 kPa, Airgas, 99.999%) at electrode potentials between -0.2 and +0.6 V vs NHE. These measurements were repeated at multiple rotation rates of between 50 and 1250 rpm to evaluate the resulting voltammograms using a Koutecky-Levich analysis,14 in which electrocatalytic rate constants were measured as a function of electrode potential and used to calculate intrinsic rate constants and charge transfer coefficients for the HOR and ORR (vide infra). Complementary measurements of CO stripping were performed on Pt/C materials, which were used to renormalize electrochemical rate constants by the total moles of surface atoms. Such experiments were

performed by dosing CO over the sample followed by potentiometric measurements to oxidize the adsorbed CO species (section S10 in the Supporting Information). These voltammograms were subtracted from a reference voltammogram on the same material at the same potentials (~0.6–0.9 V vs NHE), and the integration of this peak yields a Faradaic current, proportional to the number of surface atoms on the catalyst.

2.5. Pressurized Electrochemical Potential Measurements. Pressurized open-circuit potentiometry and voltammetry measurements were carried out on the catalytic materials in a custom-built electrochemical cell (150 cm<sup>3</sup>) with a Teflon interior, as shown in Figure S4. This experimental setup mimics the conditions of the trickle-bed reactor during thermocatalytic reaction measurements. At open circuit, there is no current flow between the electrodes, which allows for direct measurements of the electrode potential on metal nanoparticles under a given condition. The leaktight cell contained three insulated orifices that accommodated a glassy-carbon working electrode (BASi, 3.0 mm diameter), a Ag/AgCl reference electrode connected via a salt bridge, and a carbon counter electrode that was used for cyclic voltammetry measurements. Warning: the use of a metallic (e.g., Pt) counter electrode was avoided to prevent explosive gas mixtures when they are in contact with an exposed metal surface; for similar reasons, the electrode surfaces were always kept immersed in the electrolyte. Catalytic materials were drop-casted onto the working electrode using 5.0 µL of the catalyst slurry described in section 2.4. The material was dried under an infrared lamp for  $\sim 1$  h and then coated with a 1 wt % Nafion solution to bind the catalyst to the electrode surface. During measurements, the electrodes were submerged in the cell (100 cm<sup>3</sup> of deionized H<sub>2</sub>O, >17.8 M $\Omega$  cm), and the liquid phase was sparged with H<sub>2</sub> and O<sub>2</sub> gas. Here, the H<sub>2</sub> and O<sub>2</sub> compositions in the cell were controlled by flowing certified gas mixtures (25%  $H_2/N_2$  and 5%  $O_2/N_2$ , Airgas, 99.999%) through digital mass-flow controllers (Parker Porter, 601 series) at 110-180 cm<sup>3</sup> min<sup>-1</sup>, and a back-pressure regulator (Andon Specialties, BP3-1A11QCK11L) maintained the operating pressure. The potential of the working electrode was measured using open-circuit potentiometry while the gas pressure was modified in the range 60-400 kPa of H<sub>2</sub> and a constant 60 kPa of O2. The cell was held at each pressure for 30-60 min, and the last 5 min of each period were averaged to determine the operating potential at open circuit. For pressurized voltammetry measurements, a supporting electrolyte (0.1 M NaClO<sub>4</sub>) was added to the aqueous solution, and these experiments followed a methodology similar to that shown in section 2.4.

## 3. RESULTS AND DISCUSSION

3.1. Effects of H<sub>2</sub> and O<sub>2</sub> Pressures on the Electrode Potential of Nanoparticle Catalysts. Figure 1 depicts the mechanism for H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O formation and implies that these electron transfer reactions should confer an electrical potential on the metal nanoparticle catalysts during the thermochemical reactions of H<sub>2</sub> and O<sub>2</sub> gases. Consequently, the operating potential of the metal nanoparticles should depend upon the relative rate of heterolytic hydrogen oxidation and oxygen reduction steps, which are influenced by differences in kinetic barriers and reactant activities ( $[H_2]$ ,  $[O_2]$ ). Past work shows that rates of  $H_2O_2$  and  $H_2O$  formation on metal nanoparticles increase in proportion with the hydrogen pressure  $(0-80 \text{ kPa of } H_2, 60 \text{ kPa of } O_2)$ .<sup>13,16,22</sup> Thus, oxygen reduction rates can increase by orders of magnitude by changing either the hydrogen chemical potential or the electrode potential  $(\phi)$  of the catalyst. However, these rates do not depend on H<sub>2</sub> pressure at higher values (100-400 kPa of H<sub>2</sub>, 60 kPa of O<sub>2</sub>),<sup>11</sup> which suggests that hydrogenderived intermediates occupy most catalytic sites under these conditions. As the coverage of hydrogen increases on the catalyst surface, there is a higher probability that it will donate

an electron to the nanoparticle, leading to a more negative electrode potential.

Potentiometry at open circuit (i.e., at zero current) allows us to probe charge transfer reactions from the HOR or ORR on the catalyst without perturbing their steady-state reaction rates. These measurements define the operating potential ( $\Phi^{op}$ ) at which direct synthesis reactions occur. Figure 3 shows the



**Figure 3.** Open-circuit potentiometry measurements of operating potentials for Pd, PdNi, PtAu<sub>60</sub>, PtCo, and Pt catalysts as functions of  $H_2$  pressure (60–400 kPa of  $H_2$ , 60 kPa of  $O_2$ , 298 K) in comparison to the Nernstian response for the ORR and HOR paths, described by eqs 4 and 5. Nernstian expressions were calculated using the unit activities of  $H_3O^+$  and  $H_2O$  species, while the ORR expression was calculated using 0.1 mM concentrations of  $H_2O_2$  and 60 kPa of  $O_2$  to mimic open-circuit potentiometry measurements.

operating potential for Pd, PdNi, PtAu<sub>60</sub>, PtCo, and Pt catalysts as a function of the  $H_2$  pressure (60-400 kPa) at a constant pressure of O<sub>2</sub> (60 kPa) at 298 K. Over this range, PtCo shows the greatest operating potential of 0.65 V vs NHE, which decreases to 0.40 V vs NHE as the H<sub>2</sub> pressure is increased. In contrast, PtAu<sub>60</sub> shows a  $\Phi^{op}$  value of 0.46 V vs NHE, which decreases to the lowest observed value of 0.35 V vs NHE. All other materials show a similar negative shift in the operating potential within this range (0.35-0.65 V vs NHE), as discussed in Figures S5-S17 of section S3 in the Supporting Information. These results suggest that each catalyst facilitates a heterolytic reaction among hydrogen, oxygen, and water during the direct synthesis. In the absence of a catalyst, the glassy-carbon electrode shows a much higher  $\Phi^{op}$  value of ~0.75 V vs NHE (Figure S18) and is mostly insensitive to  $H_2$ pressure, which agrees with the unmeasurably low HOR rates observed on it. Overall, these results suggest that oxygen reduction follows a similar heterolytic mechanism on metal nanoparticles under both electrochemical and thermal conditions.

Figure 3 demonstrates that hydrogen transfers charge to nanoparticles, yet it is unclear how the operating potential depends on the elementary steps depicted in Figure 1. Therefore, we compared these values to the predicted operating potentials of quantitative models that consider the rates of elementary steps and the activity of the  $H_2$  and  $O_2$  reactants. First, we examine the broadly simplifying assumption that the reactants are in equilibrium with the ORR products (i.e., steps 1–11 are quasi-equilibrated) by rearranging eqs 1 and 2 to derive the Nernst equations for the HOR and  $2e^{-1}$ 

ORR half-reactions (section S4 in the Supporting Information).<sup>14</sup>

$$\Phi^{0} = \Phi_{\text{HOR}}^{0} + \frac{RT}{2F} \ln \left( \frac{[\text{H}_{3}\text{O}^{+}]^{2}}{[\text{H}_{2}][\text{H}_{2}\text{O}]^{2}} \right)$$
$$= \frac{RT}{2F} \left( \ln K_{\text{HOR}}^{0} - \ln \left( \frac{[\text{H}_{3}\text{O}^{+}]^{2}}{[\text{H}_{2}][\text{H}_{2}\text{O}]^{2}} \right) \right)$$
(4)

$$\Phi^{0} = \Phi^{0}_{H_{2}O_{2}} - \frac{RT}{2F} \ln \left( \frac{[H_{2}O_{2}][H_{2}O]^{2}}{[H_{3}O^{+}]^{2}[O_{2}]} \right)$$
$$= \frac{RT}{2F} \left( \ln K^{0}_{H_{2}O_{2}} - \ln \left( \frac{[H_{2}O_{2}][H_{2}O]^{2}}{[H_{3}O^{+}]^{2}[O_{2}]} \right) \right)$$
(5)

where the equilibrium potential ( $\Phi^0$ ) of the HOR (H<sub>2</sub> + 2H<sub>2</sub>O  $\leftrightarrow 2e^- + 2H_3O^+$ ) and the 2e<sup>-</sup> ORR (2e<sup>-</sup> + 2H<sub>3</sub>O<sup>+</sup>  $\leftrightarrow H_2O_2 +$ 2H<sub>2</sub>O) depend on their standard potentials of reaction ( $\Phi^0_{HOR}$ ,  $\Phi^0_{H_2O_2}$ ) and the activities of reactants and products in these systems ([H<sub>2</sub>], [O<sub>2</sub>], [H<sub>2</sub>O], [H<sub>3</sub>O<sup>+</sup>], [H<sub>2</sub>O<sub>2</sub>]). Here, the standard potential is related to the equilibrium constants of these reactions ( $K^0_{HOR}$ ,  $K^0_{H_2O_2}$ ) at the standard state. Section S4 in the Supporting Information presents derivations of these expressions and analogous equations for the formation of H<sub>2</sub>O. In each case, these Nernst expressions only consider the thermodynamics of the reaction ( $\Phi^{op} = \Phi^0$ ) and neglect the activation barriers of the HOR or ORR on the catalytic surface. Thus, the Nernst equations of the HOR and ORR describe a system that behaves with infinitely fast reaction rates toward these pathways.

Figure 3 shows that the materials produce operating potentials that lie between the Nernstian predictions for the HOR and the ORR. These observations suggest that the  $\Phi^{op}$ value depends on the activation barriers of these reactions and other kinetic properties of the materials, preventing equilibrium predictions for either the pure HOR or ORR paths. Figure 3 also shows that the operating potential decreases with hydrogen pressure on each catalyst, consistent with the trend displayed by the HOR Nernst equation. Materials also show different slopes between the measured  $\Phi^{op}$  value versus hydrogen pressure. Thus, greater hydrogen pressures result in a more negative operating potential on the nanoparticles, but the efficiency and extent of charge transfer are sensitive to the identity of the catalyst. Therefore, a more rigorous model is needed to capture these subtle differences between materials.

