On the stability of TiN-based electrocatalysts for fuel cell applications

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ABSTRACT

The transition metal compound – titanium nitride (TiN), with its high electrical conductivity and corrosion resistance, can be a potential fuel cell material, particularly in the development of durable electrocatalysts replacing the state-of-the-art Pt/C. Compared to conventional carbon black, TiN nanoparticle (TiN NP) catalyst supports have a lower rate of corrosion under fuel cell conditions. The current research is a follow up study on the stability of TiN based fuel cell electrodes and its impact on the electrochemical activity of the Pt based electrocatalysts when used as an alternative to the state-of-the-art carbon black support in commercial fuel cell catalyst systems under fuel cell operating conditions. Through this paper, we report that an active behavior of TiN NP can be observed at the optimal conditions of 0.5 M H2SO4 and 60 °C. But under increased temperature or acidic conditions, the native layer on TiN tends to dissolve in the electrolyte exposing the underlying nitride surface which then gets passivated with hydroxide groups. Electrochemical and XPS characterization is used to validate our hypothesis of active or passive nature of TiN NP due to presence or absence of surface passivating -OH groups, respectively. The synthesized Pt/TiN electrocatalyst, upon subjecting to accelerated durability test, showed the performance trends which agree well with the active and passive nature of the TiN NP supports.

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1. Introduction

The fuel cell technology has made significant strides towards commercialization in the past decade but many aspects of this promising technology requires further development for it to compete against the conventional power sources. Of the various types of fuel cells, proton exchange membrane (PEM) fuel cells received broad attention due to their low operating temperature, low emissions and a quick startup time; suitable for automotive and stationary-power applications. But the cost and the lifetime of a PEM fuel cell system are the major challenges that are hindering its large scale commercialization [1,2]. Lifetime of a PEM fuel cell is mainly dependent on the durability of its material components [3]. As the fuel cell operates under corrosive conditions, high-performance materials are required to withstand the degradation and maintain the stability of the fuel cell system. 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 and Vulcan XC-72 carbon black is the most popular catalyst support currently used in the Pt/C electrocatalysts. But, through extensive literature [6,7], it has been shown that carbon undergoes corrosion under the oxidizing conditions of a fuel cell, thereby degrading the electrocatalyst and significantly reducing the durability of a PEM fuel cell system.

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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 [8–10] and potential cycling can further increase the rate of carbon support corrosion [6]. Significant oxidation of carbon support can be expected to decrease the performance of a fuel cell [10,11], due to the loss and/or agglomeration of Pt particles caused by the mass loss of carbon supports. Surface C/O groups can also decrease the conductivity of catalysts [11,12] and weaken its interaction with the support resulting in an accelerated Pt sintering [13–15]; thus drastically affecting the performance of a PEM fuel cell. These results indicate the vulnerability of carbon supports under fuel cell operating conditions. For a fast approaching energy gap and climate crisis, the improvement of long-term performance of PEM fuel cell technology is a critical requirement for it to compete against the conventional energy technologies, an aspect which is significantly influenced by the stability of electrocatalysts and its catalyst support.

2. Titanium nitride as an electrocatalyst material

Titanium nitride is a triple–bond transition metal compound which has an inert nature, high mechanical hardness and a high melting point [16]. The properties of TiN that make it attractive for its application in fuel cells are its electrical conductivity and corrosion resistance. TiN has a higher electrical conductivity (4000 S cm⁻¹) relative to carbon (1190 S cm⁻¹) [17] (and values higher than 4000 S cm⁻¹ have also been reported [16,18,19]); which arises from a lone unpaired electron going into a metal localized sp hybrid orbital on Ti resulting in the non-zero electron density at Fermi level [16].

TiN is also 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 [16,20–22]. The oxide and oxynitride components are also formed during the electrochemical oxidation of titanium nitride under potential scanning conditions [16].

