Electrochemical oxidation behavior of titanium nitride based electrocatalysts under PEM fuel cell conditions

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**Abstract**

Titanium nitride (TiN) is attracting attention as a promising material for low temperature proton exchange membrane fuel cells. With its high electrical conductivity and resistance to oxidation, TiN has a potential to act as a durable electrocatalyst material. Using electrochemical and spectroscopic techniques, the electrochemical oxidation properties of TiN nanoparticles (NP) are studied under PEM fuel cell conditions and compared with conventional carbon black supports. It is observed that TiN NP has a significantly lower rate of electrochemical oxidation than carbon black due to its inert nature and the presence of a native oxide/oxynitride layer on its surface. Depending on the temperature and the acidic media used in the electrochemical conditions, the open circuit potential (OCP) curves shows the overlayer dissolved in the acidic solution leading to the passivation of the exposed nitride surface. It is shown that TiN NP displays passive behavior under the tested conditions. The XPS characterization further supports the dissolution argument and shows that the surface becomes passivated with the O–H groups reducing the electrical conductivity of TiN NP. The long-term stability of the Pt/TiN electrocatalysts is tested under PEM fuel cell conditions and the trends of the measured electrochemical surface area at different temperatures is shown to agree with the proposed passivation model.

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**1. Introduction**

In the past decade, fuel cell technology has made significant strides towards commercialization but much work needs to be done in many aspects of this promising alternative energy source for it to compete against the conventional energy sources. Of the various types of fuel cells, proton exchange membrane (PEM) fuel cells have received broad attention due to their low operating temperature, low emissions and a quick startup time. But the cost and durability can also play a crucial role in its ability accomplish. Apart from the lifetime costs, durability can also hinder the reliability of the PEM fuel cell technology against its counterparts.

Investigations have revealed that a considerable part of the performance loss is due to degradation of the electrocatalyst [4] during extended operation and repeated cycling [5], especially for PEM fuel cells in automotive applications. Currently, the carbon black supported platinum nanoparticles (Pt/C) remains the state of the art electrocatalyst for PEM fuel cells. Under the corrosive operating conditions, the Pt/C degrades via Pt dissolution, Pt particle agglomeration and carbon support corrosion mechanisms resulting, primarily, in the loss of electrochemical surface area. Furthermore, the catalytic metal, especially Pt, catalyzes the oxidation of carbon [6,7] and the oxidation of carbon black accelerates Pt sintering [8]. Vulcan XC-72 carbon black is the most popular catalyst support currently used in the Pt/C electrocatalysts but its durability, under the oxidizing conditions of a PEM fuel cell, needs significant improvement [9,10].

An ideal catalyst support material should have corrosion resistance properties under strongly oxidizing conditions of PEM fuel cell: high water content, low pH (<1), high temperature (50–90 °C), high potentials (>0.9 V) and high oxygen concentration. But carbon is known to undergo electrochemical oxidation to form surface oxides and CO/CO2 under these conditions [11–13]. Significant oxidation of carbon support can be expected to decrease the performance of a PEM fuel cell [13,14], due to the loss and/or agglomeration of Pt particles caused by the carbon corrosion. It has also been reported [14,15] that oxygen containing groups (e.g.,
carboxyl, carbonyl, hydroxyl, phenol) can be formed on the carbon surface at high temperatures and/or high potentials (>1.0 V vs. RHE at room temperature or >0.8 V vs. RHE at 65 °C) which decrease the conductivity of catalysts and weaken its interaction with the support resulting in an accelerated Pt sintering [8,16,17]; thus drastically affecting the performance of PEM fuel cell. In our report [9], we showed that carbon black supports have a higher rate of corrosion under potential cycling compared to constant potential conditions and tend to form significant amount of surface oxide groups. These studies indicate towards the vulnerability of carbon support under prolonged fuel cell operating conditions.

In our recent publication [18], we introduced titanium nitride (TiN) nanoparticles as catalyst supports for synthesizing Pt/TiN electrocatalyst and showed that it can outperform the Pt/C electro-catalyst in electrochemical surface area and catalytic activity for the same Pt particle size and loading [18]. With its unique properties of higher electrical conductivity (relative to carbon) and an outstanding oxidation and acid corrosion resistance [19–21], TiN has a high potential for developing durable electrocatalysts. Research is also being pursued on the materials of transition metal carbide and nitride family for their application in low temperature fuel cells, as described in a review by Ham and Lee [22]. Recently Musthafa and Sampath [23] reported the application of TiN films for direct methanol based fuel cells and other groups [24,25] have reported the application of Ti-based compounds for fuel cells [24,25]. But the stability and the long-term durability aspect of the electrocatalyst material under above room temperature fuel cell operating conditions is not discussed. As titanium nitride gains attention as an electrocatalyst material, its behavior under PEM fuel cell conditions remains to be investigated. Considerable research has been done in the past in electrochemically evaluating TiN thin films in electrolytes of a wide-pH range. But behavior of TiN vis-à-vis – high surface area porous material, above RT conditions, cyclic/high potentials, highly acidic conditions (pH < 1) – which are the typical conditional variables of an electrocatalyst material in a fuel cell, has not been reported in the literature. Through this paper, we extend upon our research on the TiN based electrocatalysts and report the electrochemical behavior of titanium nitride nanoparticles by evaluating them under the operating conditions of a PEM fuel cell. Along with the bare supports, we also report the electrochemical behavior of synthesized Pt/TiN electrocatalyst and its stability under prolonged exposure conditions.