These results were analyzed by assuming that a mixed potential develops when anodic (e.g., HOR) and cathodic (e.g., ORR) currents are equal on a metal surface,<sup>23-25</sup> which are described as bipolar electrodes. This theory describes the corrosion of surfaces,<sup>23</sup> electroless deposition of metals,<sup>26</sup> and production of H<sub>2</sub> and Cl<sub>2</sub> (from reactions of a redox mediator with nanoparticles).<sup>27</sup> This concept, however, has not been demonstrated for an ostensible thermocatalytic reaction of gaseous reagents on supported catalytic nanoparticles, such as the direct synthesis of H<sub>2</sub>O<sub>2</sub>. Here, the coupled HOR and ORR reactions govern the rates and selectivities of H<sub>2</sub>O<sub>2</sub> formation at a steady state in a continuous-flow reactor in the absence of an externally applied electrode potential or a pathway to conduct electrons away from the nanoparticles. Therefore, electron transfer rates for the HOR and ORR must be equal upon a given nanoparticle (Figure 1b) to balance the

mass and charge at the steady state. Since both the HOR and the ORR involve distinct steps with barriers sensitive to the identity and structure of the nanoparticle surface,<sup>28–30</sup> this model indicates that the disparities in  $\Phi^{op}$  and catalyst performance during direct synthesis result from the differences in ORR and HOR kinetics.

We quantitatively describe these differences with a Butler– Volmer model to predict changes in operating potential on the nanoparticle materials. This treatment assumes that the apparent Gibbs free energy barrier ( $\Delta G_{app}^{\dagger}$ ) of the reaction decreases as the difference in  $\Phi$  and  $\Phi^0$  increases for the reaction, and the sensitivity of this change is proportional to the charge transfer coefficient ( $\alpha$ ).<sup>14</sup> This difference (also known as overpotential) reflects the favorability of a reaction on given material, and materials that present high barriers will require greater overpotentials to achieve the same rate.

$$\Delta G_{\rm app}^{\ \ \dagger} = \Delta G_{\rm int}^{\ \ \dagger} - \alpha z F (\Phi - \Phi^0) \tag{6}$$

where  $\alpha$  is analogous to the symmetry factor of the Bells– Evans–Polanyi principle, whereby the apparent barrier depends on the position of the transition state along the reaction coordinate of the elementary step.<sup>31</sup> The value of  $\alpha$ also depends on the reorganization energy, which accounts for inner- and outer-sphere interactions that affect the transition state of electron transfer reactions.<sup>14</sup> The value of  $\Delta G_{app}^{\dagger}$  also accounts for the intrinsic barrier of the elementary process ( $\Delta G_{int}^{\dagger}$ ) that the catalyst surface presents to the reactants when the electrode potential equals the equilibrium potential. The apparent barrier affects the rate constant of the reaction ( $k_{app}$ ), while the rate of the reaction ( $r_{app}$ ) depends on both  $k_{app}$  and the reactant activity ([j]) at the catalyst surface, as shown in the Eyring equation:

$$\frac{r_{\rm app}}{[L]} = k_{\rm app}[j]\theta = \frac{k_{\rm b}T}{h} e^{-\Delta G_{\rm app}^{\dagger}/RT}[j]\theta$$
(7)

where  $k_{\rm b}$  is the Boltzmann constant, h is the Planck constant,  $\theta$  is the fraction of unoccupied reactive sites, and [L] is the total available sites on an electrode or electrocatalyst that can facilitate charge transfer to species j. By combining eqs 6 and 7, we connect core relationships from electrochemistry and chemical kinetics that yield the general Butler–Volmer expression for the forward rate of reaction as a function of the electrode potential

$$\frac{r_{\text{app}}}{[L]} = \frac{k_{\text{b}}T}{h} e^{-\Delta G_{\text{int}}^{\ddagger}/RT} e^{\alpha z F(\Phi - \Phi^0)/RT}[j]\theta$$
$$= k^0 e^{\alpha z F(\Phi - \Phi^0)/RT}[j]\theta$$
(8)

where  $k^0$  is the intrinsic rate constant of electron transfer to species j at the equilibrium potential. Here, the coverage of hydrogen- and oxygen-derived species on the nanoparticle surface increases in proportion to the reactant activity at low surface coverages. Thus, we restate eq 8 in terms of the electrical current on an electrode (section S5 in the Supporting Information) and extract relationships that resemble more traditional treatments of the HOR and ORR, reported elsewhere.<sup>15,32,33</sup>

$$\frac{i_{\text{HOR}}}{[\text{L}]} = -n_{\text{HOR}}F\frac{r_{\text{HOR}}}{[\text{L}]}$$
$$= n_{\text{HOR}}Fk_{\text{HOR}}^0 e^{\alpha_{\text{HOR}}F(\Phi - \Phi_{\text{HOR}}^0)/RT}[\text{H}_2][\text{H}_2\text{O}]\theta \qquad (9)$$

$$\frac{t_{\text{ORR}}}{[L]} = n_{\text{ORR}} F \frac{r_{\text{ORR}}}{[L]}$$
$$= n_{\text{ORR}} F k_{\text{ORR}}^0 e^{-\alpha_{\text{ORR}} F (\Phi - \Phi_{\text{ORR}}^0) / RT} [O_2] \theta$$
(10)

where the currents for the HOR  $(i_{HOR})$  and ORR  $(i_{ORR})$ depend on their respective intrinsic rate constants  $(k_{HOR}^0, k_{ORR}^0)$ , charge transfer coefficients  $(\alpha_{HOR}, \alpha_{ORR})$ , and the total number of electrons transferred  $(n_{HOR} = 2, n_{ORR} = 2-4)$ . Values of  $\Phi_{HOR}^0$  and  $\Phi_{ORR}^0$  implicitly depend on the pH of the solution, as shown in eqs 4 and 5. Note that the apparent ORR current considers the lumped average of the 2e<sup>-</sup> and 4e<sup>-</sup> paths. Moreover, eqs 9 and 10 assume that the activity of hydrogen  $([H_2])$  and oxygen  $([O_2])$  on the catalyst surface equals that of the gas phase. For fitting purposes, however, we account for the mass transfer limitations of our electrochemical system, which we consider in the complete Butler–Volmer formalism (section S5 and Figures S19–S43 in the Supporting Information).<sup>14</sup>

Applying the mixed potential model to the HOR and ORR (i.e.,  $i_{HOR} = i_{ORR}$ ), we set eqs 9 and 10 equal and derive the functional form of the operating potential of a nanoparticle. The resulting expression uses kinetic parameters measured for the HOR and ORR (related to  $\Delta G_{app}^{\dagger}$  and  $\alpha$  for elementary steps in Figure 1) to solve for the  $\Phi^{op}$  of each material as a function of the activity of hydrogen and oxygen:

$$\Phi^{\rm op} = \frac{\alpha_{\rm ORR} \Phi^0_{\rm ORR} + \alpha_{\rm HOR} \Phi^0_{\rm HOR}}{\alpha_{\rm ORR} + \alpha_{\rm HOR}} - \frac{RT}{F(\alpha_{\rm ORR} + \alpha_{\rm HOR})}$$
$$\ln \left( \frac{n_{\rm HOR} k^0_{\rm HOR} [H_2] [H_2 O]}{n_{\rm ORR} k^0_{\rm ORR} [O_2]} \right) \tag{11}$$

where RRDE methods determine values for  $k^0$  and  $\alpha$  for the HOR and ORR of each catalyst (section S5, Table S2, and Figures S19–S43 in the Supporting Information), which can predict  $\Phi^{op}$  under thermocatalytic conditions. Note that the operating potential is constrained by the reactant activities during direct synthesis, whereas the electrochemical techniques independently control the electrode potential.

Figure 4a shows HOR and ORR currents for a carbonsupported Pd catalyst calculated as functions of electrode potential ( $\Phi = -0.7$ to +0.2 V vs NHE) at different H<sub>2</sub> (60– 400 kPa of H<sub>2</sub>) and O<sub>2</sub> (60 kPa of O<sub>2</sub>) pressures, respectively. The intersection of the HOR and ORR lines predicts the  $\Phi^{op}$ for Pd nanoparticle catalysts at each combination of H<sub>2</sub> and O<sub>2</sub> pressure, which occurs when the rates of ORR and HOR are equal. For simplicity, Figure 4a,b depicts linear Tafel slopes (calculated from fitted values of  $k^0$  and  $\alpha$ ) over the 600 mV window shown in Figure 4a,b. We expect reasonable predictions across the potentials observed during open-circuit potentiometry measurements ( $\Phi^{op} = 0.35-0.65$  V vs NHE) due to overlap with the potentials used for the Tafel analysis (Figures S19–S43); however, nonlinearities would emerge at the most extreme potentials.<sup>15,34–37</sup>

Like the Nernst equation of the HOR in Figure 3, this model predicts that  $\Phi^{op}$  becomes more negative as the H<sub>2</sub> pressure increases. These relationships (Figure 4 and eq 11) reflect increasing steady-state coverages of hydrogen atoms that transfer electrons to the nanoparticle in the presence of oxygen. These trends are consistent with data in Figure 3, but this model predicts the values of the  $\Phi^{op}$  more accurately in comparison to the Nernstian predictions on these materials (Figure 3). Moreover, this Butler–Volmer model reveals the



**Figure 4.** Predicted currents as a function of potential, which derive the operating potential calculated from eq 11 using kinetics parameters ( $k_{\text{HOR}}^{\theta}$ ,  $k_{\text{ORR}}^{\theta}$ ,  $\alpha_{\text{HOR}}$ , and  $\alpha_{\text{ORR}}$ ) from RRDE measurements of the HOR and the ORR obtained independently on monometallic (a) Pd and (b) Pt catalysts. (c) Predicted operating potentials ( $\Phi$ white shown as a function of  $\Phi$ , measured at open circuit on Pd (black ●), PdCo (red  $\Delta$ ), PdNi (blue ♥), PdZn (cyan ♦), PdAu ( $\bigcirc$ ), PdCu (purple ▶), PdPt (yellow ●), Pt (green ■), PtCo (orange  $\bigcirc$ ), PtAu<sub>60</sub> (black ★), PtAu<sub>15</sub> (orange ▲), and PtAu<sub>5</sub> (purple □) nanoparticles supported on Vulcan XC-72 between 20 and 400 kPa of H<sub>2</sub> and 60 kPa of O<sub>2</sub> at 298 K.

reasons for a ~200 mV difference between values of  $\Phi^{op}$  for Pt and Pd over the range of H<sub>2</sub> pressures examined (60–400 kPa of H<sub>2</sub>). In Figures 4a,b, the ORR rates are similar between Pt and Pd (Figures S19 and S20), but the HOR currents on Pt (Figure S37) are much higher than on Pd (Figure S32) at similar electrode potentials (i.e., Pd requires a higher overpotential to reach the same rate). Thus, Pt more readily oxidizes H<sub>2</sub> and generates electrons on the nanoparticle surface, which agrees with lower hydrogen oxidation overpotentials on Pt materials in comparison to Pd.<sup>38,39</sup> Consequently, Pt shows more negative values of  $\Phi^{op}$  and greater operating currents (Figure 4b).

