

Nafion-stabilised platinum nanoparticles supported on titanium nitride: An efficient and durable electrocatalyst for phosphoric acid based polymer electrolyte fuel cells

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Abstract

Nafion derived platinum nanoparticles were produced and successfully anchored on titanium nitride (TiN) support (Pt/TiN) and its suitability for phosphoric acid based polymer electrolyte membrane fuel cells is reported. Electrochemical cycling of Nafion stabilised Pt/TiN electrocatalyst exhibits good stability, durability and better electrocatalytic activity than the traditionally employed carbon supported Pt (Pt/C). Platinum supported on TiN exhibits better oxygen reduction reaction (ORR) activity as compared to carbon black (Vulcan XC 72). Nafion stabilised Pt/TiN shows a positive shift of 20 mV in half-wave potential measured from ORR polarisation curve in relation to Pt/C. Nafion stabilised Pt/TiN shows approximately two-fold increase in mass and specific activities than the Pt/C calculated from ORR data at 0.9 V. The improved durability of Pt/TiN catalyst arises from Nafion layer surrounding the Pt nanoparticles and corrosion resistant TiN support. Transition metal nitride based electrocatalysts are more active for cathode due to synergistic effect, which is observed in oxygen reduction reaction.

1. Introduction

The successful development of polymer electrolyte membrane fuel cell (PEMFC) technology is hindered by significant performance losses under extended operating conditions [1,2]. Platinum nanoparticles supported on carbon (Pt/C) remains the state-of-the-art cathode electrocatalyst in PEMFCs, despite its significant degradation of electrocatalytic activity under long term operation, affecting the fuel cell performance [3]. Corrosion of carbon support results in the detachment of Pt particles leading to particle size growth by agglomeration, resulting in loss of active electrochemical surface area [4]. Carbon black (Vulcan XC-72) is the widely used support for anchoring active metal nanoparticles but carbon undergoes corrosion due to harsh operating conditions of fuel cells. Furthermore, Pt enhances the carbon corrosion by reducing the oxidation potential, resulting in Pt sintering [5,6].

A suitable support material should possess corrosion resistance properties to operate under corrosive fuel cell operating conditions [7]. In order to alleviate carbon support corrosion and to minimise Pt sintering and dissolution process, an alternative

support could be used to replace the carbon [8,9]. In this regard, it is important to explore non-carbon based materials, with corrosion resistance and good durability. Considerable research efforts have been devoted to design corrosion resistant electrocatalyst support based on transition metal nitrides and carbides [7]. In general, transition metal nitrides exhibit more activity than transition metal carbides for oxygen reduction reaction (ORR). Of special interest, titanium nitride (TiN) shows more activity for ORR than titanium carbide [10].

TiN is considered as a promising catalyst support for noble metal catalyst like platinum [11]. Owing to its unique properties like good electrical conductivity, outstanding corrosion resistance TiN can outperform the carbon support in stability and activity under fuel cell operating conditions. Pt supported on titanium nitride nanoparticles catalytic activity has been evaluated and showed that Pt/TiN exhibits outstanding performance compared to conventional Pt/C by Avasarala and Haldar [12].

In the present study, Nafion stabilised Pt nanoparticles supported on TiN has been prepared and evaluated in phosphoric acid. Phosphoric acid doped membrane based fuel cells can operate above 100 °C, resulting in reduced catalyst loading with increased CO tolerance. Also higher operating temperature is expected to enhance the electrode kinetics. However, in phosphoric acid based fuel cells the strong adsorption of phosphate anion poisoning the Pt particles is detrimental to catalytic activity. Nafion layer surrounding the Pt nanoparticles could prevent the poisoning of Pt from adsorption of phosphate anion. Pt undergoes corrosion in phosphoric acid resulting in reduced activity; however presence of Nafion layer could protect the Pt from corrosion.