With these unique properties of electrical conductivity and oxidation/corrosion resistance [17,23,24], TiN can be applied in fuel cells to develop durable electrocatalysts. Various research groups have reported the application of transition metal carbide and nitride family materials in low temperature fuel cells, as mentioned in a review article by Ham and Lee [25]. Recently, researchers have reported the application of TiN films [26] and titanium nitride [27–32] as electrocatalysts in polymer electrolyte fuel cell applications. Although the application of TiN-based compounds as electrocatalyst is reported, its stability and long-term durability under corrosive fuel cell conditions is not discussed. As the material further gains attention as an electrocatalyst material, its electrochemical behavior and stability under fuel cell conditions still 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 nanoparticles, above RT conditions, cyclic/ high potentials, highly acidic conditions (pH < 1) — which are the typical conditional variables faced by electrocatalyst material in fuel cells, has not been reported in the literature.

Through our recent publications [33,34], we introduced titanium nitride nanoparticles as a suitable catalyst support material to develop Pt/TiN electrocatalysts for application in PEM fuel cells. Upon synthesizing Pt/TiN, we showed that it can outperform the conventional Pt/C electrocatalyst in electrochemical surface area (ECSA) and catalytic activity for the same Pt loading [33]. On the durability aspect of TiN NP and Pt/ TiN electrocatalysts, we showed [34] that TiN NP acts as a stable electrode material at room temperature (RT) but passivates with increase in temperature of perchloric acid electrolyte. It was shown by us [34] that, depending on the temperature and thus the ionic strength of the electrolyte, the native oxide/oxynitride layer on TiN NP dissolves in the solution leading to the exposure of the underlying nitride surface. The nitride surface then reacts with the acidic media to form a Ti–OH group which attracts the oppositely charged anions in the electrolyte and passivate the surface. It was shown [34] that a passivated surface of TiN NP reduces its electrical conductivity thereby retarding the catalytic activity of Pt/TiN electrocatalysts and negatively affecting its durability.

In the concluding part of our previous report [34], we proposed that the passivation of the TiN NP under electrochemical conditions can be avoided by identifying factors, that influence the ionic strength of the acidic media, where TiN NP can be active. As the rate of corrosion of TiN in acidic conditions is significantly lower to that of carbon [35], identifying the operating conditions under which TiN is active (with a constant dissolution rate) can help in increasing the durability of TiN based electrocatalysts. In this paper, we study the behavior of titanium nitride catalyst supports in sulfuric acid electrolyte and electrochemically evaluate them under the PEM fuel cell operating conditions. Through our results, we show that an active behavior of TiN NP can be attained under a specific set of temperature and acidic conditions that entirely fall in the operating window of standard PEM fuel cell working conditions. The synthesized Pt/TiN electrocatalyst is subjected to accelerated durability test under different electrochemical conditions and the performance of the material is measured by calculating the ECSA. The ECSA trends and the durable characteristics of Pt/TiN are shown to agree well with the proposed temperature/ionic strength dependent, active-passive behavior of the TiN NP and are explained using an adsorption model.
The Pt/TiN electrocatalyst was synthesized using the polvyl process as described in Ref [33,34] and briefly discussed here. 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 to 160 °C for 3 h in a N2 atmosphere under refluxing conditions. The solution is stirred overnight at room temperature, washed in copious amounts of DI water and dried in air at 80 °C for 4 h. The resulting electrocatalyst had an average Pt particle size of 2.4 nm, as measured using X-ray diffraction and transmission electron microscopy characterization methods [34].

3.2. Electrochemical testing and half-cell performance

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.

For spectroscopic characterization, the TiN NP were coated on a carbon cloth and this working electrode was cycled between zero and positive potentials at 50 mV s⁻¹ in Ar saturated 0.5 M H2SO4 (pH < 0.5) electrolyte at 60 °C. After the electrochemical treatment, the TiN NP coated electrode is dried and used for XPS characterization. For electrochemical testing under open circuit potential (OCP) conditions, the TiN NP were sonicated in ethanol and an aliquot was deposited on a polished glassy carbon electrode (GCE, 5 mm dia., 0.1962 cm², Pine Instruments) for a material loading of 0.1 mg cm⁻² and the solvent is allowed to evaporate. The TiN NP coated GCE is immersed in sulfuric acid media and used as a working electrode in a three-electrode cell set-up for OCP measurements.

