**Re-examination of the Pt Particle Size Effect on the Oxygen Reduction Reaction
for Ultrathin Uniform Pt/C Catalyst Layers without Influence from Nafion**

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The platinum ‘particle size effect’ on the oxygen reduction reaction (ORR) has been re-evaluated using commercial Pt/C catalysts (2–10 nm Pt particle) and polycrystalline Pt (poly-Pt) in 0.1 M HClO₄ with a rotating disk electrode method. Nafion-free catalyst layers were employed to obtain specific activities (SA) that were not perturbed (suppressed) by sulfonate anion adsorption/blocking. By using ultrathin uniform catalyst layers, O₂ diffusion limitation was minimized as confirmed from the high SAs of our supported catalysts that were comparable to unsupported sputtered Pt having controlled sizes. The specific activity (SA) steeply increased for the particle sizes in the range ~2–10 nm (0.8–1.8 mA/cm²_{Pt} at 0.9 V vs. RHE) and plateaued over ~10 nm to 2.7 mA/cm²_{Pt} for bulk poly-Pt. On the basis of the activity trend for the range of particle sizes studied, it appears that the effect of carbon support on activity is negligible. The experimental results and the concomitant profile of SA vs. particle size was found to be in an agreement to a truncated octahedral particle model that assumes active terrace sites.

Keywords

Oxygen reduction reaction; Platinum; Particle size effect; Rotating disk electrode method; Nafion-free activity

1. Introduction

Although the platinum loading has been significantly reduced for automotive fuel cells over the last couple of decades, further reduction is necessary from current values of 20–40 g·vehicle⁻¹ to 5–10 g·vehicle⁻¹ for successful commercialization [1-3]. A fundamental understanding of the impact of Pt particle size, nature of support, alloying, and heat treatment on the ORR activity and durability is essential to achieve the cost targets. In this work, we primarily address the particle size effect on the ORR activity of cathode catalysts.

The so-called ‘particle size effect’ (SA vs. Pt particle diameter based on XRD, TEM, CO adsorption, electrochemical area estimated from underpotentially deposited hydrogen (H_{UPD}) or CO stripping) for the ORR on Pt-based catalysts has been debated since 1960’s [4-40]. Early works were related to the particle size effect on Teflon-bonded electrodes in phosphoric and sulfuric acid electrolytes (strongly adsorbing anion species) in an attempt to raise phosphoric acid fuel cell (PAFC) performance [4-16]. Some of these studies concluded that there was no specific activity (SA) dependence on Pt particle size; these reports may have suffered from errors caused by extrapolation over several orders of magnitude to obtain the exchange current density (j_0) [4-7]. A number of subsequent studies have reported an increase in SA with an

increase in particle size [6, 9, 11, 12, 16]. Bregoli et al. [9] first reported a clear SA dependence on the particle size between ~3.5 nm and 30 nm on the basis of SA at 0.9 V vs. RHE rather than j_0 . Other groups expanded the range of particle size (~1 nm to 50 nm) and reported a peak in mass activity (MA) at 3–5 nm [11, 12]. Kinoshita [14] rationalized the SA and MA dependence on the particle size, in the range ~1–12 nm, using a truncated octahedral particle model assuming (100) surfaces to be active sites. Markovic et al. [20] demonstrated the activity in dilute sulfuric acid depends on crystallite orientation in the following order: (111) $\ll$ (100) $<$ (110); this observation agrees with the model reported by Kinoshita [14]. Kabbabi et al. [17] examined the SA and MA in the entire particle size range from 1.8 nm to bulk polycrystalline Pt (poly-Pt) for Nafion-coated catalysts in dilute sulfuric acid solution using the rotating disk electrode (RDE) method. They found a similar trend with a steep slope for SA and MA vs. particle size in the range less than ~6 nm; they qualitatively correlated the trend (2–4.5 nm) to the amount of oxygenated species. Additionally they observed that the slope for the particle size effect was shallower from ~6 nm to bulk Pt. In contrast, Sarapuu et al. [41] reported no clear particle size dependence of the SA from ~2 nm to bulk Pt in dilute sulfuric acid solution using Pt thin film fabricated on GCs by electron beam deposition. Nesselberger et al. [31] also observed no clear particle size

dependence in the range from ~1 nm to ~5 nm but a total of x4 increase from 1–5 nm particles to bulk Pt, and reported linear MA increase with increasing Pt particle size.

