Suppression of Oxygen Reduction Reaction Activity on Pt-based Electrocatalysts from Ionomer Incorporation

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The impact of Nafion on the oxygen reduction reaction (ORR) activity **is** studied for Pt/C and Pt-alloy/C catalysts using thin-film rotating disk electrode (TF-RDE) methods in 0.1 M HClO₄. Ultrathin uniform catalyst layers and standardized activity measurement protocols **are** employed to obtain accurate and reproducible ORR activity. Nafion lowers the ORR activity which plateaus with increasing loading **on Pt catalysts**. **Pt particle size is found not to have significant influence on the extent of the SA decrease upon Nafion incorporation.** Catalysts using high surface area carbon (HSC) support **exhibits** attenuated activity loss resulting from lower ionomer coverage on catalyst particles located within the deep pores. **The impact of metallic composition on the activity loss due to Nafion incorporation is also discussed.**

Keywords

Oxygen reduction reaction; Platinum; Platinum Alloy; Nafion ionomer; Rotating disk electrode method; Ionomer coverage

1. Introduction

Automotive manufacturers have recently started launching proton exchange membrane fuel cell (PEMFC) vehicles in a small scale (1000 vehicles/year production). For successful commercialization, a further reduction of Pt catalyst usage from ~30 g to ~10 g (100kW_{stack}) is necessary [1-3]. The Pt loading can be reduced by employing novel higher activity catalysts, improving the Pt utilization, and optimizing the cathode catalyst layer.

Ionomers such as Nafion are commonly incorporated into catalyst layers of PEMFCs to provide protonic pathways for efficient platinum utilization [4]; it is well-known that excessive ionomer can block the pores in the catalyst layer and sub-optimal levels can lead to increase catalyst layer resistance and lower performance. Even for catalyst layers with optimal ionomer-to-carbon (I/C) weight ratios, recent studies using low platinum loading PEMFCs suggest that fuel cell performance at high current density is partly limited by O₂ transport through Pt/ionomer interface [5-12]. Fundamental studies using RDE methods also indicate that Nafion lowers the oxygen reduction reaction (ORR) activity on single crystalline, polycrystalline Pt and Pt alloy surfaces and nanostructured thin film (3M NSTF) [13-17]. In these studies, thin films (10's of nm) were applied to the electrode surfaces by capping with Nafion ionomer. A

positive shift on the onset potential for OH and other oxide species formation and a suppression of the ORR activity are typically observed after capping with Nafion. Subbaraman et al. [13] attributed the features observed on cyclic voltammograms under inert atmosphere to sulfonate anion adsorption on Pt surfaces using a CO displacement method [18]. Moreover, the % ORR activity loss on Nafion-capped Pt (hkl) in perchloric acid solution (weakly-adsorbing anions) was found to follow the same order, Pt (111) > (110) > (100), as that on Nafion-free surfaces in sulfuric acid; this fact led them to conclude that sulfonate anion adsorption was the main cause for lowered ORR activity. In contrast to these detailed kinetics studies on well-defined bulk Pt surfaces, little work has been reported on practical carbon supported nanoparticle platinum (Pt/C) catalysts [14, 19-21]. The lack of studies is first of all due to the fact that the ionomer cannot be simply eliminated from PEMFCs since the ionomer is crucial and indispensable for providing facile protonic pathways. However, ionomer is not necessary as a proton conducting component in half cell studies in acid electrolyte. The early work of Guilminot et al. [22] used ultramicroelectrodes with cavity technique and demonstrated that the presence of Nafion alters the ORR activity of a Pt/C catalyst by employing catalyst layers with and without recast Nafion. In contrast, Studies using thin film RDE (TF-RDE) methods have not been applied traditionally because of the

following actual and perceived difficulties: (i) elimination of ionomer can result in a low ink dispersion and poor catalyst film quality—uncontrolled catalyst mass on glassy carbon (GC) substrates and limited O₂ diffusion within catalyst layer (ii) catalysts can detach from GC substrate surfaces during experiments without ionomer adhesion—uncontrolled catalyst mass on GC substrates [23].

