Durability and degradation mechanism of titanium nitride based electrocatalysts for PEM (proton exchange membrane) fuel cell applications

Bharat Avasarala*, Pradeep Haldar

College of Nanoscale Science & Engineering, University at Albany, State University of New York, Albany, NY 12203, United States

A R T I C L E   I N F O

Article history:
Received 20 November 2012
Received in revised form 11 May 2013
Accepted 18 May 2013
Available online xxx

Keywords:
Pt/TiN
Electrocatalyst
TiN
PEM fuel cells
Catalyst support corrosion
XPS

A B S T R A C T

Titanium nitride (TiN) is a promising material that has a higher potential for increasing electrocatalyst durability in PEM (proton exchange membrane) fuel cells. In this report we provide an explanation for the higher catalytic performance of titanium nitride nanoparticles (TiN NP) based electrocatalyst (Pt/TiN) when compared to that of Pt/C, using XPS (X-ray photoelectron spectroscopy). We also compare its durability with that of the conventional Pt/C electrocatalyst and explain its degradation mechanism under fuel cell conditions. Unlike Pt/C which degrades significantly via the Pt agglomeration and carbon support corrosion mechanisms, we show that Pt/TiN degrades predominantly via Pt agglomeration mechanism. TiN has a higher resistance to corrosion than carbon (C) under electrochemical conditions; as a result catalyst support corrosion mechanism plays a minor role in the degradation of Pt/TiN. For a given mass and particle diameter, TiN has higher no. of catalyst support particles than C due its higher material density. As a result it is hypothesized that, for the same amount of catalyst loading on both supports, the Pt/TiN has a higher Pt particle density on its surface compared to Pt/C and can result in a faster rate of Pt particle agglomeration during the electrocatalyst degradation. This hypothesis is tested theoretically by calculating the support to catalyst particle ratio. It is observed that the support to catalyst particle ratio is 1:21 for 20 wt% Pt/C and 1:60 for 20 wt% Pt/TiN. The hypothesis is also tested experimentally by two different methods, the first of which is by measuring and comparing the Pt particle sizes after subjecting the Pt/TiN and Pt/C to accelerated durability tests (ADT: 0–1.3 V RHE (reversible hydrogen electrode), 1100 cyc). Secondly, the Pt particle density on the electrocatalysts is changed by varying the amount of Pt loading (10 wt% and 30 wt%) and the Pt particle size is measured at the end of ADT. Both methods lead to the same conclusion that Pt/TiN has a significantly higher Pt particle size at the end of ADT (compared to Pt/C) indicating towards its increased rate of Pt agglomeration mechanism. Furthermore, a new approach is suggested where the oxynitride layer is grown on Pt/TiN resulting in partial encapsulation of Pt particles on the surface of TiN catalyst support thereby reducing the Pt agglomeration during fuel cell operation.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

In the past decade, proton exchange membrane (PEM) fuel cell technology has made significant strides towards commercialization but its durability needs considerable improvement for the technology to compete against the conventional energy sources [1–4]. Longevity of a PEM fuel cell is mainly dependent on the durability of its components material [5], especially the electrocatalysts, which degrade under the corrosive operating conditions of the fuel cell [6]. Currently, Pt nanoparticles (Pt NP) and Vulcan XC-72 carbon black (C) are the state-of-the-art catalyst and catalyst support materials respectively; but the durability of Pt/C electrocatalyst, during extended operation and repeated cycling (e.g., automotive applications) [7], needs significant improvement [8,9].

Carbon support (of Pt/C) undergoes electrochemical oxidation under fuel cell conditions forming surface oxides and CO/CO$_2$ [10–12]; with potential cycling significantly enhancing these effects [8]. Carbon corrosion leads to extreme loss of fuel cell performance [12,13] as observed through the kinetic, mass transportation and ohmic losses. The kinetic losses arise due to the loss of catalyst sites, mass transportation losses as a result of adsorption of $–OH$ groups...
by surface oxides on carbon and ohmic losses from poor contact between carbon particles in the electrode.

Although alternative carbon and non-carbon based catalyst support materials have been proposed [14–20], many of these novel materials trade-off between a relative improvement in its catalytic performance and durability. Through our research, we introduced titanium nitride nanoparticles (TiN NP) as an alternative catalyst support material and showed that the synthesized Pt/TiN electrocatalyst has higher catalytic performance relative to conventional Pt/C (catalytic performance plots Figs. A1–A2 and Tables A1–A2 are shown in Appendix) [21]. Titanium nitride, with its inert nature [22], higher electrical conductivity (relatively to carbon) [23, 24] and resistance to oxidation [23, 25–27], is a suitable catalyst support material for developing durable electrocatalysts without compromising on its catalytic performance.

After the synthesis and development of Pt/TiN electrocatalyst and evaluating its catalytic performance, our group focused on studying the physical, chemical and electrochemical behavior of TiN NP as an electrode material. We reported [24, 28] that TiN NP has a non-uniformly distributed native oxide/oxynitride layer on its surface, which is basic in nature. The oxide/oxynitride layer on TiN NP gets dissolved in the acidic fuel cell electrolyte exposing the nitride surface beneath. The oxide component of the native layer dissolves immediately while the oxynitride component undergoes dissolution over a period of time. Further, we showed that TiN NP displays active or passive nature depending on temperature and acidic concentration of the electrolyte used in fuel cell testing conditions. When the electrochemical conditions are passive, the surface of TiN NP will be covered by –OH groups in the solution leading to its poor electrical conductivity. But under conditions where TiN NP is active, surface passivation does not occur and the TiN NP catalyst support displays its naturally high electrical conductivity and low corrosion rate [24]. We showed [24, 28] that the electrochemical conditions under which TiN NP is active in nature fall within the range of the PEM fuel cell operating conditions.