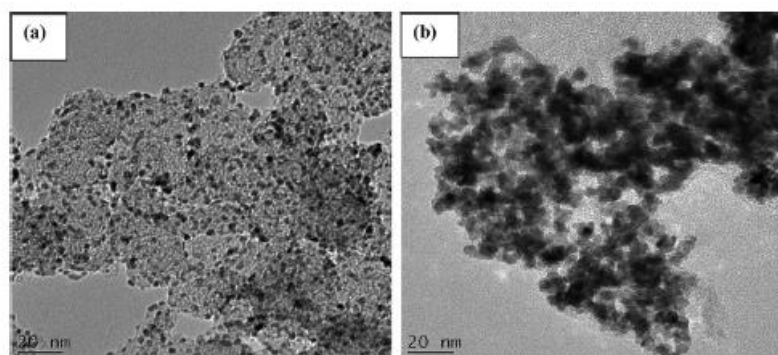


Fig. 1. HRTEM images (a) 20% Pt/C and (b) 20% Pt/TiN.

2. Experimental

The synthesis of Nafion stabilised Platinum nanoparticles (20 wt% Pt/TiN) was carried out by chemical reduction method using TiN, hexachloroplatinic acid hexa hydrates ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), Nafion (10%) and sodium borohydride (NaBH_4). In brief, hexachloroplatinic acid is stirred with Nafion (10%; Pt:Nafion mass ratio is 1:30) for 1 h. 5 ml of 87 mM NaBH_4 is added drop by drop to produce Nafion stabilised Pt colloid. Excess Nafion was removed by washing the colloid with 1:1 v/v acetone and water. A TiN powder (average size 3 μm ; BET surface area 12 $\text{m}^2 \text{g}^{-1}$ and density is 5.4 g/cm^3) is added to the purified Pt colloid and sonicated for 1 h.

The samples were characterised by transmission electron microscopy (TEM) and X-ray diffraction (XRD). Electrocatalytic activity of Nafion derived Pt/TiN was performed in a standard three electrode set up using rotating disc electrode (RDE) with a potentiostat (Autolab PGSTAT302N, Echochemie) and rotation control. A silver/silver chloride electrode (3 M KCl) is used as a reference electrode and potentials are referred to reversible hydrogen electrode (RHE). Glassy carbon electrode disc (5 mm diameter, 0.1962 cm²) is used as the working electrode substrate. Catalyst ink was prepared by ultrasonically mixing Pt/TiN in water and pipetting 5 µl of suspension onto the glassy carbon disc electrode to achieve a Pt loading of 20 µg cm⁻². After drying, a drop of Nafion (5%) solution is pipeted onto glassy carbon electrode surface as a binder to attach the catalyst and also acts as a proton carrier.

Cyclic voltammetry was performed at 25 mV s⁻¹ between 0 and +1.2 V in an N₂ saturated 0.5 M H₃PO₄ at room temperature. Electrochemical surface area in m² Pt g⁻¹ was measured from the area under the hydrogen adsorption/desorption peaks of CV curves after double-layer corrections. Accelerated catalyst degradation test was performed between 0.6 and 1.2 V at 25 mVs⁻¹ with 1000 cycles. The oxygen reduction reaction (ORR) was studied for the electrode scanned at 5 mV in oxygen saturated H₃PO₄ at 1600 rpm. The Nafion derived Pt/TiN was compared with commercial 20% Pt/C (from Alfa aesar).

