Ta modified TiO₂ supports exhibit exceptional durability in polymer electrolyte fuel cells

Amod Kumar and Vijay Ramani
Center for Electrochemical Science and Engineering
Department of Chemical and Biological Engineering
Illinois Institute of Technology
Chicago, IL 60616

Abstract

Carbon possesses many desirable properties for a suitable catalyst support in a polymer electrolyte fuel cell (PEFC) such as high electron conductivity and high surface area, which allows high dispersion of catalyst metal. Therefore, it is widely used as a catalyst support material in PEFCs. However, carbon suffers from electrochemical degradation under conditions of high temperature, high electrode potential, and low pH [1]. Carbon corrosion occurs by the following reaction:

$$C + H_2O \rightarrow CO_2 + 4H^+ + 4e^- \quad 0.207 \text{ V vs. RHE (1)}$$
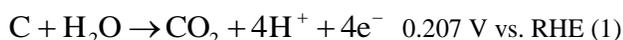
The lifetime of PEFC stacks is greatly reduced by carbon support corrosion. The reaction rate for the electrooxidation of carbon can increase significantly under certain transient operating conditions (e.g., PEFC start-up/shut-down; fuel starvation). To avoid the issue of carbon corrosion, a non-carbon corrosion resistant support possessing the desirable properties of carbon is proposed.

In this study, Ta modified TiO₂ was investigated as a possible corrosion-resistant catalyst support for PEFC applications. The main objectives of this study were: a) to investigate whether uncatalyzed Ta modified TiO₂ possessed adequate conductivity and higher electrochemical stability than commercial carbon black; and b) to compare the stability and activity of the catalyzed Ta modified TiO₂ to that of commercial Pt/C in a PEFC. The microstructure of the support and catalyst was elucidated using XRD, TEM/XEDS, XPS and BET. AC Impedance spectroscopy was carried out to measure electronic conductivity. The catalyst performance and durability were evaluated in the rotating disk electrode (RDE).

The ECSA, mass-specific activity and area-specific activity of $Pt/Ta_{0.3}Ti_{0.7}O_2$ and Pt/C catalysts are all reported in Table 1. The lower value of ECSA of $Pt/Ta_{0.3}Ti_{0.7}O_2$ compared to baseline Pt/C was attributed to the differences in platinum particle size (around 4-5 nm average for the $Pt/Ta_{0.3}Ti_{0.7}O_2$ and 2-3 nm average for the Pt/C catalyst) and to the non-optimized ionomer/support ratio in the $Pt/Ta_{0.3}Ti_{0.7}O_2$ electrode.

Table 1 Comparison of figures of merit obtained from RDE studies.

Sample	ECSA (m²/g)	I_m (mA/mg$_{Pt}$) @0.9 V	I_s (μA/cm²$_{Pt}$) @0.9 V
46% Pt/C	72±3	145±6	201±11
20% Pt/Ta₀.₃Ti₀.₇O₂	41±1	62±5	151±7
46% Pt/Cᵃ	86±7	160	210

ᵃ Extracted from literature, Gasteiger et al.[2]

The stability of the catalyzed support was estimated from the change in the Electrochemical Surface Area (ECSA) over 10,000 cycles of an accelerated load cycling test designed to mimic full load-no load transients in an operating PEFC. The response from load cycling tests (shown in Fig. 1) revealed that the ECSA of the commercial Pt/C catalyst decreased substantially, with a 47% loss after 10000 cycles. The $Pt/Ta_{0.3}Ti_{0.7}O_2$ electrocatalyst exhibited a lower, but still significant, ECSA loss of ~35% over 10,000 cycles. The lower extent of degradation was partly attributed to strong metal support interactions (SMSI) as confirmed from XPS results. TEM images of pre and post cycled Pt/C and $Pt/Ta_{0.3}Ti_{0.7}O_2$ catalysts, shown in Fig. 2, confirm the presence of greater corrosion resistance in $Pt/Ta_{0.3}Ti_{0.7}O_2$. Intensive growth of Pt particles was observed on Pt/C, which was consistent with prior reports in the literature [3]. Three main paths have been proposed for the degradation of Pt/C catalysts: Pt dissolution and re-deposition (growth via Ostwald ripening), coalescence via crystal migration, and detachment of Pt particles from the carbon support.
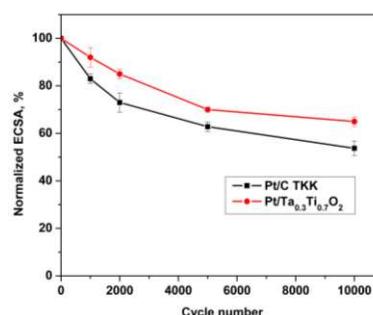
Figure 1. Normalized ECSA of Pt/C and $Pt/Ta_{0.3}Ti_{0.7}O_2$ as a function of cycle number under an accelerated potential cycling test designed to test electrocatalyst stability.
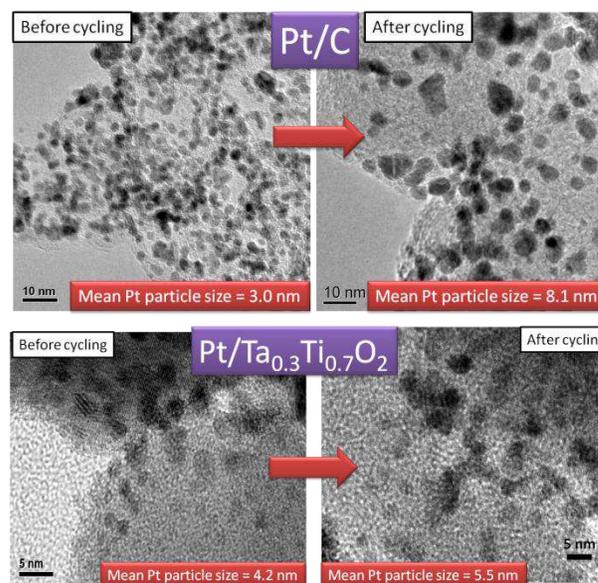
Figure 2. TEM images of Pt/C and $Pt/Ta_{0.3}Ti_{0.7}O_2$ catalyst particles before and after 10000 potential cycles. Potential cycling conditions: 0.6/0.95 V vs. RHE, rectangular wave, hold at each potential: 3 s.

References

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