

# Effect of mass transfer on the oxygen reduction reaction catalyzed by platinum dendrimer encapsulated nanoparticles

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Here we report on the effect of the mass transfer rate ( $k_t$ ) on the oxygen reduction reaction (ORR) catalyzed by Pt dendrimer-encapsulated nanoparticles (DENs) comprised of 147 and 55 atoms (Pt<sub>147</sub> and Pt<sub>55</sub>). The experiments were carried out using a dual-electrode microelectrochemical device, which enables the study of the ORR under high  $k_t$  conditions with simultaneous detection of H<sub>2</sub>O<sub>2</sub>. At low  $k_t$  (0.02 to 0.12 cm s<sup>-1</sup>) the effective number of electrons involved in ORR,  $n_{\text{eff}}$ , is 3.7 for Pt<sub>147</sub> and 3.4 for Pt<sub>55</sub>. As  $k_t$  is increased, the mass-transfer-limited current for the ORR becomes significantly lower than the value predicted by the Levich equation for a 4-electron process regardless of catalyst size. However, the percentage of H<sub>2</sub>O<sub>2</sub> detected remains constant, such that  $n_{\text{eff}}$  barely changes over the entire  $k_t$  range explored (0.02 cm s<sup>-1</sup>). This suggests that mass transfer does not affect  $n_{\text{eff}}$ , which has implications for the mechanism of the ORR on Pt nanoparticles. Interestingly, there is a significant difference in  $n_{\text{eff}}$  for the two sizes of Pt DENs ( $n_{\text{eff}} = 3.7$  and 3.5 for Pt<sub>147</sub> and Pt<sub>55</sub>, respectively) that cannot be assigned to mass transfer effects and that we therefore attribute to a particle size effect.

electrocatalysis | platinum nanoparticle

Here we report on the effect of mass transfer rate ( $k_t$ ) on the oxygen reduction reaction (ORR) catalyzed by Pt dendrimer-encapsulated nanoparticles (DENs) comprised of 147 and 55 atoms (Pt<sub>147</sub> and Pt<sub>55</sub>, respectively). The experiments were carried out in the dual-electrode microelectrochemical device shown in Fig. 1 (1). This configuration enables the study of the ORR under high  $k_t$  conditions with simultaneous detection of H<sub>2</sub>O<sub>2</sub>. This is important because the methods currently used to study ORR at high  $k_t$ , such as ultramicroelectrodes (UMEs) (2), nanoelectrodes (3), and microjet electrodes (4) do not incorporate H<sub>2</sub>O<sub>2</sub> detection. Accordingly, ORR data is generally interpreted based on steady-state, mass-transfer-limited currents alone. Using the microelectrochemical device, two principal effects are evident as  $k_t$  is increased. First, the ORR current becomes significantly smaller than predicted by the Levich equation (5). Second, the effective number of electrons involved in the ORR,  $n_{\text{eff}}$ , remains constant over the entire  $k_t$  range, for both Pt<sub>147</sub> and Pt<sub>55</sub>. We draw three conclusions from these observations: (i) The decrease in ORR current at high  $k_t$  is caused by kinetic effects; (ii) increasing  $k_t$  does not affect the mechanism of the ORR catalyzed by Pt DENs; and (iii) there is a difference in  $n_{\text{eff}}$  between Pt<sub>147</sub> and Pt<sub>55</sub> that cannot be attributed to mass-transfer effects.

The electrochemical ORR has been the subject of extensive research and has been reviewed on several occasions (6–10). The generally accepted mechanism for the ORR at a metallic surface is a multielectron reaction with intermediates as shown in Scheme 1 (2, 7, 9, 11). Specifically, at the electrode surface, O<sub>2</sub> can be reduced directly to H<sub>2</sub>O or H<sub>2</sub>O<sub>2</sub> in 4- or 2-electron processes, respectively. Subsequently, electrogenerated H<sub>2</sub>O<sub>2</sub> can disproportionate into H<sub>2</sub>O and O<sub>2</sub>, or by addition of two electrons, form H<sub>2</sub>O. According to Scheme 1, the yield of H<sub>2</sub>O<sub>2</sub>,

quantified by  $n_{\text{eff}}$ , is determined by the relative rates of steps c, d, and e, as well as the rate of mass transfer of H<sub>2</sub>O<sub>2</sub> away from the electrode surface (2).

