INVESTIGATION OF TiO₂/CARBON ELECTROCATALYST SUPPORTS PREPARED USING GLUCOSE AS A MODIFIER

Odetola Christopher, *Easton E. Bradley, *Trevani Liliana,

University of Ontario Institute of Technology, Faculty of Science
2000 Simcoe Street North, Oshawa (L1H 7K4), Ontario, Canada.

*Corresponding authors: brad.easton@uoit.ca and Liliana.trevani@uoit.ca

Keywords: glucose, titanium dioxide, Vulcan carbon, electrochemically active surface area; beginning of life

ABSTRACT
Carbon black (Vulcan XC-72R) is the most widely used support for Pt and Pt-alloy catalysts in fuel cell applications, mainly because of its excellent electrical properties, high surface area, and low cost. However, it can corrode at high electrode potentials (> 0.9 V vs. NHE) under acidic conditions. More chemically stable materials, like TiO₂, can significantly improve the performance and extend the life of the catalyst when used in combination with carbon, but there are still some drawbacks in terms of electrical conduction and activity retention. In this study, we have developed a method based on the use of glucose as molecular seed for the deposition of TiO₂ nanoparticles on carbon substrates. The introduction of –OH functional groups on the surface of carbon eliminates the need for acid treatment functionalization prior to the deposition of TiO₂. For comparison, glucose doped (G-PV) and acid treated (ATV) Vulcan XC-72R carbon were coated with TiO₂ and used as substrates for the preparation of Pt/TiO₂/Vulcan carbon composites. The catalysts’ performance on these materials was evaluated using cyclic voltammetry and a rotatory disc electrode system in 0.5 M H₂SO₄. The beginning of life-electrochemical active surface area (BOL-ESCA) of Pt on TiO₂/Vulcan glucose doped Vulcan® carbon (Pt/TiO₂/G-PV) with 14% TiO₂, 46.2 m²/g Pt showed to be significantly higher than that for the two reference samples prepared with acid-treated carbon, Pt/ATV (35.5 m²/g Pt) and Pt/14wt% TiO₂/ATV (18.8 m²/g Pt). A similar trend was observed after 4000 potential cycles (0 to 1.5 V vs. NHE), despite the values were significantly lower.

1. INTRODUCTION
Proton exchange membrane fuel cells (PEMFCs) have shown to be an attractive alternative power source for mobile and stationary applications. However, carbon corrosion and platinum aggregation during long-term operation and start-up-shut-down cycles in automotive applications result in a significant reduction of the catalyst electrochemical surface area (ECSA). The problem is more severe in the cathode due to the combination of oxidizing and acidic conditions (Wang et al., 2011, Debe 2012 and Shao et al., 2006).

Other materials that are chemically stable under these conditions do not have sufficient electrical conductivity for this application. Thus, the synthesis and characterization of metal oxides/carbon composite materials have become a very active area of research (Ioroi et al., 2005). Numerous metal oxides have been studies, with TiO₂ being the most studied, either alone or in combination with other transition metals and/or carbon (Ioroi et al., 2005, Bauer et al., 2010,Beak et al., 2010,Shanmugam et al., 2007,Huang et al., 2012,Camacho et al.,2013 and Vogel et al., 2010). TiO₂/carbon nanotubes (Huang et al., 2012 and Vogel et al., 2010) and TiO₂/graphene (Tiido et al., 2013) are perhaps the most successful materials in terms of electronic conductivity, chemical inertness, and long-term stability under accelerated test conditions. However, carbon nanotubes and graphene are still expensive and other materials are required to make PEMFCs competitive devices.

This work was aimed to synthesize uniform core/shell TiO₂/C nanostructured materials that could be used to get a better understanding of the role of TiO₂ on the stability of carbon, as well as on the enhancement of the catalytic activity of Pt toward the oxygen reduction reaction (ORR). In our approach, glucose is used to modify the surface of Vulcan XC-72R carbon and to control the deposition of TiO₂ nanoparticles on carbon. While glucose functionalization has been employed in the past for the preparation of carbon composite materials such as hollow TiO₂/C nanotubes (Cong et al., 2014) and riveted Pt/TiO₂-C (Jiang et al., 2011). The
synthesis and/or morphology of the products were different, and consequently, their potential applications and electrochemical performance were also different than the work reported here. The list of support materials investigated in this work includes: (i) Vulcan® XC-72R (PC), (ii) TiO$_2$/ acid-treated Vulcan® XC-72R (ATV), and (iii) TiO$_2$/ glucose treated Vulcan® XC-72R (G-PV). The will also enable us to better understand how glucose modification influences the electrochemical performance and properties of these materials.