2. Titanium nitride

Titanium nitride belongs to the transition metal nitride family and displays similar formation and physiochemical properties of other nitrides in the family. Many of its properties are caused by a special feature of its electronic structure, i.e., transfer of part of s- and d-valency electrons of the atoms of Ti to the 2p-states of the N thereby depleting the electron population of the d-states of Ti, which are responsible for its covalent bonding with foreign atoms [26,27]. According to Ham and Lee [22], this deficiency in the d-band occupation near the Fermi level should make the TiN surface to have a reduced ability to donate d-electrons to adsorbates; thus making it a better electron acceptor.

The triple bond between Ti and N and the mixed p and d characteristics of the interaction between Ti 3d and N 2p represents an essential aspect of covalent bonding between titanium and nitrogen atoms and is responsible for its inert nature, mechanical hardness and high melting point [28]. The metallic character arises with one unpaired electron going into a metal localized sp hybrid orbital on Ti resulting in the non-zero electron density at Fermi level (E_F) [28] contributing to its relatively high electrical conductivity. Oyaama [19] reported the electrical conductivity of bulk TiN as 4000 S cm⁻¹ and that of C as 1190 S cm⁻¹ while other groups have reported values ranging from 3125 S cm⁻¹ [29] to 33,000 S cm⁻¹ [30] for polycrystalline TiN thin films to ~55,500 S cm⁻¹ [28 and Refs. within] for TiN single crystal, conductivities that are higher than that of carbon.

TiN is well known for its oxidation resistance property, an aspect contributed to the native oxide/oxynitride layer which partially covers its surface and is formed due to atmospheric oxidation [28,31–33]. The titanium–oxygen–nitrogen system [34] has been well researched and the composition of the native layer has been attributed to a non-uniformly distributed mixture of oxynitride and oxide [28,31,32,35–38] components on its surface that prevent the surface from further oxidation. The oxide and oxynitride components are also formed during the electrochemical oxidation of titanium nitride under potential scanning conditions [28].

2.1. Oxidation

TiN undergoes a thermodynamically favorable oxidation reaction when exposed to air [28,34]:

\[
2\text{TiN} + O_2 \rightarrow 2\text{TiO}_2 + 2\text{N}_2 \uparrow \quad \Delta G^\circ = -611.8 \text{kJ mol}^{-1}(298 \text{K}) \quad (1)
\]

The oxidation process takes place in three stages [35,39]: stage 1: oxygen diffuses into the TiN lattice resulting in replacement of N by O, leading to the formation of titanium oxynitride. Stage 2: the natural protective films of the phases of TiO₂₊₁ are formed on the oxynitride layer during this stage, representing a diffusion-controlled oxidation [40]. Stage 3: slow oxidation of the residual material of TiN coated with TiO₂.

A major portion of the replaced nitrogen is released in the interstitial positions of surface oxide layers as molecular nitrogen, which gets released from the surface upon further oxidation [35].

2.2. Electrochemical oxidation of TiN

Many research papers have evaluated the electrochemical oxidation behavior of titanium nitride films in various media [28,32,36–38], and showed the high stability of TiN against oxidation process in a wide-pH range. The electrochemical oxidation resistive properties were attributed to the presence of the nitrogen enriched surface layer of titanium oxynitride with a large electron density that screens the underlying titanium ions and inhibits the oxidation reaction [20,28].

The electrochemical oxidation of TiN follows a similar path of oxidation process, where: 0.5 V to 0.8–0.9 V: the formation and growth of oxide/oxynitride films on the surface of TiN by reaction (2) predominantly leads to the retardation (or passivation) of these processes.

\[
\begin{align*}
\text{TiN} + 2\text{H}_2\text{O} &\rightarrow \text{TiO}_2 + 1/2\text{N}_2 + 4\text{H}^+ + 4\text{e}^- \quad [28, 41] \\
\text{TiN} &\rightarrow \text{Ti}^{3+} + 1/2\text{N}_2 + 3\text{e}^- \\
&\sim 1.0–1.5 \text{V: oxidation resulting in formation of hydroxides} \quad [41],
\end{align*}
\]

\[
\begin{align*}
\text{TiN} + 3\text{H}_2\text{O} &\rightarrow \text{Ti(OH)}_3 + \text{N}_2 + 3\text{H}^+ + 3\text{e}^- \\
\text{TiN} + 3\text{H}_2\text{O} &\rightarrow \text{TiO}_2\cdot\text{H}_2\text{O} + 1/2\text{N}_2 + 4\text{H}^+ + 4\text{e}^- \quad (5)
\end{align*}
\]

Miščev et al. [28] attributed the increase in current in this potential region to the formation of TiO₂ on the surface of TiN rather than hydroxide (reaction 4), but accompanied by a similar liberation of N₂. The reasoning being that the hydroxides are more soluble and less protective than the oxides, and can cause the rise of currents in this region. Above 2.0 V: at these potentials, oxygen evolution takes place with a simultaneous oxidation of titanium nitride to TiO₂.

Through the above discussion in oxidation and electrochemical oxidation processes, we intend to better address the nature of TiN.
nanoparticles under PEM fuel cell conditions by fully considering the reported electrochemical behavior of TiN in the literature.

3. Experimental

3.1. Catalyst support materials

The TiN nanoparticles or TiN NP that are used as catalyst supports in this study were commercially purchased (NanoAmor Inc., USA) and have an average particle size (APS) of 20 nm and a specific surface area (SSA) of 40–55 m² g⁻¹ [42]. The mean particle size, derived from the transmission electron microscopic (TEM) image (Fig. 1) and the X-ray diffraction pattern of TiN(1 1 1) peak (Fig. 2) using Debye–Scherer equation, match closely to the vendor reported value. The purity ascribed to the TiN was >97% and an energy-dispersive spectroscopy was performed to verify the presence of impurities, as shown in Fig. A1 of Appendix. For a comparative investigation with carbon, commercially purchased Vulcan XC-72R carbon black (Cabot Inc., USA) of a known surface area of ~250 m² g⁻¹ is used.

