# Catalytic Activity and Stability of Tungsten Oxide Electrocatalyst for Fuel Cell Applications

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Introduction

The degradation of the electrocatalyst in the polymer electrolyte membrane fuel cell (PEMFC) is a major failure mode by which the performance of PEMFC deteriorates. Several factors - acting independently or in concert with each other - give rise to catalyst degradation. These factors include catalyst particle ripening (sintering), catalyst dissolution and catalyst support corrosion. Thus, different degradation mechanisms can occur on the electrode/electrocatalyst layer. The support physically separates the catalyst nanoparticles and may also influence the adsorptive properties of the catalyst active center. High electronic conductivity is a key performance requirement for any electrocatalyst support but unfortunately it also forms the basis of corrosion degradation. The presence of water in the catalyst/electrode layer promotes the corrosion of fuel cell components. Thus, carbon or graphitic carbon being the most commonly used support material in fuel cells is subject to corrosion degradation at very low potentials:

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e \qquad E_0 = 0.207\,V \quad vs. \quad RHE$$
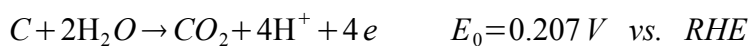
However, because the rate of carbon corrosion at 0.207 V is slow, it can still be used as catalyst support. In fact Jarvi *et al.* [1] showed that for Vulan XC72, a substantial surface oxidation occurs at 65°C when the potential is cycled beyond 0.8 V vs. RHE. Platinum is the most active catalyst for fuel cells. However, the Pt deposited on the carbon substrate is known to catalyze the corrosion or oxidation of the carbon substrate with the formation of carbon dioxide as well as other active surface species such as quinone group [2]. Understanding the degradation mechanism is pertinent to proferring a viable solution. Efforts abound in the literature in understanding the underlying issues and evaluation of alternative catalyst supports that may be resistant to corrosion [3 – 6]. Some of the alternative materials to carbon that have been studied to date include the oxides and carbides of titanium and tungsten [3 – 6]. Because of the low conductivity of the oxides and carbides, efforts have been put in examining optimal combination of carbon (for improved conductivity) and oxides (or carbides) (for improved corrosion) that will result in durable and stable fuel cell.

For the oxide supports examined in the literature, Pt deposited through the impregnation method has often been the active catalyst most discussed. The performance degradation of Pt deposited by classical impregnation method has therefore been thoroughly examined by Gasteiger *et al.* [7] and reviewed in [8 – 9]. In the present work, cyclic voltammetric method is used to examine the catalytic activity of tungsten oxide support catalyzed by electroless method for oxygen reduction. Both Co-Ni and Pd catalysts are examined for their oxygen reduction performance as catalysts. Catalytic activity of C/WO$_3$ mixture for oxygen reduction is also examined.

Experimental Method

In preparing electroless Co-Ni catalyzed WO_3 (Co-Ni/WO_3) or (Co-Ni/WO_3-C), we started with polymer-stabilized Pd nanoparticles for the activation of the substrate for electroless deposition. The polymer-stabilized palladium catalyst solution was prepared by dissolving 0.2 g analytical reagent grade palladium acetate $[CH_3CO_2)_2Pd]$ (47.05 % Pd) from Aldrich-Sigma Co, in 2.0 ml NH_4OH. The palladium mixture was then added with stirring to a 44 g methanol-poly(vinyl) butyral (Solutia Inc.'s Butvar B-98) mixture formed by dissolving 22 g PVB in 140 ml methanol. This is referred to as the Pd-ink. A known amount of tungsten oxide (Aldrich, St. Louis, MO)-carbon (Vulcan X72) was mixed with known amount of the Pd-ink and sonicated for 15 minutes. The Pd-ink/WO_3-C mixture was dried at 50^oC in an oven and then subjected to 300^oC temperature in a furnace for 24 hours. The different WO_3/C ratios investigated are: 100%/0%, 80%/20%, 50%/50% and 0%/100%.