Since the temperature affects the active or passive behavior of the TiN NP, the durability of the Pt/TiN electrocatalyst (synthesized using TiN NP) is invariably affected. In our previous report [24], we studied the durability of Pt/TiN electrocatalyst at various fuel cell temperatures and directly correlated it to the open circuit potential (OCP) of the TiN NP catalyst support. As the temperature of the acidic electrolyte increases, the ionic strength of the acidic solution increases thus causing a faster dissolution of oxynitride layer on the surface of TiN NP and exposing the nitride surface. The faster dissolution of the oxynitride layer on TiN NP leads to a rapid drop of its OCP and the subsequent formation of the Ti(OH)₂⁺ groups on its surface. This hydroxide layer prevents the TiN NP supports (of Pt/TiN electrocatalyst) to conduct electrons from Pt catalyst particles resulting in near zero electro-chemical surface area or ECSA. Thus, the ECSA of the Pt/TiN electrocatalyst operating in such an electrolyte undergoes rapid decline in a very short time and continues to plateau near zero for the remaining duration. Similarly, when the TiN NP is subjected to OCP in an acidic electrolyte at lower temperatures, the dissolution of the oxynitride layer takes significantly longer time. Hence, the process of the –OH groups forming on the surface of TiN NP occurs slowly. The ECSA of the Pt/TiN electrocatalyst operating in such an electrolyte undergoes gradual decline over a relatively longer period of time (Fig. 8 & 10 in Ref. [24]). In a follow up report [28] on the stability of Pt/TiN electrocatalyst in acidic media, we showed that the TiN NP catalyst supports show “active” nature in sulfuric acid media at higher temperatures (as high as 60 °C) showing a low dissolution rate with no passivation. Pt/TiN electrocatalyst, when subjected to ADT in sulfuric acid media at 60 °C agreed well with the proposed active/passive behavior of the TiN NP under the electrochemical conditions.

To summarize our related prior research work, we have studied the physical, chemical and electrochemical properties of TiN NP as an electrode and catalyst support material. Upon synthesizing Pt/TiN electrocatalyst, we showed that it has a higher catalytic performance when compared with that of Pt/C. We reported that the durability of Pt/TiN is dependent on the active/passive nature of the TiN NP catalyst supports, which varies based on the acid media and temperature. In this paper, we study the surface composition of Pt/TiN electrocatalyst using XPS (X-ray photoelectron spectroscopy) characterization and explain the reasoning behind its higher catalytic performance. Through theoretical calculations, we reveal that the Pt/TiN has a higher catalyst to support particle ratio than that of Pt/C. These explanations acts as a precursor that will lead the discussion to the main focus of this paper—investigation of the degradation mechanism of Pt/TiN electrocatalyst and its durability comparison with conventional Pt/C electrocatalyst under extreme fuel cell operating conditions.

2. Experimental section

2.1. Materials

TiN NP (NanoAmor Inc, USA) used as catalyst supports have an average particle size (APS) of 20 nm and a specific surface area (SSA) of 40–55 m² g⁻¹ [24, 29]. For synthesizing Pt/TiN electrocatalyst [21], TiN NP is mixed in ethylene glycol and ultrasonically treated before adding H₂PtCl₆·6H₂O drop wise. Sodium hydroxide is added to control the size of Pt nanoparticles by adjusting the pH of the solution (~12). The solution is stirred well before heating at 160 °C for 3 h in a N₂ atmosphere under refluxing conditions and upon cooling down, it is washed, filtered and dried in air at 80 °C for 4 h. The resulting electrocatalyst has a Pt APS of 2.4 nm, as measured using X-ray diffraction (XRD) and transmission electron microscopy (TEM) [24].

2.2. Half-cell performance and characterization of electrocatalysts

Electrochemical tests were performed in a standard 3-electrode cell set up with a PARSTAT 2273 potentiostat (Princeton Applied Research, USA). A reversible hydrogen electrode (RHE) (Gaskatel GmbBH, Germany) is used as a reference electrode with a Pt mesh acting as a counter electrode. Half-cell performance of electrocatalyst is measured by the ECSA using the CV technique. The electrocatalyst dispersions are prepared by ultrasonically mixing the Pt/TiN in ethanol and pipetting an aliquot of the dispersion onto the glassy carbon electrode (GCE) for a catalyst loading of 20 mµg/cm². After drying, a drop of aqueous Nafion (5 wt%) solution is pipetted onto the electrode surface in order to attach the catalyst particles onto the electrode surface. The electrocatalyst deposited GCE is immersed in 0.5 M H₂SO₄ (at 60 °C) and scanned between 0 and 1.2 V at 50 mV s⁻¹. ECSA is calculated from the area under the hydrogen adsorption and desorption peaks of CV curves after double-layer correction. For the accelerated durability test (ADT), the electrocatalyst deposited GCE is cycled between 0 and −1.3 V RHE at 50 mV s⁻¹ for 12 h (or 1100 cycles) in 0.5 M H₂SO₄ at 60 °C. Open circuit potential (OCP) of the catalyst support materials (TiN NP and C) is measured by depositing the powders on the GCE and inserting the electrode in 0.5 M H₂SO₄ at 60 °C.