The development of O<sub>2</sub>/H<sub>2</sub> polymer electrolyte membrane fuel cells (PE-MFCs) as sustainable energy sources (12, 13) has led to increased interest in developing efficient, non-Pt catalysts for the ORR (14–18). In spite of this, Pt is still considered to be the most effective catalyst for the ORR, even though it is not optimal for this application due to its high overpotential and its low Earth abundance. In the absence of viable alternatives, interest has been focused on reducing the amount of Pt required for fuel cell applications. There are two ways to do this: dilute it with a second metal or decrease the size or total number of Pt monometallic catalyst particles. However, a decrease in Pt surface coverage (or, correspondingly, an increase in  $k_t$ ) has been associated with slower ORR kinetics (19, 20) and an increase in the amount of H<sub>2</sub>O<sub>2</sub> produced (21–23). The presence of H<sub>2</sub>O<sub>2</sub> is a major concern for fuel cell applications due to its corrosive nature and because it lowers the maximum attainable voltage (24, 25).

A number of studies have been reported that focus on the role of mass transfer in ORR efficiency. The analytical tools used for this purpose include the rotating disk and rotating ring-disk electrodes (RDE and RRDE) (21, 26–28), UMEs (2, 29), nanoelectrodes (3), microjet electrodes (4), and microfluidic thin-layer cells (22, 23). In most of these studies,  $k_t$  is increased by decreasing the surface coverage of the catalyst (21–23, 27, 28). For example, Behm and coworkers studied the ORR using two-dimensional arrays of 100-nm Pt islands immobilized on glassy carbon (GC) electrodes (22, 23). The key finding was that the amount of electrogenerated H<sub>2</sub>O<sub>2</sub> increased with decreasing catalyst coverage. A “desorption + readsorption + reaction” mechanism was proposed to explain this effect (26, 30). Under this assumption, more H<sub>2</sub>O<sub>2</sub> is obtained at high  $k_t$  (low catalyst loading or high flow rates), due to lower probability for H<sub>2</sub>O<sub>2</sub> readsorption and further reaction on different Pt sites (Scheme 1) (26, 30). Kucernak and coworkers studied the effect of high  $k_t$  conditions (up to 2 cm s<sup>-1</sup>) on the ORR catalyzed by single, submicron Pt particles affixed to the ends of nanoelectrodes (3). It was found that the steady-state mass-transfer-limited current for the ORR decreased with increasing  $k_t$ . This was attributed to a shift in  $n_{\text{eff}}$  from 4 at  $k_t = 0.01$  cm s<sup>-1</sup> to 3.5 at  $k_t = 2$  cm s<sup>-1</sup> (3). However, because a collector electrode was not present, it was not possible to correlate these results to the presence of H<sub>2</sub>O<sub>2</sub>.

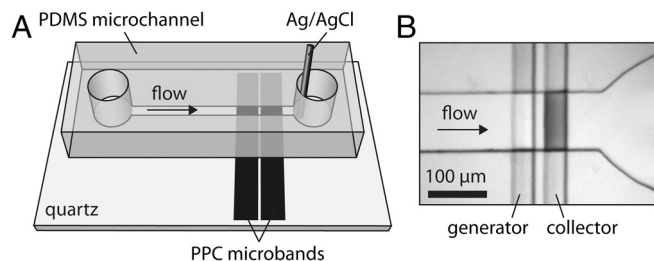
Here we study the effect of  $k_t$  on the ORR using Pt DENs having diameters of 1–2 nm and low (<0.3 nm) size polydispersity. In the microelectrochemical device shown in Fig. 1, Pt<sub>147</sub> or

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**Fig. 1.** (A) Schematic representation of the hybrid PDMS/quartz microelectrochemical device used for ORR studies. Solution is introduced to the microchannel using a syringe pump connected to the reservoir on the left. A combined reference/counter electrode is placed in the other reservoir so that it is in close proximity to PPC microband electrodes. Note that this drawing is not to scale. In the actual device, the length of the microband electrodes is typically 40  $\mu\text{m}$  with a gap of 15  $\mu\text{m}$  between them. (B) Optical micrograph of the PPC microbands and the microchannel after platinization of the collector electrode and electrochemical deposition of Pt DENs onto the generator electrode. The outlet reservoir is visible to the right of the electrodes.

