

The Influence of the Oxygen Partial Pressure on the Oxygen Reduction Reaction Kinetics for the Low Platinum Loading Catalysts

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Two different platinum catalysts (8.3 and 12.4wt% Pt based on molybdenum carbide derived carbon) were characterized by the high resolution transmission electron microscopy and X-ray diffraction methods. The oxygen reduction reaction (ORR) kinetics was studied on synthesized catalysts and commercially available 20wt% Pt-Vulcan in 0.1M KOH electrolyte solution saturated with oxygen or various O₂/N₂ gas mixtures at atmospheric pressure. The current density values increase five-fold as the oxygen concentration increases from 20% to 100%. This refers to first-order reaction with respect of oxygen for all catalyst studied. Two different approaches have been proposed for calculating the reaction order.

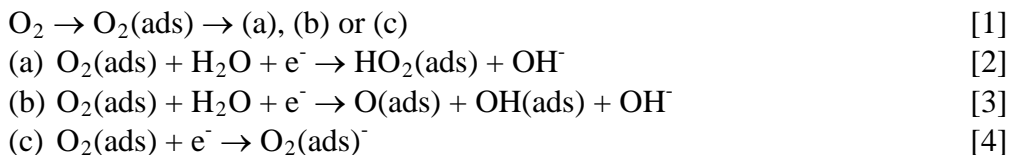
The ORR electrochemical activity for catalysts increases in the following sequence: 8.3wt% Pt-C (half of the loading) ≤ 20wt% Pt-Vulcan < 8.3wt% Pt-C ≈ 12.4wt% Pt-C at all O₂ partial pressures studied. The most promising catalyst for ORR was found to be 8.3 wt% Pt-C.

Introduction

The performance of fuel cells is first and foremost determined by the kinetics of the oxygen reduction reaction (ORR). The electrocatalysts have to conform among the others with the following requirements set by the Department of Energy (DOE): reduced precious metal loading, increased activity, improved durability/stability, and increased tolerance to air, fuel and system-derived impurities (1). One possibility to ensure the excellent performance of the electrode is using the electrocatalyst with the small size platinum nanoparticles deposited onto the hierarchically porous carbon support. In this way, the reactant gas (oxygen or air) can be uniformly distributed over the catalyst.

Many authors have been reported the influence of the oxygen/air pressure on the kinetics of the ORR and demonstrated that the effect of pressure on the oxygen solubility

is more significant in dilute electrolyte solutions compared to the concentrated ones (2-5). Oxygen partial pressure is known to affect the Pt oxidation kinetics and the proposed mechanisms of breaking the adsorbed O-O bond during or after ORR rate determining step are following (4,5):



The oxygen reduction reaction at Pt or Pt containing catalysts (e.g. polycrystalline platinum, Vulcan supported platinum) is found to be first-order kinetics indicating that a similar reaction mechanism is valid for such type of catalysts (2-8).

The experimental data reported in the literature to meet the requirements set by DOE have been mostly performed at the oxygen saturated conditions similar to our previous works, where we demonstrated that comparable current density values obtained for 20wt% Pt-Vulcan electrode could be achieved for 20wt% Pt-C with 30% lower catalyst loading and with Pt nanoparticle size of 4.2 nm (9,10). In addition, the further optimization of the Pt loading lead us to the conclusion that for ORR in 0.1M KOH solution saturated with oxygen an optimum amount is nearly 8.3wt% Pt deposited on the molybdenum carbide derived carbon (11).

Therefore, in this work the emphasis has been placed studying the ORR at various oxygen concentrations (100%, 60%, 20%) (i.e., to control the catalysts tolerance to air) in 0.1M KOH electrolyte solution saturated the respective gas mixture for previously optimized catalysts (8.3wt% Pt-C, 12.4wt% Pt-C) and the 20wt% Pt-Vulcan for comparison (11).