Since the 1990's, researchers have attempted to investigate the particle size effect in dilute perchloric acid (weakly-adsorbing anion species) to simulate Nafion membrane/ionomer employed in proton exchange membrane fuel cell using RDE methods [19-22, 25-37, 39, 40, 42-45]. Although a few reports have concluded an absence of the particle size dependence on the ORR activity [27, 28], the vast majority have reported varying degrees of the effect [19-22, 25, 26, 29-35, 37, 39, 45]. Fabbri et al. [45] recently summarized the particle size dependence reported in 6 articles and compared them to their results; the SA vs. particle size was essentially identical in all the reports when plotted with SA normalized to values at ~10 nm in each study. The SA dependence was observed to be shallow in the range less than ~10 nm and steep in the range less than ~10 nm to bulk poly-Pt. Several research groups have attempted to correlate the particle size effect trend described in Fabbri et al. [45] to the following properties: i) oxide coverage—smaller particles are more oxophilic [19], ii) geometric effect—fraction of terrace/step sites that have different sensitivity to anion adsorption from electrolyte and oxide species [31, 42], iii) surface electronic effects—electrochemical potential of total zero charge (pztc) [25], and, iv) electronic

effects—binding energy of core (4f) electrons [19], d-band vacancy/position of d-band center [22, 32, 37]. These attempts have succeeded in qualitatively correlating the SA to some of the listed properties in limited ranges; however, none of analyses using practical Pt catalysts provide a reasonable explanation for the SA dependence over the entire particle size range (1 nm particle to bulk). This discrepancy may stem from inaccurate (low) ORR activity determination especially for nanoparticle catalysts as discussed extensively in our previous studies [46-48]. Several factors have been identified that affect the measured ORR activity and consequently the observed particle size effect in 0.1 M HClO₄ using RDE methods: i) anion adsorption/blocking by Nafion ionomer—typically, incorporated in Pt/C catalyst layers but not for poly-Pt (impact of Nafion may also depend on particle size) [46, 49-56], ii) catalyst layer thickness and uniformity—O₂ diffusion within the catalyst layer [33, 35, 45, 46, 57-63], iii) ORR activity measurement protocols [29, 47, 64, 65], iv) *iR* and background current corrections [21, 31, 47, 66-68], and, v) impurity levels in the electrochemical system [47, 49, 59, 64, 69-76].

Nesselberger et al. [31] used Nafion-free catalysts and applied *iR* and background current corrections in an attempt to obtain a more reliable measure of the particle size effect. However, although their measured activities were higher, the trend essentially

followed the literature comparison conducted in Fabbri et al. [45]. In order to take into account O₂ diffusion limitation within catalyst layer as well, Perez-Alonso et al. [34] employed model Pt nanoparticle ultrathin catalyst layers directly formed on GC substrates (Pt/GC) using an advanced sputtering technique. They reported i) steep SA increase from 2 nm to 11 nm particle, ii) similar SA for 11 nm particle and poly-Pt, and, iii) MA peak at 3 nm. This trend is in sharp contrast to all the literature studies reported using practical Pt catalysts in 0.1 M HClO₄ using RDE methods. Their data closely agrees with a theoretical model that assumes truncated octahedral particles with dissolved edges and corners and terrace sites that function as active sites [42]. Since the model experiments using ultrathin catalyst layers, in principle, provide more reliable activity values than the literature experiments using practical Pt catalysts (supported Pt/C, Pt black), the agreement of the model experiment results with the theoretical model has tremendous significance. However, it is possible that the sputtered highly uniform Pt particles on GC may simulate an ideal nanoparticle catalyst system that may not provide the Pt particle size effect on practical Pt catalyst systems such as Pt/C and Pt black.

In this work, we report the ORR activity dependence on Pt particle size for practical Pt/C catalysts using highly refined thin-film RDE (TF-RDE) methods. In order to obtain

the intrinsic ORR activity of Pt surfaces, we employed well-dispersed, Nafion-free ultrathin uniform catalyst layers with ORR activity measured using well-defined protocols determined in our previous study [46].