A Co-Ni electroless solution for the deposition of electrocatalyst on the catalyzed substrate was prepared with analytical grade chemicals and deionized water. The solution contained 2.1 g $CuSO_4$, 4.9 g $NiSO_4$, 28g Tartrate, 20g NaH_2PO_2, 10g Boric Acid and 15g Gluconic Acid in a 1000 mL solution. The electroless plating temperature was fixed between $55 – 65^0C$ and the pH maintained between 9.3 and 9.6 pH units with ammonium hydroxide used for the adjustment. Electroless plating was carried out for 2 minutes, 5 minutes and 10 minutes with three repeats for each time condition. The plated sample was filtered and washed with DI water. After drying the sample in an oven at 50^oC, it was annealed at 250^oC for 15 minutes.

The catalyst ink for oxygen reduction was prepared by mixing the electroless Co-Ni catalyzed powder (100 mg), Nafion solution (Dupont, 5% solution), water and n-propanol. Typically, equal volumes of Nafion, water and propanol is mixed and sonicated prior to the addition of the catalyzed powder. The resulting ink mixture was sonicated for about 15 minutes and about 2 µL drop applied on 3mm graphite electrode. After drying at room temperature, the resulting electrode was tested in a three-electrode set-up for oxygen reduction in 0.5 M H_2SO_4 solution.

Results and Discussion

Electrochemical Characterization

Fig. 1 shows the cyclic voltammetry (CV) of Co-Ni catalyzed substrates in oxygen saturated 0.5 M sulfuric acid. The Co-Ni was electrolessly plated for 2 minutes in each case. At 0.8 V (vs. Ag/AgCl), the figure shows that the WO_3/C ratio of 80%/20% mixture was the most active for oxygen reduction. This is unexpected since the low performing WO_3 would have been expected to decrease the activity of carbon. The figure thus suggests that the limitations in the activity of WO_3 is probably related to its low electronic conductivity as compared to carbon. A further comparison is made in figure 2 for oxygen reduction using different catalyzed substrates at 0.5 V (vs. Ag/AgCl). Again, similar to our findings in Fig. 1, the 80% WO_3/20% C mixture was most active for the Co-Ni catalyzed samples. This was followed by the 50% mixture. Here again, the performance of the mixed substrates show improvement over the individual components. In fig. 2, we observe that for both WO_3 and C, the deposition of electroless Co-Ni on Pd-catalyzed substrate conferred an improved activity over the Pd-catalyzed substrate. In Fig. 3, the effect of tungsten oxide composition on the catalyst activity for the reduction of oxygen is compared at 3 different CV scan rates. The trend observed is the same for each scan rate. The results suggest that an optimized mixture of WO_3/C can be obtained for an improved activity.

The effect of annealing time on the catalytic activity of Pd-catalyzed substrate was evaluated for

WO_3. Fig. 4 compares the catalytic activity of Pd-catalyzed WO_3 annealed for different time lengths. The sample annealed for a longer time period performed better – evidence that some left-over polymer could be covering the Pd nanoparticles. Annealing temperature and time are critical parameters for the polymer-stabilized nanoparticles.

Microstructure Characterization

Fig. 5a and 5b show the surface morphology of a 50% WO_3/50% C substrate and a spectrum (EDAX) of a selected area on the substrate, respectively. The spectrum shows the presence of Co, Ni and P deposited from the electroless process. The X-ray diffraction (XRD) results of Co-Ni catalyzed substrates and Pd catalyzed WO_3 are shown in Fig. 6. The absence of any strong peaks for the carbon catalyzed sample is noted. The peaks associated with tungsten oxide at different phases are evident. The presence of Co-Ni solid solution is not pronounced because of the interactions with tungsten oxide peaks.

Catalyst Stability

For a simple stability test, the catalysts were subjected to a constant potential hold at 1.7 V (vs. Ag/AgCl) for 30 minutes and this was followed by a cyclic voltammetry. At 1.7 V, it is expected that the metal-nanoparticle catalyst will be oxidized and carrying out a simple CV will indicate the reduction of this oxide in the cathodic direction. Based on the results, one can relate the stability of the catalyst to the reduction current of the oxide formed. Our results are inconclusive since the stability test was carried out in the presence of oxygen.