In our previous study, we reported that the use of extremely thin and uniform films is indispensable to the kinetics study of ORR catalysts without hindrance from O₂ diffusion limitations within the catalyst layer, and demonstrated that ionomer is not essential to obtain well-dispersed stable thin catalyst films with extremely high ORR activity [24]. The impact of ionomer on the ORR activity can now be studied using the Nafion-free thin uniform catalyst layers and Nafion capped catalyst layers using the pre-formed Nafion-free catalyst layers.

In this work, we present results on the effect of Nafion ionomer on the ORR activity as well as CVs under inert atmosphere for several commercial Pt/C and Pt-alloy/C catalysts using a TF-RDE method by employing thin-uniform catalyst layers obtained with advanced catalyst layer fabrication techniques [24].

2. Experimental

2.1. Catalysts, chemicals and reactant gases.

Pt/C and Pt-alloy/C catalysts employed in this study were manufactured by Tanaka Kikinzoku Kyogyo (TKK, Japan) and Umicore (Germany), and the detailed specifications along with the nomenclature for the catalysts are listed in Table 1. Surface area obtained from CO chemisorption and crystallite size from XRD were provided by the manufacturer. Bulk poly-Pt ($\phi = 5$ mm, 0.196 cm^2 , embedded in a PTFE cylinder, Pine Instruments) were employed in RDE measurements. Deionized (DI) water ($>18.2\text{ M}\Omega\cdot\text{cm}$, 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), non-ionic surfactant (Triton X-100, Sigma, #T-9284), Nafion solution (DE520, EW1000, 5 wt%, $0.924\text{ g}\cdot\text{mL}^{-1}$, Sigma-Aldrich), $0.05\text{ }\mu\text{m}$ 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% HClO_4 were diluted with DI water 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 (N₂, 99.9999%, H₂, 99.999%, O₂, 99.9999%, CO 99.998% Matheson Gas).

Table 1. Electrocatalyst specifications.

Supplier	Pt Metal content (wt%)	Carbon	Nomenclature for this work	Supplier nomenclature	Surface Area CO (m ² · g ⁻¹)	Crystallite size XRD (nm)
TKK	26.1 Pt	HSC	Pt/HSC	NA	271	1.8
TKK	46.4 Pt	HSC	Pt/HSC	TEC10E50E	132.6	2.6
TKK	29 Pt	Vulcan	Pt/V	TEC10V30E	157.3	2.5
TKK	46.4 Pt	Vulcan	Pt/V	TEC10V50E	77.6	2.5
Umicore	20 Pt	Low Surface Area Carbon (LSC)	Pt/LSC	Elyst Pt20 0380	NA	3.0-3.5
Umicore	48 Pt	LSC	Pt/LSC	Elyst Pt50 0380	NA	3.6-4.2
TKK	Pt:Co = 46.4:5.0	HSC	Pt ₃ Co/HSC	TEC36E52	351	3.9
TKK	Pt:Co:Mn = 46.9:3.4:1.2	HSC	PtCoMn/HSC	NA	98.0	NA
Umicore	Pt:Co = 27.4:2.6	HSC	Pt ₃ Co/HSC	Elyst Pt30 0670	NA	4.0-4.5

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) and ORR current-potential (I - E) curves, and to apply iR correction during CV and I - E curve measurements. 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 GC. A JEOL JSM-7000F Field Emission Microscope was employed to obtain SEM images.

2.3. Electrochemical cell setup.

The electrochemical cell design (130 mL; 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 [25]. The electrochemical cell was meticulously cleaned as described in detail in our previous work [25]. The GC and poly-Pt RDE tips were polished using $0.05\text{ }\mu\text{m}$ alumina slurry before each experiment as described in detail in our previous work [24, 25].

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 [24-26]. 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} charge was obtained from **H adsorption current observed between ~0.05 V (inflection point) and ~0.4 V (double layer region)** in 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 $210 \mu\text{C}\cdot\text{cm}^{-2}_{\text{Pt}}$ [27-30]. 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. Correction for background (b.g.) currents was applied to all ORR I - E curves measured with in-situ correction of solution resistance (R_{soln}). All measurements were conducted at $23 \pm 2^\circ\text{C}$. ORR kinetic currents have been corrected to 100 kPa O_2 and Koutecký-Levich equation was applied to correct for O_2 diffusion in electrolyte solution to obtain the SA ($\text{mA}\cdot\text{cm}^{-2}_{\text{Pt}}$) 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.