3.2. Preparation of catalyst support coated electrodes and electrochemical tests

For electrochemical comparison of TiN and C, the TiN NP is sonicated in ethanol and an aliquot is deposited on a polished glassy carbon electrode (GCE, 5 mm dia., 0.1962 cm², Pine Instruments) for a material loading of 0.15 mg cm⁻² and the solvent is allowed to evaporate. The TiN NP coated GCE is used as a working electrode in a three-electrode cell set-up and a similar procedure is followed for depositing carbon black (CB) on polished GCE.

For spectroscopic characterization of TiN, carbon cloth (E-Tek®) is used as a substrate on which TiN NP is coated. The coating is prepared by ultrasonically mixing TiN NP, isopropyl alcohol and 0.05 wt% Nafion® for a loading of 3 mg cm⁻², with 95 wt% of TiN NP. Electrodes were dried at 80°C for 10 min for the evaporation of any remaining solvent.

Electrochemical tests were performed in a standard three-electrode cell set-up with a PARSTAT 2273 potentiostat (Princeton Applied Research, USA). A reversible hydrogen electrode (RHE) (Gaskatel GmBH, Germany) is used as a reference electrode with a Pt mesh acting as a counter electrode. All potentials are reported with respect to RHE. Using cyclic voltammetry (CV) techniques, the GCE was cycled between 0 and 1.0 V potentials at 50 mV s⁻¹ in Ar saturated 0.1 M HClO₄ (pH < 0.5) electrolyte at 60°C for 24 h. The maximum potential of 1.0 V is chosen as it is near to fuel cell idle conditions. Similarly, the TiN NP coated carbon cloth electrode is held vertically inside the electrolyte chamber under the same conditions but cycled between 0 and 1.2 V potentials at 50 mV s⁻¹ for 16 h. Potential cycling is chosen for the electrochemical evaluation as it is one of the extreme operating conditions in a PEM fuel cell where the electrode is exposed to repeat variations in load due to changing potentials that result in the application of oxidation/reduction processes on the electrode surface.

3.3. Synthesis of Pt/TiN electrocatalyst

TiN NP is mixed in ethylene glycol (EG) and ultrasonically treated before adding H₂PtCl₆·6H₂O drop wise. Sodium hydroxide (NaOH) 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. The solution is stirred overnight at room temperature, after which it is washed and filtered. The filtrate removed powder is dried in air at 80°C for 4 h.

![Fig. 1. (a) Transmission electron micrograph showing the TiN nanoparticles and (b) a histogram showing the TiN nanoparticles distribution with average particle size at 18.9 nm.](Image)

![Fig. 2. X-ray diffraction pattern of TiN nanoparticles.](Image)
3.4. Preparation of Pt/TiN electrocatalyst coated electrodes and half-cell performance

For determining the electrochemical surface area (ECSA) of Pt/TiN, the CV technique is used. The electrocatalyst dispersions are prepared by ultrasonically mixing the Pt/TiN in ethanol and pipetting an aliquot of the dispersion onto the GCE for a catalyst loading of 20 mg Pt cm$^{-2}$. After drying, 10 µL of aqueous Nafion (5 wt%) solution is pipetted onto the electrode surface in order to attach the catalyst particles onto the electrode surface and also to create pathways for the H$^+$ ions in the electrolyte to access the catalytic sites. The Pt/TiN deposited GCE is immersed in the Ar saturated 0.1 M HClO$_4$ which is at 60 °C and scanned between 0 and 1.2 V at 50 mV s$^{-1}$. Half-cell performance is measured by the electrochemical surface area (ECSA) which is calculated from the area under the hydrogen adsorption and desorption peaks of CV curves after double-layer correction.

3.5. Surface characterization

X-ray photoelectron spectroscopy (XPS) analysis was performed using a ThermoFisher Theta Probe system which has a 2-dimensional detector that will allow simultaneous collection of spectral data from all angles without tilting the sample. The spectrometer was equipped with a hemispherical analyzer and a monochromator and all XPS data presented here are acquired using Al Kα X-rays (1486.6 eV) operated at 100 W. Sputter cleaning was done with a differentially pumped Ar$^+$ sputter gun. The sample to analyzer takeoff angle was 45°. Survey spectra were collected at pass energy (PE) of 125 eV over the binding energy range 0–1300 eV. High binding energy resolution multiplex data for the individual elements were collected at a PE of 29.55 eV. The XPS spectra were background subtracted using the non-linear, Shirley method. The binding energies of the Ti 2p, N 1s, O 1s and C 1s component on the surface. Based on these two arguments, it can be predominantly, a result of the electrochemical oxidation of nitride nature of TiN and the presence of an oxide/oxynitride layer on its surface attribute to its initial lower current densities (TiN (0.5 h) vs. C (0.5 h) in Fig. 3). Since the native oxide/oxynitride layer on TiN NP acts as a barrier, the low oxidation current densities observed are, predominantly, a result of the electrochemical oxidation of nitride component on the surface. Based on these two arguments, it can be reasoned that the composition of oxynitride and oxide components will increase while that of nitride decreases after the potential cycling (as the nitride essentially converts to oxide and oxynitride components due to electrochemical oxidation).

In the case of CV curve for TiN NP electrode shown in Fig. 3, there is a wide margin of current density drop after 0.5 h with the later cycles 8 h, 16 h (not shown in Fig. 3) and 24 h having the same nitride and oxide peaks is attributed to the oxynitride which has an oxidation state between TiN and TiO$_2$ [28, 35].