The Pt particle size is measured before and after the electrochemical treatment by performing a two-theta X-ray diffraction scan using XDS 2000 (Scintag Inc., USA) on the electrocatalyst coated Toray carbon paper electrode (wavelength of X-rays from Cu source is 1.54 Å). X-ray photoelectron spectroscopy (XPS) analysis was performed using a ThermoFisher Theta Probe system which has a 2-dimensional detector, a hemispherical analyzer and a
monochromator and all XPS data presented here are acquired using the source Al Kα X-rays (1486.6 eV) operated at 100 W. The XPS spectra were background subtracted using the non-linear, Shirley method. The binding energies of the Pt 4f were calibrated with respect to C 1s peak at 284.6 eV.

3. Results and discussion

3.1. Titanium nitride as electrocatalyst material

Due to its thermodynamic properties, TiN NP undergoes atmospheric oxidation when exposed to air, resulting in the formation of a non-uniform oxide/oxynitride layer that partially covers its surface. This native surface layer also prevents any further diffusion of oxygen in to the bulk of titanium nitride. Due to their basic nature, the native oxide/oxynitride components of TiN NP dissolve in the acidic electrolytes [24,28].

The native layer on TiN NP is a combination of TiO, TiOxNy phases, with no complete phase separation to TiO2 [24,28]. Between the two components—oxide and oxynitride, the former largely exists in a sub-stoichiometric composition (TiOxNy) of Magneli phase, which shows electrical conductivity [17]. The oxynitride component is also electrically conductive due to its NaCl fcc crystal structure (similar to TiN’s fcc structure) and due to the significant presence of nitrogen in its lattice [30]. It has been reported [31] that titanium oxynitride thin films with low oxygen content (<40 at. %) are partly metallic. In case of TiN NP used in our research, the total surface oxygen composition measured using XPS was found to be 35–40 at. % [28]; therefore the oxygen composition in the oxynitride layer will be a fraction of the above value. Thus, based on our XPS study of TiN NP [28] and the scientific literature on TiN [17,30,31], it can be interpreted that the native layer does not act as an insulator on the surface of TiN NP.

The synthesized Pt/TiN electrocatalyst has an oxide/oxynitride layer on the surface of its TiN NP catalyst supports. But, as interpreted above, the initial cycles of the CV and ORR tests on Pt/TiN (presented in Appendix) showed no indication of ohmic resistance due to the presence of native layer on TiN NP. In fact, 20 wt% Pt/TiN showed higher ECSA and catalytic activity compared to the 20 wt% BASF Pt/C [21]. Thus, we can reasonably conclude that the conductive nature of the native layer components of TiN NP and the dissolution of oxide/oxynitride in the acidic electrolytes have minimum contribution towards the inhibition of electron transport at the TiN NP surface during initial cycles.

3.2. Pt/C vs. Pt/TiN: a spectroscopic comparison

To understand the surface chemical composition of 20 wt% Pt/TiN and Pt/C electrocatalysts, XPS is employed. The spectroscopic surface characterization technique allows one to understand the elemental and binding energy differences between the two electrocatalysts. Fig. 1 shows the survey scan spectra of the electrocatalysts with their dominant signals of Pt 4f, Ti 2p, N 1s, O 1s, and C 1s. Based on the spectral survey scan, the atomic concentrations (in at %) of the elements of both electrocatalysts are calculated and presented in the inset of Fig. 1(a) and (b).

The composition of Pt in both electrocatalysts is lower than the intended 20 wt % loading due to the fact that not all Pt is readily available on the surface of the electrocatalyst under the scanning area of the beam during XPS characterization. One can observe a 3.4 at. % of oxygen on Pt/C in Fig. 1(a), which is likely due to surface contamination of C and/or the Pt oxides/oxynitrides [32–34]. In case of Pt/TiN, the high presence of oxygen is mainly due to the native layer of TiN NP [24,28] and not because of the Pt oxides/oxynitrides in the electrocatalyst, as seen in the later sections. The C composition (~10 at. %) on the surface of Pt/TiN is the organic residue resulting from the oxidation of ethylene glycol in polyol process. Usually the surface carbon contamination is not a major issue as it gets dissolved when the Pt/TiN is washed in copious amounts of DI water (at 80 °C) after the synthesis is completed. Additionally, before any measurement, the electrocatalyst coated GCE is scanned between 0.6 and 1.4 V RHE at 100 mV s⁻¹ for multiple cycles to oxidize any surface carbon contamination on the catalyst particles.

In the inset of Fig. 1(b) one can see a higher at. % of Pt on TiN than on C catalyst supports; suggesting that an increased amount of catalyst is present on the surface of Pt/TiN that is readily accessible to reactants. To further understand the functional groups associated with Pt, the Pt 4f spectra of 20 wt% Pt/C and 20 wt% Pt/TiN are deconvoluted and shown in Fig. 2(a) and (b) respectively. According to Alderucci et al. [35], there are 2 or 3 pairs of Pt peaks in typical Pt 4f/XPS spectra of Pt metal. The most intense one, located around the binding energy (BE) values of ~71 and ~74 eV, are due to metallic platinum—Pt 4f7/2 and Pt 4f5/2, and their peak positions are affected by the interactions between Pt and the catalyst support [35]. The second and third pairs of Pt
The Pt 4f XPS signals appear around 1.5–2.8 eV and 3.4–4.3 eV, respectively, higher than that for metallic Pt [35].