Conclusion

Electroless deposition was used to catalyze tungsten oxide and carbon/tungsten oxide mixtures for electrocatalysis of oxygen. The preliminary results obtained showed that this approach is feasible in improving the catalytic activity of carbon. Further optimization and stability studies are required in order to evaluate the potential of the approach. The use of polymer-stabilized nanoparticles for the catalyzation of substrate for fuel cell applications is demonstrated.
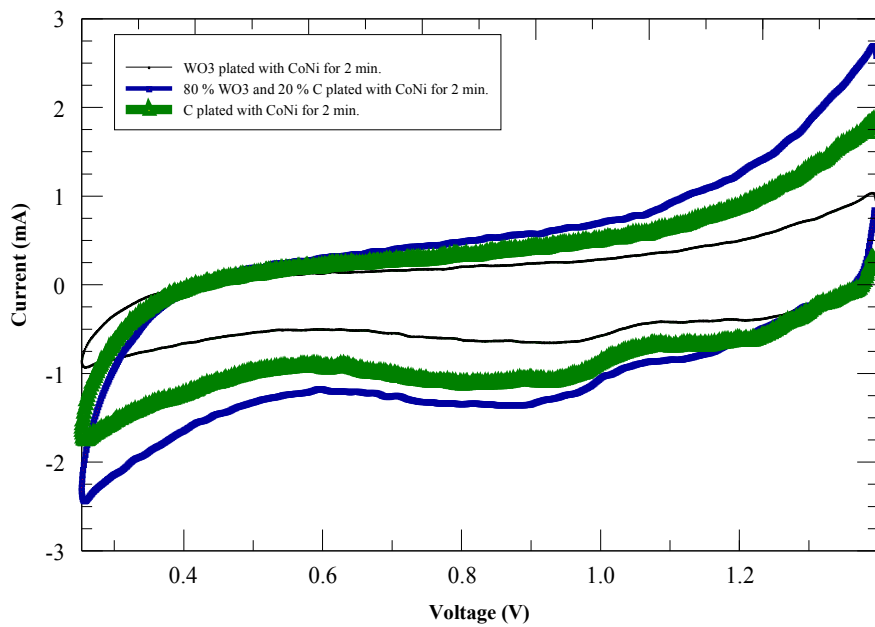
Figure 1. The Cyclic Volatmmetry graph of WO$_3$, 80% WO$_3$ and 20 % C, and Carbon all plated with CoNi for 2 minutes.
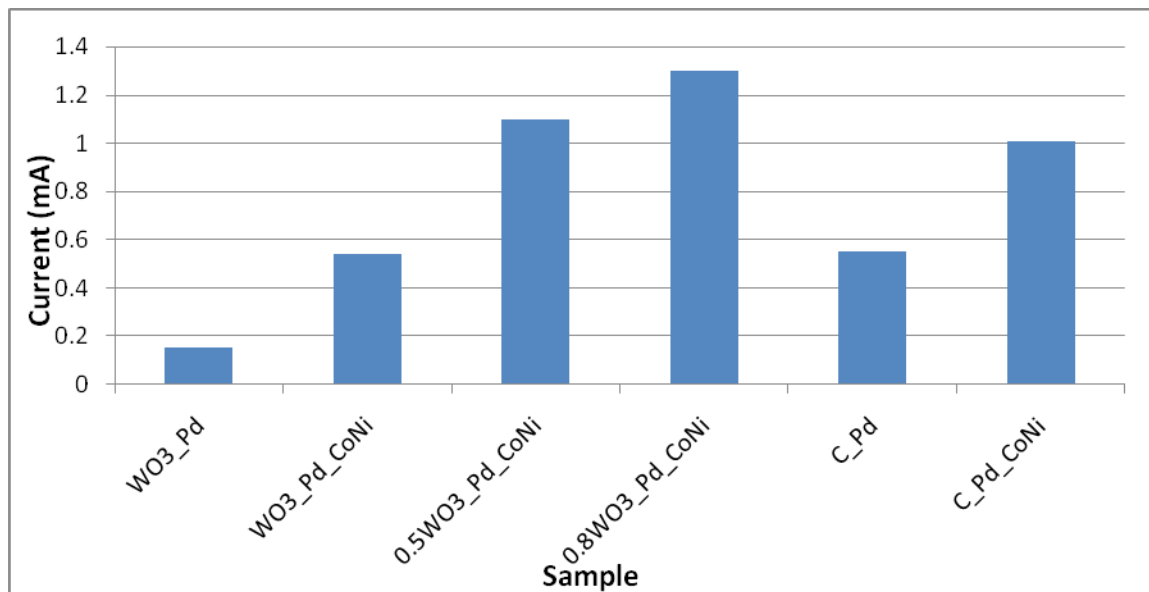

