# Ruthenium Titanium Oxide (RTO) electrocatalyst supports exhibit exceptional start-stop durability

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## Introduction

Corrosion of the carbon support used in electrocatalysts during fuel cell operation has been well documented. The carbon corrosion phenomenon is accelerated during startup and shut-down of the fuel cell, when electrode potential excursions to above 1.5 V is not uncommon for brief periods of time [1]. The irreversible carbon corrosion is accompanied by a loss in electrochemical activity and functionality of the electrode, resulting in significant and irreversible loss in performance. This factor has been one of the key obstacles in the context of automotive fuel cell commercialization. A number of noncarbon support materials have been investigated in the past to overcome this hurdle [2]. However, to be considered a suitable replacement for carbon, the support must meet requirements of surface area, electronic conductivity and porosity, besides overcoming the issue of stability. Therefore, it is a challenge to match the high activity of state-of-the-art platinum on carbon (Pt/C) catalysts while improving durability.

Titanium oxide (TiO<sub>2</sub>) is a cheap, non-toxic and widely available material that possesses high surface area. It is known to be stable in oxidative and acidic environments [3], however, it is non-conducting. In this study, titanium oxide doped with ruthenium oxide (RuO<sub>2</sub>) as an electron-conducting moiety (abbreviated as RTO) have been prepared and investigated to ascertain microstructure, materials properties of interest and most importantly, corrosion resistance under aggressive accelerated tests designed to simulate automotive start-stop cycles.

### Experimental

TiO<sub>2</sub>-RuO<sub>2</sub> powders were prepared as follows: TiO<sub>2</sub> was dispersed in 250 ml DI water and sonicated for 30 minutes. Depending on the desired composition, a desired amount of RuCl<sub>3</sub>.xH<sub>2</sub>O was added into the mixture under stirring for 30 minutes. 0.05 N KOH(aq) was then dropped into the mixture under stirring until desired pH of the solution was attained. The black powder obtained was filtered out and washed repeatedly with deionized water. The powders were then dried at 120 °C for 8 hours and further calcined at 450°C for 3 hours in air to yield anhydrous RTO. Platinum nanoparticles were supported on the RTO by the chemical reduction of Pt precursor with formic acid. The microstructure and properties of the RTO were elucidated using XRD, TEM, BET and linear sweep voltammetry. The catalyst performance and durability were evaluated using both a rotating disk electrode (RDE) and in a membrane electrode assembly (MEA). Accelerated potential cyclic test specifically developed to simulate stack start-stop conditions were employed to evaluate support and elecrocatalyst durability (potential cycling between 1 and 1.5 V; 1,000 cycles). For all studies, 46 wt% Pt/C (TEC10E50E from TKK) was used as a benchmark.

#### Results

RTO The resultant supports and derived electrocatalysts possessed the requisite electronic conductivity and surface area for use in fuel cell MEAs (details will be presented in the talk due to space constraints in this abstract). Importantly, the RTO supports exhibited outstanding corrosion resistance compared to benchmark Pt/C when exposed to identical harsh potential cycling tests, as illustrated by Figures 1. While a five-fold drop in performance was seen for the benchmark Pt/C catalyst (as shown in the Figure 1 inset) when comparing the beginning of life (BOL) and end of life (EOL) performances, the polarization curves for the Pt/RTO catalyst BOL and EOL were identical. Independent measurements on uncatalyzed supports (data not shown in abstract) also clearly revealed that the RTO materials exhibited exceptional resistance to oxidation and corrosion under harsh conditions.

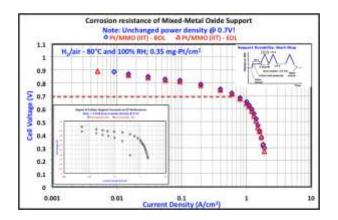
These results represent a significant advancement in the state-of-the-art in the automotive fuel cell sector.

#### References

[1] F. Takasaki, S. Matsuie, Y. Takabatake, Z. Noda, A. Hayashi, Y. Shiratori, K. Ito and K. Sasaki, *J. Electrochem. Soc.*, **158** (10), B1270, (2011).

[2] E. Antolini and E.R. Gonzalez, *Solid State Ionics*, **180**, 746 (2009);

[3] Y.-J. Wang, D. P. Wilkinson and J. Zhang, *Chem. Rev.*, **111** (12), 7625, (2011).



**Figure 1.** BOL vs. EOL performance for Pt/RTO electrocatalyst under an accelerated start-stop test compared with Pt/C benchmark data (inset).