

## Composite Carbon Nanotube and Titania Catalyst Supports for Enhanced Activity and Durability

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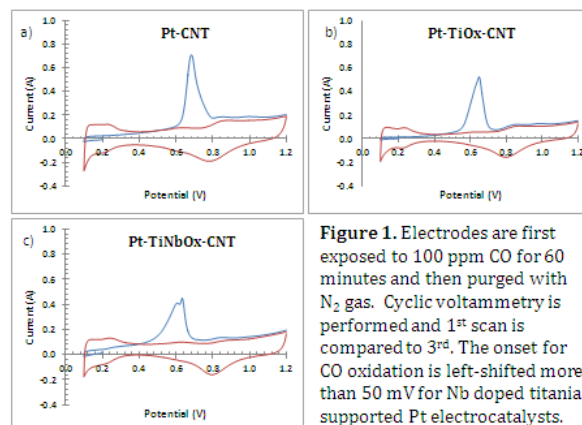
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Catalyst supports can influence the activity and durability of the precious noble metal. In this investigation, platinum (Pt) is bonded to composite carbon nanotubes (CNT) covered with metal oxides, namely titanium (Ti) oxides or titania. Composite catalysts were characterized for benefits to the hydrogen ( $H_2$ ) oxidation half reaction. The materials were constructed into working membrane electrode assemblies (MEA) used in polymer electrolyte cells. The  $H_2$  supplied to the anode is often subject to contamination from carbon monoxide (CO) which can be found in  $H_2$  derived from reforming natural gas or other organic fuels and exposure to the catalyst can poison its activity. Tolerance to CO prevents the loss of performance which is recovered by subjecting the electrode to corrosive conditions.

Modification of the support can improve both the activity and durability for Pt. Graphitic CNTs are a good framework and offer durability benefits over carbon black supports. Addition of titania can enhance the stability of Pt on support while establishing the ideal defect chemistry can improve its electrocatalytic properties. Niobium (Nb) doped titania offers several specific traits making it very attractive in the anode. As proof, in-situ electrochemical measurements for CO stripping, impedance spectroscopy, and  $H_2$  pump polarization were used to demonstrate activity advantages. Durability of the catalyst supports is revealed by continuous monitoring of corrosion through carbon dioxide ( $CO_2$ ) evolution using a mass spectrometer while cell potential is cycled according to an accelerated protocol. Comparisons are made between materials and our work demonstrates the constructive modifications

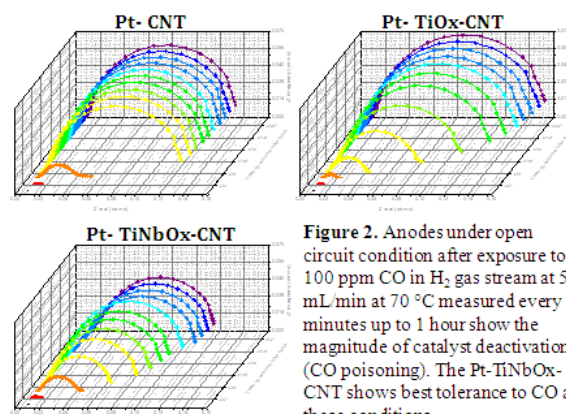
Electrocatalyst composites were synthesized in the laboratory in sequential steps that is critical to their success. Multi-wall CNTs were first oxidized in a concentrated mix of acids to prepare functional groups on their surface. The degree of disorder introduced was examined via Raman spectroscopy. Then CNT were dispersed in a sol-gel with metal alkoxides. Hydrolysis, condensation, and growth were controlled to form a thin oxide coverage. Composite supports were calcined to induce phase transformation of anatase crystal structure. Supports were prepared with only 5% metal oxide mass addition and the oxidation state of Ti was reduced by introducing 10% donor dopant of Nb atoms. The dopant selection is based on ionic radii, valence, and coordination to create oxygen vacancies balanced by n-type charge carriers for conductivity. The choice of metals, Ti and Nb, are also chosen for their stability in this environment [1]. These transition metal oxides demonstrate a strong metal support interaction with Pt [2]. This can serve to form a stronger bond with Pt than directly to carbon and is also attributed to an effect on activity through a bifunctional catalytic mechanism for CO oxidation [3, 4]. Pt deposition was carried out by the polyol reduction method assisted by microwave heating. The chemically bonded composites were investigated by several techniques including XPS, XRD, and electron microscopy.

The resulting electrocatalysts were mixed into an ink with ionomer which is deposited directly on to the polymer using an ultrasonic spray process. Engineered MEAs in cell hardware were prepared with  $0.3 \text{ mg}_{Pt}/\text{cm}^2$  for characterization. From Figure 1, CO stripping tests in cell show how different catalysts performed; a) Pt-CNT, b) Pt-TiO<sub>x</sub>-CNT, and c) Pt-Ti<sub>0.9</sub>Nb<sub>0.1</sub>O<sub>x</sub>-CNT.



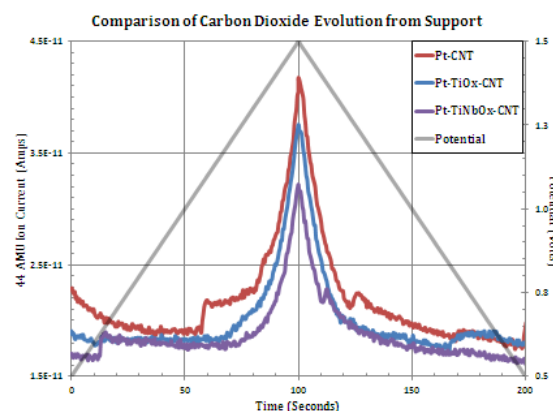
**Figure 1.** Electrodes are first exposed to 100 ppm CO for 60 minutes and then purged with  $N_2$  gas. Cyclic voltammetry is performed and 1<sup>st</sup> scan is compared to 3<sup>rd</sup>. The onset for CO oxidation is left-shifted more than 50 mV for Nb doped titania supported Pt electrocatalysts.

Figure 2 shows Nyquist plots of the impedance spectroscopy analysis dynamic for CO deactivation of Pt.



**Figure 2.** Anodes under open circuit condition after exposure to 100 ppm CO in  $H_2$  gas stream at 50 mL/min at 70 °C measured every 5 minutes up to 1 hour show the magnitude of catalyst deactivation (CO poisoning). The Pt-TiNbO<sub>x</sub>-CNT shows best tolerance to CO at these conditions.

Figure 3 depicts carbon corrosion from the catalysts.



**Figure 3.** Electrocatalyst from Pt-TiNbO<sub>x</sub>-CNT shows lowest  $CO_2$  evolution after 10<sup>th</sup> potential cycle from 0.5 to 1.5 Volts at 80 °C

### Acknowledgements

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### References

- [1] M. Pourbaix. *Atlas of Electrochemical Equilibria in Aqueous Solutions*, NACE (1974).
- [2] S. J. Tauster, S. C. Fung and R. L. Garten, *J. of Amer. Chem. Soc.*, **100** (1), 170-175 (1978).
- [3] K. Huang, K. Sasaki, R. R. Adzic, Y. Xing. *J. Mater. Chem.*, **22**, 16824-16832 (2012).
- [4] D. Wang, C. V. Subban, H. Wang, E. Rus, F. J. DiSalvo, H. D. Abruña. *J. Amer. Chem. Soc.*, **132**, 10218-10220 (2010).