Evaluation of Tungsten Carbide and Tungsten Oxide as Pt Supports for Oxygen Reduction Reaction

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Electrochemical energy conversion devices, fuel cells, have received considerable attention over the past few decades, because they have the potential to provide high efficiency power since electrochemical processes are not limited by traditional Carnot or Rankine heat cycles [1]. Over the past two decades, the most widely investigated fuel cell is the proton exchange membrane fuel cell (PEMFC) [2-3].

Taking the electron equivalence for each reaction into account, HOR and ORR yield the noncombustive redox reaction of two hydrogen molecules and one oxygen molecule, yielding two water molecules.

$$H_2 \rightarrow 2H^+ + 2e^- E^0 = 0.0 V$$
 (1)

$$O_2 + 4H^+ + 4e^- \rightarrow H_2O_{,} E^o = 1.23 V$$
 (2)

$$2H_2 + O_2 \rightarrow 2H_2O \tag{3}$$

The ORR (Eqn. 2) is the performance limiting reaction in PEMFCs [4]. The most common, highly efficient anode electrocatalyst for the hydrogen oxidation reaction (HOR), nanometer-sized clusters of platinum dispersed on high surface area carbon (Pt/C), unfortunately, are plagued by rapid performance loss with time. One of the reasons is that surface carbon atoms are oxidized electrochemically at potentials greater than 0.207 V vs. NHE, leading to the activated carbon species to react with nearby water molecules, eventually yielding CO₂[5].

Unconventional supports have been proposed over the past several years to not only reduce support corrosion, but also improve Pt cluster stability and dispersion, thus enhance Pt electrocatalytic activity. Some materials include transition metal oxides, carbides.

In this study, the ORR activity and stability of the Pt clusters supported on tungsten carbide (WC) and tungsten oxide (WO₃) catalysts are evaluated [6-7]. Figure 1 shows the proposed mechanism for ORR activity loss and Pt agglomeration for Pt/WC and Pt/WO₃. On WC, performance degradation is initiated by electrochemical oxidation of WC to WO_x at E > 0.8V. Then, the surface is further oxidized to WO_3 ; These WO_3 sites are gradually reduced during the ORR to hydrogen tungsten bronze species, which are soluble in acid media and facilitates the detachment of Pt particles from the surface. Detached Pt particles not only lose the high synergistic activity, they also agglomerate, severely reducing the Pt mass activity over time.



Figure 1. Mechanism for ORR activity loss and Pt agglomeration on Pt/WC, Pt/WO₃ Electrocatalysts.

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