The XPS analysis of Pt 4f in 20 wt% Pt/C revealed all 3 pairs of Pt peaks, as can be seen in Fig. 2(a), indicating that there is more than one chemical environment on the surface of Pt/C. The B.E. of Pt 4f7/2 at 71.9 eV agrees well with the published value of Pt metal at 71.1 eV [36,37] or 71.2 eV [32]. The second pair of Pt signals of Pt/C appears around 1.5–2.3 eV higher than that for metallic Pt, agreeing well with the values reported in literature [35,38]. The similarities, in the B.E values for the elements, with the literature suggest the appropriateness in which the XPS characterization is used for the analysis. The relative atomic percentage concentrations (rel. at. %) of various functional groups on Pt in Pt/C are presented in the Table 1 below. The Pt 4f signal of Pt/C contains metal platinum, Pt (0), of ~70 rel. at. % along with an appreciable contribution from higher B.E components—Pt (II) or PtO/Pt(OH)2 and Pt (IV) or PtO2xH2O/Pt(OH)4. Apart from the metallic Pt i.e. Pt (0), the remaining Pt (II) and Pt(IV) oxide species, constituting ~30 rel. at. %, are rendered inactive. Only ~70 rel. at. % of Pt is effectively available on Pt/C for oxidation and reduction of reactants.

In case of Pt 4f spectra of Pt/TiN (Fig. 2(b)), the B.E of Pt f7/2 is 71.9 eV, similar to that of Pt/C and well within the range to be identified as Pt (0). The relative atomic percentage concentrations (rel. at. %) of various functional groups of Pt in Pt/TiN are presented in the Table 2. Firstly, the Pt (0) in Pt/TiN constitutes 86 rel. at. %, a value significantly higher when compared to the ~70 rel. at. % of Pt (0) in Pt/C. Secondly, the non-catalyzing Pt (II) species in Pt/TiN are significantly lower (14.5 rel. at. %) when compared to the same in Pt/C (~23 rel. at. %). Thirdly, the Pt (IV) species, which can further render the Pt catalyst inactive [34], are completely absent in Pt/TiN but constitute ~7 rel. at. % in Pt/C. Finally, the full-width-at-half-maximum (FWHM) of Pt (0) peak in Pt 4f7/2 of Pt/TiN is higher and that of Pt (II) peak is lower when compared to that of Pt/C, indicating the increased coverage of metallic Pt and lower surface coverage of oxides on the surface of Pt in Pt/TiN. Through the above points, it can be concluded that the higher catalytic activity of Pt/TiN over Pt/C [21] can be attributed to the higher amount of metallic Pt (0) sites and lower amount of inactive Pt (II) or Pt(IV) in Pt/TiN.

The behavior of Pt, in forming the Pt(II) and Pt(IV) species, may be described as a continuous transition from hydroxyl adsorption to bulk hydroxide formation [33]. Thus, a Pt oxide film growth reaction at all potentials may be written as [33]:

$$\text{Pt} + \text{H}_2\text{O} \rightarrow \text{PtOH} + \text{H}^+ + \text{e}^-$$

As the film thickness increases beyond 1 or 2 monolayers of hydroxide, a place exchange mechanism between metal atom and hydroxide anions at the metal/hydroxide interface may become rate determining [33]. Considering that the Pt of Pt/C has a higher composition of Pt(II) and Pt(IV) species on the surface, the formation of these species could be attributed to the reaction (1) based surface oxidation of Pt. The lower percentage of Pt(II) and the absence of Pt(IV) species on Pt/TiN indicates that TiN based catalyst support could be playing an important role in further limiting the rate-determining step of Pt oxidation.

Apart from the Pt peak positions in the XPS graphs, the peak shapes and the peak area-ratio can provide additional information on the oxidation states of Pt. According to Kim et al. [38], the peak area ratio of Pt 4f7/2 and Pt 4f5/2 of bulk Pt metal has a theoretical value of 1.33 while Delgas et al. [39] reported that a lower ratio (i.e. < 1.33) is an indicator of the presence of Pt-oxide on the surface. As seen in the Table 3, the peak area ratio of Pt in Pt/C is lower when compared to that of Pt/TiN, further supporting the argument that Pt/C has higher presence of oxides on its catalyst

---

**Table 1**

<table>
<thead>
<tr>
<th>XPS peak (Pt/C)</th>
<th>B.E (eV)</th>
<th>At. %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4f7/2</td>
<td>4f5/2</td>
</tr>
<tr>
<td>Pt(0)</td>
<td>71.9</td>
<td>75.0</td>
</tr>
<tr>
<td>Pt(II)</td>
<td>73.2</td>
<td>77.4</td>
</tr>
<tr>
<td>Pt(IV)</td>
<td>73.7</td>
<td>80.0</td>
</tr>
</tbody>
</table>