Various fabrication techniques reported in our previous studies were applied for each catalyst to find a suitable technique for each catalyst to reproducibly obtain thin-uniform catalyst layers. Because such a suitable technique depends on catalysts,

employed techniques are described for each catalyst. For a TKK Pt/HSC (TEC10E50E), all the techniques can provide thin-uniform catalyst layers. Although one of the techniques described below incorporates slight amount of Nafion in the ink, obtained catalyst layers for the Pt/HSC exhibit as high activity values as catalyst layers fabricated using the other two techniques as reported in our previous studies [24, 31]. Therefore, we treat activity values obtained using the fabrication technique with an inclusion of slight amount of Nafion as Nafion-free activity values. We note that some of the catalyst layers fabricated using the techniques still have thin (~ 10 μm -wide) coffee ring structure on the periphery of GC substrates [24]. Therefore, we estimated effective (vol% weighted) thickness from thickness of catalyst layer on periphery and on the rest of GC area and vol% of catalysts located on the two area [24, 26].

For TKK Pt/HSC (TEC10E50E) and Pt/V catalysts, catalyst inks were prepared by mixing Pt/C catalyst powder with 7.6 mL DI water and 2.4 mL 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 μL aliquot of the catalyst ink ($3\text{--}4.5$ $\mu\text{g}_{\text{Pt}}\cdot\text{cm}^{-2}$) was pipetted onto the polished GC tip placed on a custom-built stainless steel holder and positioned in a beaker (400 mL) filled with 5 mL 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 (~13 kPa) and form the catalyst layer [19, 24]. The estimated effective thickness was 0.7 μm for a 46 wt% Pt/HSC catalyst layer, and 0.4 μm for a 46 wt% Pt/V catalyst layer.

For TKK Pt₃Co/HSC, catalyst inks were prepared by mixing the catalyst powder with 7.6 mL DI water, 2.4 mL IPA and 2.5 μL of 10 times diluted TRITON X-100 with DI water, and sonicating with the same procedure as applied for other catalysts [24]. A 2.5 μL aliquot of the catalyst ink ($4.5 \mu\text{g}_{\text{Pt}} \cdot \text{cm}^{-2}$) was pipetted onto the polished GC tip placed on a custom-built stainless steel holder and placed in an oven heated to 40°C to dry under the inks under air atmosphere.

For the other Pt/C and Pt-alloy/HSC catalysts, catalyst inks were prepared by mixing Pt/C catalyst powder with 7.6 mL DI water, 2.4 mL IPA and 10 times diluted Nafion IPA solution with ionomer to carbon ratio: I/C = 0.008 for Umicore Pt/C, 0.04 for TKK PtCoMn/C and Umicore PtCo/HSC, and sonicating with the same procedure as applied for other catalysts. A 10 μL aliquot of the catalyst ink ($3\text{--}9 \mu\text{g}_{\text{Pt}} \cdot \text{cm}^{-2}$) 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 [24, 32]. The estimated effective thickness was 1.0 μm for a 46 wt% Pt/HSC catalyst layer.

2.6. Nafion caps on poly-Pt and Pt/HSC.

Subsequent to an ORR activity evaluation on bare poly-Pt, the electrode was rinsed, covered with DI water and soaked in 1 mM KBr aqueous solution for 15 sec [16]; on rinsing with DI water, the poly-Pt surface was observed to become hydrophobic. A 2 μL aliquot of 0.025 wt% Nafion solution (x200 diluted with IPA) was dropped on poly-Pt surface with the electrode dried at 23°C followed by annealing in an oven at 140°C for 15 min to increase physicochemical stability [13, 17]. Alternatively, direct application of Nafion solution on bare poly-Pt surface (N_2 -dried, DI water rinsed) followed by the identical annealing process also produced the same results. For the case of Pt/C and Pt-alloy/C catalysts, diluted Nafion solution (2.5 μL) was dropped on the films followed by drying at 23°C. On the basis of limited analysis of Nafion capped Pt/C catalyst layers using SEM, Nafion seems to penetrate through the entire thickness of catalyst layer; we observed materials that were burnt by electron beam during SEM analysis through the entire catalyst layer thickness direction after Nafion capping. I/C ratio in the range 0.5–3.0 were obtained for a given electrode through a series of steps involving

measurement of ORR I - E , capping and drying. The entire sequence was repeated for up to 8 independent samples. The films were visually inspected for integrity before and after Nafion capping.