Certain catalysts, such as PdAu<sub>60</sub>, show a  $\Phi^{op}$  value similar to that for Pt but react at a lower ORR current density (Figures S10 and S16). This discrepancy results from the higher transfer coefficients of the HOR ( $\alpha_{HOR}$ ) and ORR ( $\alpha_{ORR}$ ) pathways and the greater H<sub>2</sub>O<sub>2</sub> selectivity on the PdAu<sub>60</sub> material in comparison to Pt. Thus, the operating potential of a material is a strong function of the number of electrons transmitted ( $n_{ORR}$ ), the intrinsic rate constants of reaction, and the charge transfer coefficients of the HOR and ORR pathways. Figure 4c shows that the predicted  $\Phi^{op}$  correlates with measured values of  $\Phi^{op}$ , determined by open-circuit potentiometry measurements over multiple combinations of hydrogen and oxygen



**Figure 5.** (a)  $H_2O_2$  and (b)  $H_2O$  formation rates as a function of  $H_2$  partial pressure on Pd (black  $\bullet$ ), PdCo (red  $\triangle$ ), PdNi (blue  $\blacktriangledown$ ), PdZn (cyan  $\blacklozenge$ ), PdAu (red  $\bigcirc$ ), PdCu (purple  $\blacktriangleright$ ), PdPt (yellow  $\bullet$ ), Pt (green  $\blacksquare$ ), PtCo (orange  $\triangle$ ), PtAu<sub>60</sub> (black  $\bigstar$ ), PtAu<sub>15</sub> (orange  $\blacktriangle$ ), and PtAu<sub>5</sub> (purple  $\square$ ) nanoparticles supported on Vulcan XC-72 (20–400 kPa of  $H_2$ , 60 kPa of  $O_2$ ) at 298 K. Note that the formation rates are normalized by the total moles of Pd or Pt in each sample. Dashed lines represent fits of eq 16 to measurements for each material, which assume constant values of  $\Phi^{op}$ .

pressures (60-400 kPa of  $H_2$ , 60 kPa of  $O_2$ ). Generally, the model agrees with the data with an  $R^2$  value of 0.74, and the discrepancies observed likely originate from slight (but unavoidable) differences between the conditions used for RRDE and open-circuit potentiometry measurements. Specifically, the presence of electrolyte in the RRDE experiments may indirectly influence kinetic parameters in ways that are absent from open-circuit potentiometry measurements. Moreover, measurements of  $\Phi^{op}$  were necessarily conducted with both H<sub>2</sub> and O<sub>2</sub>, whereas RRDE measurements were performed with either H2 or O2 but never both. These variations in the reaction environment likely give rise to subtle differences in the surface coverages of reactants not reflected in Tafel slopes (Figure 4a,b). Nevertheless, independent electrochemical measurements of HOR and ORR parameters enable accurate predictions of the expected  $\Phi^{op}$  value for a catalyst during direct synthesis across the 12 materials, which serve as useful tools to inform the design of catalytic materials.

3.2. Relating Operating Potential to H<sub>2</sub> Pressure through Rate Expressions for H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O Formation. The model presented in the previous section made a few assumptions regarding the mechanism of H<sub>2</sub>O<sub>2</sub> or H<sub>2</sub>O formation and relied on empirically measured rate constants. Subsequently, we endeavored to derive a molecularly detailed model based upon the series of elementary reactions proposed for the formation of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O under both thermochemical and electrochemical conditions. This understanding provides insight into the relationships among operating potential, product formation rates, and reactant activity. Initially, we considered a homolytic reaction mechanism, which is commonly described by Langmuir-Hinshelwood kinetics throughout the direct synthesis literature.<sup>22,40,41</sup> This model, however, does not explain the role of protic solvents in the direct synthesis reaction, since H<sub>2</sub>O<sub>2</sub> formation rates are negligible in aprotic solutions. Furthermore, the Langmuir-Hinshelwood predictions do not agree with H<sub>2</sub>O<sub>2</sub> formation rates independent of oxygen pressure (50-400 kPa of O2, 60 kPa H<sub>2</sub>).<sup>11,16</sup> Recent kinetic measurements and DFT calculations indicate that oxygen reduction barriers are much greater for homolytic surface reactions than for protonelectron transfer (PET) steps  $(\Delta \Delta E_{app}^{\dagger} = 22 \text{ kJ mol}^{-1}).^{12,42}$ Therefore, we considered a PET mechanism (depicted in

Figure 1), in which water facilitates the heterolytic oxidation of hydrogen to generate hydronium ions in solution and electrons on adsorbed oxygen intermediates ( $O_2^*$ , OH\*, or OOH\*). Then, water molecules may shuttle protons to anionic oxygen intermediates ( $O_2^{-*}$ , OH<sup>-</sup>, or OOH<sup>-\*</sup>) to complete the reduction of these species. Overall, the rate expressions derived from these elementary steps accurately capture changes in both  $H_2O_2$  and  $H_2O$  formation rates with  $H_2$  and  $O_2$  pressure upon all catalysts examined (Sections S6 and S7 in the Supporting Information). Notably, this mechanism aligns closely with proposed mechanisms for the ORR.<sup>42</sup>

We hypothesize that the electrocatalytic and thermocatalytic systems should show similar selectivities toward H<sub>2</sub>O<sub>2</sub> if oxygen reduction follows the same reaction pathways. Figure 5 shows steady-state H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O formation rates (and selectivities by comparison) as functions of H<sub>2</sub> pressure for each material used in this study. On each catalyst, the rates increase in proportion with the  $H_2$  pressure (<100 kPa, 60 kPa of O<sub>2</sub>, 298 K) before reaching a constant value at the highest pressures (150-400 kPa of  $H_{21}$  60 kPa of  $O_{21}$  298 K). These results agree with past observations on both bimetallic and monometallic Pd materials<sup>13,16</sup> and suggest that the coverage of H atoms increases with H<sub>2</sub> pressure before saturating the available active sites. These rates, however, do not depend upon the  $O_2$  pressure under these conditions<sup>11,13,16</sup> because oxygen-derived intermediates saturate distinct surface sites and do not compete with hydrogen for surface sites. Each catalyst exhibits a similar functional dependence on the pressure of hydrogen, which suggests a similar PET mechanism facilitates  $H_2O_2$  and  $H_2O$  formation on these materials.

Figure 1 shows a series of elementary steps that produce  $H_2O_2$  and  $H_2O$  through PET reactions of  $H_2$  and  $O_2$ , in which oxygen and hydrogen intermediates adsorb to distinct sites (denoted as \* and  $\square$ , respectively). The dominant hydrogen oxidation reaction mechanism on noble metals is debated in the electrochemical literature, and some studies suggest that a combination of the Heyrovsky (step 1), Tafel (step 2), and Volmer steps (step 3) occurs.<sup>15,38</sup> Similarly, it is possible for any of these steps to be kinetically relevant, depending on what steps present the greatest apparent barriers on a given material.<sup>28,43</sup> The reverse of these reactions (steps 1–3) also occur under the reaction conditions, and their rates depend on

the pH and operating potential of the nanoparticle. We compare all of these steps and their implications on the apparent rate expressions (section S6 in the Supporting Information) and find that both Heyrovsky–Volmer and Tafel–Volmer kinetics lead to rate expressions that agree with the data in Figure 5. For simplicity, we treat the Heyrovsky–Volmer mechanism and assume that the Heyrovsky step (step 1) is kinetically relevant, as proposed by Takanabe.<sup>15</sup> Similarly, we assume that steps 1 and 3 are primarily irreversible (section S6 in the Supporting Information), since these experiments occur at neutral pH. However, these assumptions may not hold at lower pH values or highly negative potentials. With these approximations, the rate expression for the HOR simplifies to

$$i_{\rm HOR} = -2Fk_1^0[{\rm H}^{\Box}][{\rm H}_2{\rm O}] \,\mathrm{e}\frac{F\alpha_1(\Phi^{\rm op} - \Phi_1^0)}{RT}$$
(12)

where  $k_{xy}^0 \Phi_{xy}^0$  and  $\alpha_x$  are the intrinsic rate constant, equilibrium potential, and charge transfer coefficient, respectively, for each step x. This expression is analogous to eq 9 and suggests that the net current of hydrogen oxidation  $(i_{HOR})$  increases with the activity of water in the solution  $([H_2O])$  and the coverage of hydrogen  $([H^{\Box}])$  on the catalyst surface.