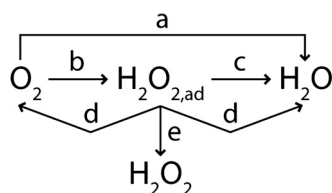
Pt<sub>55</sub> DENs are electrochemically immobilized onto a pyrolyzed photoresist carbon (PPC) generator electrode (1). This results in robust attachment of approximately 1 monolayer of Pt DENs onto the PPC surface (1). Importantly, a collector electrode is present downstream for amperometric detection of H<sub>2</sub>O<sub>2</sub>. By controlling the flow rate through the microchannel, it is possible to vary  $k_t$  between 0.02 and 0.12  $\text{cm s}^{-1}$ . Indeed, such high mass transfer conditions are not achievable using the RRDE or UMEs with diameters larger than 2  $\mu\text{m}$ . At low  $k_t$  (0.02  $\text{cm s}^{-1}$ ), which is similar to that achieved at the upper end of  $k_t$  values accessible with the RRDE,  $n_{\text{eff}}$  is 3.7 for Pt<sub>147</sub> and 3.4 for Pt<sub>55</sub>, in agreement with our previous findings (31). As  $k_t$  increases, the mass-transfer-limited current for the ORR becomes significantly lower than the value predicted by the Levich equation for a 4-electron process for both Pt<sub>147</sub> and Pt<sub>55</sub>. However, the percentage of H<sub>2</sub>O<sub>2</sub> detected remains constant, such that  $n_{\text{eff}}$  does not change over the entire  $k_t$  range employed. Interestingly, there is a significant difference in  $n_{\text{eff}}$  for the two sizes of Pt DENs (average  $n_{\text{eff}} = 3.7$  and 3.5 for Pt<sub>147</sub> and Pt<sub>55</sub>, respectively) that cannot be assigned to mass transfer effects.

The results reported here are significant for several reasons. First, we show that simultaneous measurement of the H<sub>2</sub>O<sub>2</sub> current is vital for correct interpretation of ORR data. Second, while others have previously shown that the ORR catalyzed by large Pt nanoparticles is affected by changes in  $k_t$  (22, 23) we show here that this does not apply for smaller Pt materials. Finally, we show that the size of very small Pt nanoparticles (diameters <2 nm) has an effect on the mechanism of the ORR, and hence its product distribution. These observations are relevant to the development of efficient Pt electrocatalysts for the ORR.

## Results and Discussion

### Evaluation of ORR Activity for Pt<sub>147</sub> and Pt<sub>55</sub> at Low Mass Transfer Rates.

The ORR activity of Pt<sub>147</sub> and Pt<sub>55</sub> DENs was evaluated using the poly(dimethylsiloxane) (PDMS)/quartz hybrid microelectrochemical device shown in Fig. 1 and discussed in detail elsewhere (1). Following platinization of the collector (Fig. 1B) and immobilization of Pt DENs on the generator (1), the ORR measurements were carried out in air-saturated 0.10 M HClO<sub>4</sub>



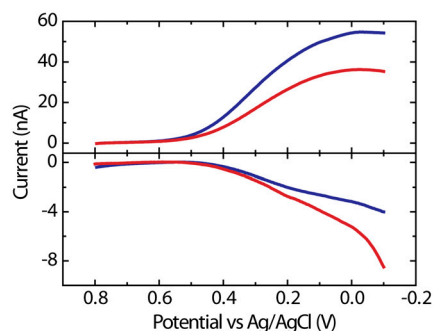
**Scheme 1.**

electrolyte solution. To evaluate the ORR kinetics at low  $k_t$ , solution was flowed through the device at 0.05  $\mu\text{L min}^{-1}$  (0.04  $\text{cm s}^{-1}$ ), corresponding to a  $k_t$  value of 0.02  $\text{cm s}^{-1}$ . This is on the same order as that achieved using an RRDE.

We previously used the RDE to evaluate the ORR characteristics of Pt DENs having different sizes (31). The results showed that the steady-state limiting current for Pt<sub>147</sub> was higher than for Pt<sub>55</sub>, an effect that was tentatively assigned to H<sub>2</sub>O<sub>2</sub> becoming a significant product of the ORR for the smaller catalytic particles (31). We pointed out that if this were correct, it was a rare case of a very slight change in particle size resulting in a shift in product distribution. Fig. 2 shows generation-collection linear scan voltammograms (LSVs) for the ORR obtained using the microelectrochemical device for Pt<sub>147</sub> (blue lines) and Pt<sub>55</sub> (red lines) DENs at  $k_t = 0.02 \text{ cm s}^{-1}$ . The potential of the generator electrode was swept from +0.80 to -0.10 V (vs. Ag/AgCl) at 50  $\text{mV s}^{-1}$ . The potential of the collector electrode was held at +1.10 V, where we observed reliable and stable mass-transfer-limited currents for H<sub>2</sub>O<sub>2</sub> oxidation (1). The onset of catalytic current is at  $\sim +0.60$  V, and a steady-state, mass-transfer-limited current is apparent over the range 0.00 to -0.10 V. There is a slight decrease in the ORR current at potentials more negative than 0 V due to hydrogen adsorption onto the catalyst (32). In addition, the adsorption of hydrogen is accompanied by an increase in hydrogen peroxide formation (manifested as an increase in the collector electrode current), an effect previously observed by others (32). To minimize artifacts arising from hydrogen adsorption, generator-collector current pairs were measured at the potential where the ORR current reached its maximum value.