For determination of ECSA of Pt/TiN, the CV technique was performed on the electrode using a 3-electrode cell set-up. 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 cm⁻². After drying, a drop of aqueous Nafion (5 wt%) solution is stirred well before heating to 160 °C for 3 h in a N₂ atmosphere under refluxing conditions. The solution is stirred overnight at room temperature, washed in copious amounts of DI water and dried in air at 80 °C for 4 h.

The resulting electrocatalyst had an average Pt particle size of 2.4 nm, as measured using X-ray diffraction and transmission electron microscopy characterization methods [34].

4. Results and discussion

4.1. Surface composition of TiN nanoparticles

TiN forms a native oxide/oxynitride layer on its surface due to atmospheric oxidation. As the TiN NP with high surface area is exposed to atmospheric conditions, the native surface layer can have a significant influence on its role as a catalyst support. It was shown [34] that the surface of TiN NP is covered with an oxide/oxynitride layer using X-ray diffraction (XRD) technique, which showed that the pure NaCl-type structure (S.G. Fm3m [225]) of TiN NP has a lattice constant of 4.212 Å which lies between the lattice constants of TiO (4.241 Å) and TiO2 (4.185 Å); thus indicating the intermediate phase of TiO2N (34,37) [38]. Further evidence of the oxynitride layer is also shown using x-ray photoelectron spectroscopy in Fig. 7(a), where the deconvoluted peak between nitride and oxide peaks of Ti 2p can be attributed to the oxynitride which has an oxidation state in-between that of TiO and TiO2. It is emphasized that no complete phase separation of the surface oxide to TiO2 [16] is seen to occur as the XRD pattern of the TiN NP showed no predominance of TiO2 peaks [34].

For quantification and for chemical state determination, high-resolution XPS survey scan spectra along with atomic concentration of the “as is” TiN NP electrode is recorded showing C1s, Ti2p, O1s, and N1s in Fig. 1. The XPS peaks in the figure correspond well with those reported in the literature [16,20,22,39-42].

As can be seen in Fig. 1, the significant oxygen composition (34.24 at.%) is due to the oxide/oxynitride layer on the surface of TiN nanoparticles [34]. The higher composition of Ti (38.86 at.%) over N (22.42 at.%) further shows that the surface is not purely titanium nitride [35]. The titanium–oxygen–nitrogen system [40] has been well researched and the oxygen composition of the native layer has been attributed to a non-uniformly distributed mixture of oxynitride and oxide [16,20,21,39-41,43] components on its surface that prevent the surface from further oxidation [34,44]. Although Saha et al. [20] proposed a method to calculate the thickness of native layer on TiN films using a uniform oxide monolayer model, we believe that the same may not yield an accurate result in this case; considering that the substrate is in the form of high surface area nanoparticles.
and shows strongly the mixed-characteristics of oxide and oxynitride components. An etch profile of the particles can indicate the non-uniform distribution of these components on the surface.

An XPS depth profile was performed on TiN NP by sputtering the surface using Ar ions and is shown in Fig. 2(a). The surface composition of the TiN NP at the start of sputtering agrees well with the atomic concentration of O1s from survey scan of TiN NP in Fig. 1. The decrease in C after a short sputtering time, from 4.99 to 0 at.%, confirms that its presence is due to the surface contamination on TiN NP. Interestingly, the elemental trends change significantly after a depth equivalent to 5 min of sputtering time. This shows that the oxygen component (or oxide) is relatively thin and its dominance is limited to the top layers of the surface of TiN NP.

Fig. 2(b) supports the above explanation where the oxide component (of Ti 2p3/2) steeply declines with a corresponding increase of nitride component. After the sputtering time of 5 min, one can see the plateauing of the curves which reveals that the nitride component is dominant right below the surface while a certain amount of oxide is always seen to be present on TiN [45]. The oxynitride component is seen to be fairly stable in composition throughout the etch profile, attributed to its inert nature [34].