The kinetically relevant steps of oxygen reduction involve electron transfer to oxygen-derived species, because the reaction rates on Pd do not depend on the isotopic label of the proton (e.g.,  $k_{\rm H_2O}^0/k_{\rm D_2O}^0 \approx 1$ ).<sup>44,12</sup> Specifically, the electrochemical literature suggests that the first electron transfer to O<sub>2</sub>\* (step 5a) is the kinetically relevant step for both H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O formation on Pd and Pt materials.<sup>42,44–46</sup> We also assume that subsequent reduction steps are irreversible (Figure 1), since density functional theory (DFT) calculations indicate that each of these reactions.<sup>12,42</sup> Consequently, the reverse reactions are slow except at operating potentials much more positive than are observed during open-circuit potentiometry measurements.<sup>47</sup> Thus, we derive the apparent current expression for the ORR

$$i_{\text{ORR}} = i_{\text{H}_2\text{O}_2} + i_{\text{H}_2\text{O}} = n_{\text{ORR}} F k_{5a}^0 e^{-\alpha_{5a} F (\Phi^{op} - \Phi_{5a}^0)/RT} [\text{O}_2^*]$$
(13)

where the total ORR current  $(i_{ORR})$  equals the currents associated with the formation of  $H_2O_2$   $(i_{H_2O_2})$  and  $H_2O$   $(i_{H_2O})$ , which increases with the coverage of  $O_2^*$  ( $[O_2^*]$ ) and the operating potential of the nanoparticle. Here, the total number of electrons transferred  $(n_{ORR})$  depends on the relative rate of the  $2e^-$  or  $4e^-$  pathways. Equation 13 reflects values for the intrinsic rate constant  $(k_{5a}^0)$  and charge transfer coefficient  $(\alpha_{5a})$  of the kinetically relevant electron transfer to  $O_2^*$ (analogous to eq 10). This expression was solved explicitly from the pseudo-steady-state coverage of each oxygen-derived intermediate ( $[O_2^*]$ ,  $[O^*]$ ,  $[OH^*]$ ,  $[OOH^*]$ ; Section S7 in the Supporting Information), while  $\Phi^{op48}$  relates to the electron chemical potental of the metal and was calculated by setting eqs 12 and 13 equal to each other (i.e.,  $i_{HOR} = i_{ORR}$ )

$$\Phi^{\rm op} = \frac{(\alpha_{5a} \Phi_{5a}^{0} + \alpha_{1} \Phi_{1}^{0})}{(\alpha_{5a} + \alpha_{1})} - \frac{RT}{F(\alpha_{5a} + \alpha_{1})}$$
$$\ln\left(\frac{2k_{1}^{0}[H_{2}][H_{2}O]\theta_{\Box}}{n_{\rm ORR}k_{5a}^{0}K_{4}[O_{2}]\theta_{*}}\right)$$
(14)

where the operating potential of the nanoparticle depends on the apparent equilibrium potential  $(\Phi_{5a}^0, \Phi_1^0)$  and the ratios of hydrogen oxidation  $(k_{1}^0, \alpha_1)$  versus oxygen reduction  $(k_{5a}^0, \alpha_{5a})$ rates.  $\Phi^{op}$  also depends on the temperature, the selectivity of  $H_2O_2$  (related to  $n_{ORR}$ ), and the coverage of sites that bind hydrogen  $(\theta_{\Box} = f([H^{\Box}]))$  and oxygen  $(\theta_* = f([O_2^*], [O^*]))$ [OH\*],[OOH\*])) species. Equation 14 resembles the functional form of eq 11 where  $\alpha_{ORR}$ ,  $\alpha_{HOR}$ ,  $k_{HOR}^0$ , and  $k_{ORR}^0$  reflect the apparent charge transfer coefficients and rate constants measured experimentally, which change with surface coverage  $(\theta_{\Box}, \theta_*)$  over a given range of conditions. Overall, these findings predict that the operating potential will decrease with the activity of hydrogen and increase with the activity of oxygen, which agrees with observations in Figure 4. Thus, H<sub>2</sub> pressure controls the value of  $\Phi^{op}$  on nanoparticle catalysts during the thermocatalytic ORR; however, material-dependent parameters (e.g.,  $k_i$ ,  $\alpha_i$ , and  $\Phi_i^0$ ) also contribute.

Functional forms of  $n_{\text{ORR}}$ ,  $\theta_{\Box}$ , and  $\theta_*$  were solved and substituted into eqs 13 and 14, which results in an expression showing the total rate of oxygen reduction under thermocatalytic conditions:

$$\frac{r_{\text{ORR}}}{[L_*]} = \left(\frac{\frac{n_{\text{ORR}}}{2}k_{\text{5a}}^0 K_4[O_2]}{1 + K_{\text{app},O_2}[O_2]}\right)^{\alpha_1/(\alpha_1 + \alpha_{\text{5a}})} \\ \left(\frac{k_1^0[H_2][H_2O]}{1 + K_{\text{app},H_2}[H_2]}\right)^{\alpha_{\text{5a}}/(\alpha_1 + \alpha_{\text{5a}})} \\ e^{F\alpha_1\alpha_{\text{5a}}(\Phi_{\text{5a}}^0 - \Phi_1^0)/(\alpha_{\text{5a}} + \alpha_1)RT}$$
(15)

This equation shows that the thermocatalytic rate of the ORR depends on expressions for both the hydrogen oxidation and oxygen reduction reactions. Here, these terms are multiplied by an exponential term, reflecting the difference in equilibrium potentials of the HOR and ORR paths ( $\Phi_{5a}^0 - \Phi_1^0$ ). The turnover rate of the ORR also carries an exponential dependence upon parameters that depend on the relative magnitude of the charge transfer coefficients of the ORR and HOR. Empirically, we observe greater values of  $\alpha_{ORR}$  versus  $\alpha_{HOR}$  (Table S2), suggesting that eq 15 should simplify to

$$\frac{r_{\text{ORR}}}{[L_*]} \approx \left(\frac{\frac{n_{\text{ORR}}}{2}k_{5a}^0 K_4[O_2]}{1 + K_{\text{app},O_2}[O_2]}\right)^{\alpha_1/\alpha_{5a}} \left(\frac{k_1^0[H_2][H_2O]}{1 + K_{\text{app},H_2}[H_2]}\right) e^{F\alpha_1(\Phi_{5a}^0 - \Phi_1^0)/RT}$$
(16)

This expression indicates that rates should increase in proportion with  $[H_2]$  and should show a weak dependence on  $[O_2]$ . Similarly, the model predicts that rates should be independent of pressure when the surface is saturated with hydrogen- and oxygen-derived intermediates ( $[H^{\Box}]$ ,  $[O_2^*]$ ,  $[O^*]$ ,  $[OH^*]$ ,  $[OH^*]$ ). The steady-state coverage of such species depends on the apparent adsorption constants of hydrogen ( $K_{app,H_2}$ ) and oxygen ( $K_{app,O_2}$ ), which reflect the relative rate that surface intermediates are generated and consumed. More specifically,  $K_{app,H_2}$  depends on the relative rate of steps 1 and 3 (i.e.,  $K_{app,H_2} = r_1/r_3$ ) while  $K_{app,O_2}$  depends on numerous elementary reactions that reduce oxygen (steps 4–9, 12, and 13). Rearrangement of eq 16 yields individual expressions for the formation of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O:

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$$\frac{r_{\rm H_2O_2}}{[\rm L_*]} + \frac{r_{\rm H_2O}}{[\rm L_*]} = (S_{\rm H_2O_2}(\Phi^{\rm op}) + S_{\rm H_2O}(\Phi^{\rm op}))\frac{r_{\rm ORR}}{[\rm L_*]}$$
(17)

$$S_{\rm H_2O_2}(\Phi^{\rm op}) = \frac{\frac{k_{12}^0 k_{6a}^0 e^{-\alpha_{6a}F(\Phi^{\rm op} - \Phi_{6a}^0)/RT}}{(k_{12}^0 + k_{13}^0 e^{-\alpha_{13}F(\Phi^{\rm op} - \Phi_{13}^0)/RT})}}{(k_{6a}^0 e^{-\alpha_{6a}F(\Phi^{\rm op} - \Phi_{6a}^0)/RT} + 2k_7^0 e^{-\alpha_7 F(\Phi^{\rm op} - \Phi_7^0)/RT}) + \frac{k_{13}^0 k_{6a}^0 e^{-\alpha_{13}F(\Phi^{\rm op} - \Phi_{13}^0)/RT} e^{-\alpha_{6a}F(\Phi^{\rm op} - \Phi_{6a}^0)/RT}}{(k_{12}^0 + k_{13}^0 e^{-\alpha_{13}F(\Phi^{\rm op} - \Phi_{13}^0)/RT})}$$
(18)

$$S_{\rm H_2O}(\Phi^{\rm op}) = 1 - S_{\rm H_2O_2}(\Phi^{\rm op})$$
<sup>(19)</sup>

where  $S_{\rm H_2 \ O_2}$  and  $S_{\rm H_2 O}$  are functions of  $\Phi^{\rm op}$  and represent the selectivities toward H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O, respectively. Here, the H<sub>2</sub>O<sub>2</sub> selectivity depends on the rate that OOH\* reduces to  $H_2O_2$   $(k_{6a}^0, \alpha_{6a})$  versus the rate that OOH\*  $(k_{7}^0, \alpha_7)$  or  $H_2O_2^*$  $(k_{13}^0, \alpha_{13})$  dissociate during H<sub>2</sub>O formation. These expressions also contain terms describing the relative rate that H<sub>2</sub>O<sub>2</sub> desorbs  $(r_{12})$  into solution versus the rate that it is reduced to  $H_2O(r_{13})$ . Moreover, these equations quantify how selectivities depend on the operating potential and temperature (vide infra). These equations also suggest that the selectivities in electrocatalytic and thermocatalytic measurements will be equivalent if the materials operate at the same potential ( $\Phi$  =  $\Phi^{op}$ ), present similar kinetic constants, and possess identical reactant coverages and nanoparticle phase. These expressions also define the apparent value of  $n_{ORR}$  in relation to the values of  $S_{H_2O_2}$  and  $S_{H_2O_2}$ .

$$n_{\rm ORR} = \frac{4}{1 + S_{\rm H_2O_2}(\Phi^{\rm op})}$$
(20)

Thus, eq 20 shows that the average number of electrons transmitted during the ORR ranges from 2 to 4, depending on whether the  $H_2O_2$  or  $H_2O$  formation pathway dominates.

When coverages of hydrogen atoms are low (i.e.,  $[L_{\Box}] = [\Box]$ ) and the surface is saturated with oxygenates (i.e.,  $[L_*] \neq [*]$ ), eq 16 takes the form

$$\frac{r_{\rm H_2O_2}}{[\rm L_*]} \approx S_{\rm H_2O_2}(\Phi^{\rm op}) \left( \frac{n_{\rm ORR} k_{\rm 5a}^0 \rm K_4}{2K_{\rm app,O_2}} \right)^{\alpha_1/\alpha_{\rm 5a}} (k_1^0[\rm H_2][\rm H_2O]) \\ e^{F(\alpha_1(\Phi_{\rm 5a}^0 - \Phi_1^0))/RT}$$
(21)

which predicts that the rate of the ORR increases in proportion with hydrogen pressure at the lowest values of  $[H_2]$  and the overall rate depends mostly on the Heyrovsky step. This rate also depends on the apparent rate constant of electron transfer to oxygen-derived species and the relative charge transfer coefficients of the HOR and ORR.