Importantly, the ORR limiting current for Pt<sub>147</sub> DENs (55 nA) is noticeably higher than for Pt<sub>55</sub> DENs (37 nA), although the LSVs have the same general shape. The downstream collector electrode makes it possible to determine the amount of H<sub>2</sub>O<sub>2</sub> produced during ORR, at the same time the mass-transfer-limited currents are measured at the generator. The LSVs in Fig. 2 show that the amount of H<sub>2</sub>O<sub>2</sub> oxidized at the collector electrode is higher for Pt<sub>55</sub> DENs. As we hypothesized in our earlier publication, this indicates that the peroxide pathways play a more important role in the ORR catalyzed by smaller nanoparticles (31).

The value of  $n_{\text{eff}}$  was determined using the ratio of the steady-state mass-transfer-limited current for the ORR ( $i_{\text{gen}}$ ) and the oxidation current for H<sub>2</sub>O<sub>2</sub> ( $i_{\text{col}}$ ); that is,  $n_{\text{eff}} = 4 - [(2i_{\text{col}})/(\eta i_{\text{gen}})]$ , where  $\eta$  represents the collection efficiency of the device (details on how  $\eta$  is calculated are provided in *Materials and Methods*) (33). In Fig. 2,  $i_{\text{col}}$  has been background subtracted against the current value obtained by holding the collector electrode at a potential (1.10 V), where the ORR does not proceed. The measured  $\eta$  at 0.05  $\mu\text{L min}^{-1}$  was 40.0%. Note that the collector cur-



**Fig. 2.** Generation (upper curves) and collection (lower curves) LSVs obtained using Pt<sub>147</sub> (blue lines) and Pt<sub>55</sub> (red lines) DENs in air-saturated, aqueous 0.10 M HClO<sub>4</sub>. The potential of the generator electrode was scanned from +0.80 to -0.10 V (vs. Ag/AgCl) while holding the potential of the platinized collector at +1.10 V. The flow rate was 0.05  $\mu\text{L min}^{-1}$  corresponding to  $k_t = 0.02 \text{ cm s}^{-1}$ , and  $\eta$  was 40.0%. The scan rate was 50  $\text{mV s}^{-1}$ .

rent does not exhibit a clear, steady-state plateau (*vide supra*), and, as such,  $i_{\text{col}}$  was measured at the potential where  $i_{\text{gen}}$  attained its maximum value (0 V). The calculated values of  $n_{\text{eff}}$  are  $3.7 \pm 0.1$  and  $3.4 \pm 0.1$  (average of three independent measurements), for Pt<sub>147</sub> and Pt<sub>55</sub>, respectively. Using these values for  $n_{\text{eff}}$ ,  $i_{\text{gen}}$  can be estimated using the Levich equation (Eq. 1) (5), as follows:

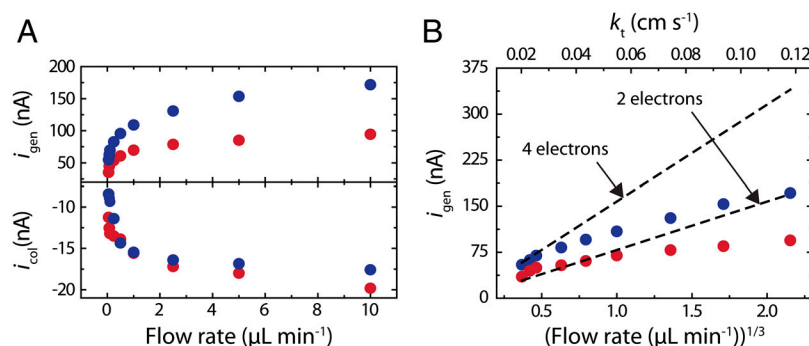
$$i_{\text{gen}} = 0.925n_{\text{eff}}Fc_{\text{O}_2}D_{\text{O}_2}^{2/3}V_f^{1/3}\left(\frac{h^2d}{4}\right)^{-1/3}wx_c^{2/3}. \quad [1]$$