4.2. Oxide/oxynitride dissolution in sulfuric acid media

The surface oxides of TiN NP, due to their strong basic character, dissolve in acidic media to form colorless titanium (IV or +4) oxysalts that decompose in water, as was seen in the case of TiN NP in perchloric acid media [34]. To confirm the oxide dissolution in sulfuric acid, a few ml of H₂O₂ was added to a mixture of TiN NP dispersed in 0.5 M H₂SO₄ 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 to orange hydrated (Ti(III)OH)⁺ ions according to the reaction 1 [46] thus confirming the presence of dissolved Ti(IV) species:

\[
(Ti(OH)₃)⁺ + H₂O₂ → (Ti(III)OH)⁺ + 2H₂O
\]  

(1)

The immediate change in color of the solution suggests the rapid dissolution of titanium oxides in the acidic media [34]. Further evidence to the dissolution of oxide component is shown in the analysis of Table 1, where one can see a decrease in 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. The dissolution of oxynitride of TiN NP can be interpreted from the variation of its open circuit potential (OCP) with time. OCP or the corrosion potential (Ecorr) measures the equilibrium potential above which the oxidation is initiated on the surface of the electrode. A stable OCP indicates the stable nature of the electrode while the surface reactions cause the OCP to fluctuate. Fig. 3 shows the changes of OCP of TiN NP with
immersion time at various temperatures of sulfuric acid electrolyte. The OCP of TiN NP (at 60, 70, 80 °C), in Fig. 3, shifts rapidly downward during the initial stages 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 [40,47], which increasingly exposes the nitride surface directly to the acidic solution. As the temperature of the sulfuric acid electrolyte increases from 60 to 80 °C, the hydrogen ion strength in the acid increases thus causing a faster dissolution of oxynitride component. This can be seen in Fig. 3 as an increase in negative slope and a reduction of dissolution time during the initial stage of immersion. The anodic chemical reaction that can be related to TiN at these OCP conditions can be expressed as [40]:

\[
\text{TiN} + \text{H}_2\text{O} \rightarrow \text{Ti(OH)}^{2+} + \frac{1}{2}\text{N}_2 + \text{H}^+ + 3\text{e}^- \tag{2}
\]

Furthermore, the Potential–pH (or Pourbaix) diagram of Ti–H$_2$O predicts that the possible thermodynamically stable state of Ti ion under the OCP conditions is 3 + valence, which is also the oxidation state of Ti in reaction (2). The above two arguments suggest that the dissociated titanium, Ti(III), is most likely a Ti(OH)$^{2+}$ [40,43].

The rapid decrease of OCP, along with the generation of currents during the initial stage of immersion of Fig. 3, can thus be related to the formation of the corrosion product of Ti (OH)$^{2+}$ (according to reaction 2) on the nitride surface of TiN NP; with its nature of positive charge [40]. The formation of these positively charged corrosion products on the TiN surface leads to a subsequent adsorption of other negatively charged anions existing in the sulfuric acid solution such as HSO$_4^-$ and/or SO$_4^{2-}$. As a result, an adsorption configuration is likely to be set up where the surface area of TiN NP will be covered with a layer of such oppositely charged ions, naturally prohibiting the dissolution of TiN and thus making the electrode passive and attain more noble potentials. The rise of temperature of electrolyte to 70 and 80 °C increases the ionic strength of H$_2$SO$_4$ solution (due to further dissociation of H$^+$ and SO$_4^{2-}$ ions) resulting in an increased coverage of TiN NP and causing faster rate of oxynitride dissolution and rapidly exposing the nitride surface to the electrolyte. The Ti(OH)$^{2+}$ that is formed on the surface of TiN NP further attracts the SO$_4^{2-}$/HSO$_4^-$ ions resulting in a faster rate of passivation of surface. Hence, one can see that the OCP curve (at 70 and 80 °C) drops steeply in the initial stage of immersion after which it gradually increases to noble potentials before plateauing for the rest of the immersion.