The native layer on the surface of TiN nanoparticles used in our study is a combination of Stage 1 (TiO$_x$N$_{2-x}$ phase) and Stage 2 (Ti$_2$O$_{3n-m}$ phase) of the oxidation process (Section 2.1), with the latter being predominant while no complete phase separation to TiO$_2$ [28] is seen to occur from the XRD plot in Fig. 2.

Using the TiN NP with partially covered native oxide/oxynitride layer, the Pt/TiN electrocatalyst was synthesized and its electrochemical evaluation has been reported in our previous paper [18]. The cyclic voltammogram (CV) or the oxygen reduction reaction (ORR) curves for Pt/TiN showed no indication of an ohmic resistance due to the oxide/oxynitride layer on the surface of TiN nanoparticles. In fact, 20 wt% Pt/TiN showed higher electrochemical surface area and catalytic activity compared to the conventional 20 wt% BASF® Pt/C [18] for the same Pt loading. If the oxide/oxynitride layer were to act as a poor electrical conductor, then the ohmic losses (due to the inhibition of electron transportation from the catalyst particle to the support) should cause retardation in the kinetics of the catalytic reactions; which was not observed in our tests suggesting an alternative possibility. In the later part of this report, an explanation to this behavior and the role of the oxide/oxynitride layer on TiN nanoparticles are discussed.

4.2. Electrochemical comparison of CB and TiN NP under PEM fuel cell operating conditions

Fig. 3 shows the CV curves of TiN NP and CB electrodes, where the current densities generated by TiN NP are significantly lower when compared to those of CB under identical test conditions. The inert nature of TiN and the presence of an oxide/oxynitride layer on its surface attribute to its initial lower current densities (TiN (0.5 h) vs. C (0.5 h) in Fig. 3). Since the native oxide/oxynitride layer on TiN NP acts as a barrier, the low oxidation current densities observed are, predominantly, a result of the electrochemical oxidation of nitride component on the surface. Based on these two arguments, it can be reasoned that the composition of oxynitride and oxide components will increase while that of nitride decreases after the potential cycling (as the nitride essentially converts to oxide and oxynitride components due to electrochemical oxidation).

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untreated: TiN nanoparticles (TiN NP), as is treated: TiN NP coated carbon cloth, 16 h of potential cycling.

Surface conditions, (A) and (B).

tion and analysis, the TiN electrodes were exposed to two different useful technique in observing these changes. For XPS characterization, the TiN support surface. As the catalyst support corrosion in low temperature fuel cells usually occurs at the surface, XPS can be a temperature fuel cells usually occurs at the surface, XPS can be a

dation at 0.55 V (hydroquinone/quinone peak). TiN shows highly passivating behavior, due to its oxide/oxynitride components and also, possibly due to the titanium dioxide and hydroxide groups that can be formed at these potentials according to reactions (4) and (5). To study the surface changes on the TiN NP due to electrochemical oxidation, XPS characterization is performed on TiN NP coated electrodes.

4.3 Spectroscopic analysis of TiN NP electrodes

XPS is a surface analysis technique which can provide a better understanding of the changes on the surface due to electrochemical oxidation, along with the atomic concentration of elements on the TiN support surface. As the catalyst support corrosion in low temperature fuel cells usually occurs at the surface, XPS can be a useful technique in observing these changes. For XPS characterization and analysis, the TiN electrodes were exposed to two different surface conditions, (A) and (B).

(A) Untreated: TiN nanoparticles (TiN NP), as is
(B) Treated: TiN NP coated carbon cloth, 16 h of potential cycling between 0 and 1.2 V at 50 mV s⁻¹ in 60 °C argon saturated 0.1 M HClO₄ electrolyte.

The XPS survey spectra of untreated and treated TiN NP electrodes exhibited the characteristic Ti 2p, O 1s and N 1s peaks at the corresponding binding energies of 528.2, 456.5 and 396.2 eV, respectively, in accordance with values reported in literature [28,31,33,35,37,38,46]. Based on the elemental peaks in the survey spectra and the sensitivity factors of individual elements, the relative atomic concentration on the surface of untreated and treated TiN electrodes are plotted in Fig. 5.

The initial oxygen composition on the ‘untreated’ TiN NP electrode (in Fig. 5) is attributed to the native oxide/oxynitride layer on its surface; other surface groups such as TiN–O*, TiN–OH, adsorbed H₂O may also be contributing to oxygen composition, although minimally. The increase in the composition of Ti is a result of the electrochemical oxidation of TiN into Ti ions (through reaction (3)). Similarly, the decrease of N can be attributed to the decrease in nitride composition due to its oxidation. From the electrochemical reactions, the oxygen composition should increase as an outcome of the oxidation of TiN due to potential cycling. But, as seen in Fig. 5, a slight decrease of oxygen composition is observed for the ‘treated’ TiN NP electrode.

The atomic concentration ratios of the elements on ‘treated’ TiN electrodes, drawn from their respective peak intensities are presented in Table 1. The O/Ti ratio of the TiN electrodes decreases after the electrochemical treatment due to the relative increase of Ti while the increase of O/N ratio indicates towards the relative decrease of N over O. This suggests that the electrochemical oxidation does not necessarily replace one-to-one of N with O. Based on these arguments, the decrease of O/Ti ratios from 0.39 to 0.35, suggests a relative increase in TiN composition after the electrochemical treatment, the increase attributed to the increase in Ti composition.