Experimental

Pt catalysts for the oxygen reduction reaction (ORR) were synthesized by the sodium borohydride reduction method (12,13). The high-temperature chlorination method was used for preparation of the micro-mesoporous carbon (Mo_2C , Sigma-Aldrich) support (14). The amount of the Pt nanoparticles deposited onto the carbon support was found to be 8.3 and 12.4 wt% according to the triple quadrupole inductively coupled plasma mass spectrometry (ICP-MS) analysis and named as 8.3wt% Pt-C and 12.4% Pt-C, respectively (11). Additionally, various physical characterization methods have been applied: X-ray photoelectron spectroscopy (XPS), low-temperature nitrogen sorption analysis, *in situ* atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD). The detailed analysis and discussion of physical characterization results have been described in elsewhere (10,11). Shortly, XPS analysis showed that deposited Pt nanoparticles in the catalyst have an oxidation state of 0. The low temperature nitrogen sorption analysis confirmed that the initial pore size distribution of the carbon support remains the same and after the modification with Pt nanoparticles the specific surface area of the synthesized catalyst is around $1700 \pm 50 \text{ m}^2 \text{ g}^{-1}$. The surface sensitive AFM method indicated that the Pt nanoparticles are stable under the electrochemical cycling conditions. The mean particle size of the platinum nanoparticles was estimated using the surface imaging (SEM and TEM) methods as well as the XRD technique for determining the atomic structure of the

Pt nanoparticles (Figure 1), and the values were comparable (11). TEM imaging demonstrated that the Pt nanoparticles are favorably situated on the edges of the graphitized carbon areas, contributing to the part of the conducting and catalytically more active triple phase boundaries (10).

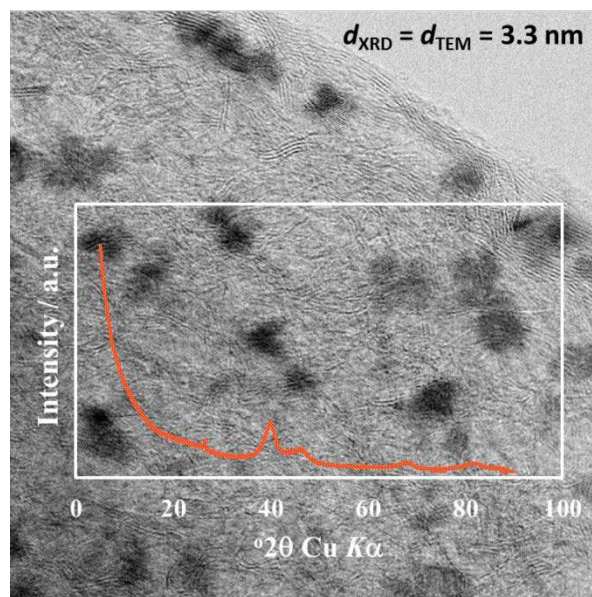


Figure. 1. TEM and XRD data for 8.3wt% Pt-C.

To investigate the influence of the oxygen partial pressure on the kinetics of ORR, the rotating disk electrode (RDE) and the cyclic voltammetry (CV) methods (*Gamry Instruments Inc, Reference 600™*) were used. Certain portion of the Pt catalyst powder, Milli-Q⁺ water, the isopropanol and the Nafion[®] dispersion solution (Aldrich) were mixed to receive the catalyst ink. Thereafter, the ink was deposited onto the surface of the working electrode (glassy carbon disk electrode, *Pine Research Instrumentation, 0.196 cm²*) and dried (15-17).

Experiments were carried out in 0.1 M KOH (Sigma-Aldrich, 99,99%) solution saturated with the various O₂/N₂ gas mixtures. 8.3wt% Pt-C catalyst with two different loadings (0.5 to 1.0 mg cm⁻²) and 12.4wt% Pt-C, and commercial 20wt% Pt-VulcanXC72[®] catalyst for comparison (*Fuel Cell Earth, LLC, Wakefield, Massachusetts, USA, 20%Pt-V*) were studied.

All working electrode potentials were measured against Hg|HgO|0.1M KOH reference electrode. The RDE and CV data presented have been corrected against the ohmic potential drop (high frequency series resistance $R_{el} \approx 37 \Omega$) (16,17).

Results

The ORR polarization curves, i.e. corrected current density (j_c) vs. electrode potential (E) plots, for 8.3wt% Pt-C are given in Figure 2 for different oxygen concentrations at the constant electrode rotation rate 3000 rpm measured in 0.1M KOH solution.