The above described adsorption model, proposed by S.D.Chyou et al. [40] for TiN thin films in varying concentrations of sulfuric acid solutions, accurately explains the electrochemical behavior of TiN NP under 0.5 M sulfuric acid at varying temperature conditions. By increasing the concentration of sulfuric acid solution, S.D.Chyou et al. [40] reported that TiN thin film electrode changes from active to a passive state under RT conditions. Here, we show that a similar phenomenon can be observed by exposing the TiN NP electrode in sulfuric acid media to increased temperatures ranging from RT to 80 °C.

Unlike at higher temperatures, the hydrogen ion strength of 0.5 M H$_2$SO$_4$ at RT is insufficient to dissolve the surface oxynitride layer on the TiN NP. Hence, the OCP curve (at RT) in Fig. 3 is seen to decrease very slowly with time suggesting the slow process of oxynitride dissolution. With an increase in temperature of 0.5 M sulfuric acid solution from RT to 60 °C, one can see in Fig. 3 that the slope of the OCP curve becomes steeper suggesting a faster rate of oxynitride dissolution at 60 °C than at RT.

Of the OCP curves of TiN NP in Fig. 3, the OCP of 60 °C is uniquely positioned, because, after the oxynitride dissolution which is indicated by the drop of OCP, the OCP lies in the active region (~0.0 V vs. RHE) of the plot with a constant (and low) corrosion rate. It can be interpreted that, at this temperature, the exposed nitride surface forms the Ti(OH)$^{2+}$ as a corrosion product (according to reaction (2)) which easily dissolves in the electrolyte rather than of forming a passive layer on the surface of TiN NP by adsorbing anions from the solution. It can be explained that the 0.5 M sulfuric acid at 60 °C has an optimal ionic strength that is sufficient to dissolve the oxynitride layer but lacks the required concentration of oppositely charged ions that can passivate the surface of TiN NP; resulting in an increase of OCP towards nobler potentials.

It was reported [40] that, according to the mixed-potential theory, the cross-over of anodic and cathodic curves of TiN films (at RT) lies in the active regions of its anodic plot; due to which an active dissolution of TiN occurs in sulfuric acid of concentration between 0.1 and 16N. TiN acts as a non-passive metal in these conditions with a low-rate of corrosion. But above the critical concentration of 20N, TiN spontaneously undergoes passivation due to an increase in the ionic strength of acidic media due to dissociated H$^+$ and SO$_4^{2-}$. In the case of TiN NP in 0.5 M H$_2$SO$_4$, it is observed that the surface shows an active behavior until 60 °C, above which passivation occurs.

To confirm the above explanation of active and passive behavior of TiN NP with respect to temperature, XPS is performed on TiN NP electrodes exposed to OCP conditions of 60 °C and 80 °C in 0.5 M H$_2$SO$_4$ solution. After a certain immersion time, marked in Fig. 3 as Point 1 and Point 2, the

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Fig. 3 – Changes in open circuit potential (OCP) with the immersion time (4 h) for TiN NP in 0.5 M H$_2$SO$_4$ solution saturated with argon.
electrodes are taken out of the solution and dried before XPS characterization. As the OCP of TiN NP electrode at 60 °C lies in the active region in Fig. 3 (at Point 1), the XPS O 1s spectra of TiN NP at point 1 should have no passivating (OH) groups on its surface; while the XPS O 1s spectra of TiN NP electrode at point 2 of the OCP curve at 80 °C should indicate dominating presence of (OH) groups suggesting the increase of OCP to noble potentials due to surface passivation. These trends can be seen to match exactly in Fig. 4 (a) and (b) for point 1 and 2 respectively, where O 1s spectra of TiN NP at 80 °C shows the dominating –OH peak while O 1s spectra of TiN NP at 60 °C shows no such –OH peaks but ads. H2O.

XPS results support the explanation that TiN is active under the conditions of 0.5 M H2SO4 at 60 °C but undergoes passivation at higher temperatures. These results indicate that TiN NP, under the “active” conditions, acts as a stable electrode with its naturally low corrosion rate.