The significant increase in Ti/N ratio suggests that the N decreases while Ti increases simultaneously, presumably from the same compound. Since the oxidation of TiN inevitably results in nitrogen as a by-product in the form of N₂, NO₂, NO, etc. [37] one can see the decrease in nitrogen composition. The increase of Ti, with a decrease of O and N, suggests that the surface is not predominated by the oxide layer after the electrochemical treatment. Further investigation of the elemental peaks can provide information on the nature of surface groups formed on the surface of TiN and their trends after the electrochemical treatment.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>O/Ti</th>
<th>O/N</th>
<th>O/TiN</th>
<th>Ti/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.60</td>
<td>1.15</td>
<td>0.39</td>
<td>1.91</td>
</tr>
<tr>
<td>Treated</td>
<td>0.50</td>
<td>1.22</td>
<td>0.35</td>
<td>2.42</td>
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</table>

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Deconvoluted Ti 2p XPS spectra of: (a) untreated; (b) treated TiN NP electrode. The peak positions and their assignments are based on the reported literature [28,31,33,35,37,38,46]. Using XPS technique, which is strictly a surface characterization technique, the oxide peak at 459.1 eV is assigned to TiO$_2$ (IIa) but a distinct phase of the same is not observed in the XRD plot in Fig. 2.

Comparing the spectra of Ti 2p in Fig. 6(a) and (b), one can observe the changes in peak areas and heights after the electrochemical treatment. The binding energies of Ti 2p$_{3/2}$ and 2p$_{1/2}$ of ‘untreated’ electrode are assigned to TiN (Ia) and TiN (Ib), respectively, with 455.6 and 461.7 eV as their respective peak positions. After the electrochemical treatment, both the binding energies of Ti 2p$_{3/2}$ and 2p$_{1/2}$ shifted to 460.7 eV (A) and 466.2 eV (B), respectively, as shown in Fig. 6(b). These characteristic peaks of ‘A’ and ‘B’ are related to the tetravalent titanium ion, Ti(OH)$_2$$^{2+}$, where the Ti ion possibly oxidized to the states of higher valence during potential cycling following reaction (6) [37]:

$$\text{TiN} + 3\text{H}_2\text{O} = \text{Ti(OH)}_2$$^{2+} + NO + 4\text{H}^+ + 6\text{e}^- \quad (6)$$

For Ti in acidic media, the Pourbaix diagram predicts that the thermodynamically stable states of Ti ions under the condition of anodic polarization have 3+ and 4+ valence, with the dissociated titanium, most likely, as Ti$^{4+}$, Ti(OH)$_2$$^{2+}$ and Ti(OH)$_2$$^{2+}$ [36,37]. Considering the XPS peak positions of ‘A’ and ‘B’ of Ti 2p in Fig. 6(b) and the tetravalence of Ti ion according to the Pourbaix diagram of Ti in acidic media, it is reasoned that the Ti ion could be taking the form of Ti(OH)$_2$$^{2+}$ with a 4+ oxidation state, after the electrochemical treatment.

The areas under the deconvoluted peaks of Ti 2p$_{3/2}$ are presented in Table 3 where one can see a significant presence of oxide and oxynitride components on the surface of the untreated TiN electrode, suggesting that the process of atmospheric oxidation has been initiated to certain extent, supporting the earlier statements. Due to their inert nature, the existing oxide/oxynitride layer present on the surface of TiN NP does not oxidize any further. It should be noted that the overlayer was never transformed to a pure titanium oxide even after 2 years of air exposure, but rather remained a mixture of oxynitride and oxide. This implies that the oxidation mainly occurs on the nitride part of the surface on TiN nanoparticles resulting in the decrease of its composition, with a corresponding increase in the oxide and oxynitride components [28] by the same magnitude.

In Table 3, it can be seen that the nitride component, TiN (Ia), decreases by 17.2% after the electrochemical treatment, with a 10.4% increase in the relative composition of TiO$_2$. This increase agrees well with the reported literature [28], where the electrochemical oxidation of TiN forms TiO$_2$ compound on the surface. The remaining percentage of decrease in nitride should be attributed to the increase of oxide composition. But the increase in the oxynitride composition is not accompanied by a corresponding increase in the oxide component. In fact, the oxide component, as shown in Table 3, significantly decreases by a relative composition of 46.7%. The area ratio of nitride (Ia) and oxide (IIa) peaks, ($A_{\text{TiN}}/A_{\text{TiO}_2}$), in Ti 2p$_{3/2}$ (Fig. 6) increases from 0.51 to 0.95 suggesting the significant decrease of oxide after the electrochemical treatment.

![Fig. 6. Deconvoluted Ti 2p XPS spectra of: (a) untreated; (b) treated TiN NP electrode.](image)

<table>
<thead>
<tr>
<th>Functional groups</th>
<th>Untreated (%)</th>
<th>Treated (%)</th>
<th>Change in relative composition, Δ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN</td>
<td>31.5</td>
<td>14.3</td>
<td>17.2</td>
</tr>
<tr>
<td>TiO$_2$N$_y$</td>
<td>6.8</td>
<td>17.2</td>
<td>10.4</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>14.8</td>
<td>14.8</td>
<td>0</td>
</tr>
<tr>
<td>Ti(OH)$_2$$^{2+}$</td>
<td>–</td>
<td>53.7</td>
<td>–</td>
</tr>
</tbody>
</table>
treatment. The oxide on TiN NP surface dissolves in the acidic media exposing the nitride surface which further reacts with the acidic media to form Ti–OH compound according to reaction (8). The above proposed mechanism explains the significant increase in Ti(OH)22+, the magnitude (53.7%) of which can be equaled to the dissolution of oxide component (46.7%) and the dissolution of oxide (6.8%) which is newly formed due to the electrochemical oxidation of nitride component. Although an elaborate discussion on this topic is provided later in Section 4.4, it is emphasized that electrochemical treatment under cycling potentials will lead to the formation of oxide/oxynitride layer [28]. But, unlike in buffer solutions (pH ~ 7), perchloric acid solution tends to dissolve the layer exposing the nitride surface underneath.