Here,  $F$  is the Faraday constant,  $c_{\text{O}_2}$  and  $D_{\text{O}_2}$  are the bulk concentration and diffusion coefficient, respectively, of O<sub>2</sub> [ $c_{\text{O}_2} = 0.20$  mM, (34)  $D_{\text{O}_2} = 1.67 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>] (35),  $V_f$  is the volume flow rate (0.05  $\mu\text{L min}^{-1}$ ),  $x_c$  and  $w$  are the length (40  $\mu\text{m}$ ) and the width (100  $\mu\text{m}$ ) of the electrode, respectively,  $d$  is the width of the microchannel (100  $\mu\text{m}$ ), and  $h$  is the height of the microchannel (20  $\mu\text{m}$ ). Using the previously determined  $n_{\text{eff}}$  values,  $i_{\text{gen}}$  is calculated to be 55 nA for Pt<sub>147</sub> and 50 nA for Pt<sub>55</sub>. For Pt<sub>147</sub>, the calculated value is in excellent agreement with the measured  $i_{\text{gen}}$  of 55 nA. However, for Pt<sub>55</sub>, the calculated value is substantially higher than the experimentally determined  $i_{\text{gen}}$  (37 nA). Although we do not understand this result, such inconsistencies are common in the ORR RRDE literature (36, 37). It is possible that the relatively high scan rate employed (50 mV s<sup>-1</sup>) also contributes to this effect.

**ORR Measurements at High Mass Transfer Rates.** To learn more about the effect of the mass transfer rate of O<sub>2</sub> on  $n_{\text{eff}}$ , we acquired ORR generation collection LSVs while flowing air-saturated 0.10 M HClO<sub>4</sub> through the microchannel at flow rates ranging from 0.05 to 10  $\mu\text{L min}^{-1}$  (0.04 to 8.3 cm s<sup>-1</sup>). This corresponds to  $k_t$  values from 0.02 to 0.12 cm s<sup>-1</sup>. This range is considerably higher than that accessible with the RRDE. Indeed, to achieve the upper limit of  $k_t = 0.12$  cm s<sup>-1</sup>, a RRDE would have to be rotated at 150,000 rpm, which is well above the typical maximum rotation rate of 7,000 rpm. Fig. 3A shows a plot of  $i_{\text{gen}}$  and simultaneously measured  $i_{\text{col}}$  values obtained for Pt<sub>147</sub> (blue dots) and Pt<sub>55</sub> (red dots) as a function of flow. Values for  $i_{\text{gen}}$  and  $i_{\text{col}}$  were obtained from both low-to-high and high-to-low flow rates, and were found to be independent of this parameter. This confirms that the Pt coverage is constant throughout the experiments (that is, that the Pt DENs remain attached to the electrode surface). In Fig. 3A,  $i_{\text{col}}$  was normalized with respect to  $\eta$  for each flow rate. Recall that  $i_{\text{gen}} - i_{\text{col}}$  current pairs were measured at the potential where  $i_{\text{gen}}$  reached its maximum value and  $i_{\text{col}}$  values were background subtracted (*vide supra*). Fig. 3A shows that, for both Pt<sub>147</sub> and Pt<sub>55</sub> DENs, as  $k_t$  increases,  $i_{\text{gen}}$  increases and begins to level off at flow rates higher than 2  $\mu\text{L min}^{-1}$ . The same pattern is observed for  $i_{\text{col}}$ . Furthermore, across the entire flow-rate range,

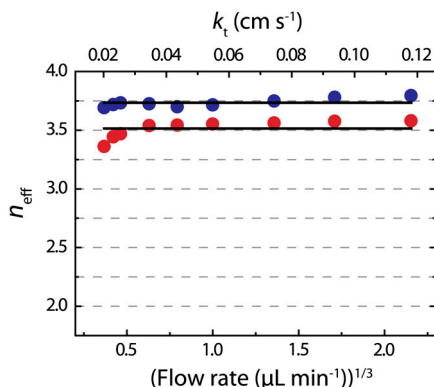
the ORR limiting current for Pt<sub>147</sub> remains higher than that for Pt<sub>55</sub>.

