

Influence of Film Morphology on the Oxygen Reduction Reaction Activity in Rotating Disk Electrode Studies

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Thin-film rotating disk electrode (TF-RDE) measurements have been utilized to benchmark the oxygen reduction reaction (ORR) activity of baseline Pt/C and novel electrocatalysts (available in small amounts) for polymer electrolyte membrane fuel cells (PEMFCs). The experiments are typically carried out under the assumption that the deposited films are extremely thin and that the smooth surface diffusion layer model and associated analyses are valid.¹⁻⁴ Despite refinement of the technique over several decades, the results obtained for the ORR activity differ within the literature by as much as a factor of 2 even for conventional Pt/C electrocatalysts used as baseline electrocatalyst material.³⁻⁹

In order to reproducibly obtain accurate and precise ORR activity parameters for electrocatalysts in RDE experiments, two groups have examined the effect of film uniformity and thickness.⁶⁻⁸ Although the methodologies used to obtain the uniform films differed, these studies emphasized the importance of forming a thin and uniform film structure to limit the impact of mass transport on the measured ORR activity.

Most studies that involve thin films have a Nafion cap or Nafion mixed in with the catalyst and justified as a method to prevent flaking off of the films under rotation. In our previous TF-RDE study,⁹ Nafion-free Pt/C electrodes were fabricated and shown to exhibit 1.8 times higher specific and mass activities than electrodes with Nafion incorporation. For the first time, in this study 30–50 electrodes of each ink formulation were evaluated in order to demonstrate clear evidence of reproducibility and sufficient data to obtain valid normal distributions.⁹ Based on the analysis of Tafel plots, onset of surface oxide species and effect of Pt loading ($\mu\text{g}/\text{cm}^2$), the change in activity was attributed to a combination of mass transport and electronic resistance caused by the ionomer, while eliminating sulfonate anion adsorption. Since the film formation process (deposition, drying) in our previous work was not as well-controlled as in the literature⁶⁻⁸, a further refinement and isolation of the sources of activity loss was not possible.

In this work, we proceed with further investigations into Pt-based electrocatalysts using inks formulated with and without incorporation of

Nafion with much lower catalyst loadings to minimize the film structural effect. Preliminary results obtained for Pt/Vulcan in 0.1 M HClO_4 exhibited higher mass activity for extremely low loadings ($<2.3 \mu\text{g}_{\text{Pt}}/\text{cm}^2$) as compared to typical loadings ($\sim 18 \mu\text{g}_{\text{Pt}}/\text{cm}^2$) with Nafion incorporation as shown in Fig. 1. We also address the issues involved in obtaining accurate measurements of the electrochemical area from HUPD areas of cyclic voltammograms (CVs) for extremely low loadings and film thicknesses. Increased film uniformity obtained by drying water–isopropanol (IPA) inks under an IPA atmosphere will also be presented. Complementary studies on the effect of Nafion coating on bulk polycrystalline Pt electrodes will be discussed.

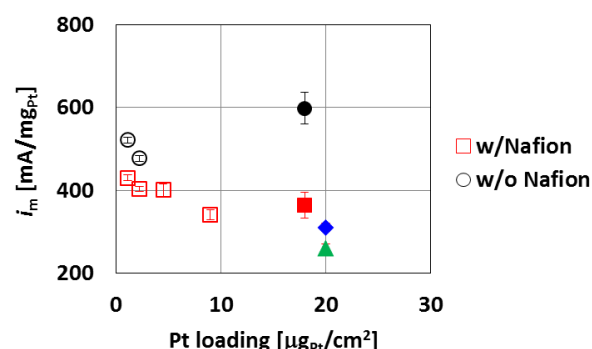


Figure 1 Mass activity of Pt/Vulcan for various catalyst loadings on RDE tips with/without Nafion incorporation obtained in 0.1 M HClO_4 at room temperature. Each bar shows standard deviation for 4–13 measurements. Hollow squares/circles ($\square$, $\circ$) represent results from this study. Solid square/circle ($\blacksquare$, $\bullet$) show previously reported data.⁹ The solid diamond ($\blacklozenge$) and triangle ($\blacktriangle$) represent literature values obtained for 19.7% Pt/Vulcan (E-TEK) and 40% Pt/Vulcan (JM) with Nafion incorporation prepared by a rotational drying process, respectively.⁷

References

1. T. J. Schmidt, H. A. Gasteiger, O. D. Staeb, P. M. Urban, D. M. Kolb and R. J. Behm, *J. Electrochem. Soc.*, **145**, 2354 (1998).
2. K. J. J. Mayrhofer, D. Strmcnik, B. B. Blizanac, V. Stamenkovic, M. Arenz and N. M. Markovic, *Electrochim. Acta*, **53**, 3181 (2008).
3. H. A. Gasteiger, S. S. Kocha, B. Sompalli, F. T. Wagner, *Applied Catalysis B-Environmental* **2005**, 56, 9.
4. I. Takahashi, S. S. Kocha, *J. Power Sources*, **195**, 63,12-6322 (2010).
5. D. van der Vliet, D. S. Strmcnik, C. Wang, V. R. Stamenkovic, N. M. Markovic and M. T. M. Koper, *J. Electroanal. Chem.*, **647**, 29-34 (2010).
6. Y. Garsany, O. A. Baturina, K. E. Swider-Lyons, S. S. Kocha, *Anal. Chem.*, **82**, 6321-6328 (2010).
7. Y. Garsany, I. L. Singer, K. E. Swider-Lyons, *J. Electroanal. Chem.*, **662**, 396–406 (2011).
8. K. Ke, K. Hiroshima, Y. Kamitaka, T. Hatanaka, and Y. Morimoto, *Electrochim. Acta*, **72**, 120-128 (2012).
9. S. S. Kocha, J. W. Zack, S. M. Alia, K. C. Neyerlin, B. S. Pivovar, *ECS Trans.*, **50** (2), 1475-1485 (2012).