**Table 2**

<table>
<thead>
<tr>
<th>XPS peak (Pt/TiN)</th>
<th>B.E (eV)</th>
<th>At. %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4f7/2</td>
<td>4f5/2</td>
</tr>
<tr>
<td>Pt(0)</td>
<td>72.5</td>
<td>75.6</td>
</tr>
<tr>
<td>Pt(II)</td>
<td>73.8</td>
<td>77.7</td>
</tr>
</tbody>
</table>

**Table 3**

<table>
<thead>
<tr>
<th>Peak ratio</th>
<th>Pt 4f5/2:Pt 4f7/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>0.83</td>
</tr>
<tr>
<td>Pt/TiN</td>
<td>1.08</td>
</tr>
<tr>
<td>Theoretical value for bulk Pt (zero Pt-oxides)</td>
<td>1.33</td>
</tr>
</tbody>
</table>

---

Please cite this article in press as: Avasarala B, Haldar P, Durability and degradation mechanism of titanium nitride based electrocatalysts for PEM (proton exchange membrane) fuel cell applications, Energy (2013), http://dx.doi.org/10.1016/j.energy.2013.05.021
surface. Further research is required to understand the role of TiN support in minimizing the oxygen species on Pt catalyst.

3.3. Durability performance

3.3.1. Catalyst particle density

One of the fundamental differences between the catalyst support materials of titanium nitride and carbon is their material density—TiN (5.4 g cm$^{-3}$) vs. C (1.9 g cm$^{-3}$) [23]. For a given mass, density is inversely related to the volume of the material and in this case, the volume of each particle ($V_C$ or $V_{TiN}$) times the no. of nanoparticles ($N_C$ or $N_{TiN}$) for a constant mass. Assuming that both catalyst support particles have same particle diameter, then for an equal mass, TiN will have a lower no. of particles compared to C (i.e. $N_{TiN} < N_C$).

In synthesizing ‘x’ wt% electrocatalyst, an amount of precursor is added whose metal content, by weight, is ‘x’ percentage of the weight of catalyst supports. For synthesizing a 20 wt% electrocatalyst using 1 g of catalyst supports, a precursor containing 0.2 g of metal is added to the catalyst supports. In case of the synthesis of 20 wt% Pt/C or 20 wt% Pt/TiN, for a given mass of catalyst supports of TiN or C, the amount of Pt precursor added will be equal in both cases. This is because the Pt precursor amount will be dependent on the mass of the supports (20% of the mass of supports, in both cases) and not on the material type (C or TiN) or the no. of its particles ($N_C$ or $N_{TiN}$). As explained in previous paragraph, for the same mass of C and TiN catalyst supports, TiN has less no. of particles than that of C due to its higher material density i.e. $N_{TiN} < N_C$. When an equal amount of Pt precursor (20% of mass of supports) is added to both C and TiN supports, it will result in a less-dense precursor coating on C supports than on TiN supports. This is due to the fact that there are more C support particles and the Pt precursor coats a larger surface area (~250 m$^2$ g$^{-1}$) and spreads thin forming a less-dense coating. But TiN support particles are fewer in number and have a lower surface area (40–55 m$^2$ g$^{-1}$), hence Pt precursor has lesser surface area to cover thus forming a dense-coating on TiN supports. As Pt nucleation proceeds in the synthesis of Pt/TiN, Pt particles tend to occupy the limited surface area on TiN NP resulting in an increased Pt particle density. During the synthesis of Pt/C, the Pt particles occupy sites on carbon supports of wider surface area resulting in a lower Pt particle density. Based on the above understanding, theoretical calculations were performed to estimate the Pt particle density on both electrocatalysts.

3.3.2. Support: catalyst particle ratio

For convenience and ease of calculations, consider 1.2 g of 20 wt% Pt/C—implying 0.2 g of Pt and 1 g of C. Since density of a given material is its mass divided by its volume, density of carbon, 1.9 (g cm$^{-3}$) = 1 (g)/$V_C$ (cm$^{-3}$), which implies,

$$V_C = 1/1.9\ (\text{cm}^3)$$  

(2)

where $V_C$ = volume occupied by carbon supports in 1.2 g of 20 wt% Pt/C.

Let the carbon support particles be ‘$N_C$’ in number in 1.2 g of 20 wt% Pt/C (assuming spherical in shape),

$$N_C = [\text{Vol. of 1 gram of C}, \frac{V_C}{[\text{Vol. of a single C particle}]}$$  

(3)

The average diameter of one C particle: ~20 nm, which implies that the volume of a single C particle = 4180 nm$^3$. Substituting above value in equation (3), we get,

$$N_C = \frac{1}{1.9} \left(\frac{1}{4180}\right) = 2E12,$$  

(4)

which implies, there are 2E12 C particles in 1.2 g of 20 wt% Pt/C.

The amount of Pt present in 1.2 g of 20 wt% Pt/C is 0.2 g. Density of Pt, 21.45 (g cm$^{-3}$) = 0.2 g/(Pt$V_P$ cm$^3$, where $V_P$ = volume occupied by Pt particles in 1.2 g of 20 wt% Pt/C.

$$V_P = \frac{21.45 \text{ (g cm}^{-3})}{0.2 \text{ (g)}}$$  

(5)

Assuming there are ‘$n_{Pt}$’ spherical shaped Pt particles with diameter of 2 nm,

$$n_{Pt} = \frac{\text{Vol. of 0.2 g of Pt}}{\text{Vol. of a single Pt particle}}$$

$$n_{Pt} = \left(\frac{4\pi/3}{(2/2)^3}\right) = 4.29E13,$$  

(6)

which implies that there are 4.29E13 Pt particles on 1.2 g of 20 wt% Pt/C.