It is interesting to compare the experimental values of  $i_{\text{gen}}$  with the theoretical values predicted by the Levich equation (Eq. 1) for 4- and 2-electron ORR processes. In Fig. 3B, the  $i_{\text{gen}}$  values from Fig. 3A are plotted vs.  $V_f^{1/3}$  and  $k_t$ . The current for 4- and 2-electron ORR processes are plotted on the same graph (dashed lines). For Pt<sub>147</sub>, Fig. 3B indicates that as  $k_t$  increases,  $i_{\text{gen}}$  appears to drift from the 4-electron to the 2-electron ORR pathway (Scheme 1). Interestingly, at  $V_f$  higher than 1  $\mu\text{L min}^{-1}$ , the measured  $i_{\text{gen}}$  for Pt<sub>55</sub> is smaller than the value predicted by Eq. 1 for a 2-electron process, an observation that will be discussed later. Importantly, for both Pt<sub>147</sub> and Pt<sub>55</sub> DENs, the plot of  $i_{\text{gen}}$  vs.  $V_f^{1/3}$  is not linear. A similar trend in the ORR limiting current was observed during Pt-catalyzed ORR studies using UMEs (2) and nanoelectrodes (3), and for Cu using hydrodynamic electrodes (4). These results were interpreted in terms of O<sub>2</sub> reduction not following a simple 4- or 2-electron transfer process, but instead undergoing a transition from 4 electrons at the lowest  $k_t$  values towards 2 electrons as the mass transfer rate increased. It is important to note that in these earlier reports a collector electrode was not used, and therefore the amount of H<sub>2</sub>O<sub>2</sub> generator could not be measured directly and then correlated to the ORR current. Because we (1) and others (36, 37) have noted that the mass-transfer-limited current for the ORR is often unreliable for the determination of  $n_{\text{eff}}$ , an accurate calculation requires the ratio of  $i_{\text{col}}$  to  $i_{\text{gen}}$ . Here, the concomitant measurement of H<sub>2</sub>O<sub>2</sub> oxidation current allows the calculation of  $n_{\text{eff}}$  at each  $k_t$  value. Fig. 4 shows a plot of  $n_{\text{eff}}$  vs.  $V_f$  and  $k_t$ , calculated for data presented in Fig. 3A. At all but the lowest flow rates, the value of  $n_{\text{eff}}$  (that is, the percentage of H<sub>2</sub>O<sub>2</sub> collected during ORR) is nearly constant. Consequently, although the magnitude of  $i_{\text{gen}}$  suggests a shift in the mechanism of ORR with the change in mass transfer rate,  $n_{\text{eff}}$  remains constant over the entire  $k_t$  range. The average  $n_{\text{eff}}$  is 3.7 and 3.5 for Pt<sub>147</sub> and Pt<sub>55</sub>, respectively, similar to the values calculated at  $k_t = 0.02$  cm s<sup>-1</sup> (3.7 for Pt<sub>147</sub> and 3.4 for Pt<sub>55</sub>). We attribute the shift in  $i_{\text{gen}}$  observed here, and previously by others (2–4) to kinetic effects: As  $k_t$  increases, some O<sub>2</sub> molecules flow past the generator electrode faster than they can be reduced. This results in a decrease in  $i_{\text{gen}}$  from its theoretical mass-transfer-limited value. However, the mechanism of ORR remains unaffected. Although we do not currently have a definitive explanation for the difference in  $n_{\text{eff}}$  between Pt DENs of different sizes, it is possible that the decrease in particle size leads to a different O<sub>2</sub> binding mechanism onto the Pt surface, which ultimately affects the ORR pathway. For small Pt NPs, molecular O<sub>2</sub> can bind to corner and edge sites in the so-called single-bond binding geometry, in which one oxygen atom is against the metal surface



**Fig. 3.** (A) Plot of  $i_{\text{gen}}$  (ORR mass-transfer-limited current) and simultaneously acquired  $i_{\text{col}}$  (H<sub>2</sub>O<sub>2</sub> oxidation current) for Pt<sub>147</sub> (blue circles) and Pt<sub>55</sub> (red circles) measured while flowing air-saturated, aqueous 0.10 M HClO<sub>4</sub> through the microchannel at flow rates ranging from 0.05 to 10  $\mu\text{L min}^{-1}$  ( $k_t$  from 0.02 to 0.12 cm s<sup>-1</sup>). Note that  $i_{\text{col}}$  was normalized with respect to  $\eta$  ( $\eta$  values for 0.05, 0.075, 0.1, 0.25, 0.5, 1, 2.5, 5, and 10  $\mu\text{L min}^{-1}$  flow rates were 40.0, 37.2, 36.3, 34.7, 34.2, 34.0, 33.5, 33.3 and 32.7%, respectively). (B) Plot of  $i_{\text{gen}}$  from A vs.  $V_f^{1/3}$  and  $k_t$ , for Pt<sub>147</sub> (blue circles) and Pt<sub>55</sub> (red circles). The dashed black lines were calculated using the Levich equation (Eq. 1) for a 4-electron (upper line) and a 2-electron (lower line) process.