2. Experimental

2.1. Catalysts, chemicals and reactant gases.

Pt/C catalysts employed in this study were manufactured by Tanaka Kikinzoku Kyogyo (TKK, Japan), Johnson Matthey (JM, UK) and Umicore (Germany), and the detailed specifications along with the nomenclature for the catalysts are listed in Table 1. Surface area obtained from BET method and CO chemisorption and crystallite size from XRD were provided by the manufacturer. Pt/C catalyst with 10 nm Pt particle (average) was obtained by heat treating Umicore 48 weight% (wt%) Pt/C catalyst at 500 °C under H₂ atmosphere for 2 hours. Bulk poly-Pt ($\phi = 5$ mm, 0.196 cm², embedded in a PTFE cylinder, Pine Instruments) were employed in RDE measurements. Deionized (DI) water (>18.2 M Ω ·cm, TOC <5 ppb) from a Milli Q system (Millipore) was used for acid dilutions and glassware cleaning. The following chemicals were used in electrolyte preparation and ink formulation: isopropanol (IPA, CHROMASOLV[®] Plus, for HPLC, 99.9%, Sigma-Aldrich), Nafion solution (DE520, EW1000, 5 wt%, 0.924 g·cm⁻³,

Sigma-Aldrich), 0.05 μm alumina dispersion (Buehler Inc.), concentrated (conc.) sulfuric acid (Certified ACS Plus, Fisher Scientific), Nochromix[®] (Godax Laboratories, Inc.), and 70% perchloric acid Veritas[®] Doubly Distilled (GFS chemicals). 70% HClO_4 were poured directly from the original acid container into clean perfluoroalkoxy alkane (PFA) or fluorinated ethylene propylene (FEP) bottles placed on a scale, and the HClO_4 was poured into DI water in another PFA or FEP bottle to prepare 0.1 M HClO_4 electrolyte. All electrochemical measurements were carried out in 0.1 M HClO_4 . Gases used in this study were all classified as ultrapure grade (N_2 , 99.9999%, H_2 , 99.999%, O_2 , 99.9999%, CO 99.998% Matheson Gas).

Table 1. Electrocatalyst specification.

Supplier	Pt content (wt%)	Carbon	Nomenclature for this work	Supplier nomenclature	Surface Area CO ($\text{m}^2 \cdot \text{g}^{-1}$)	Crystallite size XRD (nm)
TKK	26.1	High Surface Area Carbon (HSC)	Pt/HSC	NA	271	1.8
TKK	46.4	HSC	Pt/HSC	TEC10E50E	132.6	2.6
TKK	29	Vulcan	Pt/V	TEC10V30E	157.3	2.5
TKK	46.4	Vulcan	Pt/V	TEC10V50E	77.6	2.5
TKK	46.2	Graphitized Vulcan	Pt/G-V	NA	70.7	2.3
JM	38	HSC	Pt/HSC	NA	81	<2
Umicore	19.5	Low Surface Area Carbon (LSC)	Pt/LSC	Elyst Pt20 0380	NA	3.0-3.5
Umicore	48	LSC	Pt/LSC	Elyst Pt50 0380	NA	3.6-4.2

2.2. Instrumentation.

A microbalance (UMX2, Mettler Toledo), bath sonicator (FS30H, Fisher Scientific, output: 42 kHz, 100 W) and horn sonicator (S-4000, Q_{SONICA}, LLC., output: 20 kHz, 600 W max) were employed in the preparation of catalyst inks. Autolab PGSTAT302N potentiostat operated with NOVA software from Metrohm was used to obtain cyclic voltammograms (CVs), ORR current-potential (*I-E*) polarization curves, and to conduct *iR* correction dynamically during the electrochemical measurements and electrochemical impedance spectroscopy (EIS). RDE rotators, PTFE rotator shafts and GC tips ($\phi = 5$ mm, 0.196 cm^2 , embedded in a PTFE cylinder) were obtained from Pine Instruments. An optical microscope (AM4815ZT Dino-Lite Edge, Dino-Lite Digital Microscope) was routinely used to facilitate inspection of catalyst layers on glassy carbon (GC) substrates. A JEOL JSM-7000F Field Emission Microscope was employed to obtain SEM images.