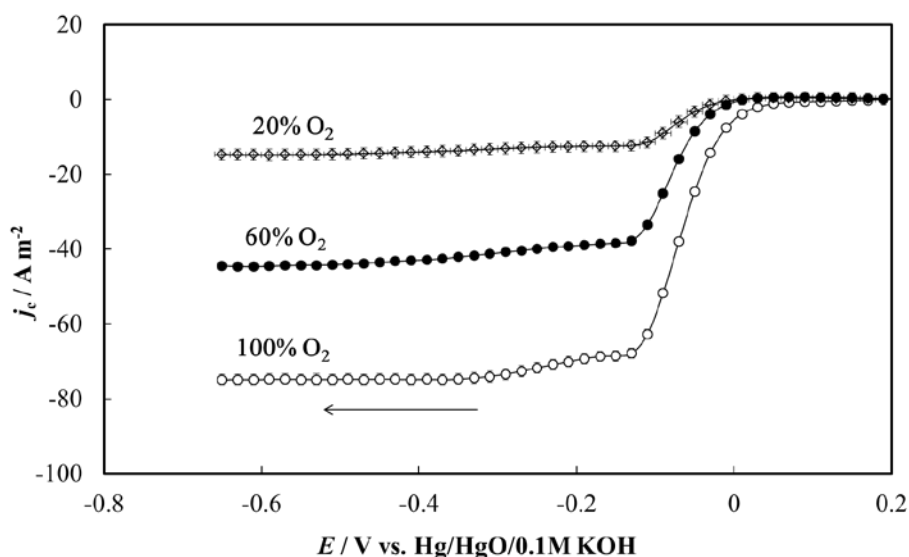


Figure 2. j_c vs. E curves for 8.3wt% Pt-C for different oxygen concentrations at $\omega = 3000$ rpm in 0.1M KOH solution (noted in Figure).

The summarized data for all studied catalysts in the mixed kinetic potential region ($E = -0.07$ V vs. Hg|HgO| 0.1 M KOH, at $\omega = 3000$ rpm) are presented in Figure 3.

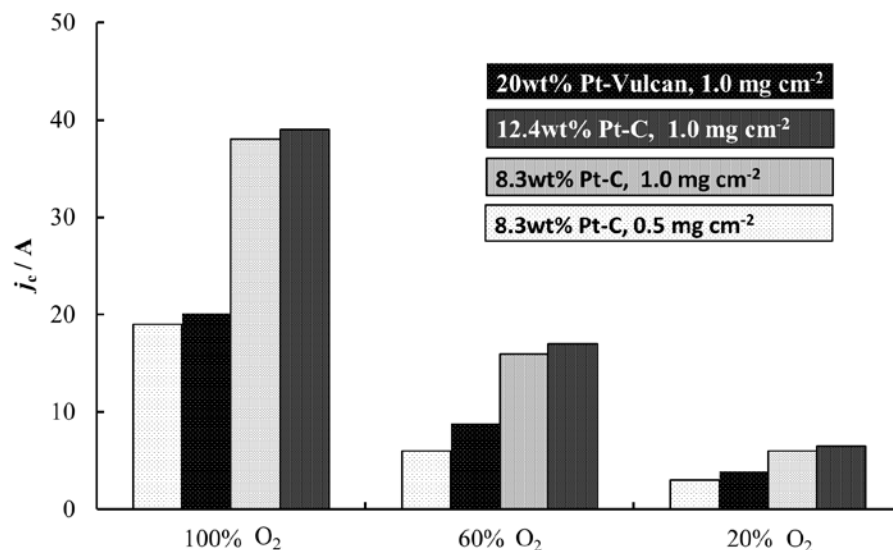


Figure 3. The comparison of the ORR activity for catalysts studied.

The main results are the following:

1. The 8.3 and 12.4wt% Pt-C catalysts demonstrated comparable electrochemical activity toward ORR at all O₂ partial pressures studied, and showed approximately 2 times higher current density values than the 20wt% Pt-Vulcan at saturated oxygen conditions.
2. At saturated oxygen conditions, comparable ORR activity for the 8.3wt% Pt-C at half of the initial loading (0.5 mg cm⁻²) and the 20wt% Pt-Vulcan (1 mg cm⁻²) was achieved.