**Fig. 4.** The value of  $n_{\text{eff}}$  calculated from the experimental results in Fig. 3A for Pt<sub>147</sub> (blue circles) and Pt<sub>55</sub> (red circles) vs.  $V_f^{1/3}$  and  $k_t$ . The black lines represent the average values of  $n_{\text{eff}}$  across the entire mass transfer range shown.

and the second is exposed to the solvent. Such single-bond binding can lead to the formation of OOH groups, and ultimately, H<sub>2</sub>O<sub>2</sub>. Experimental and theoretical work is currently underway to fully understand this effect.

### Conclusions

Using a dual-electrode microelectrochemical device we investigated the effect of mass transfer on the ORR catalyzed by Pt<sub>147</sub> and Pt<sub>55</sub> DENs. At low values of  $k_t$  (0.02 cm s<sup>-1</sup>),  $n_{\text{eff}}$  was 3.7 for Pt<sub>147</sub> and 3.4 for Pt<sub>55</sub>, in agreement with previous findings obtained using a RDE (31). As  $k_t$  was increased from 0.02 to 0.12 cm s<sup>-1</sup>, the measured ORR mass-transfer-limited current for both Pt<sub>147</sub> and Pt<sub>55</sub> was smaller than the value predicted by the Levich equation, similar to results obtained by others (2–4). Previously, this was interpreted as a transition of the ORR from four electrons at the lowest  $k_t$  values towards two electrons as the mass transfer rate increased. Here, we observed that the percentage of H<sub>2</sub>O<sub>2</sub> produced was unaffected by  $k_t$ , and  $n_{\text{eff}}$  was nearly constant across the entire  $k_t$  range. Hence, the concomitant measurement of H<sub>2</sub>O<sub>2</sub> allows us to conclude that the decrease in the expected mass-transfer-limited current for ORR at high  $k_t$  is in fact due to kinetic effects, rather than a change in the ORR mechanism.

Importantly, we also observed an unambiguous nanoparticle size effect on the mechanism of ORR, with an average  $n_{\text{eff}}$  higher for Pt<sub>147</sub> (3.7) than for Pt<sub>55</sub> (3.5). It is certainly surprising that a change in particle size of just 100 atoms is able to shift the reaction mechanism. Accordingly, we are investigating this effect in more detail, as it may have an important role to play in ORR electrocatalysis specifically and electrocatalysis generally. The results of these studies will be reported in due course.

### Materials and Methods

**Chemicals.** PDMS channels were prepared using a Sylgard 184 elastomer kit obtained from K. R. Anderson, Inc. Quartz microscope slides (25 mm × 75 mm, 1 mm thick) were purchased from Technical Glass Products. Positive-tone photoresist (AZ 1518) and developer (AZ 400K) were purchased from Capitol Scientific, Inc. Sixth-generation poly(amidoamine) dendrimers terminated with hydroxyl groups (G6-OH) were purchased as a 5% (wt/wt) solution in methanol (Dendritech, Inc.). Prior to use, the methanol was removed under vacuum and the dendrimer was reconstituted in water at a concentration of 100 μM. K<sub>2</sub>PtCl<sub>4</sub> (99.99%), NaBH<sub>4</sub> (99.99%), and LiClO<sub>4</sub> (99.99%) were purchased from Sigma-Aldrich, Inc.; HClO<sub>4</sub> (Ultrapure II) was from J. T. Baker and ferrocenemethanol (FcMeOH, 97%) was from Acros Organics. These reagents were used without further purification. Deionized water having a resistivity of 18.2 MΩ cm was used for all experiments (Milli-Q gradient system, Millipore).

**Preparation of Microelectrochemical Devices.** The procedure for fabricating PPC microband electrodes is described in detail elsewhere (1). Briefly, PPC microbands, 40 μm wide and separated by a 15 μm gap, were fabricated by slow pyrolysis of patterned AZ 1518 photoresist at 1,000 °C under a forming gas of 5% H<sub>2</sub> and 95% N<sub>2</sub> (1). The thickness of the resulting PPC features, measured using profilometry, was 300 nm. PDMS microfluidic channels, 6 mm long, 100 μm wide and 20 μm high, were prepared using a previously described replica micromolding method (1, 38). Two reservoirs (1.0 mm diameter) were punched at the ends of each channel to accommodate introduction of solution. The PDMS layer and quartz substrate were exposed to an air plasma (60 W, model PDC-32G, Harrick Scientific) for 45 s, joined together under an optical microscope, and then placed over a hot plate at 80 °C for 5 min. A syringe pump (Pump 11, Pico Plus Elite, Harvard Apparatus), connected to the inlet (left side) reservoir using Teflon tubing, was used to push solution through the microelectrochemical device.