2.3. Electrochemical cell setup.

The electrochemical cell design (130 cm^3 ; counter electrode: Pt gauze; reference electrode: RHE; working electrode: poly-Pt or GC with catalyst layer) as well as

detailed cleaning procedure are described in our previous work [47]. The electrochemical cell was meticulously cleaned as described in detail in our previous work [47]. The GC and poly-Pt RDE tips were polished using 0.05 μm alumina slurry before each experiment as described in detail in our previous work [46, 47].

2.4. Standardized electrochemical measurement protocols.

Protocols for conditioning, CVs for electrochemical area (ECA) estimation and ORR *I-E* curve measurements established on the basis of our comprehensive experimental studies have been meticulously adhered to in this manuscript and we briefly state these measurement protocols [46-48]. For conditioning, potential cycling was conducted in the range 0.025–1.2 V at 500 $\text{mV}\cdot\text{s}^{-1}$ for 50–100 cycles. H_{UPD} (adsorption) charge was obtained from the third cycle of CV measured in 0.025–1.0 V at 20 $\text{mV}\cdot\text{s}^{-1}$ under N_2 atmosphere and ECA was estimated using $210 \mu\text{C}\cdot\text{cm}^{-2}_{\text{Pt}}$ [77-80]. We note that HUPD charge estimated in this method resulted in one half of CO stripping charge for Pt/C catalysts [47]. ORR *I-E* curve was measured from –0.01 to 1.0 V at 20 $\text{mV}\cdot\text{s}^{-1}$ and 1600 rpm under O_2 atmosphere, and correction for solution resistance (R_{soln} , typically ~21 ohm) obtained by EIS was applied dynamically during the measurement. Background (b.g.) currents were measured under N_2 atmosphere and used for correction for all ORR

I-E curves. All measurements were conducted at $23 \pm 2^\circ\text{C}$. ORR kinetic currents at 82 kPa (~ 1800 m) have been corrected to 100 kPa O_2 using reaction order ($m = 1$) [81-83] and Koutecký-Levich equation was applied to correct for O_2 diffusion in electrolyte solution to obtain the SA ($\mu\text{A}\cdot\text{cm}^{-2}_{\text{Pt}}$) and MA ($\text{mA}\cdot\text{mg}^{-1}_{\text{Pt}}$). The SA and MA are reported at 0.9 V vs. RHE in this manuscript.

2.5. Catalyst layer fabrication.

For TKK Pt/HSC (TEC10E50E), Pt/V and Pt/G-V catalysts, catalyst inks were prepared by mixing Pt/C catalyst powders (46 wt% Pt/C catalyst: 3.8 mg, 29 wt% Pt/V: 4.1 mg) with 7.6 cm^3 DI water and 2.4 cm^3 IPA, and sonicating in the ice-water bath sonicator (10 min) followed by sonication using the horn sonicator (6 W, 30 s) with sample vial placed in an ice-water bath. A 5 mm^3 aliquot of the catalyst ink ($3\text{--}4.5\text{ }\mu\text{g}_{\text{Pt}}\cdot\text{cm}^{-2}$) was pipetted onto the polished GC tip placed on a custom-built stainless steel holder and positioned in a beaker (400 cm^3) filled with 5 cm^3 of IPA. The beaker was sealed with a polymer film that was perforated. The beaker with the electrodes and IPA were placed in an oven heated to 40°C to gradually (~ 3 hours) dry the inks under IPA vapor ($\sim 13\text{ kPa}$) and form the catalyst layer [46, 58].

For other catalysts (TKK Pt/C except for TEC10E50E, JM Pt/HSC and Umicore Pt/LSC), a high-quality thin layer was not possible without the addition of an extremely small amount of Nafion: catalyst inks were prepared by mixing Pt/C catalyst powder (26.1 wt% Pt/HSC: 2.3 mg, 38 wt% Pt/HSC: 2.4 mg, 19.5 wt% Pt/LSC: 4.5 or 9.1 mg, 48 wt% Pt/LSC: 3.7 mg) with 7.6 cm³ DI water, 2.4 cm³ IPA and 0.5 wt% Nafion IPA solution (diluted from 5 wt% Nafion) with ionomer to carbon weight ratio: I/C = 0.008 for 48 wt% Pt/LSC (0.5 wt% Nafion: 4 mm³), 0.02-0.04 for 26.1 wt% Pt/HSC (14 mm³), 38 wt% Pt/HSC (13 mm³), 19.5 wt% Pt/LSC (29 mm³), and sonicating with the same procedure as stated above for other Pt/C catalysts. A 10 mm³ aliquot of the catalyst ink (3–9 μg_{Pt}·cm⁻²) was pipetted onto the polished GC tip on an inverted rotator shaft at 100 rpm. The ink was subsequently dried under ambient conditions by increasing and maintaining the rotator speed at 700 rpm for a period of 15 min [46, 59].