2. EXPERIMENTAL

2.1. Samples preparation

**Carbon Modification and TiO$_2$ Deposition**

The as received Vulcan XC72 carbon black (PV) from Cabot Corporation was subjected to two alternative treatments: (i) acid functionalization (ATV), and (ii) glucose doping (G). In the first case, carbon black was refluxed in 3 M HNO$_3$ solution at 120 °C for 3 hours and stirred to cool. The suspension was filtered and washed with distilled water until neutral pH conditions, after which the sample was dried in a vacuum oven at 80 °C. Glucose doping on acid treated and pristine carbon was carried out in a solution of glucose in an ethanol/water mixture (80 wt% ethanol) in an ultrasonic bath for 120 minutes at room temperature. The carbon/glucose products were filtered and washed with the same ethanol/water solution to remove any excess of glucose. The solids were dried in a vacuum oven overnight at 60 °C.

ATV and G-PV samples were suspended in isopropanol and sonicated for 2 hours before the addition of 2 mL of 0.2 M titanium tetraisopropoxide (TTIP) diluted in isopropanol under vigorous stirring. The mixture was refluxed at 110 °C under constant stirring for three hours before the drop-wise addition of 200 µL water, after which refluxing was continued for an additional 5 hours. The solution was left to stand with continuous stirring for four days and the resultant gel was washed with deionized water. The solid products were dried in a vacuum oven at 80 °C and then annealed at 500 °C in a nitrogen atmosphere for 2 hours to promote TiO$_2$ crystallization.

**Deposition of Platinum Nanoparticles**

Briefly, a mass of modified carbon (TiO$_2$/ATV or TiO$_2$/G-PV) was suspended in deionized water at room temperature and subjected to sonication for 20 min before the addition of H$_2$PtCl$_6$. After 3 hours of stirring, the temperature was lowered to 0 °C and the reducing agent, NaBH$_4$, added. The reduction was allowed to proceed for 6 hours; the solid products were filtered, washed with distilled water and dried at 80 °C overnight. The composite catalysts are henceforth denoted as Pt/xx wt% TiO$_2$/G-PV for the glucose doped carbon substrate and Pt/xx wt% TiO$_2$/ATV for acid-treated carbon without glucose. For comparison, Pt nanoparticles were also deposited on ATV to form Pt/ ATV.

**Working Electrodes Preparation**

A glassy carbon electrode (0.196 cm$^2$) was used to support the catalyst films for the oxygen reduction reaction studies. The catalyst inks were prepared by adding 5 mg of catalyst in a solution containing, 100 µL of a 5% Nafion® solution and 400 µL of an isopropyl alcohol/deionized water (50:50 V/V) mixture. The catalyst ink was put in an ultrasonic bath for 30 min, and 5 µL of ink was deposited onto the glassy carbon surface and dried for 5 minutes. The average catalyst loading was 0.05 mg/cm$^2$ with 30 wt% Nafion loading. Between studies, the electrode was polished with alumina (0.05 µm) and rinsed with deionized water. The electrode was then placed in an ultrasonic bath for 5 min and rinsed again with deionized water and dried in air.

2.2. Characterization Methods

The composition of the samples was determined by thermogravimetric analysis (TGA) using a Q600 SDT Thermal Analyzer from TA Instruments controlled by Q Series software. The experimental runs were carried out with ~ 10 to 15 mg of sample in alumina pans under air (Praxair A10.0XD-T 99.99%) or argon (AR 5.00-H-T 99.999% Praxair) at a gas flow rate of 50 mL min$^{-1}$ and a heating rate of 20 °C min$^{-1}$. The phases present were identified from X-ray diffraction data obtained with a Rigaku Ultima IV X-ray diffractometer equipped with a graphite monochromator, k-β filter, and a Cu Ka 0.154 nm X-ray source. For these studies, samples were scanned from 10 to 85 2θ angles with a step size of 0.02 °. Surface area determination studies were carried out by nitrogen adsorption measurements using the Brunauer, Emmett and Teller (BET) equation with a Quantachrome NOVA 1200e BET analyzer. For this determination, ~ 100 mg of sample was degassed under nitrogen flow at 300 °C for a minimum of 2 hours prior to the actual measurement.
2.3. Electrochemical Studies

The electrochemical measurements were performed in 0.5 M H$_2$SO$_4$ at room temperature using a three-electrode cell with an Ag/AgCl/0.1M KCl reference electrode [0.197V vs. NHE] and a Pt counter electrode. The working electrode was a glassy carbon disc electrode (0.196 cm$^2$) that it was used to support the catalyst films. All the potentials were converted to the normal hydrogen electrode (NHE) scale for comparison with other studies.