3. Results and Discussion

3.1. Impact of Nafion on poly-Pt

Before conducting a detailed investigation on the effect of ionomer on the ORR activity of Pt/C and Pt-alloy/C, we verified and reproduced the results presented in literature for the simpler poly-Pt system [13, 33-35]. The electrochemically conditioned poly-Pt was either capped directly with ionomer or after pre-soaking in a KBr solution to produce similar results. Figure 1a captures the effects ascribable to the ionomer on CVs under N_2 and Fig. 1b and the inset on ORR I - E curves. A negative shift in the onset of H_{UPD} current and new peaks that manifest at 0.15 V (cathodic peak) and 0.18 V (anodic peak) are observed in Fig. 1a in close qualitative agreement with literature [13, 33-35]; Small differences on CVs between our study and the literature studies probably stem from a number of artifacts including the cleaning process of the poly-Pt surface, viz., electrochemical cleaning/inductive heating, type of Nafion ionomer, solvent used to dilute the ionomer, thickness of the ionomer film and its heat treatment. The H_{UPD} area

decreased (by 2%) from Nafion capping accompanied by slight shifts on the onset potential of oxide formation/reduction regime.

In Fig. 1b, Nafion-capped surface exhibits reduced current density in diffusion regime from ~0.7 V to ~0.3 V. This is likely because of the anion adsorption. Recent PEMFC studies showed that a Nafion thin film has a large interfacial O₂ transport resistance [9, 12] and that large interfacial O₂ transport resistance was shown to stem from a very thin high density ionomer layer formed on ionomer/Pt interface by MD studies by Jinnouchi et al. [11].

Precipitous ORR activity losses were observed accompanied by a potential dependent shift of the entire curve (Fig. 1b, inset): ~60% loss at 0.95 V, ~70% loss at 0.9 V (from 2.8 mA·cm⁻²_{Pt} to 0.80 mA·cm⁻²_{Pt}), ~80% loss at 0.8 V. Recent fundamental studies using well-defined catalyst surfaces reported that sulfonate adsorption is the main source that lowers the ORR activity [13-17]. Since anion species adsorb more strongly at higher potentials, one might expect to observe larger %difference in activity at higher potentials originating from growing sulfonate coverage between Tafel curves for bare and Nafion-coated Pt surfaces. However, in the inset of Fig. 1b, the %loss of activity with Nafion capping on poly-Pt is larger at lower potentials. This is likely because, at higher potential, the anion coverage is reduced by the growth of oxide [17].

The difference in extents of the onset potential shift **on CVs under N₂** and the shift in the Tafel plot appears to indicate different sensitivities for the effect of Nafion.

Figure 1. (a) CVs under N₂ and (b) ORR *I-E* curves (inset: Tafel plot) in 0.1 M HClO₄

at $20\text{ mV}\cdot\text{s}^{-1}$ for poly-Pt with and without Nafion cap.

3.2. Impact of Nafion on Pt-based catalysts on various carbon black supports

High surface area carbon blacks (HSC) such as Ketjen Black have micropores within which >50% of the Pt nanoparticles reside [36-39]; on the other hand, low surface area supports (LSC) such as Vulcan or graphitized carbons lack micropores so that most of the Pt particles are on the outer surface. CVs under N₂ and ORR Tafel plots for 46 wt% Pt/HSC and 48 wt% Pt/LSC are shown in Fig. 2a–2d as examples to illustrate two extreme cases of supports. In Fig. 2a, 46 wt% Pt/HSC exhibits neither peak shifts in H_{UPD} region as is observed for poly-Pt nor onset potential shifts in oxide formation/reduction region. Correspondingly, in Fig. 2b, shifts in the ORR Tafel curves are not clearly observable until I/C ratio becomes high ($I/C \geq 1.5$). In contrast, in Fig. 2c, 48 wt% Pt/LSC exhibits observable peak shifts in H_{UPD} region and slight shift on the onset potential of oxide formation regime with increasing I/C ratio as is observed for poly-Pt. In the ORR Tafel curves (Fig. 2d), larger shifts are observed with increasing I/C ratio and the extent of the shift at the highest I/C ratio is similar to the shift observed for poly-Pt (the inset of Fig. 1b). **In contrast to the observable potential dependence of %loss in activity for poly-Pt surfaces as depicted in 3.1., such dependence was not observed for Pt/C catalysts.**