### 4.3. TiN NP electrodes under active dissolution

To study the surface characteristics of TiN NP during its active dissolution, the TiN NP electrodes are exposed to idle and extreme fuel cell operating conditions and studied using XPS characterization. The TiN NP was exposed to the following surface conditions:

(A) TiN NP, 12 h of immersion in 60 °C, Ar saturated, 0.5 M H2SO4

(B) TiN NP, 12 h (900 cycles) of potential cycling between 0 and 1.2 V at 50 mV s⁻¹ in 60 °C, Ar saturated, 0.5 M H2SO4

The XPS survey spectra of TiN NP electrodes, in Fig. 5(a) and (b), 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 [16,20,22,39,42]. The atomic concentrations of TiN NP electrodes show no significant difference between the two treatments after immersion or potential cycling in sulfuric acid electrolyte for prolonged times. But compared to the ‘as is’ TiN NP of Fig. 1, there is a significant increase in the atomic concentration of oxygen when TiN NP is exposed to conditions A and B. It can be hypothesized that the increase in oxygen composition on TiN NP is due to an increase in –oxide/oxy-nitride, OH groups or adsorbed H2O on the surface of TiN NP. The individual XPS spectra of oxygen, O 1s in Fig. 6, are inspected to explain the increase in oxygen composition on the surface of TiN NP. While the dominating peak at 530.9 eV on the surface of TiN NP (without any treatment) in Fig. 6(a), is oxide [16,20,22,39,41,42,48], a significant presence of the characteristic adsorbed H2O peak at 532.6 eV [16,39,40,42,49] is seen only in Fig. 6(b) and (c), which are exposed to conditions A and B in sulfuric acid media. The above results further support the explanation for Fig. 4 as no OH groups are formed on the surface of TiN NP as it is active under these conditions.

The dissolution of oxides of titanium in the acidic media can also be seen from the significant drop of the atomic concentration of oxide after conditions A and B, as shown in Table 1. It is interesting to note that the potential cycling has the same impact on the surface of TiN NP as does the immersion in 0.5 M sulfuric acid media at 60 °C, without an increase in the formation of oxide and oxy-nitride components. These results (O 1s spectra of Fig. 6 (b) and (c) and Table 1) further support the argument that the TiN NP surface does not get passivated at 60 °C sulfuric acid but undergoes low rate of corrosion with a strong presence of ads H2O. The surface adsorption of H2O on TiN NP is further supported by the Ti 2p spectra of TiN NP electrodes. The deconvoluted Ti 2p peaks of the electrode are shown in Fig. 7 whose peak positions match well with the literature [16,20,39,41,42].

![Fig. 4 - XPS spectra of O 1s for TiN NP electrodes taken at (a) point 1 and (b) point 2 on OCP curves shown in Fig. 3.](image-url)
In our previous report [34], it was shown that potential cycling of TiN NP in perchloric acid (at 60 °C) results in the formation of Ti(OH)$_2$ groups which passivate the surface and reduce its electrical conductivity thereby inhibiting the electron transportation in Pt/TiN electrocatalysts. In the present case of potential cycling of TiN NP electrode in sulfuric acid media (at 60 °C), no Ti(OH)$_2$ peak is observed in the Ti 2p spectra of TiN NP electrodes that can lead to the surface passivation. But a dominating peak is observed at 495.5 eV of Ti 2p which is generally characteristic of TiO$_2$ or TiO$_2$.H$_2$O component of Ti 2p$^{3/2}$. This dominant peak cannot be attributed to oxide as it is known to dissolve in acidic media and the Table 1 (along with O1s) further shows the significant decrease in its composition. But the similarity in the XPS peak positions of TiO$_2$ and TiO$_2$.H$_2$O and the presence of adsorbed H$_2$O in O1s spectra of Fig. 6 indicate that the dominant peak on Ti 2p spectra in Fig. 7(b) and (c) represents TiO$_2$.H$_2$O. From these results it is clear that the nitride surface undergoes active dissolution in sulfuric acid (at 60 °C) resulting in surface adsorption of H$_2$O.

### 4.4. Dependence of durability of TiN NP on acidic media

As the temperature (at given concentration of acidic media) 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 influence of temperature on the durability of Pt/TiN electrocatalyst in 0.1 M perchloric acid electrolyte is shown in our previous report [34]. As the TiN NP electrode became passive at the tested temperatures in 0.1 M HClO$_4$, the ECSA of the Pt/TiN decreased drastically in a short span of time to ~0 m$^2$.g$^{-1}$.