From (4) and (6), the ratio of C to Pt particles =

$$N_C/n_{Pt} = (2E12)/(4.29E13) = 1/21.45,$$  

which implies that there are ~21 Pt particles for every 1 C particle support.

Similarly, the support to catalyst ratio ($N_{TiN}/n_{Pt}$) for 20 wt% Pt/TiN is 1:61, which means that there are approximately 61 Pt particles on a single TiN NP support. These ratios show that there are ~3 times more Pt particles on TiN NP than on C for the same Pt loading thus supporting the reasoning of higher Pt particle density on TiN NP supports in Section 3.3.1. Further, the higher Pt particle density on Pt/TiN also explains the increased amount of A1 % of Pt on Pt/TiN, as seen in XPS plot of Fig. 1. The above calculations and comparison of Pt particle densities play a very important role in understanding the dominant degradation mechanisms of Pt/TiN when compared to Pt/C, as discussed in the next Section 3.3.3.

3.3.3. Electrocatalyst degradation mechanism

The degradation of a conventional Pt/C electrocatalyst has been reported to take place via the following three mechanisms—Pt agglomeration, Pt dissolution and catalyst support corrosion. Irrespective of the mechanistic pathway, the final outcome of the electrocatalyst degradation is the decline of fuel cell performance primarily due to the loss of electro-chemical surface area (ECSA) or the no. of active catalyst sites. Various studies have been reported in the recent years in identifying the contribution of each pathway to the electrocatalyst degradation [40,41]. Also, the influence of one mechanism over the other has also been reported where Pt catalyst influences the carbon support corrosion and at the same time, the corrosion of carbon leads to Pt agglomeration and/or the loss of Pt particles due to the mass loss of the support [14].

To compare the durability of the electrocatalysts in our case, the synthesized 20 wt% Pt/TiN and a commercially obtained BASF® 20 wt% Pt/C are subjected to accelerated durability test (ADT) under electrochemical conditions which are akin to the extreme fuel cell operating conditions. In Fig. 3, the ECSA trends of both the electrocatalysts at various stages of ADT can be observed. At a peripheral level, one can see that both electrocatalysts degrade in a similar manner, with a minor improvement in the durability of Pt/TiN. Now the question arises if the two electrocatalysts have similar degradation mechanisms.

As specified earlier, the degradation of the electrocatalysts can take place via—Pt dissolution, Pt agglomeration and catalyst support corrosion. The acidic electrolytes (in which the ADT is conducted for Pt/C and Pt/TiN), when tested for Pt presence using Inductively Coupled Plasma (ICP) trace analysis method (Adirondack Environmental Services, NY, USA), showed an insignificant <0.5 ppm value. This suggests that the Pt dissolution may not be the dominant degradation pathway for either of the
electrocatalysts under given conditions. In case of support corrosion mechanism, we have already shown that the TiN NP catalyst supports have a higher resistance to corrosion than carbon black under potential cycling conditions [24,28] such as used in ADT. Here, we compare the long term electrochemical stability of catalyst supports under open circuit potential (OCP) conditions. The OCP of C and TiN NP is tested using a RDE in a 3-electrode set-up under typical electrochemical conditions of a fuel cell and is shown in Fig. 4. As explained through our previous reports [24,28], the native oxide/oxynitride layer on TiN NP dissolves in the acidic electrolyte exposing the nitride surface. This dissolution is reflected in the Fig. 4 as an initial steep decline of the OCP. One can see that the later part of the OCP of TiN NP is quite stable with minimal changes despite the prolonged exposure. In the given acidic and temperature conditions, the exposed nitride surface does not get passivated with hydroxyl groups and shows minimal corrosion [28]. The other plot in Fig. 4 is the OCP of C, which declines continuously suggesting that the carbon undergoes corrosion when exposed to fuel cell conditions. As the exposure time proceeds, one can see an increase in the slope of declination of the OCP of C suggesting an increase in the rate of carbon corrosion with time.

From the Fig. 4, we reasoned that TiN NP has a stable nature in the tested conditions while C undergoes significant corrosion with time. Upon evaluating C and TiN under potential cycling [24] and OCP conditions, we concluded that, unlike C, catalyst support corrosion may not be the dominant degradation mechanism for Pt/TiN electrocatalyst. Hence, we hypothesized that Pt agglomeration or particle growth could be the dominant mechanism for Pt/TiN electrocatalyst degradation.

Researchers such as Borup et al. [1] suggested that the degradation of an electrocatalyst during potential cycling, such as in ADT is best described by a Pt agglomeration mechanism which is a combination of Pt particle coalescence and Pt dissolution/re-precipitation. To study the Pt agglomeration mechanism in our case, XRD technique is applied on both the electrocatalysts to measure the change in Pt particle sizes and the results are shown in Fig. 5. The Pt particle size for 20 wt% Pt/C increased from 2.7 to 5.6 nm—a 107% increase; while that of 20 wt% Pt/TiN changed from 2.3 (before ADT) to 7.9 nm (after ADT)—an increase of 243%. The significant increase of Pt particle size in Pt/TiN over that of Pt/C proves our hypothesis that Pt agglomeration is significantly higher for Pt particles on TiN NP and is the dominant pathway for Pt/TiN degradation.