At the highest hydrogen pressures, hydrogen atoms saturate the available surface sites (i.e.,  $[L_{\Box}] = H^{\Box}$ ) and eq 16 simplifies to

$$\frac{r_{\rm H_2O_2}}{[\rm L_*]} \approx S_{\rm H_2O_2}(\Phi^{\rm op}) \left(\frac{n_{\rm ORR} k_{5a}^0 K_4}{2K_{\rm app,O_2}}\right)^{\alpha_3/\alpha_{5a}} (k_3^0[\rm H_2O]) e^{F(\alpha_3(\Phi_{5a}^0 - \Phi_3^0))/RT}$$
(22)

where the rate of ORR does not depend on hydrogen pressure and the overall rate is mostly dependent on the Volmer step. Under such conditions, the Volmer step acts as the kinetically relevant step of the HOR, which leads to slight changes in the apparent rate constant and charge transfer coefficients.

Equation 16 was fit to the reaction rates shown in Figure 5 by assuming a constant value for each variable other than  $[H_2]$ . While the intrinsic rate constants  $(k_x^0)$ , charge transfer coefficients  $(\alpha_x)$ , and other terms (e.g.,  $\Phi_x^0$ ,  $n_{\text{ORR}}$ ) change as a function of the potential and the coverage of hydrogen (vide infra), we treat these parameters as constants since we do not have data showing the functional dependence of these values over this range of conditions. Still, eq 16 captures the functional change in rates shown in Figure 5, suggesting that the proposed electrochemical reactions can reasonably describe the trends in data for thermocatalytic systems. Specifically, eq 16 explains why rates increase in proportion with hydrogen pressure (eq 21) as the surface eventually saturates with  $H^{\square}$  (eq 22). Yet, most Pd materials showed a considerable increase in H2O2 selectivity at these higher pressures of hydrogen (150–400 kPa of  $H_2$ ) in comparison to the lower pressures  $(20-60 \text{ kPa of } H_2)$ . Consequently, most Pd materials showed unexpected deviations in their fits of  $k_{6a}^0$ and  $k_{7}^0$ , which suggest that the rate of H<sub>2</sub>O<sub>2</sub> formation  $(k_{63}^0)$ increases relative to the rate of H<sub>2</sub>O formation  $(k_7^0)$  at higher coverages of  $H^{\Box}$ . Such findings agree with the formation of the  $\beta$ -PdH, phase, which presents lower barriers to generate H<sub>2</sub>O<sub>2</sub> and greater O-O dissociation barriers in comparison to metallic Pd (vide infra).<sup>12</sup> Thus, eq 16 captures the functional change in rates, but the formation of  $\beta$ -PdH<sub>r</sub> convolutes the functions related to selectivity (eqs 18 and 19). Nevertheless, this analysis suggests that a nanoparticle will facilitate a high rate of H<sub>2</sub>O<sub>2</sub> formation if the surface presents a low barrier to both oxidize hydrogen and reduce oxygen through the 2e<sup>-</sup> route.

3.3. Comparing Catalyst Performance between Thermocatalysis and Electrocatalysis. The H<sub>2</sub>O<sub>2</sub> selectivity of a metal nanoparticle material depends upon the metal identity, the temperature, and the coverage of reactants on the catalyst surface. The selectivity for each catalyst also reflects the electrode potential under electrochemical ORR conditions or the operating potential under direct synthesis conditions. This selectivity is a function of the competing rates of reactions that consume OOH\* intermediates by simple electron transfer  $(k_{6a}^0)$  or dissociative electron transfer  $(k_7^0, k_{13}^0)$  pathways (eqs 18 and 19). Ultimately, H<sub>2</sub>O<sub>2</sub> selectivities reflect the ability of the catalyst to cleave the O-O bond,<sup>6,9,11,49</sup> which occurs irreversibly under direct synthesis conditions, as shown during the reduction of <sup>18</sup>O<sub>2</sub>-<sup>16</sup>O<sub>2</sub> mixtures.<sup>50</sup> Consequently, metals that prevent the O–O bond rupture in dioxygen species  $(O_2^*, O_2)$ OOH\*, and  $H_2O_2^*$ ) and provide high oxygen reduction rates give the highest rates and selectivities for  $H_2O_2$  formation. Our model also gives greater insight into the molecular phenomena that dictate selectivity changes under varying reaction conditions. Thus, we compared the selectivities of Pd and  $PtAu_{15}$  catalysts over ranges of electrode potentials (-0.1 to +0.6 V vs NHE), hydrogen pressures (20–400 kPa of  $H_2$ , 60 kPa of  $O_2$ ), and temperatures (278–308 K), as shown in Figure 6.



**Figure 6.** Selectivity of  $H_2O_2$  formation on PtAu<sub>15</sub> and Pd nanoparticles as a function of (a) electrode potential (-0.1 to +0.6 V vs NHE, rotating ring-disk electrode), (b)  $H_2$  and  $O_2$  pressure (20-400 kPa of  $H_2$ , 60 kPa of  $O_2$ , 278 K, trickle-bed reactor), and (c) inverse temperature (200 kPa of  $H_2$ , 60 kPa of  $O_2$ , 278–308 K, trickle-bed reactor). The best fit of eq 23 is shown as the dashed line in (a).

3.3.1. Selectivity of H<sub>2</sub>O<sub>2</sub> Formation as a Function of Electrode Potential. Figure 6a shows that H<sub>2</sub>O<sub>2</sub> selectivities of Pd and PtAu<sub>15</sub> catalysts increase exponentially to maximum values of 60 and 90%, respectively, between electrode potentials of 0.45–0.6 V vs NHE. At lower electrode potentials (-0.1 to +0.3 V vs NHE), however, the selectivity of the PtAu<sub>15</sub> material gradually decreases to 50%, while the selectivity of Pd decreases more sharply and approaches a constant value of ~20%. All catalysts examined present selectivity profiles with similar functional forms (Figures S44-S56), consistent with analogous electrocatalytic measurements reported elsewhere.<sup>49</sup> The decrease in selectivities at lower potentials suggests that the apparent free energy barrier for  $H_2O_2$  decomposition pathways becomes comparable to the primary H<sub>2</sub>O<sub>2</sub> formation pathway at the lowest potentials. Here, both the disproportionation of  $H_2O_2$  ( $2H_2O_2 \rightarrow O_2 +$  $2H_2O$  and the direct electroreduction of  $H_2O_2$  (step 13) may contribute to this decrease in selectivity, <sup>49,51</sup> but such reactions are challenging to deconvolute. Therefore, we have considered only the electroreduction of  $H_2O_2$ , which yields equations that reasonably agree with the corresponding data (Figure 6a). Below, we show the generalized form of eq 18, which applies for any electrode potential

$$S_{\rm H_2O_2}(\Phi) = \frac{\frac{k_{12}^0 k_{03}^0 e^{-\alpha_{6a}F(\Phi - \Phi_{6a}^0)/RT}}{(k_{12}^0 + k_{13}^0 e^{-\alpha_{13}F(\Phi - \Phi_{13}^0)/RT})}}{(k_{6a}^0 e^{-\alpha_{6a}F(\Phi - \Phi_{6a}^0)/RT} + 2k_7^0 e^{-\alpha_7 F(\Phi - \Phi_7^0)/RT}) + \frac{k_{13}^0 k_{6a}^0 e^{-\alpha_{13}F(\Phi - \Phi_{13}^0)/RT} e^{-\alpha_{6a}F(\Phi - \Phi_{6a}^0)/RT}}{(k_{12}^0 + k_{13}^0 e^{-\alpha_{13}F(\Phi - \Phi_{13}^0)/RT})}$$
(23)

where the selectivity of H2O2 formation depends on the relative ratio of the primary 2e<sup>-</sup> path (step 6a) versus the primary 4e<sup>-</sup> (step 7) and secondary 2e<sup>-</sup> (step 13) pathways that form H<sub>2</sub>O. Equation 23 reasonably reproduces selectivities measured as functions of electrode potential (Figures S44-S56), and Table S3 displays values of the fitted parameters. This expression for  $S_{H_2O_2}$  contains a ratio for the rate of  $H_2O_2$ decomposition to the rate of  $H_2O_2$  desorption (step 12). Here, H<sub>2</sub>O<sub>2</sub> desorption rates are assumed to depend more weakly on electrode potential, since this step does not involve charged intermediates or an explicit electron transfer step. Consequently, at low overpotentials, the rate of H<sub>2</sub>O<sub>2</sub> desorption is fast, and eq 23 collapses into a sigmoidal expression. At the greatest overpotentials, however, eq 23 predicts a sharp decrease in selectivity that is consistent with the behavior in Figure 6a.

Fits of  $k_{6a}^0$  and  $k_7^0$  explain why PtAu<sub>15</sub> is more selective than Pd over a broader range of electrode potentials. The greater ratio between rate constants of the primary ORR pathways  $(((k_{6a}/k_7)_{PtAu})/(k_{6a}/k_7)_{Pd} = 4)$  indicate that PtAu<sub>15</sub> shows a higher intrinsic free energy barrier to form H<sub>2</sub>O versus H<sub>2</sub>O<sub>2</sub> in comparison to Pd. The high selectivities on PtAu<sub>15</sub> resemble those for PdAu alloys,<sup>16,52</sup> on which O–O bond dissociation pathways ( $k_7$ ,  $k_{13}$ ) are inhibited as Pd atoms are isolated on the Au surface. PtAu<sub>15</sub> may form similar types of monomeric or oligomeric groupings of Pt atoms. In contrast, the surface of monometallic Pd nanoparticles provides large ensembles of contiguous Pd atoms with electronic structures that favor H<sub>2</sub>O formation.