The kinetic current (I_k) can be calculated from Koutecky–Levich equation that is expressed by

$$\frac{1}{I} = \left(\frac{1}{I_k}\right) + \left(\frac{1}{I_d}\right)$$

where I is the measured current and I_d the diffusion limited current. The I_d term can be obtained from the Levich equation:

$$I_d = 0.62nFAD^{2/3}\nu^{-1/6}\omega^{1/2}C_{O_2}$$

where n is the number of electrons transferred; F is Faraday's constant (96,485 C mol⁻¹); A is the area of the electrode (0.196 cm²); D is the diffusion coefficient of O₂ in 0.5 M H₃PO₄ solution (2.1 × 10⁻⁵ cm² s⁻¹); ν is the kinematic viscosity of the electrolyte (1.01 × 10⁻² cm² s⁻¹); ω is the angular frequency of rotation, $\omega = 2\pi f/60$, f is the rotation rate in rpm and C_{O_2} is the concentration of molecular oxygen in 0.5 M H₃PO₄ solution (1.03 × 10⁻³ M).

3. Results and discussions

3.1 Morphology and structural characterisation

Fig. 1a and b shows HRTEM images of commercial Pt/C and Nafion-stabilised Pt/TiN. Platinum nanoparticles are well dispersed on carbon support. In comparison Nafion stabilised Pt particles forms loosely agglomerated structures over TiN surface. The particle size distribution, calculated from more than 100 nanoparticles, shows that the mean particle size is about 5 nm in diameter for 20 wt% Pt/TiN as compared to Pt/C, which is slightly smaller than the value calculated from XRD.

Fig. 2 shows XRD patterns of Pt/TiN, which exhibits the sharp peaks for TiN, this pattern can be indexed to NaCl structure. The lattice parameter of TiN ' a ' is found to be 0.422 nm calculated from (1 1 1) diffraction plane of TiN. Pt shows four diffraction peaks corresponding to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes which are consistent with a face centred cubic (fcc) structure. Diffraction peaks of platinum were relatively broader due to smaller particle size. The crystallite size calculated for Pt (1 1 1) from the Scherrer formula is about 6.5 nm which is slightly more than the particle size measured from TEM images because XRD gives volume-weighted measurements that tend to overestimate the geometric particle size.

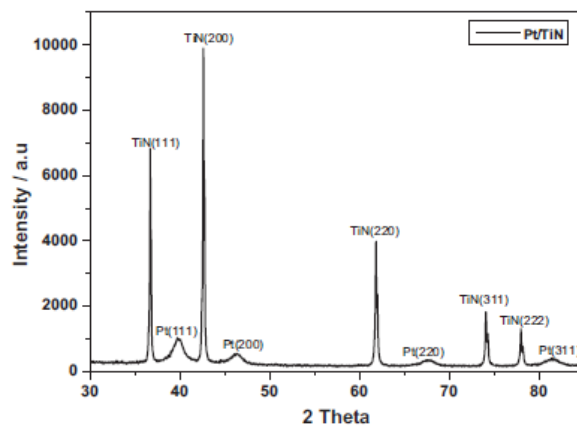


Fig. 2. X-ray spectrum of 20% Pt/TiN.