4.3.2. O 1s
The deconvoluted O 1s XPS spectra for the ‘untreated’ and ‘treated’ TiN electrode are shown in Fig. 7(a) and (b), respectively. The dominant O 1s component (IV) for ‘untreated’ electrode in Fig. 7(a) is located at 530.2 eV and is assigned to TiO2 [28,31,33,35,38,46,47] but the dominant O 1s peak for the ‘treated’ electrode has shifted to 531.2 eV, which is characteristic to O–H group [28,35,37,46,48]. The significant increase of O–H peak (V) of O 1s in Fig. 7, after the electrochemical treatment, supports the earlier argument about the formation of Ti–OH groups indicated by the peaks 'A' and 'B' of Ti 2p in Fig. 6(b) and the Pourbaix diagram of Ti in acidic media. The remaining components of the O 1s peaks are labeled in Table 3 and illustrated in Fig. 7. The dissolution of titanium oxide in acidic media can also be seen from the significant drop of the oxide peak (IV) at 530.9 eV. Similar to the oxynitride component in Ti 2p and N 1s spectra (Fig. A3, Appendix), the TiOxNy (VII) peak in O 1s is seen to increase for the ‘treated’ TiN electrode. NO (VIII) is a possible by-product formed during the electrochemical oxidation of TiN [36] along with NO2 and N2 and its peak can be seen near 535.0 eV [49].

4.4. Dissolution of oxide/oxynitride layer
It is well known [50,51] that the oxides of titanium, due to their strong basic character, dissolve in acidic media to form colorless titanium (IV or 4+) oxysalts that decompose in water. In perchloric acid media such as the one used in our case, Ti (IV) species can be present as (Ti(OH)2)2+ or TiO2+ that is derived from the salts of TiOCl42− anions [51]. To confirm the oxide dissolution in perchloric acid, a few ml of H2O2 was added TiN NP dispersed in 0.1 M HClO4 and the solution turned to intense orange color. This is due to the fact that colorless hydrated Ti(IV) ions in the solution get converted in to orange hydrated (Ti(O2)OH)+ ions according to reaction (7) [50] thus confirming the presence of dissolved Ti(IV) species:

\[
(Ti(OH)_3)^+ + H_2O_2 \rightarrow (Ti(O_2)OH)^+ + 2H_2O
\] (7)

The immediate change in color of the solution suggests the rapid dissolution of titanium oxides in the acidic media. Further evidence to the dissolution of oxide component is shown in the analysis of XPS spectra of Ti 2p and O 1s in Figs. 6 and 7, where one can see the decrease of oxide composition.

Unlike the oxides which were quick to dissolve in the acidic media, it can be reasoned that the oxynitride takes a longer time to dissolve due to its nitrogen composition. Fig. 8 shows the changes of open circuit potential (OCP) of TiN NP with immersion time at various temperatures of perchloric acid. OCP or the corrosion potential (ECorr) measures the equilibrium potential above which the oxidation is initiated on the surface. A stable OCP indicates the stable nature of the electrode while the surface reactions cause the OCP to fluctuate.

The OCP (at 60, 70, 80 °C) of TiN NP in Fig. 8 shifted rapidly downwards during the initial stage of immersion. The downward shift of OCP towards the active potentials is due to the self-activation of TiN and is an indication of a dissolution of the oxynitride on the surface of TiN [37,52], which increasingly exposes the nitride surface directly to acidic solution. The anodic chemical reaction that can be related to TiN at these OCP conditions can be expressed as [37]:

\[
TiN + H_2O \rightarrow Ti(OH)_2^{2+} + 1/2N_2 + H^+ + 3e^-
\] (8)

The potential-pH (or Pourbaix) diagram of Ti-H2O predicts that the possible thermodynamically stable state of Ti ions under the OCP conditions can be 3+ valence; and the reaction (8) indicates that...
this dissociated titanium, Ti(III), is most likely Ti(OH)$_2^{2+}$ \cite{36,37}. As the temperature of perchloric acid solution in Fig. 8 increases from 60 to 80 $^\circ$C, the hydrogen ion strength in the acid solution increases thus causing a faster dissolution of oxynitride layer during the initial stage of immersion. The steeper slope and a lower dissolution time with an increase in temperature in Fig. 8 are an indication of faster rate of oxynitride dissolution due to increased ionic strength of the acid solution.

The rapid decrease of OCP, for the curves in Fig. 8, in the initial stage of immersion is related to the formation of the corrosion product of Ti(OH)$_2^{2+}$ (according to reaction (8)) on the exposed nitride surface, with its nature of positive charge \cite{37}. The formation of these corrosion products on the TiN surface leads to a subsequent adsorption of other negative ions existing in the solution such as ClO$_4^-$. As a result, an adsorption configuration is likely to be set-up where the surface area of TiN NP will be covered with such anions, naturally prohibiting the dissolution of TiN and thus making the electrode passive and attain more noble potentials. The OCP curves of 60, 70 and 80 $^\circ$C in Fig. 8 drop steeply in the initial stages of immersion after which it gradually plateaus for the rest of the immersion, in the passive region of the plot. This increase towards nobler potentials is likely the result of subsequent adsorption of anions in the solution by the positively charged Ti(OH)$_2^{2+}$ layer on the nanoparticles surface. This adsorption model, proposed by Chyou et al. \cite{37} for TiN thin films in varying concentrations of sulfuric acid solutions, explains the electrochemical behavior of TiN NP under simulated PEM fuel cell conditions, Electrochim. Acta (2010), doi:10.1016/j.electacta.2010.08.035