Figure 2. The effect of I/C ratio on (a, c) CVs under N_2 and (b, d) ORR $I-E$ curves in 0.1 M HClO_4 at $20 \text{ mV}\cdot\text{s}^{-1}$ for (a, b) 46 wt% Pt/HSC and (c, d) 48 wt% Pt/LSC.

To illustrate the effect of Nafion on SA at 0.9 V for various Pt/C catalysts, the SA is plotted against I/C ratio in Fig. 3. The SA and MA can also be found in Tables 2 (I/C ~0) and 3 (I/C dependence). At I/C ratio ~0 (Nafion-free), the SA varies depending on average Pt particle size/ECA as reported in our previous study [31]. When a Nafion cap

is applied, the SA decreases for all catalysts in proportion to the I/C ratio. In **most** cases above certain I/C ratio, the SA plateaus. Since the addition of ionomer either increases the thickness in a uniform manner or increases the coverage of Nafion agglomerates as reported in literature, the plateau seems to indicate that either a threshold thickness or maximum coverage is reached. The implication of the plateau will be discussed to more detail later in this section.

Figure 3. I/C ratio dependence of SA at 0.9 V for various Pt/C catalysts. **Error bars** indicate standard deviation for catalysts tested using 4 or more samples (46 wt% and 26 wt% Pt/HSC, 29 wt% Pt/V and 48 wt% Pt/LSC), and maximum and minimum for catalysts tested using less than 4 samples (46 wt% Pt/V).

Table 2. ECA, SA and MA at 0.9 V vs. RHE for Pt based catalysts at I/C ~0.

Catalyst	# of samples	ECA ($\text{m}^2\cdot\text{g}^{-1}$)	SA ($\text{mA}\cdot\text{cm}^{-2}_{\text{Pt}}$)	MA ($\text{mA}\cdot\text{mg}^{-1}_{\text{Pt}}$)	Reference
26.1wt% Pt/HSC	6	136 ± 3	0.74 ± 0.03	1.01 ± 0.05	[31]
46.4wt% Pt/HSC	44	101 ± 7	0.89 ± 0.06	0.90 ± 0.09	[24]
29wt% Pt/V	6	93.5 ± 0.9	1.01 ± 0.06	0.94 ± 0.06	[31]
46.4wt% Pt/V	20	63 ± 3	1.12 ± 0.07	0.71 ± 0.04	[24]
20wt% Pt/LSC	8	66.4 ± 0.8	1.13 ± 0.03	0.75 ± 0.02	[31]
48wt% Pt/LSC	6	48.0 ± 0.3	1.79 ± 0.05	0.86 ± 0.02	[31]
46.4 Ptwt% Pt ₃ Co/HSC	17	54 ± 4	1.5 ± 0.1	0.78 ± 0.02	This work
46.9 Ptwt% PtCoMn/HSC	1	61	1.65	1.00	This work
27.4 Ptwt% Pt ₃ Co/HSC	4	70 ± 2	2.17 ± 0.06	1.53 ± 0.02	This work

Table 3. I/C dependence of SA and MA at 0.9 V vs. RHE for Pt based catalysts.