**Preparation of Pt DENs.** Pt DENs comprised of 147 and 55 atoms were prepared according to our previously published procedure (31, 39). A 0.10 mM aqueous solution of G6-OH was mixed with sufficient aqueous 0.10 M K<sub>2</sub>PtCl<sub>4</sub> such that the final Pt<sup>2+</sup>-to-dendrimer ratios were 147:1 or 55:1. After stirring for three days (40), a 10-fold molar excess of aqueous 1.00 M NaBH<sub>4</sub> was added to reduce Pt<sup>2+</sup>. This solution was kept capped for 24 h to maximize reduction of Pt<sup>2+</sup> (40). Note that we have previously shown that reduction of the Pt<sup>2+</sup>/G6-OH precursor by BH<sub>4</sub><sup>-</sup> does not yield fully reduced Pt DENs (40, 41). However, electrochemical cycling does result in complete reduction (*vide infra*) (40, 41). The average diameters and size distributions of the Pt DENs were 1.7 nm and 1.4 nm for Pt<sub>147</sub> and Pt<sub>55</sub>, respectively (31). After synthesis, the quality of the Pt DENs was verified by UV-vis absorption spectroscopy (31, 42). Before using for electrochemical experiments, Pt DENs were dialyzed for 24 h in 4.0 L of Millipore water (Milli-Q Gradient PF-06073) to remove salts and other impurities. After dialysis, but prior to immobilization onto PPC electrodes, the DEN solution was mixed with sufficient LiClO<sub>4</sub> to yield a 0.10 M solution.

**Electrochemistry.** The microelectrochemical device was configured in a three-electrode arrangement, comprising the two PPC microbands as working electrodes. A Ag/AgCl reference electrode, which also acted as a counter electrode was positioned in the outlet (right-hand side) reservoir (Scheme 1). All potentials are referenced to Ag/AgCl (3.4 M KCl, model 66-EE009 “no-leak” Ag/AgCl, Dionex). LSV with two working electrodes was carried out using a computer-based bipotentiostat (Model CHI760B potentiostat, CH Instruments). All electrochemical experiments were performed at 22 ± 1 °C.

Prior to the immobilization of Pt DENs on the generator, Pt was electro-deposited onto the PPC collector electrode to increase its sensitivity for amperometric H<sub>2</sub>O<sub>2</sub> detection (Fig. 1B) (1). After platinization, LSVs were acquired at the PPC generator electrode in the ORR region of interest (+0.80 to -0.10 V vs. Ag/AgCl) using aqueous 0.10 M HClO<sub>4</sub>, to check that the generator electrode had not been contaminated with Pt during the platinization step. Pt DENs were then immobilized on the PPC generator using a previously reported procedure (1, 31, 39). Briefly, a 10.0 μM Pt DEN solution containing 0.10 M LiClO<sub>4</sub> was flowed through the microchannel at 0.05 μL min<sup>-1</sup> while the electrode potential was swept three times between +0.10 and +1.00 V (vs. Ag/AgCl) at 10 mV s<sup>-1</sup>. We previously showed that this results in robust attachment of approximately 1 monolayer of Pt DENs onto both GC and PPC surfaces (1, 31). Before acquiring ORR generation collection LSVs, the DEN-modified electrodes were scanned 20 times at 100 mV s<sup>-1</sup> between +1.25 V and -0.20 V (vs. Ag/AgCl) in air-saturated 0.10 M HClO<sub>4</sub> solution. As we have shown previously, these conditioning scans (43) are commonplace and required to achieve stable and reproducible LSVs (39).

Upon completion of the ORR measurements,  $\eta$  was determined for each microelectrochemical device using the following method. Generation collection LSVs were recorded while pumping an aqueous solution containing 0.10 mM FcMeOH and 0.10 M KNO<sub>3</sub> through the microchannel at flow rates ranging from 0.05 to 10 μL min<sup>-1</sup> (0.04 to 8.3 cm s<sup>-1</sup>). At each flow rate, the values of  $\eta$  were calculated as the ratio of the steady-state mass-transfer-limited currents at the collector and generator electrodes, for the electrolysis of FcMeOH. The calculated values of  $\eta$  ranged from 32.7–40.0%.

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