The minimal decline of OCP curve at room temperature (RT, 23 $^\circ$C) in Fig. 8 indicates that the rate of dissolution of the oxynitride layer on the surface of TiN NP is very low at the given conditions; which imply that TiN NP will take a significantly longer time to passivate under the RT conditions of 0.1 M HClO$_4$ acid electrolyte. It should be noted that the variation in the starting OCP potential (indicating the electrode passive and attain more noble potentials. The OCP curves of 60, 70 and 80 $^\circ$C in Fig. 8 drop steeply in the initial stages of immersion after which it gradually plateaus for the rest of the immersion, in the passive region of the plot. This increase towards nobler potentials is likely the result of subsequent adsorption of anions in the solution by the positively charged Ti(OH)$_2^{2+}$ layer on the nanoparticles surface. This adsorption model, proposed by Chyou et al. \cite{37} for TiN thin films in varying concentrations of sulfuric acid solutions, explains the electrochemical behavior of TiN NP under simulated PEM fuel cell conditions, Electrochim. Acta (2010), doi:10.1016/j.electacta.2010.08.035

The oxynitride component of the native layer, TiO$_x$N$_y$, has a relatively slower rate of dissolution compared to oxide and consists of lower percentage of oxygen composition than the oxide component. TiO$_x$N$_y$ has an electrically conductive nature due to its NaCl crystal structure which is similar to TiN and also a significant presence of nitrogen in its lattice \cite{34}. It has been reported \cite{33} that titanium oxynitride thin films with low oxygen contents (<40 at.%) are partly metallic suggesting that the oxynitride layer on the surface of TiN nanoparticles may have relatively higher electrical conductivity. To further support the statement, the elemental composition of oxygen, from oxide and oxynitride components, on the ‘untreated’ TiN nanoparticles surface was measured by XPS and was found to be ~35% atomic concentration. This means that the oxynitride component will have a much lower composition of oxygen than the total value. It is reasonable to speculate that this conductive nature of oxynitride component on the surface of TiN NP resulted in the minimal ohmic resistance (or poor retardation of kinetics) from the catalyst supports during the initial cycles of CV and ORR tests of Pt/TiN presented in our previous report \cite{18}.

4.5. Electrical conductivity of oxide/oxynitride components on TiN NP surface

An aspect of concern for TiN nanoparticles is the change in its electrical conductivity due to the presence of the oxide and oxynitride components on the surface. Since the surface is not predominated with TiO$_2$, the oxide component largely exists as a sub-stoichiometric composition (Ti$_x$O$_{2n-1}$) of Magneli phase, which has electrically conductive properties \cite{24}. With an increase in surface oxygen composition due to electrochemical oxidation at high potentials, the surface layers can become titanium dioxide but get easily dissolved in the acidic conditions of fuel cell without acting as an insulator.

The oxynitride component of the native layer, TiO$_x$N$_y$, has a relatively slower rate of dissolution compared to oxide and consists of lower percentage of oxygen composition than the oxide component. TiO$_x$N$_y$ has an electrically conductive nature due to its NaCl crystal structure which is similar to TiN and also a significant presence of nitrogen in its lattice \cite{34}. It has been reported \cite{33} that titanium oxynitride thin films with low oxygen contents (<40 at.%) are partly metallic suggesting that the oxynitride layer on the surface of TiN nanoparticles may have relatively higher electrical conductivity. To further support the statement, the elemental composition of oxygen, from oxide and oxynitride components, on the ‘untreated’ TiN nanoparticles surface was measured by XPS and was found to be ~35% atomic concentration. This means that the oxynitride component will have a much lower composition of oxygen than the total value. It is reasonable to speculate that this conductive nature of oxynitride component on the surface of TiN NP resulted in the minimal ohmic resistance (or poor retardation of kinetics) from the catalyst supports during the initial cycles of CV and ORR tests of Pt/TiN presented in our previous report \cite{18}.

4.6. Stability of Pt/TiN electrocatalyst

As the temperature affects the active or passive behavior of the TiN NP, the durability of the Pt/TiN electrocatalyst (synthesized using TiN NP) will also be invariably affected in a similar manner. The synthesized Pt/TiN electrocatalyst has an average platinum particle size of 2.4 nm as measured by TEM (Fig. 9). To test the durability of the electrocatalyst, Pt/TiN was subjected to accelerated durability test (ADT) where the electrocatalyst coated electrode undergoes repeated potential cycling for a prolonged period of time under simulated PEM fuel cell conditions. The durability performance in this case was monitored by the no. of active Pt sites on the electrocatalyst i.e., the electrochemical surface area (ECSA), which was measured at intervals of 100 cycles; the plot of ECSA of Pt/TiN vs. no. of cycles at different temperatures is shown in Fig. 10.

The ECSA of Pt/TiN at 60 $^\circ$C in Fig. 10 has an initial high value of 70 m$^2$ g$^{-1}$Pt but falls to near zero within few hours of operation and continues to plateau near zero for the remaining duration. This trend can be explained by the OCP curve of TiN NP at 60 $^\circ$C (in Fig. 8) where the dissolution of oxynitride layer takes place in the initial stages and later passivation occurs due to the formation of Ti(OH) layer on its surface. XPS characterization also revealed a similar hydroxide layer on the surface of TiN NP after repeated potential cycling, which is similar to ADT. This hydroxide layer prevents the TiN NP supports (of Pt/TiN electrocatalyst) to conduct electrons from Pt catalyst particles resulting in near zero ECSA as shown...
Fig. 9. (a and b) Transmission electron micrograph showing the Pt particles on TiN catalyst supports; (c) histogram showing the Pt nanoparticles distribution with mean particle size at 2.4 nm.

