

TiO₂ nanosheets as a protective additive for Pt/C catalyst

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Long term performances of Pt/C must be improved without sacrificing initial activity in order to realize polymer electrolyte fuel cells. During fuel cell operation, various phenomena occurs such as Pt dissolution/re-deposition, Pt sintering and carbon corrosion which all lead to drastic decrease of the catalyst activity. To protect the carbon support from corrosion, the use of graphitized carbon black [1] or carbon nanotubes [2] have been proposed. Another approach is to replace the carbon support by a metal oxide that is resistant to corrosion such as TiO₂ [3]. Oxide nanosheets, such as RuO₂ and TiO₂ nanosheet, can act as a protective layer when mixed with Pt/C for both anode and cathode catalysts [4-7]. The addition of a small amount of TiO₂ nanosheet with ~1 nm thickness and lateral size of sub-micrometers can enhance the long-term stability of PtRu/C anode [6]. This study shows the effect of addition of TiO₂ nanosheet to a commercial 30wt% Pt/vulcan carbon catalyst on the Oxygen Reduction Reaction (ORR) activity and durability towards carbon corrosion.

TiO₂ nanosheet (TiO₂ns) colloid was derived from layered K₂Ti₄O₉ by slight modification of a previously reported method [9]. The colloid solution containing exfoliated TiO₂ns was slowly dropped into an aqueous dispersion of carbon supported Pt (30wt% Pt; TEC10V30E, Tanaka Kikinokogyo) to prepare the desired composite catalyst TiO₂ns-Pt/C with TiO₂:Pt=0.3:1 molar ratio. The ORR activity was measured with a rotating disk electrode (RDE) in O₂-saturated 0.1 M HClO₄ at 60°C by linear sweep voltammetry (0.05→1.2 V vs. RHE) at 10 mV s⁻¹. The ORR activity (background subtracted) of the fresh catalyst was compared to that after the accelerated durability test (ADT). ADT protocol was performed by 2000 cycles between 1.0-1.5 V vs RHE in N₂-saturated 0.1 M HClO₄ at 60°C at 500 mV s⁻¹.

Figure 1 shows the Koutecky-Levitch plots from the RDE data at 0.9 V vs RHE before and after durability. The mass activity before and after ADT for Pt/C and TiO₂ns-Pt/C catalyst are compared in Fig. 2. Both catalysts, Pt/C and TiO₂ns-Pt/C, show similar initial mass activity with $j_k=220$ A (g-Pt)⁻¹. After ADT, the mass activity of Pt/C decreases to 120 A (g-Pt)⁻¹ (45% loss in activity). The mass activity of TiO₂ns-Pt/C after ADT was 174 A (g-Pt)⁻¹, thus the loss in activity is reduced to 22%.

Acknowledgements

This work was supported in part by the "Polymer Electrolyte Fuel Cell Program" from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

- [1] H. Yano, T. Akiyama, M. Watanabe, H. Uchida, *J. Electroanal. Chem.*, **688**, 137, (2013).
- [2] Y. Shao, G. Yin, J. Zhang, Y. Gao, *Electrochim. Acta*, **51**, 5853, (2006).
- [3] N. Rajalakshmi, N. Lakshmi, K.S. Dhathathreyan, *Int. J Hydrogen Energ.*, **33**, 7521, (2008).
- [4] W. Sugimoto, T. Saida, Y. Takasu, *Electrochem. Commun.*, **8**, 411 (2006).
- [5] T. Saida, W. Sugimoto, Y. Takasu, *Electrochim. Acta*, **55**, 857 (2010).
- [6] T. Saida, N. Ogiwara, Y. Takasu, W. Sugimoto, *J. Phys. Chem. C*, **114**, 13390 (2010).
- [7] C. Chauvin, Q. Liu, T. Saida, K. Lokesh, T. Sakai, W. Sugimoto, *ECS Transaction*, **50**, 1583 (2013).
- [8] D. Takimoto, C. Chauvin, W. Sugimoto, *Electrochem. Commun.*, **in press**, available on web (2013).
- [9] W. Sugimoto, O. Terabayashi, Y. Murakami, Y. Takasu, *J. Mater. Chem.*, **12**, 3814 (2002).

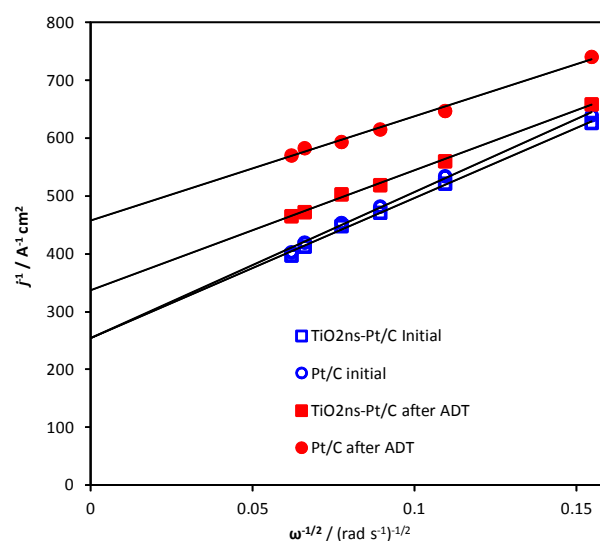


Figure 1: Koutecky-Levitch plots of Pt/C and TiO₂ns-Pt/C before and after ADT in 0.1 M HClO₄, at 0.9 V vs RHE (60°C).

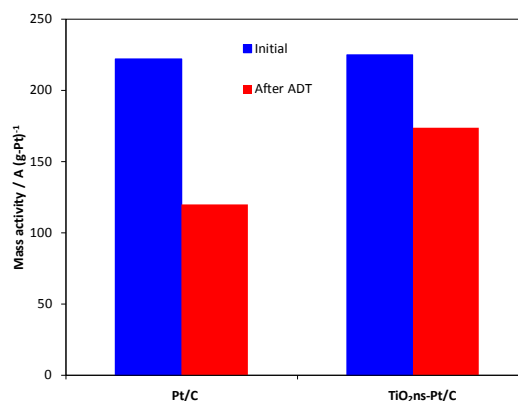


Figure 2: Mass activity of Pt/C and TiO₂ns-Pt/C catalysts before and after ADT in 0.1 M HClO₄, at 0.9 V vs RHE (60°C).