- The ORR activity of the 8.3wt% Pt-C catalyst in 60% O₂/ 40% N₂ gas mixture saturated solution was nearly the same as for the 20wt%Pt-Vulcan catalyst in 100% O₂ saturated condition.
- The 8.3wt% Pt-C catalyst showed the best performance in artificial air.

Increasing the oxygen concentration from 20% to 100%, the corrected current density values increased five-fold. For all catalysts, the $i_{100\%}/i_{20\%}$ ratio was found to be around 5 within the electrode potential range studied (Figure 4), indicating that the oxygen reduction is first-order reaction. This result is in good agreement with the literature data (4,5).

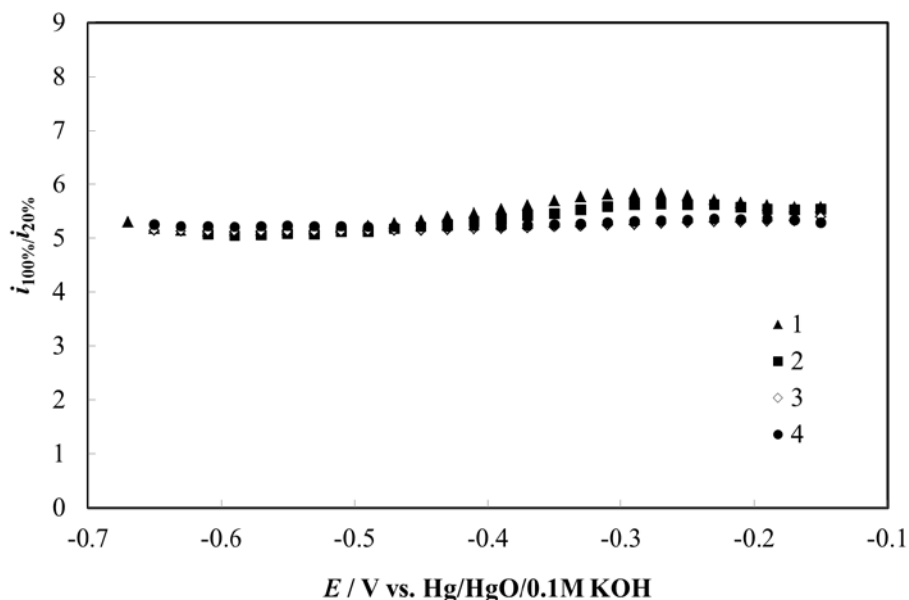


Figure 4. The $i_{100\%}/i_{20\%}$ ratio vs. E at 3000 rpm, at 10 mV s⁻¹ in 0.1M KOH solution for catalysts: 1 – 12.4wt% Pt-C; 2 – 8.3wt% Pt-C; 3 – 8.3wt% Pt-C (0.5 mg cm⁻¹) and 4 – 20wt% Pt-Vulcan.

The reaction order for ORR (n_{O_2}) can be determined from RDE measurements at various oxygen partial pressures (p_{O_2}), thus, the further information about the mechanism of oxygen reduction at platinum nanoparticles, i.e. stoichiometry of the electroactive species in the rate determining step, could be obtained (4-6).

The constructed Tafel-like dependencies, i.e. electrode potential vs. logarithmic kinetic current densities (j_k), were used for the estimation of the Tafel-like plot slope (b) values at different O₂ concentrations (summarized in the Table I). The influence of O₂ partial pressure on the Tafel-like plot slope values was found to be significant and therefore, two different approaches for calculating the reaction order were used. At first, the dependencies of the electrode potential versus logarithm oxygen partial pressure (corrected for vapor pressure of the water) at the constant current density ($j_c = 10$ A m⁻²) were established and the reaction order was calculated by dividing the slope value of the E vs. $\log p_{O_2}$ plot by the average value of the Tafel-like plot slope using following equation (2,7,8):

$$(\delta E / \delta \log p_{O_2})_{j=\text{const}} = |b| \times n_{O_2} \quad [5]$$