Figure 2. Peak Current of samples plated in the presence and absence CoNi at a scan rate of 25mV/s.
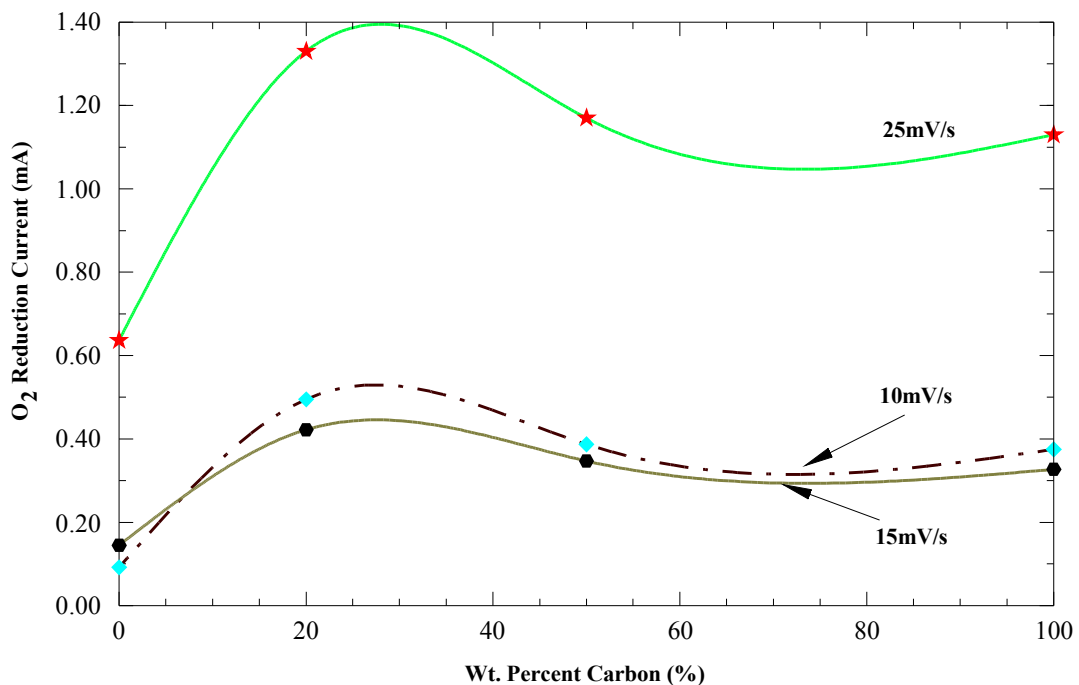
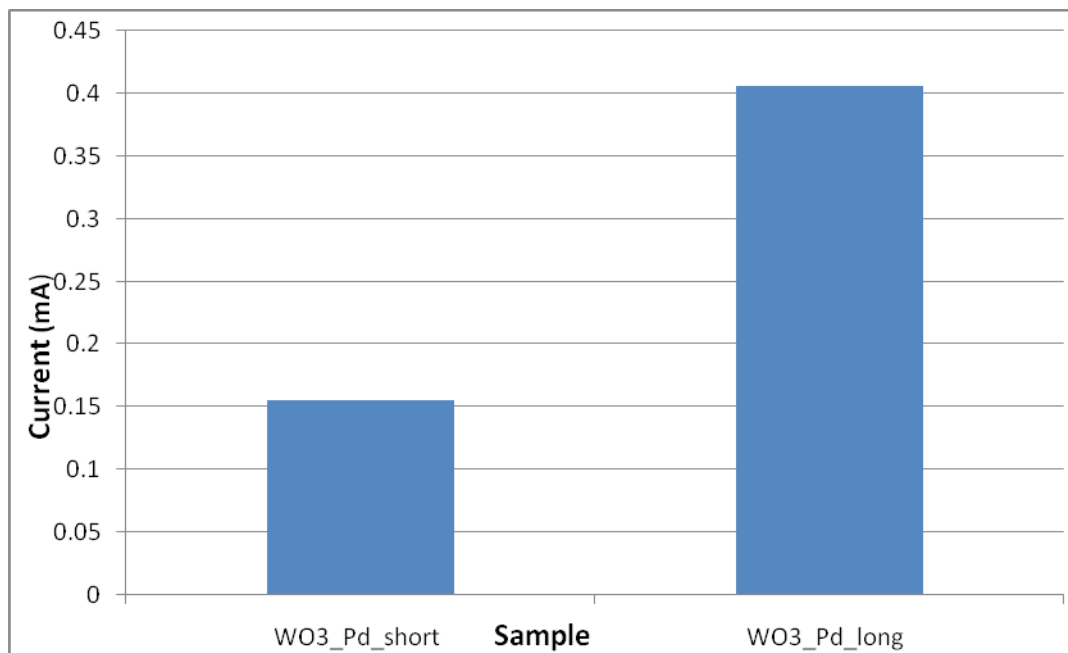**Figure 3.** Oxygen reduction current on CoNi catalyst as a function of WO₃/C composition