Finally, this derivation implies that each catalyst possesses an optimum electrode potential ( $\Phi_{opt}$ ) that provides the maximum possible H<sub>2</sub>O<sub>2</sub> selectivity, which occurs when the

derivative of eq 23 equals zero  $(dS_{H_2O_2}(\Phi)/d\Phi = 0)$  (Section S8 in the Supporting Information):

$$\Phi_{\rm opt} \approx \frac{RT}{F(\alpha_7 - \alpha_{6a})} \ln \left( \frac{k_7^0(\alpha_{6a} - \alpha_{13} - \alpha_7)}{k_{6a}^0 \times \alpha_{13}} \right) + \frac{(\alpha_7 \Phi_7^0 - \alpha_{6a} \Phi_{6a}^0)}{\alpha_7 - \alpha_{6a}}$$
(24)

This relationship shows that  $\Phi_{\text{opt}}$  depends on the difference of the charge transfer coefficients that form  $H_2O_2$  ( $\alpha_{6a}$ ) versus those that form H<sub>2</sub>O ( $\alpha_{72}$ ,  $\alpha_{13}$ ). This parameter also depends on the ratio of intrinsic rate constants that primarily form H<sub>2</sub>O  $(k_7^0)$  versus those that form H<sub>2</sub>O<sub>2</sub>  $(k_{6a}^0)$ . Thus, the value of  $\Phi_{opt}$ represents a critical point at which the metallic density of states overlaps with the OOH\* and  $H_2O_2^*$  states in a way that maximizes electron transfer toward stable H<sub>2</sub>O<sub>2</sub>\* species while preventing excessive electron transfer into the O-O antibonding states. These differences may suggest that Pt monomers and oligomers on the surface of PtAu<sub>15</sub> do not bind dioxygen intermediates with  $\eta^2$  adsorption modes that lead to the significant overlap between the d band and O-O antibonding states on Pd. Consequently, subtle changes in the coordination of reactants may lead to greater  $H_2O_2$ selectivities at  $\Phi_{opt}$  on PtAu<sub>15</sub>.

The results presented in this subsection suggest that Pd performs catalysis at a suboptimal operating potential (0.51-0.61 V vs NHE) under our tested direct synthesis conditions, which leads to H<sub>2</sub>O<sub>2</sub> selectivities between 16 and 25%. Figure 6a indicates that the optimal operating potential of this Pd material is at 0.43 V vs NHE, which leads to a selectivity as high as 60% at this condition. PtAu<sub>15</sub>, in contrast, shows values of  $\Phi^{op}$  between 0.39 and 0.45 V vs NHE, which corresponds to H<sub>2</sub>O<sub>2</sub> selectivities between 76 and 86%, as shown in Figure 6a. Therefore, PtAu15 operates more closely to its optimal operating potential (0.34 V vs NHE) under direct synthesis conditions in comparison to Pd. Thus, these results present new opportunities to design materials that result in operating potentials closer to the optimal potential by understanding factors that affect charge transfer coefficients and rate constants toward the HOR and ORR. Similarly, these principles may lead to the design of reactors that facilitate oxygen reduction at this optimum potential for H<sub>2</sub>O<sub>2</sub> generation.

3.3.2. Selectivity of  $H_2O_2$  Formation as a Function of Hydrogen and Oxygen Activity. The  $H_2O_2$  selectivity changes as a function of hydrogen pressure under direct synthesis conditions. Figure 6b shows the  $H_2O_2$  selectivity of PtAu<sub>15</sub> and Pd nanoparticles (20–400 kPa of  $H_2$ , 60 kPa of  $O_2$ , 278 K). The selectivities on PtAu<sub>15</sub> increase from ~75% toward a value of 90% over this range of  $H_2$  pressures. In contrast,  $H_2O_2$  selectivities on Pd vary between 6 and 9% at the lowest pressures (20–60 kPa of  $H_2$ ) before rising sharply and becoming constant (~60%) at the highest pressures (200–400 kPa of  $H_2$ ). The change in selectivity with respect to the thermodynamic activity of  $H_2$  is shown below, as derived in section S9 in the Supporting Information:

$$\left( \frac{dS_{H_2O_2}(\Phi^{op})}{d[H_2]} \right) \approx \left( \frac{d\Phi^{op}}{d[H_2]} \right) \left( \frac{dS_{H_2O_2}(\Phi)}{d\Phi} \right)$$

$$\propto \frac{\alpha_{6a} - \alpha_7 - \alpha_{13}}{\alpha_{5a} + \alpha_1}$$
(25)

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This expression shows that changes in  $H_2O_2$  selectivity with  $H_2$ activity reflect the change in selectivity with electrode potential (derivative of eq 23) and change in operating potential with  $H_2$ activity (derivative of eq 14). Specifically, the dependence of selectivity on potential is a function of the charge transfer coefficients that lead to  $H_2O_2$  formation ( $\alpha_{6a}$ ) versus those that lead to H<sub>2</sub>O formation ( $\alpha_{71}$ ,  $\alpha_{13}$ ). In comparison, the functional relationship of operating potential and hydrogen activity depends upon the overall charge transfer coefficients of the ORR and HOR ( $\alpha_{5a}$ ,  $\alpha_1$ ). For instance, PdAu<sub>60</sub> and PtCo present similar values of  $\alpha_{5a}$  (Table S2, 0.37 versus 0.30), but PdAu<sub>60</sub> presents much greater values of  $\alpha_1$  (Table S2, 0.93) versus 0.25). Consequently, PdAu<sub>60</sub> shows the smallest decrease in operating potential (~0.03 V, Figure S10), while PtCo shows the greatest difference in operating potential (~0.25 V, Figure S7) between 60 and 400 kPa of H<sub>2</sub>. Thus, some metals may show a modest change in selectivity over a broad range of hydrogen pressures if materials show little change in their operating potential (e.g.,  $\alpha_{5a}$  and  $\alpha_1$  are large).

The data in Figure 6b show trends in selectivity consistent with the changes in operating potential determined through open-circuit potentiometry measurements at similar pressures (Figure 4). PtAu<sub>15</sub> operates at potentials ( $\Phi^{op} = 0.39 - 0.45$  vs NHE) coinciding with a similar change in  $H_2O_2$  selectivity (75-90%) in Figures 6a,b, which agree with predictions from eq 23. Pd, in contrast, operates at more positive potentials  $(\overline{\Phi}^{op} = 0.51 - 0.61 \text{ vs NHE})$ , which correspond to a H<sub>2</sub>O<sub>2</sub> selectivity of between 16 and 25% in Figure 6a. Yet, the  $H_2O_2$ selectivity increases from 6 to 60% between 20 and 400 kPa of  $H_{22}$  significantly exceeding the expectations of eq 23 for these corresponding operating potentials. Thus, the predicted changes in selectivities over this range of hydrogen and oxygen pressures shows better agreement for PtAu<sub>15</sub> in comparison to Pd, which suggests that intrinsic rate constants  $(k_{6a}, k_7, k_{13})$ change with reactant coverages on Pd but not on PtAu15. Again, these observations coincide with a Pd to  $\beta$ -PdH<sub>x</sub> phase transition for Pd nanoparticles, as observed by operando X-ray absorption spectroscopy at  $H_2$  to  $O_2$  gas ratios of ~2:1.<sup>12,53</sup> Pt and Pt-based bimetallics do not form hydrides under these conditions, which explains why the changes in selectivity are more significant on Pd and Pd-based alloys in comparison to the Pt- based materials (Figure 5).

Thus, materials may exist at similar potentials ( $\Phi = \Phi^{op}$ ), but the coverages of H<sup> $\Box$ </sup> atoms on these nanoparticles are greater under direct synthesis conditions than under electrocatalytic conditions because of the increased chemical potential of hydrogen. Thus, these differences in the electrochemical potential lead to inconsistencies between H<sub>2</sub>O<sub>2</sub> selectivities in thermochemical and electrochemical systems. Specifically, the coverage of H<sup> $\Box$ </sup> atoms ([H<sup> $\Box$ </sup>]) during direct synthesis depends directly upon the H<sub>2</sub> pressure (section S6 in the Supporting Information):

$$[\mathrm{H}^{\Box}] = \frac{k_1^0}{k_3^0} [\mathrm{H}_2] [\Box] e^{F\alpha_1 (\Phi^{\mathrm{op}} - \Phi_1^0)/RT} e^{-F\alpha_3 (\Phi^{\mathrm{op}} - \Phi_3^0)/RT}$$
(26)

In contrast, electrochemical conditions produce  $H^{\Box}$  atoms by steps associated with the hydrogen evolution reaction on the nanoparticle surface and depend upon the applied electrode potential:

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Figure 7. Thermocatalytic  $H_2O_2$  selectivities and ORR rates compared to electrocatalytic selectivities and predicted ORR rates on (a, c) PdPt (yellow  $\spadesuit$ ), Pt (green  $\blacksquare$ ), PtCo (orange  $\triangle$ ), PtAu<sub>60</sub> (black  $\star$ ), PtAu<sub>15</sub> (orange  $\blacktriangle$ ), and PtAu<sub>5</sub> (purple  $\Box$ ) and (b, d) Pd (black  $\spadesuit$ ), PdCo (red  $\triangle$ ), PdNi (blue  $\checkmark$ ), PdZn (cyan  $\blacklozenge$ ), PdAu (red  $\bigcirc$ ), and PdCu (purple  $\blacktriangleright$ ) nanoparticles supported on Vulcan XC-72. The thermocatalytic selectivity was calculated from the  $H_2O_2$  formation rate divided by the  $H_2$  consumption rate in a trickle-bed reactor (20–400 kPa of  $H_2$ , 60 kPa of  $O_2$ ) at 298 K. The electrocatalytic selectivity was calculated from the ring and disk currents of a rotating ring–disk electrode (RRDE). Selectivities were determined at equivalent potentials ( $\Phi = \Phi^{op}$ ) from open-circuit potentiometry experiments using eq 23. The rates of the ORR were predicted from electrochemical rate constants (Table S2) using eq 16.

$$[\mathrm{H}^{\Box}] = \frac{k_{-3}^{0}}{k_{-1}^{0}} [\mathrm{H}_{2}\mathrm{O}][\Box] e^{-F\alpha_{-3}(\Phi - \Phi_{-3}^{0})/RT} e^{F\alpha_{-1}(\Phi - \Phi_{-1}^{0})/RT}$$
(27)

Comparisons of these equations demonstrate that high coverages of  $H^{\Box}$  can form by dissociative adsorption of  $H_2$ under thermochemical conditions. Under electrochemical conditions, however, the reduction of hydronium ions requires electrode potentials lower than those used for the ORR, resulting in low coverages of  $H^{\Box}$  under the conditions we investigated.<sup>54</sup> For example, voltammograms of Pd show that hydrogen evolution occurs at electrode potentials below -0.1V vs NHE (Figure S57), which is much lower than the optimum operating potential of Pd ( $\Phi_{opt}^{pd}$  = 0.43 V vs NHE). Consequently, Pd likely exists in the metallic phase during typical RRDE measurements. The formation of the  $\beta$ -PdH<sub>x</sub> phase occurs only at electrode potentials that are unselective toward the formation of H<sub>2</sub>O<sub>2</sub> because secondary decomposition pathways  $(k_{13}^0, \alpha_{13})$  become significant relative to the primary formation pathways  $(k_{6a}^0, \alpha_{6a})$  at these lower potentials. Similarly, the presence of gaseous hydrogen allows Pd to form a more selective surface structure ( $\beta$ -PdH<sub>x</sub>) but at a suboptimal potential during direct synthesis. Similarly, the

coverage of  $H^{\Box}$  is likely much lower on Pt materials under similar conditions, since these materials show much greater HOR rates in cmparison to the Pd materials (section S5 in the Supporting Information).