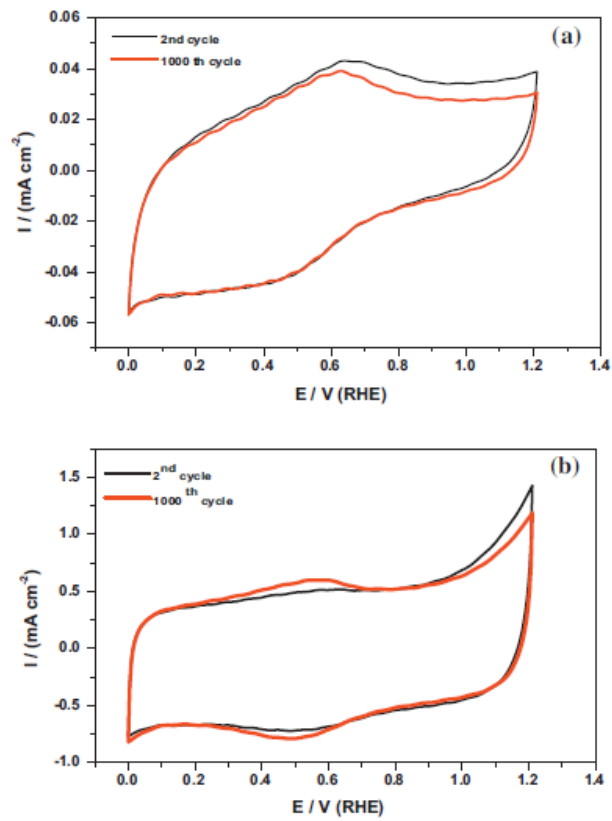


Fig. 3. (a) CVs of TiN and (b) CB in an N_2 saturated $0.5\text{ M H}_3\text{PO}_4$ at 100 mV s^{-1} .

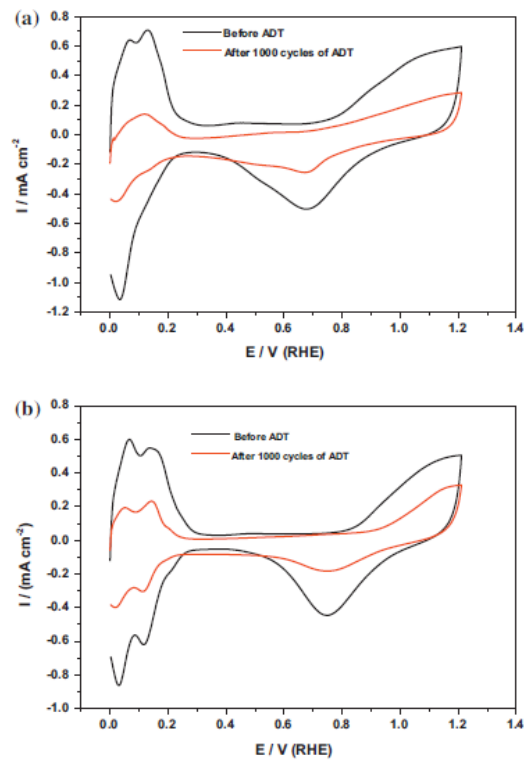


Fig. 4. (a) CVs of 20% Pt/C and (b) 20% Pt/TiN (Nafion stab) in N_2 saturated $0.5\text{ M H}_3\text{PO}_4$ at 50 mV s^{-1} .

3.2 Electrochemical comparison of carbon black (CB) and TiN in phosphoric acid medium

Fig. 3a and b shows the CV curves of TiN and CB electrodes respectively in an N₂ saturated 0.5 M H₃PO₄ at a scan rate of 100 mV s⁻¹. TiN shows significantly lower current densities than CB under same experimental conditions. TiN exhibits oxide or oxynitride layer on its surface, the presence of oxide or oxynitride creates passivating surface on TiN resulting in lower oxidation current densities, whereas carbon shows higher oxidation current densities with increasing corrosion rate. Also the inert nature of TiN attribute to lower current densities. The XRD results confirmed the presence of native oxynitride layer, this is attributed to the lattice parameter 'a', the value of 'a' for TiN is 0.424 nm; whereas for TiO is 0.418 nm. The value of 'a' calculated from XRD is 0.422 nm which lies in between the TiO and TiN. According to Vegard's law the titanium oxynitride lies between TiO and TiN.

3.3 Electrochemical characterisation

Fig. 4a and b shows CV curves of 20% Pt/C and 20 wt% Pt/TiN respectively in an N₂ saturated 0.5 M phosphoric acid medium. The comparison of cyclic voltammograms of 20 wt% Pt/TiN shows no additional current peak, which indicates that TiN is stable under potential region between 0 to 1.2 V. The ECSA measured for 20 wt% Pt/TiN is found to be 54.90 m² g⁻¹ pt and for Pt/C it was 53.33 m² g⁻¹ pt with an equal amount of pt loading in the electrodes.