Fig. 10. Decrease of ECSA of 20 wt% Pt/TiN after potential cycling between 0 and 1.3 V (50 mV s$^{-1}$) in N$_2$ saturated 0.1 M HClO$_4$ for 1200 cycles or 16 h. Pt loading: 20 μg cm$^{-2}$.

Fig. 11. CV curves of 20 wt% Pt/TiN showing the 100 and 1200 cycles during the potential cycling between 0 and 1.3 V (50 mV s$^{-1}$) in N$_2$ saturated 0.1 M HClO$_4$ at 70 $^\circ$C. Pt loading: 20 μg cm$^{-2}$.
in Fig. 10. Passivation of TiN surface due to hydroxide layer and the resulting poor conductivity of TiN particles has been reported by Qiu and Gao [21] who measured that the electrical conductivity of TiN powder decreases by an order of magnitude due to the hydrolyzed layer on the surface.

As mentioned earlier, the OCP curves in Fig. 8 show that an increase in temperature leads to faster passivation of the TiN NP surface. Hence, one can see a faster rate of decline of ECSA for test at 70 °C and significantly lower rate of decrease of ECSA at 23 °C (RT) in Fig. 10. This shows that the decreasing trends of ECSA of Pt/TiN can be explained by the adsorption model of TiN described using OCP curves.

It may be argued that the decline of ECSA for the Pt/TiN at higher temperatures (60 and 70 °C) of acidic media may also be due to the complete loss of Pt catalyst and/or a sharp increase in Pt particle size due to agglomeration. But an increase in Pt particle size does not amount to a corresponding rapid decline of ECSA as seen in Fig. 10 and the presence of Pt (on the Pt/TiN coated carbon cloth electrode) was still seen after the ADT using an energy-dispersive spectrometer. Also, an increased Pt particle shows lower current densities but retains the typical shape of the platinum CV curve unlike the 'cyc 1100' curve in Fig. 11 that shows negligible (hydrogen adsorption–desorption) HAD peaks with a complete passivation suggesting the poor conduction of support.

It can be observed that the passivation of TiN surface (plateauing of OCP in Fig. 8 at 60 °C) is attained in ~1 h whereas the passivation of TiN surface of Pt/TiN (plateauing of ECSA in Fig. 10 at 60 °C) is attained after ~4 h (or 300 potential cycles). The longer time taken by the TiN NP to passivate under potential cycling conditions, compared to the OCP conditions, agrees well with the earlier proposed mechanism of simultaneous dissolution and formation of oxide/oxynitride components during potential cycling. The illustration of the process can be seen in Fig. 12.

Though the above results of Pt/TiN electrocatalyst may seem to suggest only the strong dependence of temperature on its stability, a closer analysis indicates that factors such as concentration and type of acid media can also influence the TiN surface. It is emphasized that the passivation behavior of TiN NP shown in this study is specific to the temperature and concentration conditions of perchloric acid electrolyte. By changing the operating window to a different set of parameters of—acidic media, temperature and concentration, crystallinity of TiN powder [54], an active phase or a delayed passivation of TiN nanoparticles can be observed.

The passivation behavior of TiN NP under the prolonged electrochemical conditions may not be a limitation for its application as a catalyst support in PEM fuel cells. Unlike carbon black, TiN nanoparticles do not predominantly oxidize to gaseous oxides that can lead to a significant mass loss but forms a passivating surface that prevents further oxidation. If the chemical stability of the TiN nanoparticles towards water in acidic media can be modified to reduce surface hydrolysis, TiN NP can become a durable catalyst support that can increase the lifetime of PEM fuel cells. Zhang and Binner [55] proposed a coating of stearic acid on nitride powder as a stabilizing agent against hydrolysis while Müller et al. [56] described the protection of nanoscale non-oxidic particles from oxygen uptake by coating with N₂-containing surfactants. Though a carbon-based coating can provide a hydrophobic surface, there is a possibility that it may undergo electrochemical oxidation similar to carbon supports under PEM fuel cell conditions. Alternatively, identifying an active phase of TiN, in a set of conditions that fall in the operating window of a PEM fuel cell, can result in an increased durability of the Pt/TiN electrocatalyst.

Though carbon black supports cost less than TiN NP, an increased durability obtained from the novel TiN NP supports can reduce the lifetime costs of a PEM fuel cell system by enabling the system to function till its intended life span. Further research is being pursued to effectively use the oxidation resistance properties of titanium nitride nanoparticles for increasing the durability of electrocatalysts in PEM fuel cells. The research also opens different avenues where TiN supports can be used in combination with other catalysts or mixed with other conventional supports. But it is emphasized that attention must be paid to the stability of the nitride support over prolonged exposure under PEM fuel cell conditions as it provides the true understanding of the durability of the electrocatalyst.

5. Conclusion

The oxidation currents of TiN are significantly lower compared to that of CB at operating potentials 1.0 and 1.2 V of a PEM fuel cell thus indicating its corrosion resistance properties. XRD and XPS characterization of TiN NP revealed an existing oxide and oxynitride layer on the surface, which prevents further diffusion of oxygen into the bulk TiN. It is reported that the nitride component decreases and oxide/oxynitride components increase on the TiN surface during the potential cycling but the oxide/oxynitride layer tends to dissolve in acidic solution depending on the media and temperature. The exposed nitride surface reacts with the solution and using XPS and OCP data, it is shown to form Ti(IV) hydroxide ions that passivates the surface by adsorbing oppositely charged anions in the solution. The durability of Pt/TiN electrocatalyst also agrees well with the adsorption model of TiN NP.
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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.electacta.2010.08.035.

References