For TKK TEC10E50E, both the types of inks were prepared with and without Nafion to examine the influence of Nafion addition. This method provides as thin and uniform catalyst layers for both the types of catalyst inks as shown in Fig. 1. Figure 2 shows that the measured activities are virtually equal with and without the small amount of Nafion addition. We also note that although truly Nafion-free activity cannot be obtained for catalysts that required the addition of slight amount of Nafion to fabricate thin and

uniform catalyst layers, the impact of the Nafion addition is likely negligible for the I/C range used in this study based on the observation that the activity is invariable for 19.5 wt% Pt/LSC catalyst layers with I/C range between 0.02 and 0.04. Therefore, we treat all the activity values obtained using these two methods as Nafion-free activity values.

Figure 1

Figure 2

3. Results and Discussion

CVs for poly-Pt, 48 wt% Pt/LSC and 26.1 wt% Pt/HSC catalysts in 0.1 M HClO₄ are depicted in Fig. 3a to show the effect of ECA. In order to compare CV characteristics of catalysts with different ECAs, current was normalized with ECA after subtraction of double layer charging current (I_{dl}). Peak potentials of Pt surface oxidation and oxide reduction are more positive for catalyst with lower ECAs as reported in literature [19]. ORR *I-E* curves for these catalysts in 0.1 M HClO₄ are also plotted in Fig. 3b to demonstrate reliability of the ORR activity measurement in this study. Agreement of limiting current for the Pt/C catalysts (5.5–5.9 mA·cm⁻²) with the theoretical value at 1600 rpm (5.99 mA·cm⁻²), calculated using kinematic viscosity

($1.009 \times 10^{-2} \text{ cm}^2 \cdot \text{s}^{-1}$), solubility ($1.26 \text{ mol} \cdot \text{dm}^{-3}$) and diffusivity ($1.90 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$) [84, 85], indicates that the catalysts cover almost the entire GC area [46]. Also, i) similar slope on I - E curves for the Pt/C catalysts to that for poly-Pt at $\sim 0.85 \text{ V}$ and above, and ii) as sharp transition from mixed kinetic/diffusion regime to O_2 diffusion limiting regime on the curves for the Pt/C catalysts as that for poly-Pt, suggest that negligible mass transport limitation within Pt/C catalyst layers.

Figure 3

SA values in 0.1 M HClO_4 obtained for Pt particle size in the range from $\sim 2 \text{ nm}$ to bulk poly-Pt (4 to 44 electrodes per catalyst, 2 inks per catalyst) along with literature values are depicted in Fig. 4 [26, 31, 34, 86] and ECA, average particle size and SA can be found in Table 2. The obtained ECA does not agree well with that estimated from CO chemisorption measurements. The deviation may stem from difference in preconditioning processes and assumption of CO binding mode for ECA estimation [87]. Average particle size was calculated from ECA assuming mono-dispersed sphere having the entire area electrochemically active [26, 31, 86]. The estimated average particle size from H_{UPD} charge tends to be larger compared to the crystallite size