After electrochemical cycling (1000 cycles) in the potential region between 0.6 and 1.2 V, Pt/C exhibit significant loss of ECSA (4.76 m² g⁻¹ pt) compared to 20 wt% Pt/TiN (15.23 m² g⁻¹ pt). The better catalytic activity and stability of 20 wt% Pt/TiN is attributed to corrosion resistant behaviour of TiN and also the coordination between Nafion and Pt nanoparticles [8]. Good interfacial contact is established between Nafion and Pt, resulting in effective ionomer distribution in the catalyst layer. The enhanced electrochemical stability is due to the Nafion layer covering Pt surface inhibiting the aggregation of Pt, owing to the strong steric hindrance effect of sulfonic acid groups on Nafion. Presence of Nafion layer between the Pt particles could prevent diffusion of soluble Pt particles by redepositing at original site.

The ORR polarisation curves measured for Pt/C and 20 wt% Pt/TiN on a rotating disc electrode (RDE) in an O₂ saturated 0.5 M H₃PO₄ at 1600 rpm are shown in Fig. 5a. Nafion stabilised Pt/TiN shows a 50 mV higher ORR onset potential than Pt/C. Current approaches the mixed kinetic-diffusion regime at lower overpotentials (+0.75 to +0.95 V) and at higher overpotentials current reaches its diffusion-limited value of ~5.37 mA cm⁻². The half-wave potential of an ORR curve is often used to evaluate the activity of catalyst. 20 wt% Pt/TiN shows a positive shift in $E_{1/2}$ of 20 mV compare to Pt/C. The difference in $E_{1/2}$ showed a marked improvement in ORR activity of 20 wt% Pt/TiN. The mass activity of Nafion stabilised Pt/TiN (0.9 V; 9.95 mA mg⁻¹) which is 2 times higher than that of Pt/C (0.9 V; 4.95 mA mg⁻¹), indicating that Pt/TiN has better catalytic activity.

The specific activity calculated from ORR at 0.9 V for 20 wt% Pt/TiN and Pt/C are 18.12 and 9.2 $\mu\text{A cm}^{-2}$ Pt respectively.

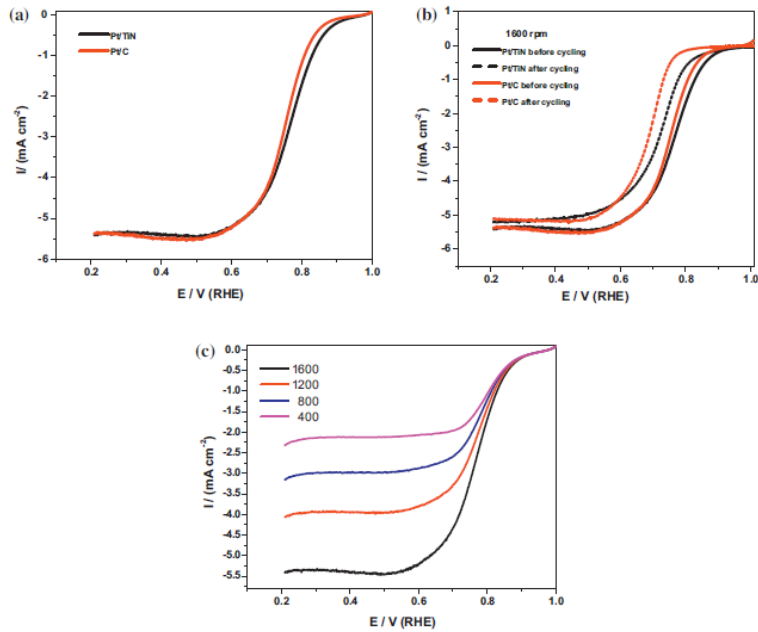


Fig. 5. (a) Oxygen reduction reaction curves of 20% Pt/C and 20% Pt/TiN in O_2 saturated 0.5 M H_3PO_4 at 1600 rpm and 5 mV s^{-1} scan rates, (b) ORR curves of 20% Pt/C and 20% Pt/TiN before and after ADT cycling and (c) rotation rate dependant ORR curves of 20% Pt/TiN.

