

The 2012 Joseph W. Richards Summer Research Fellowship — Summary Report

Catalytic Activity for ORR of a Platinum-Free Electrocatalyst in Phosphoric Acid

by Balázs B. Berkes

Platinum and its alloys are predominantly used as electrocatalysts in fuel cells for both the hydrogen oxidation and the oxygen reduction reactions (ORR). However, in fuel cells containing phosphoric acid (either as the electrolyte or the dopant for the polymer electrolyte membrane – PAFCs or PBI/PAFCs¹), phosphate anion adsorbs on platinum surfaces² and hinders the rate of the oxygen reduction reaction, thus contributing to significant overpotential even though the temperatures of PAFCs are larger than that of PEMFCs. This study examines a N4-chelated non-precious metal catalyst (NPMC)³ which is less sensitive to phosphoric acid poisoning and estimates its activity at elevated temperatures and will compare with Pt/C electrocatalyst under normal PEM conditions.

The rotating disk electrode configuration was employed for this study of high surface area electrocatalyst.^{4,5} We examined a commercial Pt/C catalyst and an iron(III) tetramethoxyphenyl porphyrin chloride supported on carbon (FeTMPPCl/C) that was prepared at Case Western Reserve University (CWRU). The catalysts were attached to the smoothly polished glassy-carbon electrode surface in the form of a suspension with Nafion[®] and a film of Nafion[®] was deposited onto the surface. The cell potentials were calibrated to the RHE as determined by hydrogen evolution under operating conditions, and ohmic corrections were made using impedance measurements at each temperature.

Catalytic activities were compared based on measured currents of polarization curves in the so called region of kinetic control (Fig. 1). For Pt/C catalyst, a potential of 0.875 V was selected, which is close to the usual value of 0.9 V where the influences of mass transport are negligible.⁶ In case of the NPMC catalyst, a potential of 0.7 V was used in the range of measurable kinetic currents. Temperature dependence of O₂ solubility on 1st order kinetics was taken into account in estimating the activation energy by Arrhenius-plots (Fig. 2.)

We found that the activation energy of ORR in the case of the NPMC is smaller than that on Pt/C. We will continue to analyze this data in more detail to estimate NPMC activity at 200 °C in phosphoric acid electrolyte and then compare with Pt/C at 80 °C in perchloric acid electrolyte which simulates PEM electrolytes such as Nafion[®].

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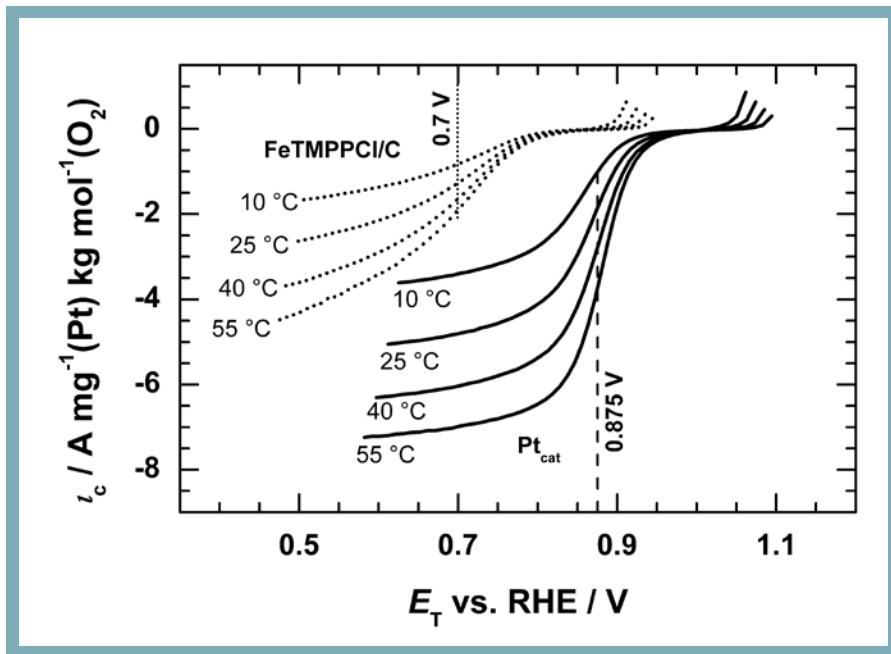