estimated from XRD pattern (Table 1). This could be due to the conditioning process conducted in electrochemical experiments to measure the ORR activity. Since the ORR activity is measured after the conditioning process, we employ average particle size estimated from H_{UPD} to discuss particle size effect. SA values obtained in our studies (filled blue circles) is observed in Fig 4 to be significantly higher ($0.74\text{--}1.8\text{ mA}\cdot\text{cm}^{-2}_{Pt}$) in the range ($\sim 2\text{--}10\text{ nm}$) than those reported in literature ($0.2\text{--}0.5\text{ mA}\cdot\text{cm}^{-2}_{Pt}$) using practical Pt catalysts [26, 31] but comparable to that of Perez-Alonso et al. [34]. On the basis of findings in our previous studies, the high values are due to i) exclusion of Nafion ionomer that lowers the ORR activity, ii) the use of thin and uniform catalyst layers with negligible O_2 diffusion limitation within the catalyst layer, iii) the use of ORR activity measurement protocols with appropriate conditioning and corrections, and iv) minimized impact of impurity in the electrochemical system on the activity. Our understanding can be rationalized when our results are compared to the results reported by Perez-Alonso et al. [34], who used model electrodes in which Pt particles were deposited directly onto GC substrates (denote as sputtered Pt/GC hereafter) by an advanced sputtering technique. Because of the nature of the deposition technique, the catalyst layers obtained in Perez-Alonso et al. [34] are extremely thin, Nafion is not incorporated and ORR activity measurement protocols are similar to the protocols

applied in this work. Thus, the catalyst layers in the sputtered Pt/GC experiments should result in ORR activities of Pt with negligible loss due to O₂ diffusion limitation. On the basis of these facts, it is reasonable to treat the high SA values in our study as approaching the intrinsic activity of Pt nanoparticles with minimal impact from O₂ diffusion limitation and impurities.

Figure 4

Table 2. Comparison of ECA, SA and MA for Pt/C catalysts

catalyst	# of samples	ECA (m ² ·g ⁻¹)	Average particle size (nm)	SA (mA·cm ⁻² _{Pt})	MA (mA·mg ⁻¹ _{Pt})	Reference
26.1 wt% Pt/HSC	6	136 ± 3	2.1	0.74 ± 0.03	1.01 ± 0.05	This work
46.4 wt% Pt/HSC	44	101 ± 7	2.8	0.89 ± 0.06	0.90 ± 0.09	[46]
29 wt% Pt/V	6	93.5 ± 0.9	3.0	1.01 ± 0.06	0.94 ± 0.06	This work
46.4 wt% Pt/V	20	63 ± 3	4.4	1.12 ± 0.07	0.71 ± 0.04	[46]
46.2 wt% Pt/G-V	6	54 ± 4	5.2	1.17 ± 0.06	0.63 ± 0.05	This work
38 wt% Pt/HSC	5	120 ± 3	2.3	0.82 ± 0.02	0.98 ± 0.04	This work
19.5 wt% Pt/LSC	8	66.4 ± 0.8	4.2	1.13 ± 0.03	0.75 ± 0.02	This work
48 wt% Pt/LSC	6	48.0 ± 0.3	5.8	1.79 ± 0.05	0.86 ± 0.02	This work
48 wt% Pt/LSC-HT*	4	28 ± 1	9.9	1.67 ± 0.09	0.471 ± 0.009	This work

*HT: heat-treated

The impurity level in the cell/electrolyte can be judged from the magnitude of SA of bulk poly-Pt; the SA of poly-Pt ranges $2\text{--}3\text{ mA}\cdot\text{cm}^{-2}_{\text{Pt}}$ in these studies (Fig. 4). By normalizing to the SA for poly-Pt, it may be possible to make a more fair comparison of the trend and be able to make a comparison to the theoretical model. Figure 4 has been re-plotted as Fig. 5 with SA normalized to poly-Pt SA for each data set [26, 31, 34, 42, 86]. Figure 5 includes a curve representing a theoretical model (truncated octahedral particle with dissolved edges and corners) reported by Tritsarlis et al. [42]. The SA value corresponding to $\sim 30\text{ nm}$ evaluated in our group using Nafion-free Pt nanotube thin catalyst layer (blue open circle) has also been added to Fig. 5. In literature studies [26, 31], SA remains low in the range from $\sim 2\text{ nm}$ to 8 nm but significantly increases in the range from $\sim 8\text{ nm}$ to bulk poly-Pt. In our study, in contrast, SA at $\sim 2\text{ nm}$ is already as high as $\sim 30\%$ of SA for poly-Pt, and SA steeply increases to $60\text{--}70\%$ of SA for poly-Pt at $\sim 10\text{ nm}$ followed by attenuated increase and plateau to reach bulk poly-Pt activity. The trend in our study is coincident with most of the sputtered Pt/GC data and is in close agreement to the theoretical model. Figure 6 is a plot of the normalized SA vs. particle size with the second ordinate representing fraction of terrace atoms obtained experimentally for the catalyst of Perez-Alonso et al. [34]. Since our data for practical catalysts falls in the same range as that of Perez-Alonso et al. [34], it follows that