Catalyst	# of samples	SA ($\text{mA}\cdot\text{cm}^{-2}_{\text{Pt}}$)				MA ($\text{mA}\cdot\text{mg}^{-1}_{\text{Pt}}$)			
		I/C 0	0.5	1.5	3	I/C 0	0.5	1.5	3
26.1wt% Pt/HSC	4	0.76 ± 0.01	0.65 ± 0.04	0.63 ± 0.04	0.62 ± 0.03	1.02 ± 0.04	0.86 ± 0.05	0.83 ± 0.06	0.82 ± 0.06
46.4wt% Pt/HSC	8	0.87 ± 0.08	0.84 ± 0.08	0.77 ± 0.09	0.64 ± 0.04	0.84 ± 0.07	0.78 ± 0.06	0.71 ± 0.08	0.57 ± 0.03
29wt% Pt/V	5	1.01 ± 0.07	0.79 ± 0.04	0.59 ± 0.03	0.51 ± 0.03	0.94 ± 0.07	0.70 ± 0.04	0.52 ± 0.04	0.43 ± 0.03
46.4wt% Pt/V	2	1.09 ± 0.03	0.82 ± 0.08	0.73 ± 0.06	0.656 ± 0.007	0.68 ± 0.02	0.48 ± 0.06	0.41 ± 0.04	0.346 ± 0.001
20wt% Pt/LSC	1	1.12	0.55	0.48	0.44	0.76	0.35	0.30	0.27
48wt% Pt/LSC	4	1.81 ± 0.04	1.31 ± 0.07	0.83 ± 0.05	0.68 ± 0.03	0.87 ± 0.02	0.59 ± 0.03	0.36 ± 0.03	0.68 ± 0.01
46.4 Ptwt% Pt ₃ Co/HSC	2	1.50 ± 0.03	1.52 ± 0.02	1.50 ± 0.01	1.41 ± 0.02	0.97 ± 0.02	0.97 ± 0.01	0.95 ± 0.01	0.91 ± 0.01
46.9 Ptwt% PtCoMn/HSC	1	1.65	1.41	1.40	1.21	1.00	0.86	0.85	0.74
27.4 Ptwt% Pt ₃ Co/HSC	1	2.10	2.01	1.78	1.69	1.55	1.39	1.27	1.25

Error in SA and MA indicate standard deviation for catalysts tested using 4 or more samples, and maximum and minimum for catalysts tested using less than 4 samples.

To investigate the SA dependence on I/C ratio further, the SA values were normalized using the value at I/C ~0 for each catalyst as shown in Fig. 4. The rate at which the SA decreases is high at low I/C ratios <1.5 and approaches zero at I/C ratios >1.5. For 46 wt% Pt/HSC, such trend is not clearly observed. This may be due to insufficient penetration of Nafion through thickness direction of catalyst layer. The SA loss at high I/C ratios shows the following trend: HSC < Vulcan < LSC. In contrast, no clear trend is observed within catalysts with similar average particle size/ECA (~97 m²·g_{Pt}⁻¹: 46 wt% Pt/HSC vs. 29 wt% Pt/V, ~65 m²·g_{Pt}⁻¹: 46 wt% Pt/V vs. 20 wt% Pt/LSC). Thus, properties of carbon, coverage or thickness of Nafion are likely to be dominant factors that determine the extent of the SA loss.

Figure 4. I/C ratio dependence of normalized SA for various Pt/C catalysts. SA at 0.9 V normalized to Nafion-free surface of each Pt/C catalyst. Error bars indicate normalized standard deviation for catalysts tested using 4 or more samples (46 wt% and 26 wt% Pt/HSC, 29 wt% Pt/V and 48 wt% Pt/LSC), and normalized maximum and minimum SA for catalysts tested using less than 4 samples (46 wt% Pt/V).

In an attempt to investigate the factors, we estimated carbon-surface-area-specific Nafion loading from I/C ratio and BET surface area of carbon supports: HSC, Vulcan $\sim 250 \text{ m}^2 \cdot \text{g}^{-1}$, LSC $\sim 80 \text{ m}^2 \cdot \text{g}^{-1}$ and replotted SA in relation to the Nafion loading (Fig. 5). The SA dependence for poly-Pt is also plotted in Fig. 5. In addition, Nafion film thickness was estimated assuming uniform coverage using the BET surface areas (Fig. 5, second abscissa). We note that BET surface area of HSC support is assumed to be the same as Vulcan support (although the actual BET surface area is $\sim 800 \text{ m}^2 \cdot \text{g}^{-1}$) because