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This decrease is mainly attributed to the poor electrical conductivity of the TiN NP caused by the surface passivation of the supports with Ti–OH groups [34]. But unlike perchloric acid media, the TiN NP does not passivate in sulfuric acid at 60 °C, as observed so far.

Fig. 8 shows the results of the accelerated durability tests (ADT) performed on Pt/TiN in sulfuric and perchloric acid media (at 60 °C). Similar to TiN NP, the oxide and oxynitride components on Pt/TiN dissolve in the acidic media exposing the nitride surface. As the surface is shown to passivate in perchloric acid media [34], one can see in Fig. 8, a steep decline in the ECSA followed by a near zero activity of the Pt/TiN electrocatalyst. Upon passivation with –OH groups, the electrical conductivity of TiN NP is reduced [24], thereby limiting the support’s ability to transport electrons. But, since the TiN supports do not passivate but undergo active dissolution in sulfuric acid media (at 60 °C), a natural declination of ECSA is seen to occur in Fig. 8. Thus a strong correlation can be seen between OCP of TiN NP and the durability of Pt/TiN electrocatalyst in different acidic electrolytes.

The above results of Pt/TiN electrocatalyst seem to suggest the strong dependence of temperature, acidic concentration and type of acidic media on its stability. But a closer analysis indicates that these factors directly influence the ionic strength of the sulfuric acid media by varying its H⁺/SO₄²⁻ concentration, which ultimately influences the TiN NP surface. 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, as it is seen that an active phase can be achieved in sulfuric acid (60 °C). These conditions, under which TiN NP is found to be active, lie in the operating window of PEM fuel cell working conditions suggesting that the Pt/TiN electrode operated under the active behavior conditions can have a lower catalyst support corrosion. It is reminded that the RT conditions do not have a significant affect on TiN NP in acidic media (as seen in Fig. 3) suggesting the material’s negligible dissolution rate. The TiN NP electrode (and the Pt/TiN electrocatalyst) can appear to be stable under RT conditions of an acidic electrolyte only in a limited time window, but does not reflect the true behavior of the material.

Though carbon black supports cost less than that of 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. For the same amount of loading and particle size, the no. of Pt particles on the surface of TiN NP support in Pt/TiN
The electrocatalyst will be higher compared to carbon black support in Pt/C electrocatalyst of same dimensions, due to the difference in density of TiN (5.1 g cm\(^{-3}\)) [17] and C (1.9 g cm\(^{-3}\)) [17]. Since there are an increased no. of Pt particles on the TiN NP supports with a reduced particle–particle distance on the support surface, the Pt agglomeration can have a stronger influence on the decline of ECSA of Pt/TiN electrocatalyst. Hence it is highly likely that the decrease in ECSA of Pt/TiN in 0.5 M sulfuric acid (at 60 °C) can be primarily due to the Pt particle agglomeration and/or dissolution rather than catalyst support corrosion. Further research is being pursued to understand the degradation mechanism of Pt/TiN electrocatalysts under the conditions where TiN NP shows an active electrochemical behavior.

5. Conclusion

We found that the TiN NP catalyst supports based electrocatalysts are significantly influenced by the temperature and acidic conditions of PEM fuel cell operation. The supports behave passively, in sulfuric acid media at temperatures higher than 60 °C, due to the formation of −OH groups on its surface which reduce its electrical conductivity thereby inhibiting its electron transportation properties. The TiN NP supports, when tested in sulfuric acid media at 60 °C, showed an active behavior with a low dissolution rate without any passivation. Using XPS and electrochemical characterization, it is shown that TiN NP acts as an ‘active’ electrode under a specific set of acidic conditions that fall under the fuel cell operating window. The synthesized Pt/TiN electrocatalyst is subjected to accelerated durability test and the stability of the electrocatalyst agreed well with the proposed active/passive behavior of the TiN NP under the electrochemical conditions.

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