The analysis in this section reveals an important distinction between the thermal and electrocatalytic systems, which only becomes apparent following these comparisons. Controlling the hydrogen and oxygen pressure allows for greater control of the coverage of surface species, which can lead to more selective intrinsic rate constants than in purely electrochemical systems. Separately, an electrode can bias the potential of a nanoparticle toward its optimal potential ( $\Phi_{opt}$ ) to favor  $H_2O_2$ formation over primary and secondary pathways that form  $H_2O$ , which may not be possible under thermocatalytic conditions. These findings imply that much greater  $H_2O_2$ selectivities may be achieved through simultaneous control of both the activities of  $H_2$  and  $O_2$  to optimize surface coverages and the electrode potential to manipulate apparent rate constants.

3.3.3. Selectivity of  $H_2O_2$  Formation as a Function of Temperature. In this subsection, we consider the selectivity of materials as a function of temperature, which gives insight into

the apparent barriers of reaction for the  $H_2O_2$  and  $H_2O$  formation pathways. Figure 6c shows the selectivity of Pd and PtAu<sub>15</sub> between 278 and 308 K at a constant pressure of 200 kPa of  $H_2$  and 60 kPa of  $O_2$ . PtAu<sub>15</sub> shows a decrease in  $H_2O_2$  selectivity from 87% to 57%, while the selectivity on Pd decreases from 52% to 47% over this range. To interpret this behavior, we differentiate the selectivity with respect to temperature (SI section S9) and derive

$$\left(\frac{\mathrm{d}S_{\mathrm{H}_{2}\mathrm{O}_{2}}(\Phi^{\mathrm{op}})}{\mathrm{d}T}\right)_{\Phi} \propto \Delta H_{7}^{\dagger} - \Delta H_{6a}^{\dagger} + F((\alpha_{7} - \alpha_{6a})\Phi^{\mathrm{op}} - (\alpha_{7}\Phi_{7}^{0} - \alpha_{6a}\Phi_{6a}^{0})) + \xi(\Phi^{\mathrm{op}}) = \Delta \Delta H_{4e\cdot2e}^{\dagger}$$
(28)

Here, the change in selectivity with temperature depends on the differences between the apparent activation enthalpies for the four-electron and two-electron ORR  $(\Delta \Delta H_{4e-2e}^{\dagger})$ . This parameter depends on the difference in the intrinsic activation enthalpies  $(\Delta H_7^{\ddagger}, \Delta H_{6a}^{\ddagger})$ , equilibrium potentials  $(\Phi_{72}^0, \Phi_{6a}^0)$ , and charge transfer coefficients ( $\alpha_7$ ,  $\alpha_{6a}$ ) of the elementary steps that form H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O from OOH\*. This expression indicates that a more negative operating potential leads to a lower apparent reaction barrier for either ORR pathway. Moreover, eq 14 suggests that an increase in temperature leads to a decrease in the operating potential, indicating that these apparent barriers should also decrease with temperature. Therefore, eq 28 indicates that the H<sub>2</sub>O<sub>2</sub> selectivity should increase if  $\Phi^{op}$  decreases at a constant temperature (assuming  $\alpha_{6a} > \alpha_7$ ). However, Figure 6c shows that the selectivity decreases as the temperature increases, indicating that intrinsic activation enthalpies  $(\Delta H_7^{\ddagger}, \Delta H_{6a}^{\ddagger})$  dictate most of the change in selectivity over the tested range of temperature (i.e., the change  $\Phi^{op}$  with temperature has a weak influence on selectivity). At lower operating potentials, however, the secondary  $H_2O_2$  decomposition pathway (step 13) becomes more dominant, and  $\xi$  contributes to a significant decrease in the selectivity (Sections S4, S5 and S9 in the Supporting Information). Therefore, the value of  $\Phi_{opt}$  coincides with the maximum value of  $\Delta\Delta H_{4e-2e}^{\ddagger}$ , leading to the maximum selectivity for a material.

These interpretations of eq 28 explain the trends in Figure 6c, where we empirically measure the apparent values of  $\Delta\Delta H_{4e-2e}^{\dagger}$  as 40 kJ mol<sup>-1</sup> on PtAu<sub>15</sub> and 7 kJ mol<sup>-1</sup> on Pd. The greater value of  $\Delta\Delta H_{4e-2e}^{\dagger}$  results in higher selectivity on PtAu<sub>15</sub> than on Pd in Figure 6, which agrees with the fits of  $k_{6a}$  and  $k_7$  by eq 23. Thus, the surface structure of PtAu<sub>15</sub> may consist of monomeric Pt species that intrinsically favor the formation of H<sub>2</sub>O<sub>2</sub> versus H<sub>2</sub>O by obstructing the dissociation of O–O bonds, while Pd consists of contiguous ensembles of Pd that more readily dissociate these bonds. Comparisons of the activation barriers at low and high hydrogen pressures show that  $\Delta\Delta H_{4e-2e}^{\dagger}$  also depends upon H<sub>2</sub> pressure (Table S4 and Figures S59–S70). We attribute these differences to changes in the coverage of reactive species (e.g., H<sup>[]</sup>), which can influence intrinsic activation enthalpies ( $\Delta H_7^{\dagger}$ ,  $\Delta H_{6a}^{\dagger}$ ) and the operating potential ( $\Phi^{op}$ ).

 $H_2O_2$  selectivities decrease as temperatures increase on all materials. This observation agrees with the value of eq 23 taken at the limit of low temperature  $(\lim_{T\to 0} S_{H_2O_2}(T) = 1)$  at a constant potential. However, eq 14 suggests that  $\Phi^{op}$  increases as the temperature decreases, indicating that this improvement

in selectivity may wane at sufficiently low temperatures. While the selectivity of  $H_2O_2$  increases at lower temperatures, the overall rate of  $H_2O_2$  formation decreases in both thermochemical and electrochemical systems. However, an applied electrode potential can compensate for the loss of oxygen reduction rates, while high  $H_2O_2$  selectivities are maintained. Thus, this analysis demonstrates a careful tradeoff between formation rates and selectivity, depending on the temperature and the potential of the nanoparticle.

3.3.4. Comparison of Rates and Selectivity of Electrochemical and Thermal Measurements. Using the results from prior sections, we compare and analyze trends in  $H_2O_2$ rates and selectivities obtained over a range of thermal and electrochemical conditions for 12 different compositions of Ptand Pd-based monometallic and bimetallic nanoparticles supported on carbon. Figure 7a,b shows that electrochemical and thermochemical H2O2 selectivities on a given catalyst correlate when they are measured at identical potentials ( $\Phi =$  $\Phi^{op}$ ). These comparisons involve measurements obtained as a function of H<sub>2</sub> pressure (Figure S5) and as a function of electrode potential (Figures S44-S56), which are related to one another using potentiometric measurements obtained in mixtures of  $H_2$  and  $O_2$  gas (Figure 4 and Figures S6–S17). The selectivities reported in Figures 7a,b collectively show parity across many of the studied materials ( $R^2 = 0.61$ ). These observations corroborate a similar reaction mechanism between the thermocatalyic and electrocatalytic systems and support the relationships described in the previous sections.

The Pt-based materials show a high level of parity (Figure 7a,  $R^2 = 0.94$ ) in comparison to Pd-based materials, which deviate more from parity (Figure 7b,  $R^2 = 0.55$ ). These deviations among the Pd-based materials are most significant at the greatest  $H_2$  pressures, which lead to high  $H^{\Box}$  coverages and form the  $\beta$ -PdH<sub>x</sub> phase.<sup>12,53</sup> This phase does not form readily during electrochemical measurements of the ORR, because  $H^{\Box}$  coverages are negligible under these conditions (vide supra). The formation of  $\beta$ -PdH<sub>x</sub> lowers barriers to generate  $H_2O_2$  ( $k_{6a}^0$ ) and increases O-O bond dissociation barriers  $(k_{7}^0, k_{13}^0)$  in comparison to metallic Pd.<sup>12</sup> Consequently, catalysts that contain Pd typically show greater similarities in H<sub>2</sub>O<sub>2</sub> selectivities between electrochemical and thermochemical conditions when the latter use lower hydrogen pressures. In contrast, the Pt materials agree better with the parity line over the given range of potentials, suggesting that these materials present more similar kinetic parameters under electrochemical and thermochemical conditions. This conclusion also agrees with the inability of Pt materials to form hydrides at reactant pressures used in trickle-bed reactor measurements.

Figure 7c,d shows the agreement of thermochemical ORR rates in comparison to the predictions of eq 16 on Pt- and Pdbased materials. Generally, reactive catalysts show high reactivity in both the electrocatalytic and thermocatalytic systems. However, the predicted ORR rates show better agreement with the rates measured on Pt materials than on Pd materials. Specifically, the electrocatalytic prediction of rates is systematically greater than those measured thermocatalytically on Pd materials. In section S10 in the Supporting Information, we evaluate the sources of these disparities and find that the overprediction of rates on Pd materials may result from differences between the apparent values of  $k_{\text{ORR}}$ ,  $k_{\text{HOR}}$ ,  $\alpha_{\text{ORR}}$ , and  $\alpha_{\text{HOR}}$  during electrocatalysis and thermocatalysis experiments. Specifically, these parameters depend strongly on the



**Figure 8.** (a) Comparison of direct synthesis turnover rates of  $H_2O_2$  formation as a function of hydrogen pressure (20–400 kPa of  $H_2$ , 60 kPa pf  $O_2$ , 298 K) on Au, PdAu, and PtAu materials. (b) Comparisons of current generated on a disk and ring electrode, which measures the total rate of the ORR and the associated  $H_2O_2$  production as a function of electrode potential (-0.1 to +0.6 V vs NHE). These currents were used to calculate (c) the  $H_2O_2$  selectivity of the materials at varying electrode potentials. (d) Comparisons between the disk current of the HOR on these materials as a function of electrode potential (0.4–1.0 V vs NHE). Formation rates are normalized by the total moles of Pd or Pt in these samples, while rates on monometallic Au are below the detection limit.

coverages of oxygen- and hydrogen-derived intermediates, and nonlinearities in our Tafel analysis exacerbate these differences. Since eq 16 includes exponential functions of  $\alpha_{ORR}$  and  $\alpha_{HOR}$ , small changes in these values can cause the apparent rate to change by orders of magnitude. This conclusion agrees also with the better parity of selectivity measurements on Pt materials versus Pd materials, which is also a strong function of coverage. Predictions on Pt materials show reasonable agreement, especially when the number of surface sites is quantified with an internal standard (e.g., CO chemisorption; Figure S71).