of similar carbon particle sizes for HSC and Vulcan, and the following understanding reported in literature: i) Pt particles are located both on the outer surface of HSC particles and within pores of the HSC [36, 38, 39], and ii) Pt particles located on the outer surface of the HSC support are in touch with ionomer whereas those located within pores of the HSC support are not [37-39]. Pt/Vulcan and Pt/LSC catalysts exhibit similarly large SA loss with increasing Nafion loadings/thickness to $\sim 1 \mu\text{g}\cdot\text{cm}^{-2}_{\text{carbon}}/\sim 5$ nm followed by plateau (red band) whereas Pt/HSC catalysts show relatively small SA loss by the plateau. It is noteworthy that Nafion thickness where the normalized SA starts to plateau (~ 5 nm) coincides with the reported minimum Nafion thickness [40]. Although researchers have assumed simplified model with thin uniform ~ 2 nm Nafion film covering the entire catalyst surface, recent microscopic study demonstrated that Nafion forms finite-sized layer and covers carbon support non-uniformly with a minimum thickness ~ 5 nm and Nafion coverage becomes higher with increasing Nafion loadings [40]. This study indicates that, in Fig.5, Nafion coverage becomes lower at the loadings less than $\sim 1 \mu\text{g}\cdot\text{cm}^{-2}_{\text{carbon}}$ ($< \sim 5$ nm in thickness) and it can reach unity at the loadings more than that. Because the SA decreases in the loading range where the coverage increases and it starts to plateau at the loading where the coverage becomes close to unity, it is plausible to consider that Nafion coverage is a dominant factor that

controls the SA loss on Pt catalysts. Comparable normalized SA values for Nafion-capped poly-Pt (coverage ~ 1) [17], Pt/Vulcan and Pt/LSC in the plateau region are consistent with the interpretation. Thus, it is reasonable to conclude that the attenuated SA loss for Pt/HSC catalysts in the plateau region is because Pt particles that are sheltered from Nafion in micropores of HSC support maintain their original activity [37-39]. The differences in the rate of SA loss observed between 46 wt% and 26 wt% Pt/HSC catalysts and between 48 wt% and 20 wt% Pt/LSC catalysts may have been caused by variation in the extent of Nafion penetration. Further studies such as the observation of sulfonate adsorption using so-called CO displacement method [13, 18] are necessary to understand the Nafion loading dependence on SA in more details.

Figure 5. Nafion loading dependence of the normalized SA at 0.9 V for Pt/C nanoparticle catalysts as well as bulk poly-Pt. Nafion loading/thickness estimated from

actual roughness factor for poly-Pt. Error bars indicate normalized standard deviation for catalysts tested using 4 or more samples (46 wt% and 26 wt% Pt/HSC, 29 wt% Pt/V and 48 wt% Pt/LSC), and normalized maximum and minimum SA for catalysts tested using less than 4 samples (46 wt% Pt/V).

The SA dependence on I/C ratio for Pt/HSC and Pt-alloy/HSC catalysts is summarized in Fig. 6a and can also be found in Table 3. At I/C ~0, Pt-alloy/HSC catalysts exhibit ~1.7 to ~2.9 times higher SA values than Pt/HSC (Table 2); the higher SA values of Pt-alloy/HSC catalysts are likely due to combined effects from alloying and larger particle size. As is observed for Pt/HSC catalysts, Nafion also lowers the SA of Pt-alloy/HSC catalysts. In normalized SA scale (Fig. 6b), similar I/C dependence is observed although there is some variation among Pt alloy catalysts. Although the relatively small SA loss for 46 wt% Pt₃Co/HSC may indicate that the impact of Nafion also depends on metallic composition of catalysts, further studies need to be conducted e.g. by employing catalysts supported on Vulcan or LSC.

Figure 6. The dependences of (a) SA and (b) normalized SA to SA for Nafion-free surface of each catalyst on I/C ratio for HSC supported Pt-based catalysts. **Error bars** indicate standard deviation for 26 wt% and 46 wt% Pt/HSC obtained for 4 and 8 samples, respectively, and maximum and minimum for 46 wt% Pt₃Co/HSC obtained for 2 samples.

3.3. Implications for MEAs

In automotive PEMFCs, membrane electrode assembly must function from low to high relative humidity (RH) at various temperatures. At low RH conditions, proton conduction to Pt surfaces can be significantly perturbed without being in touch with ionomer. For Pt/HSC catalyst layers with typically used compositions, Pt utilization defined as the ratio of electrochemical area to the total surface area can become as low as ~30% at low RH conditions while the utilization is as high as ~90% at high RH conditions [37-39]. The lowered utilization due to lower ionomer coverage can lower the ORR current. Our study, however, indicates that higher Nafion coverage on Pt and Pt alloy catalyst surfaces results in lower ORR activity. Furthermore, ionomer poisoning may become more deleterious at lower RH conditions; onset potential of oxide formation/desorption currents positively shifts to a great extent at lower RH conditions [39, 41]. Therefore, further study with this type of support structure may provide an improved PEMFC performance.