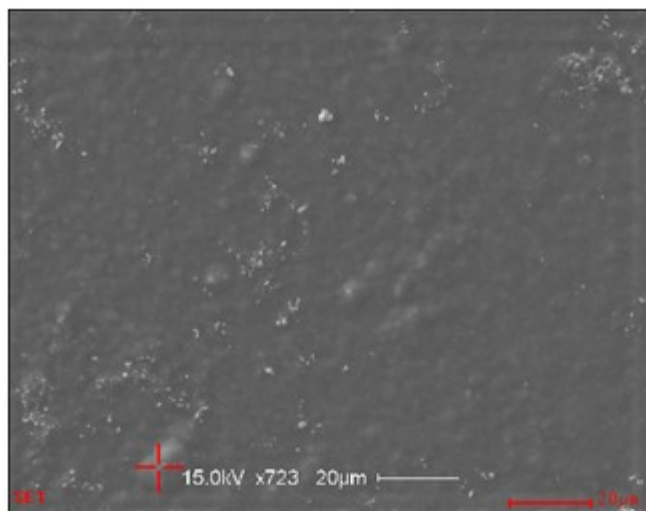**Figure 4.** A comparison of Pd catalyzed WO₃ annealed for 24 hours and for one week at a scan rate of 25mV/s

Figure 5a. EDAX results showing surface morphology of 50% WO₃/ 50% C plated with CoNi for 5 minutes
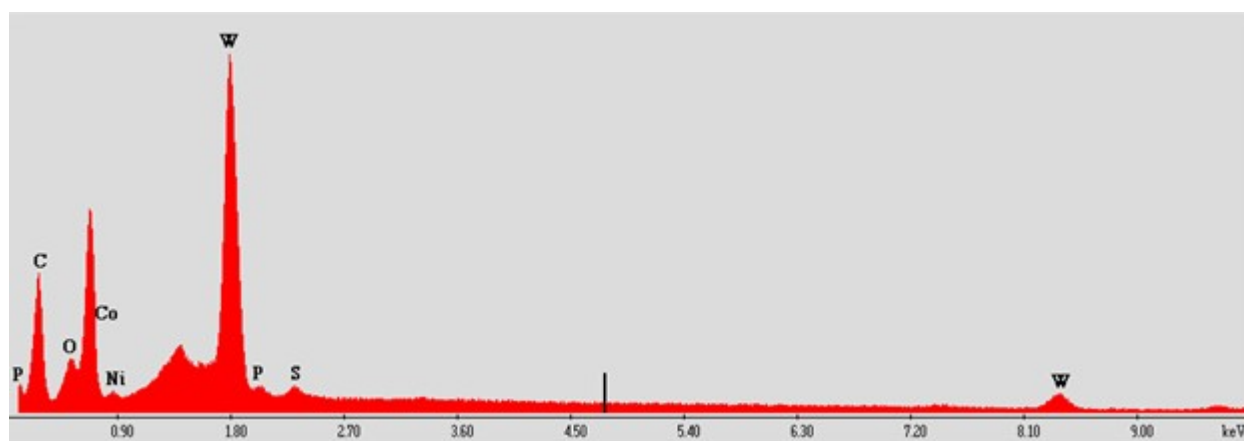