FIG. 1. RDE data for the oxygen reduction reaction at two types of catalysts in 0.1 M HClO₄. All the potentials (E_T) are temperature-corrected (to 25 °C). The kinetic current densities are normalized to mass per surface area of the examined catalyst and to the oxygen concentration at the given temperature.

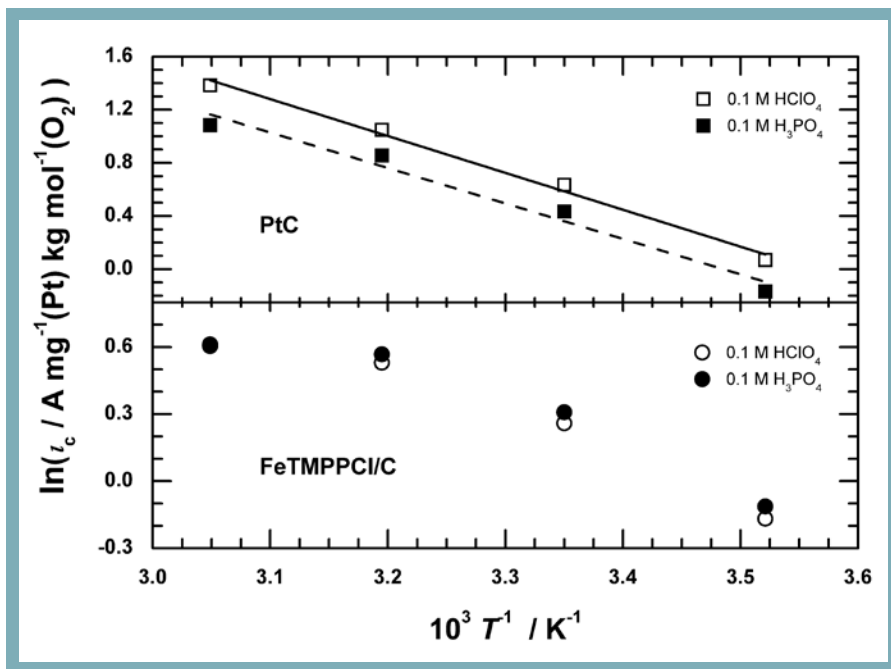


FIG. 2. Arrhenius-plots of corrected kinetic currents from RDE data. Currents are normalized to mass of the catalyst and to the solubility of oxygen. The temperature values were measured within the cell.

Acknowledgment

I would like to thank to Robert F. Savinell and all of my colleagues at CWRU for the help provided in my work during the summer. The ECS is gratefully acknowledged for supporting a stay in the U.S.

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References

1. J.-T. Wang, R. F. Savinell, J. Wainright, M. Litt, and H. Yu, *Electrochim. Acta*, **41**, 193 (1996).
2. G. Horányi, E. M. Rizmayer, and G. Inzelt, *J. Electroanal. Chem.*, **93**, 183 (1978).
3. J.-P. Dodelet, in *N4-Macrocyclic Metal Complexes*, J. H. Zagal, F. Bedioui, and J.-P. Dodelet Editors, p. 83, Springer, New York (2006).
4. F. Gloaguen, F. Andolfatto, R. Durand, and P. Ozil, *J. Appl. Electrochem.*, **24**, 863 (1994).
5. T. J. Schmidt, H. A. Gasteiger, G. D. Stäb, P. M. Urban, D. M. Kolb, and R. J. Behm, *J. Electrochem. Soc.*, **145**, 2354 (1998).
6. U. A. Paulus, T. J. Schmidt, H. A. Gasteiger, and R. J. Behm, *J. Electroanal. Chem.*, **495**, 134 (2001).

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