Overall, these disparities show that it is possible to achieve a similar potential on a nanoparticle ( $\Phi = \Phi^{op}$ ) under thermoand electrocatalytic conditions, but the electrochemical potential may vary significantly. Consequently, coverages of reactive intermediates can differ in these measurements and result in differences in the apparent charge transfer coefficients and intrinsic rate constants. Pt-based materials seem less sensitive to changes in reactant coverage, leading to better agreement with the predictions of the model. On Pd-based materials, however, differences in the coverage of hydrogenand oxygen-derived intermediates can alter the apparent values of  $k_{ORR}$ ,  $k_{HOR}$ ,  $\alpha_{ORR}$ , and  $\alpha_{HOR}$  during measurements of the HOR, ORR, and direct synthesis. Thus, this model can provide reasonable predictions for thermocatalytic rates and selectivities when kinetic parameters are determined at equivalent electrochemical potentials.

**3.4. Semiquantitative Predictions for Thermocatalytic Systems.** In previous sections, we derived a rate expression (eq 16) that accurately describes the changes in  $H_2O_2$  and  $H_2O$  formation as a function of hydrogen pressure and provided guidelines to design high-performance thermal catalysts. Equation 16 shows that the rate of  $H_2O_2$  formation depends mostly on the kinetic parameters of hydrogen oxidation ( $k_{11}^0$ ,  $\alpha_1$ ,  $k_{31}^0$ ,  $\alpha_3$ ) and  $2e^-$  oxygen reduction ( $k_{6a}^0$ ,  $\alpha_{6a}$ ). Therefore, materials with a nominally similar selectivity should show an overall higher rate of  $H_2O_2$  formation if they present lower overpotentials to oxidize hydrogen. Figure 8 shows comparisons of  $H_2O_2$  formation rates and selectivities on Au, PdAu\_{60}, and PtAu\_{60} catalysts that examine this hypothesis.

Figure 8a shows that  $H_2O_2$  formation rates on  $PtAu_{60}$  are twice those measured on  $PdAu_{60}$  over a range of  $H_2$  pressures (20–400 kPa of  $H_2$ ), while rates on Au are immeasurably low. Yet, the same materials show similar oxygen reduction rates (Figure 8b) over the examined range of electrode potentials (-0.1 to +0.9 V vs NHE), as shown by comparable current densities on both the ring and disk electrodes. Moreover, the electrocatalytic  $H_2O_2$  selectivities (Figure 8c) are similar to those measured under direct synthesis conditions at equivalent electrode potentials ( $\Phi = \Phi^{op}$ ). These discrepancies suggest that the kinetics of the hydrogen oxidation reaction produce the large differences in rates observed during the thermocatalytic reactions of H<sub>2</sub> and O<sub>2</sub>.

Figure 8d shows rotating disk voltammograms for the same Au-based catalysts performing hydrogen oxidation over a similar range of electrode potentials (-0.1 to +1.0 V vs NHE)as the ORR measurements. These data show that PtAu<sub>60</sub> catalyzes HOR rates nearly double those of PdAu<sub>60</sub> over this range, such that the HOR overpotential of PtAu<sub>60</sub> is ~150 mV lower than for PdAu<sub>60</sub>. In comparison, the Au presents HOR rates that are many orders of magnitude lower than those on either material. Thus, the Pt alloy more readily oxidizes hydrogen than the Pd alloy, while pure Au barely activates hydrogen  $(k_{1,\text{PtAu}_{60}}^0 > k_{1,\text{PdAu}_{60}}^0 \gg k_{1,\text{Au}}^0)$ . Within the framework established in Sections \$3.1 and \$3.2 in the Supporting Information, the greater HOR overpotentials on Au and PdAu<sub>60</sub> in comparison to PtAu<sub>60</sub> lead to lower rates of H<sub>2</sub>O<sub>2</sub> formation on these catalysts under thermocatalytic conditions (eq 16). Essentially, the higher barriers of the HOR on Pd<sub>1</sub>Au<sub>60</sub> and Au lead to larger apparent barriers to form H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O. Such interpretations are consistent with predictions in the literature, showing that effective catalysts must readily activate both hydrogen and oxygen to achieve high rates toward H<sub>2</sub>O<sub>2</sub>.<sup>5</sup>

This analysis also reveals that differences in HOR kinetic parameters  $(k_1^0, \alpha_1, k_3^0, \alpha_3)$  allow PtAu<sub>60</sub> to access a wider range of operating potentials in comparison to PdAu<sub>60</sub> under direct synthesis conditions. PdAu<sub>60</sub> operates between 0.39 and 0.42 V vs NHE, while PtAu<sub>60</sub> operates over a broader range of 0.35– 0.46 V vs NHE. Coincidentally, these materials operate near their optimum potentials ( $\Phi_{opt}^{PdAu_{60}} = 0.33$ ,  $\Phi_{opt}^{PtAu_{60}} = 0.37$  V vs NHE) and provide similar selectivities toward H<sub>2</sub>O<sub>2</sub> formation (~50–65%). These data suggest that even higher ORR rates and selectivities could be achieved in the direct synthesis system if the PdAu<sub>60</sub> and PdAu<sub>60</sub> catalysts operated at more negative potentials ( $\Phi^{op} = 0.33-0.23$ , Figure 8c). Thus, a higher HOR rate could further increase both the H<sub>2</sub>O<sub>2</sub> formation rate and selectivity.

Overall, these observations on PtAu and PdAu alloys help inform the design of catalytic materials for the direct synthesis of H<sub>2</sub>O<sub>2</sub>. Specifically, catalysts should contain sites that readily activate and oxidize hydrogen (e.g., Pd, Pt) to have an appreciable H<sub>2</sub>O<sub>2</sub> formation rate under thermochemical conditions. Our analysis also shows that the HOR reactivity of materials can lower their operating potential, indirectly increasing their  $H_2O_2$  selectivity by pushing it toward  $\Phi_{opt}$ . Similarly, these materials must selectively reduce oxygen toward H<sub>2</sub>O<sub>2</sub> versus H<sub>2</sub>O by presenting high barriers toward the O-O bond dissociation pathways. To achieve this end, metal nanoparticles must contain reactive moieties that bind but do not dissociate dioxygen intermediates, such as monomeric Pd or Pt sites within a Au substrate. Thus, highperformance catalysts should balance 2e<sup>-</sup> ORR and HOR rates so that they operate near their optimal potential and achieve their maximum possible selectivity.

#### 4. CONCLUSIONS

In this study, we present the relationship between electrocatalysis and thermocatalysis in aqueous oxygen reduction chemistry. We show how to predict the operating potential, reactivity, and  $H_2O_2$  selectivity on metal nanoparticles under direct synthesis conditions through independent electrochemical measurements of the hydrogen oxidation and oxygen reduction reactions. Molecularly meaningful derivations show that the operating potential depends on the relative rates of the coupled HOR and ORR reactions on a metal nanoparticle surface. For instance, increasing the pressure of hydrogen leads to higher HOR rates and lower operating potentials, which provide a greater driving force to reduce oxygen.

These observations and analyses also allow the design of high-performance oxygen reduction materials that enable high rates and selectivity for the direct synthesis of H<sub>2</sub>O<sub>2</sub> from its elements. We quantitatively described how the selectivity of H<sub>2</sub>O<sub>2</sub> approaches a maximum at its optimum operating potential  $(\Phi_{opt})$  during electrocatalytic measurements. In comparison, we show how hydrogen and oxygen activities lead to selective surfaces and catalyst structures under thermochemical conditions, which do not occur readily in electrochemical measurements. Thus, this analysis shows how catalysts can access more selective states that were unrecognized prior to direct comparisons between thermochemical and electrochemical systems. This work also shows that an increase in hydrogen oxidation rates increases the overall H<sub>2</sub>O<sub>2</sub> formation rate and can bias nanoparticles toward more selective operating potentials, as shown by comparisons of Au, PdAu<sub>60</sub>, and PtAu<sub>60</sub>. Thus, ideal materials must simultaneously present favorable barriers and charge transfer coefficients toward the 2e<sup>-</sup> ORR and HOR paths to obtain the greatest rates and selectivities toward H<sub>2</sub>O<sub>2</sub> formation. Therefore, this understanding informs the design of new direct synthesis catalysts based on electrochemical studies and may enable the economical production of H2O2 for industrial applications.

These findings yield far-reaching implications for both fundamental studies in electrocatalysis or thermocatalysis and the technological application of catalysis. This work focuses on oxygen reduction, but this analysis may extend to numerous liquid-phase reactions that involve heterolytic hydrogen transfer, such as CO<sub>2</sub> reduction and alcohol oxidation.<sup>3,4,</sup> The methodology outlined here also provides guidelines to design materials and reaction conditions that increase the selectivity and reaction rates in other systems. Specifically, investigators may design heterogeneous catalysts using electrochemical methods to independently study the barriers and charge transfer coefficients of the half-reactions involved in various redox chemistries. These measurements should also allow the prediction of thermocatalytic behavior through a careful analysis of electrochemical kinetic parameters. This work presents opportunities for catalyst discovery using electrochemical methods that are amenable to high-throughput experimentation. Finally, the control of electrode potentials and reactant activities may allow access to highly selective and reactive catalyst states for desired products.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c13399.

Characterization of catalyst materials by TEM, EDXRF, and ICP, open-circuit potentiometry measurements to determine operating potentials of catalysts in a high pressure electrochemical cell, which reflect thermocatalytic conditions, Koutcky–Levich and Tafel analysis of electrochemical measurements of the HOR and ORR, mathematical derivations for the Nernst equations, hydrogen adsorption and oxidation kinetics, formation rates of  $H_2O_2$  and  $H_2O$  formation under thermocatalytic conditions, and  $H_2O_2$  selectivity over a broad range of potentials, hydrogen pressures, and temperatures (PDF)

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The authors declare no competing financial interest.

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