Fig 5b shows the ORR curves performed after 1000 cycles of ADT, Pt/C shows a 70 mV degradation in half-wave potential whereas Nafion stabilised Pt/TiN shows about 50 mV shift. The rotation rate dependant polarisation curves for ORR of Nafion stabilised Pt/TiN is shown in Fig. 5c. Fig. 6a shows Koutecky–Levich plots obtained at 0.8–0.9 V. K–L plots are linear and parallel to each other; this indicates first-order kinetics with respect to molecular oxygen reduction. The number of electrons transferred (n), as calculated from the slopes of Koutecky–Levich plots at 0.8–0.9 V, is 3.83 (~ 4), which indicates nearly complete reduction of O_2 to H_2O . The Tafel plots of Pt/C and 20 wt% Pt/TiN are shown in Fig. 6b. It is seen from the Tafel plots, there are two regions, 60 mV/decade at lower current densities indicating one-electron transfer reaction being the rate-determining step and another region approximately at 120 mV/decade at higher current densities indicating that two-electron transfer reaction as the rate-determining step.

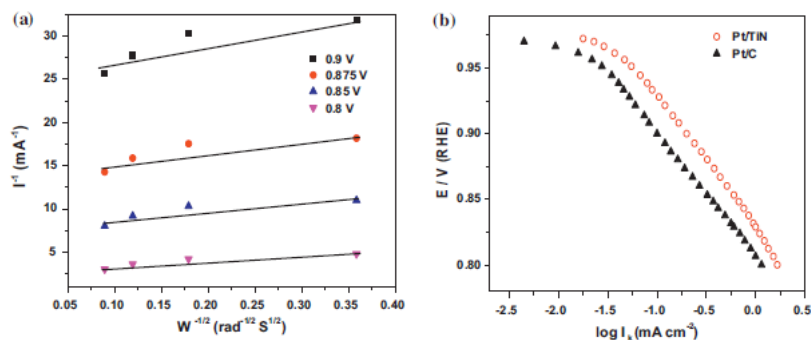


Fig. 6. (a) K–L plots of 20% Pt/TiN at different potentials and (b) Tafel plots of 20% Pt/C and 20% Pt/TiN.

The improved catalytic activities of Nafion stabilised Pt nanoparticles supported on TiN are influenced by metal support interactions as it is reported in literature for TiN supported electrocatalysts [12]. In case of carbon supported catalysts, the performance loss is mainly due to carbon corrosion, leading to agglomeration of Pt particle on the surface of support. Pt particles grow through Ostwald ripening and also electrochemical corrosion of Pt metal at anode and cathode contributes to the overall catalytic degradation [9]. Carbon is replaced with TiN to alleviate the carbon corrosion, and also the electrochemical corrosion Pt metal could be prevented with protection from Nafion layer. Moreover, the aggregation of Pt particles could be suppressed due to the steric effect of SO_3^- groups of Nafion. Nafion stabilised Pt on carbon has been reported with improved stability over commercial Pt/C, this can only control the electrochemical corrosion and aggregation of particles but carbon corrosion still exists and affects performance. Therefore, Nafion stabilised Pt/TiN is an alternative to carbon supported Pt based catalysts. The evaluation of Nafion stabilised Pt/TiN for full cell is under way.

4. Conclusions

20 wt% Pt/TiN has been developed and evaluated as electrocatalyst for fuel cells. The electrochemical analysis shows that 20 wt% Pt/TiN has better catalytic activity and stability under PEMFC operating conditions. The improved durability of 20 wt% Pt_{Na}/TiN is attributed to both the support properties and to the stabilising effect of Nafion. The results suggest that 20 wt% Pt/TiN can be a suitable cathode catalyst for phosphoric acid based high temperature polymer electrolyte membrane fuel cells.

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