

ORR Kinetics Investigation of Pt/Carbon Electrocatalysts with Varying Pt Loading and Electrode Thickness by Rotating Disk Electrode

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Platinum (Pt) and Pt-based alloys supported on high surface area carbons (HSACs) are still the most common electrocatalysts for proton exchange membrane (PEM) fuel cells for automotive applications. The performance of these catalysts can be subject to significant mass transfer limitations.¹ Fundamental understanding of both the effect of Pt loadings in terms of its dispersion on the carbon support and the intrinsic oxygen reduction reaction (ORR) activity of the catalyst can help to optimize the catalyst layer thickness for decreased Pt loadings in PEM fuel cells. The objective of this study is to investigate the effect of Pt loadings and catalyst layer thicknesses on ORR kinetics.

A rotating disk electrode (RDE) system is employed to evaluate the kinetics of various Pt/carbon catalysts. Three Tanaka Kikinzoku Kogyo (TKK) electrocatalysts with different Pt loadings (46%, 28% and 19%), similar Pt particle sizes and identical carbon supports (HSAC) were chosen for this study. Experiments were designed to study the effect of electrode Pt loadings and the catalyst layer thicknesses on the ORR kinetics of the catalyst. This is summarized in Table I. A constant ionomer/carbon ratio of 0.43 was used for all studies. Cyclic voltammetry (CV) was performed under a saturated N₂ atmosphere in order to obtain the electrochemical area (ECA, m² g_{Pt}⁻¹) of Pt. Hydrodynamic voltammetry was carried out in a saturated O₂ atmosphere to characterize ORR activity.

Table I. Disk electrode specifications to study kinetics of Pt/C catalysts with varied disk thickness.

Pt loading (wt%)	ω_{Pt} ($\mu\text{g cm}^{-2}$)	ω_C ($\mu\text{g cm}^{-2}$)	Electrode thickness L (μm)
46	17.3	20.31	1.56
28	17.3	44.04	3.37
19	17.3	73.76	5.63
46	34.6	40.6	3.11
28	34.6	88.1	6.73
19	34.6	147.5	11.26
46	86.5	101.5	7.78
28	86.5	219.9	16.83
19	86.5	368.9	28.15

ORR kinetic parameters of these three Pt/C catalysts (disk Pt loading of 17.3 $\mu\text{g}_{Pt} \text{cm}^{-2}$ and varying disk thickness) are shown in Figure 1. The disk thickness for all three catalysts at this loading was less than 10 μm . These three Pt/C catalysts demonstrated similar intrinsic ECAs and ORR activities regardless of electrode thickness. Similar results are also observed with a constant disk thickness of $\sim 1.6 \mu\text{m}$ and varying disk Pt loading (not shown here). The results showing the intrinsic area specific activity is independent of Pt loading

is consistent with the published findings.^{2,3} The limiting current densities followed the Levich equation and are also found to be consistent with the theoretical values.

Our observations also indicate that ECAs for the chosen catalysts are similar regardless of the catalyst loading and dispersion when the electrode thickness is less than 10 μm . For thicker catalyst layers ($> 10 \mu\text{m}$), accurate ECA evaluation becomes tricky using this technique due to distorted shape of the CV. When the catalyst layer on the disk is thick, a mass-transfer limitation may be introduced. Further discussion will be presented at the meeting.

The ORR kinetics of these Pt/C catalysts under the varied electrode Pt loadings and catalyst layer thicknesses will be further analyzed in terms of activity employing the Koutecky–Levich equation and Tafel slopes. It is believed that the use of an optimally loaded Pt/C catalyst with maximum Pt utilization can provide an advantage by reducing the catalyst layer thickness for better mass transport without losing kinetic activity.

References

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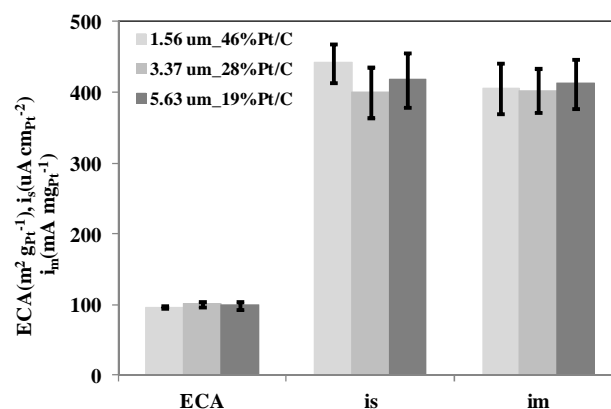


Fig.1 ECA, area specific activity (is), and mass activity (im) of Pt/carbon electrocatalysts with a constant disk Pt loading of 17.3 $\mu\text{g}_{Pt} \text{cm}^{-2}$ and varying disk thickness in 0.1 M HClO₄ at 25°C.