4. Conclusion

The effect of Nafion on the ORR activity was studied for Pt/C and Pt-alloy/C catalysts using thin-film RDE methods in 0.1 M HClO₄. In order to determine the impact of

Nafion on the ORR kinetics, mass transport limitation within catalyst layers was minimized by employing ultrathin-uniform catalyst layers. In addition, standardized activity measurement protocols were applied to obtain accurate and reproducible ORR activity. It was found that Nafion lowered the ORR activity and the SA decrease plateaued with increasing Nafion loadings for **most** catalysts. Analysis in normalized SA scale to corresponding Nafion-free surface suggests that Nafion coverage is a dominant factor that determines the extent of the SA decrease **on Pt surfaces, and Pt particle size was found not to have significant influence on the extent of the SA decrease upon Nafion incorporation. Further studies need to be conducted to determine the influence of metallic composition of catalysts on the impact of Nafion loading on SA.** Catalysts using HSC support exhibited attenuated SA loss at Nafion loadings where the SA plateaued. This attenuated loss is the result of the combination of original activity on Nafion-free Pt catalysts located within pores of HSC particles and lowered activity on Nafion-covered Pt catalysts located on the outer surface of the HSC particles. Because catalysts using HSC support lose some electrochemical area at low RH in PEMFCs, HSC support may not be an ideal from this aspect. However, our study also suggests that HSC support can maintain original Pt activity by sheltering Pt

particles in micropores from ionomer coverage. Thus, further study with this type of support structure may improve PEMFC performance.

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Figure 1

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Figure 6

Figure 6

Figure 1. (a) CVs under N₂ and (b) ORR *I-E* curves (inset: Tafel plot) in 0.1 M HClO₄ at 20 mV·s⁻¹ for poly-Pt with and without Nafion cap.

Figure 2. The effect of I/C ratio on (a, c) CVs under N₂ and (b, d) ORR *I-E* curves in 0.1 M HClO₄ at 20 mV·s⁻¹ for (a, b) 46 wt% Pt/HSC and (c, d) 48 wt% Pt/LSC.

Figure 3. I/C ratio dependence of SA at 0.9 V for various Pt/C catalysts. **Error bars** indicate standard deviation for catalysts tested using 4 or more samples (46 wt% and 26 wt% Pt/HSC, 29 wt% Pt/V and 48 wt% Pt/LSC), and maximum and minimum for catalysts tested using less than 4 samples (46 wt% Pt/V).

Figure 4. I/C ratio dependence of normalized SA for various Pt/C catalysts. SA at 0.9 V normalized to Nafion-free surface of each Pt/C catalyst. **Error bars indicate normalized** standard deviation for catalysts tested using 4 or more samples (46 wt% and 26 wt% Pt/HSC, 29 wt% Pt/V and 48 wt% Pt/LSC), and normalized maximum and minimum SA for catalysts tested using less than 4 samples (46 wt% Pt/V).

Figure 5. Nafion loading dependence of the normalized SA at 0.9 V for Pt/C nanoparticle catalysts as well as bulk poly-Pt. Nafion loading/thickness estimated from actual roughness factor for poly-Pt. Error bars indicate normalized standard deviation for catalysts tested using 4 or more samples (46 wt% and 26 wt% Pt/HSC, 29 wt% Pt/V and 48 wt% Pt/LSC), and normalized maximum and minimum SA for catalysts tested using less than 4 samples (46 wt% Pt/V).

Figure 6. The dependences of (a) SA and (b) normalized SA to SA for Nafion-free surface of each catalyst on I/C ratio for HSC supported Pt-based catalysts. Error bars indicate standard deviation for 26 wt% and 46 wt% Pt/HSC obtained for 4 and 8 samples, respectively, and maximum and minimum for 46 wt% Pt₃Co/HSC obtained for 2 samples.