The ORR activity for each sample was investigated using a rotating disc electrode (RDE) system from Pine Research Instrumentation in combination with a Gamry Reference 600 potentiostat. For these studies, the electrolyte was saturated with oxygen for 15 minutes, and the potential was swept from 1.0 to 0.3 V at a scan rate of 5 mV s$^{-1}$ at various rotation rates between 400 and 1600 rpm. The reported cyclic voltammograms were obtained under nitrogen at a sweep rate of 50 mV/s, including those used for the electrochemical surface area (ECSA) determination. The catalyst stability was investigated using a protocol that involved cycling the potential for 4000 cycles from 0.05 V to 1.5V at a sweep rate of 50 mV/s and using the ECSA as an indication of catalyst degradation.

3. RESULTS AND DISCUSSION

3.1. Materials Characterization Studies

Due to the hydrophobic nature of PV carbon, acid pre-treatment is usually required to improve the wetting condition for platinum deposition; however, the introduction of functional groups on carbon reduces its inherent inertness, and carbon corrosion can be induced under oxidizing and acidic conditions like those found in the cathode compartment in fuel cells (Guha et al., 2007 and Calvillo et al., 2009). Non-carbon supports, such as TiO$_2$, have the potential to eliminate the problem because of their more hydrophilic character and chemical stability, but transitions metals oxides are semiconductors and their performance for fuel cells applications is far from optimal (Ioroi et al., 2005). In this study, “TiO$_2$ coated carbon” was prepared in an attempt to combine the properties of both materials using a novel synthetic approach that uses glucose as a seed for the deposition of TiO$_2$ on carbon without the need of acid treatment. The content of Pt and TiO$_2$ on the composite samples was determined from the residual mass after combustion in air at temperatures over 600$^\circ$C, (Eastcott et al., 2012). Typical TGA/DSC results for glucose, PV, and G-PV are summarized in Figure 1. As shown, the onset temperatures for the decomposition of PV, 630$^\circ$C, is significantly higher than that for glucose, 240$^\circ$C, allowing the determination of glucose loading on carbon.

Similarly, the TiO$_2$-to-carbon ratio, as well as the Pt content can be obtained from TGA experiments in air. Figure 2 shows the TGA and DSC data for G-PV and TiO$_2$/G-PV, after annealing in nitrogen at 500$^\circ$C for 2 hours, before and after the decoration with Pt nanoparticles. TiO$_2$ and Pt catalyzed the decomposition of carbon (520$^\circ$C) with onset temperatures of 350$^\circ$C and 490$^\circ$C, respectively. However this does not have impact on the residual masses of TiO$_2$ and Pt/TiO$_2$. Composition of each sample is summarized in Table 1.

Figure 3 summarized the BET surface areas determined for several modified carbon samples. Acid treated Vulcan (ATV) showed a modest increase in surface area (~ 7 %) over the untreated sample (PV), that it is subsequently reduced by the adsorption and pyrolysis products of glucose (G-ATV). This is consistent with the changes observed in the case of pristine carbon (PV vs G-PV). The deposition of TiO$_2$ on ATV and G-PV carbon has a very different impact on the substrate overall area, that we can only attribute to the presence of pyrolysis products in the case of the G-PV sample. A larger area is beneficial if the material will be used as support for the deposition of Pt nanoparticles.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Weight % of TiO$_2$</th>
<th>Weight % of Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/ ATV</td>
<td>---</td>
<td>24.5</td>
</tr>
<tr>
<td>Pt/14% TiO$_2$/ATV</td>
<td>13.5</td>
<td>20.5</td>
</tr>
<tr>
<td>Pt/14% TiO$_2$/G-PV</td>
<td>13.5</td>
<td>16.5</td>
</tr>
</tbody>
</table>
Figure 1: The (a) TGA and (b) DSC curves obtained under argon for Glucose (G), Pristine Vulcan (PV) and Glucose doped pristine Vulcan (G-PV). Experimental conditions: average sample mass: 10 mg, gas flow rate: 50 mL/min and heating rate of 20 °C/min.

