Oxygen reduction on Pt/[TaOPO₄/VC], Pt/[NbOPO₄/VC], Pt/[Ta₂O₅/VC], and Pt/[Nb₂O₅/VC] electrocatalysts in alkaline electrolyte

Yannick Garsany¹, Albert Ephsteyn², and Karen E. Swider-Lyons² ¹EXCET INC. Springfield, VA 22151 ²Naval Research Laboratory, Washington, DC 20375, USA

New opportunities exist for the electrocatalysts in oxygen reduction reaction (ORR) in alkaline fuel cells (AFCs) in terms of electrocatalytic activity and material stability. In alkaline electrolyte, the electrocatalytic process is more facile than in acidic electrolyte due to the weakening of the competitive adsorption by the unreactive anion (1, 2). Compared to acid electrolytes, a much wider range of electrode materials are stable in alkaline electrolyte, including a number of less expensive materials; therefore, less platinum or even some non-noble metals (3-7) can be considered.

Recent studies have shown that platinum supported on metal oxide MOx (M=Ce, Ti, Mo, W, Nb, Ta) gave enhanced electrocatalytic activity for ORR (8-11). Recently, we reported high mass and surface area specific activity for the ORR using a 3 wt% nanoscale tantalum oxy-phosphate/Vulcan carbon supported Pt electrocatalyst (Pt/[TaOPO₄/VC]) heat treated at 660 °C in a reducing atmosphere, when tested in 0.10 M perchloric acid electrolyte using the rotating disc electrode (RDE) methodology (12, 13). At 0.90 V vs. RHE, 1600 rpm and a potential scan rate of 20 mV s⁻¹, a mass and areaspecific activity of 0.46 A mg_{Pt}^{-1} and 625 μ A cm_{Pt}^{-1} was measured for the heat treated Pt/[TaOPO₄/VC] electrocatalyst, compared to 0.24 A mg_{Pt}^{-1} and 333 μ A $cm_{Pt}^{\ -2}$ for a standard Pt/VC electrocatalyst (13). In contrast, a similarly prepared Pt/[TaOPO4/VC] and a Pt/[Ta₂O₅/VC] both heated treated at 200 °C in air showed no significant improvement over the Pt/VC standard. The high ORR activity of the Pt/[TaOPO₄/VC] electrocatalyst heat treated at 660 °C in a reducing atmosphere was attributed to an enrichment of the concentration of available protons at the Pt surface by the tantalum polyphosphate (13).

Here we present our findings on the ORR activity and selectivity measured on nanoscale platinum supported on tantalum and niobium oxy-phosphate/Vulcan carbon $(Pt/[TaOPO_4/VC] and Pt/[NbOPO_4/VC] and nanoscale$ platinum supported on tantalum and niobium oxide/Vulcan carbon (Pt/[Ta2O5/VC] and Pt/[Nb2O5/VC]), all heat treated at 660 °C in a reducing atmosphere. Both niobium and tantalum oxides are used as screens and catalyst supports in the anodes of acidic electrolyzers and are significantly more stable than any transition metal or rare earth oxides. The electrocatalytic evaluation is carried out using rotating disk electrode (RDE) voltammetry in 0.1 M KOH. The ORR kinetics and Tafel slope are discussed, along with the ORR kinetics measured on a standard Pt/VC electrocatalysts.

ACKNOWLEDGEMENTS

We are grateful to the Office of Naval Research for continued support of our research.



Figure 1. Mass and Area-specific activities of Pt/VC, Pt/[TaOPO₄/VC], Pt/[Ta₂O₅/VC], Pt/[NbOPO₄/VC] and Pt/[Nb₂O₅/VC] calculated at 0.90 V-iR corrected vs. RHE from ORR polarization curves measured in 0.10 M KOH at a potential scan rate of 20 mV s⁻¹ and an electrode rotation rate of 1600 rpm. Error bars represent the standard deviation obtained from five independent measurements.

REFERENCES

1. N. M. Marković and P. N. Ross Jr, *Surf. Sci. Rep.*, **45**, 117 (2002).

2. A. E. S. Sleightholme, J. R. Varcoe and A. R. Kucernak, *Electrochem. Commun.*, **10**, 151 (2008).

3. L. Demarconnay, C. Coutanceau and J. M. Léger, *Electrochim. Acta.*, **49**, 4513 (2004).

4. S. L. Gojković, S. Gupta and R. F. Savinell, J. *Electroanal. Chem.*, **462**, 63 (1999).

5. I. Roche, E. Chaînet, M. Chatenet and J. Vondrák, *J. Phys. Chem C*, **111**, 1434 (2006).

6. C. Song, L. Zhang and J. Zhang, *J. Electroanal. Chem.*, **587**, 293 (2006).

7. N. A. Vante and H. Tributsch, *Nature*, **323**, 431 (1986).

8. O. A. Baturina, Y. Garsany, T. J. Zega, R. M. Stroud, T. Schull and K. E. Swider-Lyons, *J. Electrochem. Soc.*, **155**, B1314 (2008).

9. T. Ioroi, Z. Siroma, N. Fujiwara, S.-i. Yamazaki and K. Yasuda, *Electrochem. Commun.*, **7**, 183 (2005).

10. P. J. Kulesza, B. Grzybowska, M. A. Malik and M. T. Galkowski, *J. Electrochem. Soc.*, **144**, 1911 (1997).

11. Z. Sun, H. C. Chiu and A. C. C. Tseung, *Electrochem. Solid-State. Lett.*, **4**, E9 (2001).

12. Y. Garsany, A. Epshteyn, A. P. Purdy, K. L. More and K. E. Swider-Lyons, *J. Phys. Chem. Lett.*, **1**, 1977 (2010).

13. A. Korovina, Y. Garsany, A. Epshteyn, A. P. Purdy, K. More, K. E. Swider-Lyons and D. E. Ramaker, *J. Phys. Chem C*, **116**, 18175 (2012).