To test our “Pt agglomeration” hypothesis, we proceeded with further experimentation. As discussed earlier (in Sec 3.3.1), Pt/TiN has a higher support to catalyst particle ratio (1:61) compared to that of Pt/C (1:20) for the similar particle dimensions and Pt loading. In case of Pt/C, the inter-particle distance between any two Pt particles is relatively higher due to its lower support to catalyst ratio. A higher support to catalyst particle ratio for Pt/TiN implies an increased Pt particle density with a lower particle-to-particle distance between any two Pt particles on the supports. The Pt particle density and particle to particle distance plays a significant role during the electrocatalyst degradation. When the Pt particles coalesce locally or migrate on the support's surface to form larger-sized agglomerates [1,40,42–50], a Pt particle on TiN NP support encounters more no. of Pt particles than a Pt particle on C support. This implies that, under same conditions and for the same duration, the Pt agglomeration mechanism causes an increased Pt particle size for Pt/TiN compared to Pt/C. This explanation supports the XRD results of Pt particle sizes after the ADT, where the Pt particle size of

Fig. 3. Accelerated durability test for 20 wt% Pt/TiN and 20 wt% Pt/C measured using RDE technique with electrocatalyst deposited on a glassy carbon electrode.

Fig. 4. Plot comparing the Open Circuit Potential or $E_{corr}$ of Vulcan XC-72 carbon black and titanium nitride nanoparticles in 0.5 M H$_2$SO$_4$ for 10 h at 60 °C.

Fig. 5. Pt particle size of electrocatalysts, measured before and after the accelerated durability test (ADT) using XRD.
20 wt% Pt/TiN increased from 2.3 to 7.9 nm while that of 20 wt% Pt/C changed from 2.7 to 5.6 nm. This explanation further adds weight to the initial hypothesis that the degradation of Pt/TiN electrocatalyst is predominantly via Pt agglomeration mechanism.

An interesting approach to test the above explanation is by varying the support to catalyst ratio i.e. by varying the inter-particle distance between Pt particles on the catalyst supports by changing the Pt loading (wt %) on electrocatalysts. A decrease in catalyst loading, from 20 to 10 wt %, will result in (1) a lower support to catalyst ratio, (2) lower Pt particle density and (3) an increase in distance between Pt particles on the catalyst supports. Similarly, applying the same logic, an increase in catalyst loading (from 20 to 30 wt %) leads to (1') a higher support to catalyst ratio, (2') an increase in Pt particle density and (3') a decrease in inter-particle distance between Pt particles on the catalyst supports. If Pt agglomeration were really the dominant degradation mechanism for Pt/TiN, altering the particle ratio should accordingly influence the Pt particle growth during Pt/TiN degradation.

Before proceeding to the synthesis of 10 wt% and 30 wt% electrocatalysts and subjecting them to ADT, a “thought experiment” is conducted to understand the Pt agglomeration possibilities with 10%, 20%, and 30% Pt catalyst loadings on TiN NPs. The support to catalyst ratio of 10 wt% Pt/TiN will be lower to that of 20 wt% Pt/TiN. Because of its higher inter-particle distance between any two Pt particles on 10 wt% Pt/TiN, a Pt particle migrating on TiN support surface will encounter relatively lower no. of other Pt particles (compared to 20 wt% Pt/TiN) to agglomerate during degradation. Hence, the post-ADT Pt particle size of the former will be smaller when compared to that of the latter. Similarly, the post-ADT particle size of 30 wt% Pt/TiN will be comparatively larger than that of 20 wt% Pt/TiN. This is because, a Pt particle on 30 wt% Pt/TiN encounters relatively higher no. of other Pt particles due to the lower inter-particle distance between Pt particles when compared to 20 wt% Pt/TiN. A Pt particle migrating on TiN support surface, of 30 wt% Pt/TiN, will encounter higher no. of Pt particles leading to a bigger Pt particle size post ADT. Thus, the post-ADT Pt particle sizes of the electrocatalysts will vary according to 30 wt% Pt/TiN > 20 wt% Pt/TiN > 10 wt% Pt/TiN. But, in general, the support to catalyst ratio of 10, 20 and 30 wt% Pt/C will always be lower to the corresponding 10, 20 and 30 wt% Pt/TiN. As a result, the post-ADT Pt particle size of Pt/C will always be lower than that of the corresponding wt% Pt/TiN.