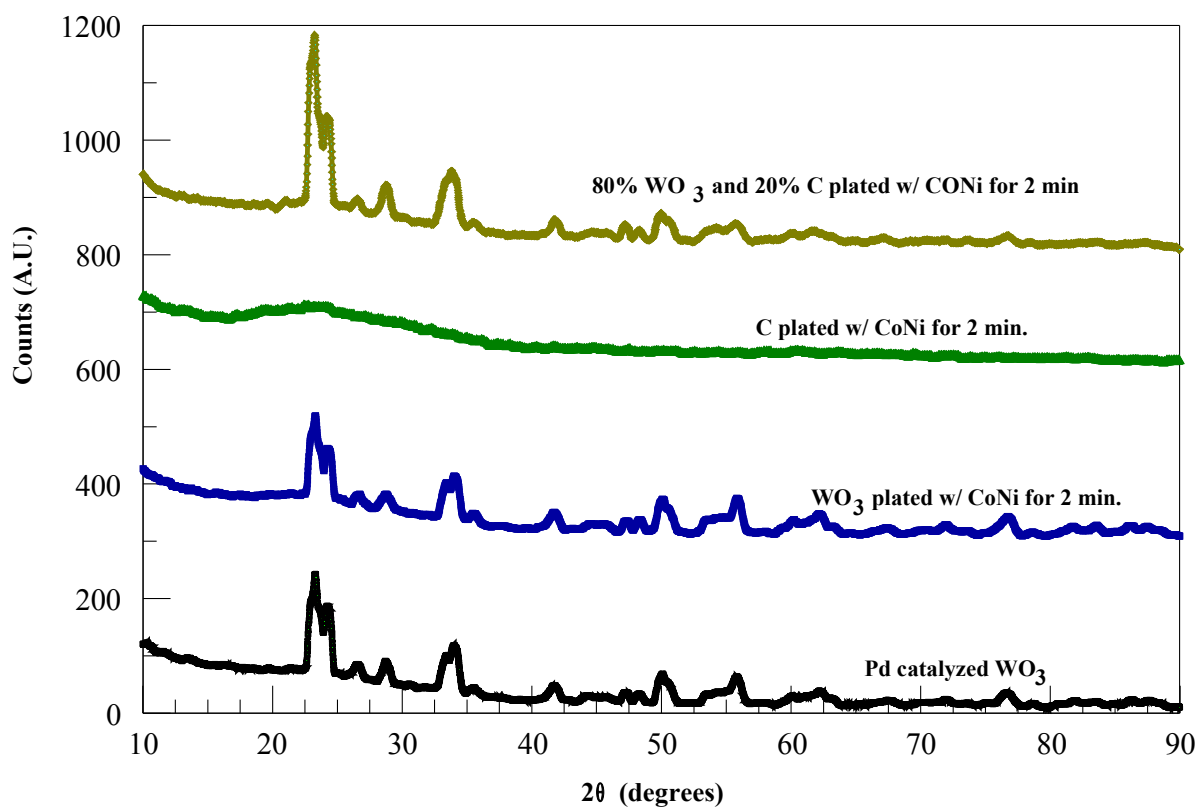**Figure 5b.** Spectrum of selected area on the surface of the 50% WO₃/50%C substrate.

Figure 6. XRD results of WO$_3$ and C both plated with CoNi for 2 minutes and the results of Pd catatalyzed WO$_3$

Acknowledgments

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