Figure 2: The (a) TGA and (b) DSC curves obtained under air for G-PV and Pt/G-PV. The (c) TGA and (b) DSC curves obtained under air for TiO$_2$/G-PV, and Pt/TiO$_2$/G-PV. Experimental conditions: average sample mass: 10 mg, gas flow rate: 50 mL/min, and heating rate 20 °C/min.
The X-ray diffraction patterns obtained for TiO$_2$/ATV and TiO$_2$/G-PV samples are presented in Figure 4. The diffraction lines for anatase and rutile are clearly visible despite the large amount of carbon and the broadening of the TiO$_2$ bands due to the small particles size ~ 5 nm for the ATV sample. The formation of rutile is rarely observed at 500 °C, but at this point it is not clear if it is due to the heat treatment or the presence of glucose.

The diffraction patterns for the Pt/ ATV, Pt/14 wt% TiO$_2$/ATV, and Pt/14 wt% TiO$_2$/G-PV catalysts do not show any significant differences. The average particle size of the Pt nanoparticles was determined from the broadening of the Pt (111) peak using the Debye–Scherrer equation was ~ 4 to 5 nm.

Figure 4: XRD patterns: (a) 14 wt% TiO$_2$/ATV and 14 wt% TiO$_2$/G-PV (b) Pt/ ATV, Pt/14 wt% TiO$_2$/ATV and Pt/ 14 wt%TiO$_2$/G-PV.
3.2. Electrochemical Studies

In an attempt to understand the impact of glucose (if any) on the activity and stability of Pt on this substrate, different electrochemical measurements were carried out to determine: the Pt specific surface area (m²/g Pt), the onset potential for the oxygen reduction reaction (ORR) along with the mechanism of the reaction, and the kinetic current at 0.65 V normalized by mass of platinum.

3.2.1. Oxygen Reduction Reaction

Figure 5 shows typical current vs. potential curves for ORR using two different Pt/substrate samples at various rotation speeds (400 to 2500 rpm). Kinetic current densities ($i_k$) and the number of electrodes involves in the ORR for each catalyst were determined using the Koutecky-Levich equation (Bard et al., 2001):

$$\frac{1}{i_d} = \frac{1}{i_k} + \frac{1}{i_{dl}}$$

(1)

where $i_d$ is the diffusion limited current density, which is given by:

$$i_{dl} = 0.62 \, n \, F \, D_{O_2}^{2/3} \, \nu^{-1/6} \, [O_2] \, \omega^{1/2}$$

(2)

$n$ is the number of electrons, $F$ is Faraday’s constant, $[O_2]$ is the concentration of dissolved oxygen (4.59x10⁻⁴ mol.L⁻¹) (Wang et al., 2011), $D_{O_2}$ is the diffusion coefficient of oxygen (2.20 x 10⁻⁵ cm²/s) (Bard et al., 2001), $\nu$ is the kinematic viscosity of 0.5M H₂SO₄ at 25 °C (0.891 x 10⁻⁵ cm²/s) (Gasteiger et al., 1995) and $\omega$ is the electrode rotation rate.

Kinetic currents and onset potentials for the ORR on Pt deposited on three different substrates: ATV, 14wt% TiO₂/ATV, 14 wt% TiO₂/G-PV at 0.65 V are compared in Table 2. From these results, it is clear that the presence of glucose has a beneficial overall positive impact on the activity of Pt that it can be associated with the presence of glucose pyrolysis products between carbon and the metal oxide film as it was observed in the case of hollow Pt/TiO₂-c nanotubes (Huang et al., 2012).

Table 2. Summary of electrocatalytic activity and stability

<table>
<thead>
<tr>
<th>Samples</th>
<th>BOL ECSA (m²/g Pt)</th>
<th>EOL ECSA (m²/g Pt)</th>
<th>Onset Potential for ORR (V)</th>
<th>$i_k^*$ (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/ ATV</td>
<td>37.5</td>
<td>0.6</td>
<td>0.89</td>
<td>14.7</td>
</tr>
<tr>
<td>Pt/14% TiO₂/ATV</td>
<td>15.6</td>
<td>3.7</td>
<td>0.92</td>
<td>14.2</td>
</tr>
<tr>
<td>Pt/14% TiO₂/G-PV</td>
<td>46.2</td>
<td>7.6</td>
<td>0.94</td>
<td>16.1</td>
</tr>
</tbody>
</table>

*i_k based on electrode geometric area (0.196 cm²)