To test if the thought experiment analysis is true, 10 wt% and 30 wt% Pt/TiN electrocatalysts are synthesized and the corresponding wt% Pt/C is purchased commercially. The Pt particle sizes of the electrocatalysts are pre-measured using XRD method and post-measured after subjecting them to ADT. Fig. 5 shows the Pt particle sizes of 10, 20 and 30 wt% Pt/C and Pt/TiN measured before and after ADT. It can be interpreted from Fig. 5 that the above mentioned possibilities ((1–3) and (1’–3’)) are true. The right-half of Fig. 5 represents Pt/TiN while the left-half represents Pt/C. Post ADT Pt particle sizes are always higher for all six electrocatalysts with different loadings suggesting that Pt agglomeration is a common degradation mechanism. As predicted in the last two paragraphs, one can see that the post-ADT Pt particle size of 20 wt% Pt/TiN is higher than that of 10 wt% Pt/TiN and lower to that of 30 wt% Pt/TiN. The same behavior is also observed in case of Pt/C. This shows that Pt loading influences the inter-particle distance, which in turn, influences the Pt agglomeration. Higher Pt wt% (such as 30 wt% Pt/C or Pt/TiN) leads to shorter inter-particle distance and therefore increased agglomeration during ADT. The lower wt% of Pt (10 wt% Pt/TiN or Pt/C) leads to larger inter-particle distance between Pt particles on a support, resulting in a smaller increase of Pt particle size post-ADT. The post-ADT Pt particle size of Pt/TiN not only increases with Pt loading but also the values are significantly higher when compared to the post-ADT Pt particle size of Pt/C. This further suggests that Pt/TiN has higher Pt particle density than that of Pt/C, for all Pt loadings. The theoretical calculations of the support to catalyst particle ratio are strongly supported by these experimental values. These results provide an accurate agreement to our analysis and support our hypothesis that Pt agglomeration is higher in case of Pt/TiN due to its higher Pt particle density compared to that of Pt/C and is the dominant degradation mechanism for Pt/TiN electrocatalysts.

Despite a higher Pt particle size after ADT, the Pt/TiN still shows higher durability when compared to Pt/C as can be seen in Fig. 6(a) and (b). This suggests that, in case of Pt/C, other mechanisms such as carbon support corrosion could be playing a significant role in its degradation. The variations in durability trends, between the electrocatalysts and their different loadings, is most likely due to the differences in synthesis techniques, variation in temperature and concentration of the electrolyte during the ADT, etc.

Our fundamental basis in choosing titanium nitride as a catalyst support material was mainly to address the durability issue faced by the electrocatalysts due to carbon corrosion. Although titanium nitride showed higher resistance to corrosion than carbon (under the fuel cell electrochemical conditions), the overall durability improvement of Pt/TiN over Pt/C is minor. The increased durability of Pt/TiN, gained from the catalyst support resistance to corrosion, is seen to be discounted to a certain extent by an increase in the rate of Pt agglomeration.
On a closer analysis of the catalyst support material and some clever techniques, the titanium nitride catalyst support can be engineered to limit the Pt agglomeration mechanism as well. It has been shown through our previous reports that the native layer on the surface of titanium nitride has an oxyinitride component which is inert and electrically conductive in nature. Unlike the oxide component which dissolves easily in the acidic electrolytes, oxyinitride shows stability for a longer period of time. A thin layer of oxyinitride can be grown on Pt/TiN electrocatalyst by annealing the material in nitrogen environment at controlled temperatures ranging between 70 and 120 °C. The oxyinitride layer grown on Pt/ TiN, can partially encapsulate the catalyst particles binding them onto the titanium nitride catalyst support surface thereby limiting the Pt particle mobility and agglomeration. Although the partial submersion of catalyst particles may result in relatively lower ECSA, the initial results of this nanoengineering approach showed significant stability and is shown in the Fig. A3 (of Appendix). Further research is required for optimizing the oxyinitride growth process and its effect on the electrocatalyst performance and durability. A similar approach has also been taken by Kakinuma et al. [51], where the Pt catalyst is supported on Sn0.96Sb0.04O2 with a network structure.

4. Conclusion

In this study, we conduct an in-depth analysis of the higher catalytic performance and durability of the novel Pt/TiN electrocatalysts, in comparison to the conventional Pt/C. We demonstrate that, unlike Pt/C, which undergoes degradation via carbon corrosion and Pt agglomeration mechanism, the Pt/TiN electrocatalyst degrades solely via surface agglomeration of Pt particles. Investigative results are summarized as follows:

1) The XPS Pt 4f spectra of Pt/TiN showed higher presence of metallic Pt(0) and lower at. % conc. of Pt(II)/Pt(IV) oxides when compared to Pt/C

2) The theoretical calculation of Pt particle density on catalyst supports shows that Pt/TiN has a higher support to Pt particle ratio when compared to that of Pt/C, for the same catalyst loading and particle sizes.

3) Supporting our earlier research, the Open Circuit Potential of TiN shows higher corrosion resistance (to that of C) under fuel cell electrochemical conditions. We show that Pt/TiN has a higher durability than Pt/C.

4) Based on the higher support to Pt particle ratio of Pt/TiN (compared to Pt/C) and the higher corrosion resistance of TiN (compared to C supports), it is hypothesized that Pt/TiN undergoes degradation in fuel cell operating conditions predominantly via the Pt particle growth mechanism. The hypothesis is tested and confirmed by measuring the Pt particle sizes of electrocatalysts after durability tests.

5) The hypothesis is further tested by varying the Pt catalyst loading (10 and 30 wt% Pt/TiN) and arriving at similar conclusion of Pt agglomeration as the degradation mechanism for titanium nitride based electrocatalysts.

6) But the overall durability improvement of Pt/TiN over Pt/C is minor as the increased durability of Pt/TiN, gained from the catalyst support resistance to corrosion, is seen to be discounted to a certain extent by an increase in the rate of Pt agglomeration mechanism.

Acknowledgment

The authors gratefully acknowledge Richard Moore for his assistance with XPS characterization of the electrocatalyst samples.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.energyc.2013.05.021.

References