despite the wider particle size distribution the SA for practical catalysts show good correlation to terrace atom fraction. The samples used in our study include various types of carbon supports as well as bulk poly-Pt; the correlation suggests that there is minimal interaction with the carbon supports that affects the ORR activity. In simple terms, we may conclude that the intrinsic activity of Pt at 0.9 V is proportional to the number of terrace sites. We note that the so-called “particle proximity effect” on the ORR activity is not likely to be affecting the SA values on Pt/C catalysts used in this study [88]; calculated average inter-particle distance (AID) or edge to edge distance using an equation reported in literature ranges from 8 nm to 23 nm for Pt/C catalysts used in our study [89]. Although the calculated AID provides only an indicative average, the AID range for catalysts used in our study are still significantly longer than inter-particle distances that have been reported to increase the ORR activity (<1.5 nm) in literature study [88].

Figure 5

Figure 6

The absolute values of MA obtained in our and literature studies are summarized in Fig. 7 [26, 31, 34, 42, 86] and can also be found in Table 2. The MA obtained in our work is significantly higher than that reported in the literature using practical Pt catalysts and is in close agreement with that for sputtered Pt/GC measurements and the theoretical model. An MA decrease for particle sizes below ~2 nm was not observed in our studies due to both a lack of available samples/data in that range as well as a finite particle size distribution for practical catalysts.

Figure 7

4. Conclusion

Pt particle size effect on the ORR activity was studied in the range from 2 nm to bulk poly-Pt using practical Pt/C catalysts and poly-Pt in 0.1 M HClO₄. By incorporating experimental advancements (Nafion-free ultrathin uniform catalyst layers and standardized protocols): i) extremely high SA and MA for practical catalysts comparable to the sputtered Pt/GC (approaching an ideal system) were obtained, ii) the particle size effect for practical catalysts in our work agreed with the theoretical model

that assumed truncated octahedral particles with terrace sites to be active, iii) no strong interaction with the carbon supports was observable.

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Figure Captions

Figure 1. SEM images of TKK 46 wt% Pt/HSC catalyst layers fabricated on GC substrates using (a) the Nafion-free method and (b) the low Nafion content method (I/C 0.02). Catalysts removed as observable as horizontal lines on both catalyst layers to facilitate observation and analysis of catalyst distribution in each local area (~80% of the catalysts located in the area of $<0.5\ \mu\text{m}$ in thickness for both catalyst layers).

Figure 2. SA at 0.9 V obtained for TKK 46 wt% Pt/HSC catalyst layers fabricated with the Nafion-free method and the low Nafion content method.

Figure 3. (a) CVs and (b) ORR I - E curves for poly-Pt and Pt/C catalyst layers at $20\ \text{mV}\cdot\text{s}^{-1}$ and 23°C in $0.1\ \text{M HClO}_4$. B.g. current correction applied for the ORR I - E curves.

Figure 4. Particle size dependence of specific activity at 0.9 V vs. RHE in $0.1\ \text{M HClO}_4$ obtained in this study in comparison with literature values.

Figure 5. Normalized SA dependence on particle size effect obtained in our study as well as literature experimental and theoretical studies. The dashed black line indicates the trend for the theoretically determined discrete values represented by the black squares.

Figure 6. Correlation between SA and fraction of surface terrace atom % estimated from CO-TPD experiments re-plotted from Perez-Alonso et al. [34] (pink cross). The SA values normalized to SA values of poly-Pt electrodes to depict correlation between SA obtained in this work (blue circles) and the fraction of surface terrace atoms.

Figure 7. MA at 0.9 V obtained in this work as well as literature experimental and theoretical studies. The absolute values of MA for the theoretical model (Tritsaridis et al. [42]) were estimated using the SA of poly-Pt in this work.

Figure 1

Figure 2

Figure 3

Figure 5

Figure 6

Figure 7