



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



Kazuma Shinozaki^{a,b,c,*}, Yu Morimoto^c, Bryan S. Pivovar^a, Shyam S. Kocha^a

^a National Renewable Energy Laboratory, Electrochemical Characterization Labs, Golden, CO 80401, USA

^b Colorado School of Mines - Department of Chemistry, Golden, CO 80401, USA

^c Toyota Central R&D Labs., Inc., Aichi, 480-1192 Japan

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ABSTRACT

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.

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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) << (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

* Corresponding author at: Toyota Central R&D Labs., Inc., Aichi, 480-1192 Japan.
E-mail address: Shinozaki@mosk.tytlabs.co.jp (K. Shinozaki).

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) *i*R 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 *i*R 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 ($\varphi = 5$ 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 μ m 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% HClO₄ were poured directly from the original acid container into clean perfluoroalkoxy alkane (PFA) or fluorinated ethylene propylene (FEP) bottles placed on a scale, and

Table 1
Electrocatalyst specification.

Supplier	Pt content (wt %)	Carbon	Nomenclature for this work	Supplier nomenclature	Surface Area CO (m ² ·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

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