In this way, the reaction order for oxygen reduction established is somewhat higher than unity (Table I). Secondly, the reaction order was calculated from the double-logarithmic kinetic current density versus oxygen partial pressure plots completed at the constant electrode potential (-0.09V vs. Hg|HgO| 0.1M KOH) for comparison (Figure 5). The slope value of this dependence is defined as the reaction order. The $\log j_k$ vs. $\log pO_2$ dependencies are linear and coincide for all studied Pt-C catalysts. The reaction order was found to be 1.0 ± 0.1 . Depending on the approach used the calculated values of the reaction order somewhat differ (Table I).

TABLE I. ORR kinetic parameters for Pt catalysts.

Catalyst material	Tafel slope (b) / mV dec ⁻¹			Reaction order	
	100% O ₂	60% O ₂	20% O ₂	nO ₂ ^a	nO ₂ ^b
8.3wt% Pt-C (0.5 mg cm ⁻²)	-73	-60	-59	1.20	1.09
8.3wt% Pt-C	-77	-76	-69	1.18	1.04
12.4wt% Pt-C	-83	-78	-71	1.17	0.89
20wt% Pt-Vulcan	-74	-64	-63	1.00	0.87

^a reaction order calculated using equation [5]

^b reaction order calculated from the slope of the $\log j_k$ vs. $\log pO_2$ plot

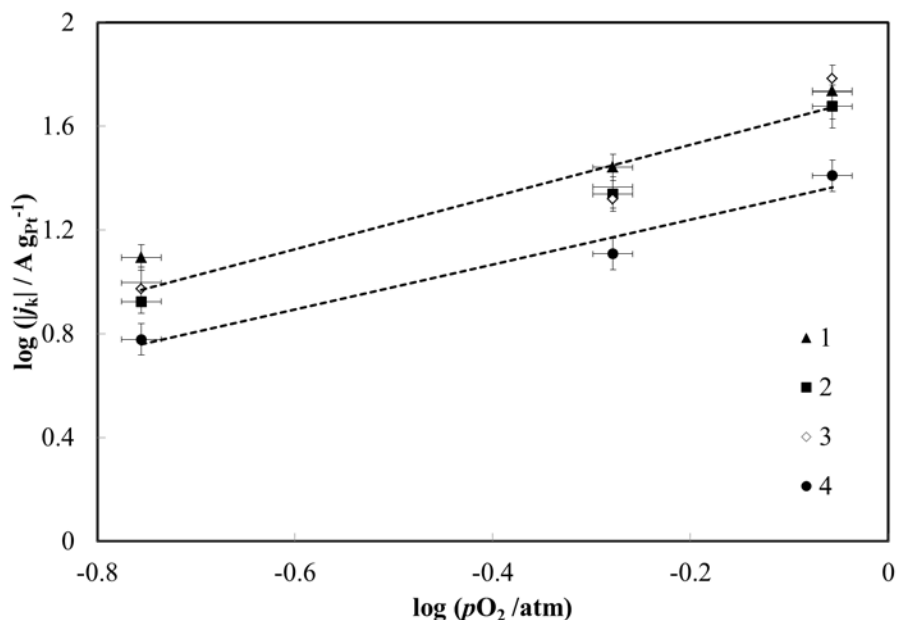


Figure 5. $\log j_k$, $\log pO_2$ dependencies for catalysts: 1 – 12.4wt% Pt-C; 2 – 8.3wt% Pt-C; 3 – 8.3wt% Pt-C (0.5mg cm⁻¹) and 4 – 20wt% Pt-Vulcan.

Cyclic voltammograms (at $\nu = 5 \text{ mV s}^{-1}$) for the 8.3wt% Pt-C (0.5mg cm⁻²) catalyst in KOH solution saturated with 100%, 60% and 20% oxygen and 100% nitrogen, are presented in Figure 6.