3.2.2. Electrochemical Active Surface Area

The electrochemical active surface area (ECSA) of Pt on different substrates was determined from cyclic voltammograms (CVs) in nitrogen-purged 0.5 M H₂SO₄ solution (Fig.6). All samples show well-defined hydrogen adsorption/desorption peaks, but the double layer capacitance and the carbon peaks due to the quinone-hydroquinone reaction (0.4 – 0.8 V) that are very visible in the case of Pt deposited on carbon are significantly reduced in the case of carbon coated with TiO₂ nanoparticles (Pt/14 wt% TiO₂/ATV and Pt/14 wt% TiO₂/G-PV).
Figure 5: ORR curves: for different rotation speeds (400-2500RPM) at a scan rate of 5 mV/s for prepared catalysts (a) Pt/14 wt% TiO\textsubscript{2}/ATV (b) Pt/14 wt% TiO\textsubscript{2}/G-PV (c) Koutecky-Levich plots at 0.65V vs. NHE. Measurements were carried out in O\textsubscript{2}-saturated 0.5M H\textsubscript{2}SO\textsubscript{4} at 25 °C. Current density based on the electrode geometric area (0.196cm\textsuperscript{2}).

The ECSA of Pt at the beginning-of-life (BOL) and after 4000 potential cycles (0 - 1.5 V vs. NHE) in nitrogen-purged 0.5 M H\textsubscript{2}SO\textsubscript{4} were determined by integrating the area of the hydrogen adsorption /desorption region after correction for double layer capacitance and assuming a monolayer coverage of hydrogen atoms on polycrystalline Pt has a standard charge density of 210 µC/cm\textsuperscript{2}. The results are summarized in Fig. 6. As shown, the BOL-ESCA of Pt on TiO\textsubscript{2}/glucose doped carbon with up to 14% TiO\textsubscript{2} content (Pt/14 wt% TiO\textsubscript{2}/G-PV) is significantly higher than that for Pt/14wt%TiO\textsubscript{2}/ATV in good agreement with the kinetic studies in O\textsubscript{2} saturated solutions and the formation of a conductive carbon layer between TiO\textsubscript{2} and Vulcan carbon. Perhaps more attractive, the BOL-ESCA of Pt/14 wt% TiO\textsubscript{2}/G-PV is also greater than that for Pt/ATV.

The significant reduction of the hydrogen adsorption and desorption area upon cycling the potential for all the catalysts studied (Fig. 5) is an aspect that needs improvement, but the observed trend is an indication that the presence of TiO\textsubscript{2} could prevent Pt agglomeration.

4. CONCLUSIONS

In this study, we have developed a method based on the use of glucose as molecular seed for the deposition of TiO\textsubscript{2} nanoparticles on carbon substrates. The introduction of –OH functional groups on the surface of carbon eliminates the need for acid treatment functionalization prior the deposition of platinum. For comparison, glucose doped (G-PV) and acid treated (ATV) Vulcan XC-72R carbon were coated with TiO\textsubscript{2} and used as substrates for the preparation of Pt/TiO\textsubscript{2}/Vulcan carbon composites. The catalysts’ performance on
these materials was evaluated using cyclic voltammetry and rotating disc electrode experiments in 0.5 M H₂SO₄ with and without dissolved oxygen.

Kinetic analysis of the composite catalysts towards ORR shows a more preferable 4-electron transfer process. The beginning of life-electrochemical active surface area (BOL-ESCA) of Pt on TiO₂/Vulcan glucose doped Vulcan® carbon (Pt/TiO₂/G-PV) with 14% TiO₂, 46.2 m²/g, was significantly higher than that of the two reference samples prepared with acid-treated carbon, Pt/ATV (37.5 m²/g) and Pt/13.5 wt% TiO₂/ATV (18.8 m²/g). The higher ECSA values for glucose doped samples can be attributed to a mutual electronic interaction of the Pt nanoparticles on these supports as well as to minimal TiO₂ segregation with better catalyst dispersion. The stability of the catalysts was evaluated by potential cycling in acidic medium. The ECSA decreased from 37.6 to 0.6 m²/g for Pt/ ATV, from 15.6 to 3.7 m²/g for Pt/14 wt% TiO₂/ATV, and from 46.2 to 7.6 m²/g for Pt/14 wt%TiO₂/G-PV. This result shows that the composite catalysts are more stable compared with Pt/ ATV catalysts.

**Figure 6:** Half-cell CVs of (a) Pt/ ATV (b) Pt/ 14 wt% TiO₂/ ATV (c) Pt/ 14 wt% TiO₂/ G-PV catalysts under aging conditions in argon-saturated 0.5M H₂SO₄ solution at a scan rate of 50 mV/s test temperature: 25 °C for 4000 potential cycles. Pt loading 0.05 ± 0.01 mg/cm² and 30 wt% Nafion loading.
5. ACKNOWLEDGEMENTS

This work was supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada through the Discovery Grants program and the Faculty of Science at the University Of Ontario Institute Of Technology.

6. REFERENCES