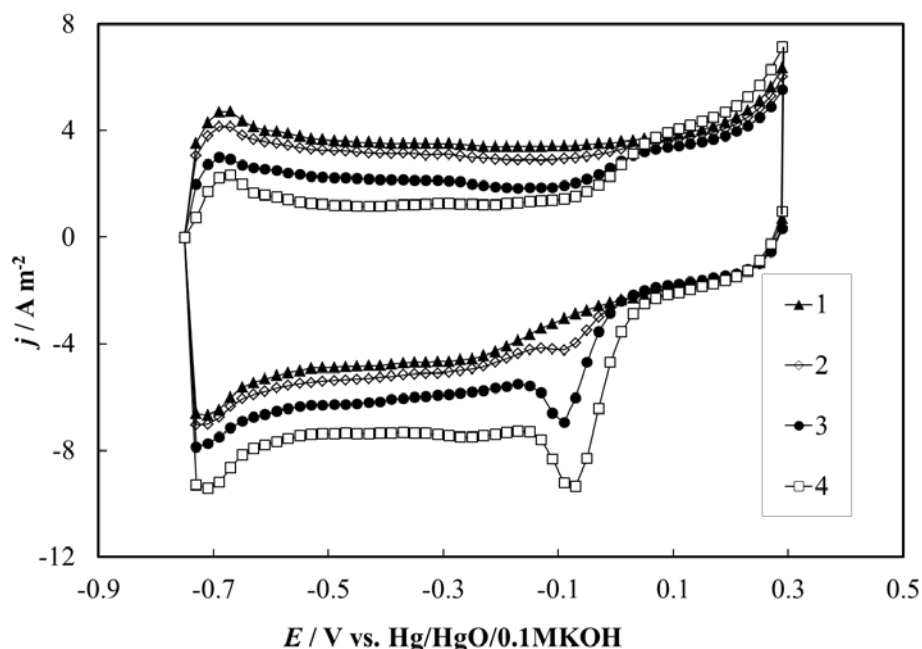


Figure 6. Cyclic voltammograms (at $\nu = 5 \text{ mV s}^{-1}$) for 8.3wt% Pt-C (0.5 mg cm^{-2}) catalyst in 0.1M KOH solution saturated with: 1- 100% N_2 ; 2- 20% O_2 ; 3- 60% O_2 and 4- 100% O_2 .

There are well expressed oxygen reduction peaks in the cathodic scan directions in j, E -curves in 0.1M KOH solution. As it can be seen in Figure 6, the peak current density (j_p) values increase with increasing O_2 concentration in the following sequence: $100\% \text{ N}_2 < 20\% \text{ O}_2 < 60\% \text{ O}_2 < 100\% \text{ O}_2$ at fixed loading and Pt weight percent in the catalyst. Thus, the current density values are significantly influenced by the chemical composition of the saturation gas used. It should be mentioned that reduction peak potential (E_p) is independent of the applied oxygen partial pressure (Figure 6).

Conclusions

In this work the electrocatalytic activity of the 8.3wt% Pt-C, 12.4wt% Pt-C and 20wt% Pt-Vulcan catalysts toward ORR was analyzed in 0.1M KOH electrolyte solution saturated with oxygen or various O_2/N_2 gas mixtures at atmospheric pressure. Increasing the oxygen concentration from 20% to 100% resulting in a five-fold increase of the corrected current density values and the reaction order established by two different approaches was found to be 1.0 ± 0.2 .

The ORR electrochemical activity of the catalysts increases in the following order: $8.3\text{wt}\% \text{ Pt-C } (0.5 \text{ mg cm}^{-2}) \leq 20\text{wt}\% \text{ Pt-Vulcan} < 8.3\text{wt}\% \text{ Pt-C} \approx 12.4\text{wt}\% \text{ Pt-C}$ at all O_2 partial pressures studied. At saturated oxygen conditions, comparable ORR activity for the 8.3wt% Pt-C (0.5 mg cm^{-2}) and the 20wt% Pt-Vulcan (1 mg cm^{-2}) was achieved.

In 60% O_2 /40% N_2 gas mixture saturated solution, the ORR activity of the 8.3 wt% Pt-C catalyst was nearly the same as measured for 20wt% Pt-Vulcan catalyst in 100% O_2 saturated solution. Thus, the most promising catalyst for ORR was found to be 8.3 wt% Pt-C.

Acknowledgements

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