

Titanium nitride nanoparticles based electrocatalysts for proton exchange membrane fuel cells†

Bharat Avasarala, Thomas Murray, Wenzhen Li and Pradeep Haldar*

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Titanium nitride nanoparticles act as a catalyst support material for proton exchange membrane fuel cells showing higher catalytic performance than conventional platinumized carbon electrocatalysts.

Proton exchange membrane fuel cells (PEMFCs) are a promising power technology with a wide variety of potential applications including stationary power sources and automotive engines. It was realized¹ that a significant challenge hindering large-scale implementation of PEMFC technology is the loss of performance during extended operation and repeated cycling. Investigations have revealed that a considerable part of the performance loss is due to the degradation of the electrocatalyst.² Currently, platinum (Pt) dispersed as nanosized particulates on high surface area carbon (Pt/C) is the preferred electrocatalyst used in PEMFC systems to obtain optimized catalytic activity and cost³ but its long term performance under chemically and electrochemically oxidizing conditions needs further improvement.⁴

In the present work, we show that titanium nitride (TiN) nanoparticles can be used as a catalyst support material for noble metals like Pt in PEMFC and can outperform the conventional Pt/C electrocatalyst in terms of catalytic activity. TiN has higher electrical conductivity, comparable to that of carbon and outstanding oxidation and acid corrosion resistance.^{5,6} These unique properties have the potential to make TiN a catalyst support for PEMFCs replacing carbon. Nanostructured TiN has proven to be a promising material for super capacitors⁷ and its application as an electrode material has also been reported^{7–13} in the past.

Recently it has been reported¹² that electrodeposited Pt on TiN film coated on a stainless steel substrate can outperform the conventional electrocatalyst in electrochemical oxidation of methanol. Datta and Kumta¹⁴ also showed higher catalytic activity of Pt 50 at% Ru/TiN as an anode catalyst support in direct methanol fuel cells. But, to our knowledge, no literature was found describing the usage of TiN nanoparticles as a catalyst support for Pt in hydrogen based PEMFCs.

Here we demonstrate the synthesis of a Pt/TiN electrocatalyst with Pt nanoparticles supported on commercial TiN nanoparticles

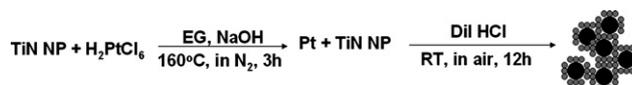


Fig. 1 Schematic illustration detailing all major steps involved in the preparation of Pt/TiN through a polyol process.

(average particle size: 20 nm, 40–55 m²/g, NanoAmor Inc, USA) and perform electrochemical tests to evaluate its electrochemical surface area (ECSA), mass and specific activities in aggressive PEM fuel cell testing conditions.

Fig. 1 summarizes all major steps involved in a typical synthesis of Pt/TiN by a polyol process¹⁵ using TiN nanopowder, ethylene glycol (EG) and hexachloroplatinic acid (H₂PtCl₆) to achieve a 20 wt% Pt on TiN.

In this process, TiN nanopowder is mixed in EG and ultrasonically treated before adding H₂PtCl₆ 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 nitrogen (N₂) atmosphere under refluxing conditions. EG serves as a reducing agent by oxidizing to glycolic acid at <160 °C. The deprotonated form of glycolic acid, glycolate ion, acts as a good stabilizer¹⁶ for the Pt colloids formed during the polyol process. The solution is stirred overnight at room temperature and washed with copious amounts of DI water at 80 °C to remove any organic residues left due to the oxidation of EG. The prepared electrocatalyst is dried in air at 80 °C for 3 h.

Transmission electron microscopy (TEM) analysis of the Pt/TiN electrocatalyst, as shown in Fig. 2 shows that the average particle size is ~2 nm with a distribution range 1–3 nm and the X-ray mapping (ESI†) suggests a uniform distribution of Pt on TiN support.

To evaluate Pt/TiN for its electrocatalyst performance, electrochemical measurements are performed in a standard three-electrode cell set up³ using a rotating disk electrode (RDE) with a potentiostat (Princeton Applied Research) and a rotation control (Pine Instruments). A reversible hydrogen electrode (RHE, HydroFlex) is used as a reference electrode and all potentials refer to that of the RHE.

A polished glassy-carbon disk electrode (5 mm diameter, 0.1962 cm², Pine Instruments) is used as the substrate for the supported catalyst. Catalyst dispersions are prepared by ultrasonically mixing the electrocatalyst in ethanol and pipetting an aliquot of the dispersion onto the electrode for a catalyst loading of 20 μg_{Pt}/cm². After drying, a drop of aqueous Nafion® (5 wt%) solution is pipetted onto the electrode surface in order to attach the catalyst particles onto the glassy-carbon electrode and also to create pathways for the H⁺ ions in the electrolyte to access the catalytic sites.

For cyclic voltammetry (CV) measurements, the electrode is cycled at 50 mV/s between 0 to +1.2 V in 0.1 M HClO₄ electrolyte saturated

College of Nanoscale Science & Engineering, University at Albany, SUNY, 255 Fuller Road, Albany, NY 12203. E-mail: phaldar@uamail.albany.edu; Fax: (+001) 518 437 8687; Tel: (+001) 518 437 8686

† Electronic supplementary information (ESI) available: The proof for the presence of surface oxide layer on TiN is presented using an XPS image and the X-ray diffraction data of lattice parameters. A TEM image of Pt/TiN is included to show that most of the Pt particles are supported on the TiN supports. An X-ray map of Pt/TiN is included for the elements Ti, N and Pt to indicate the uniformity of the Pt distribution on TiN. A TEM-based EDS image is presented to show the elements involved in Pt/TiN. See DOI: 10.1039/b819006b

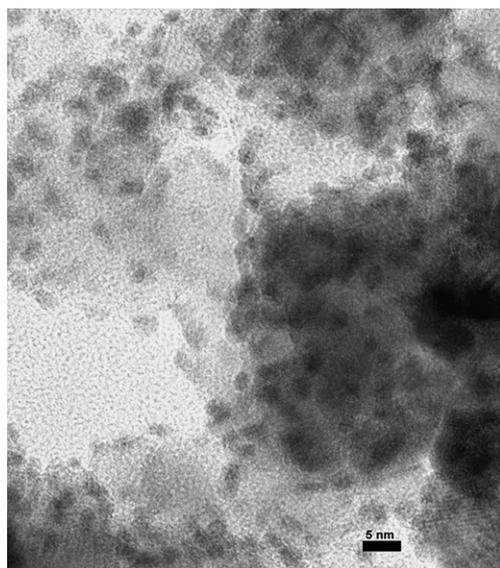


Fig. 2 TEM image of Pt/TiN showing Pt particles supported on TiN powder (scale bar: 5nm).

with argon.¹ The electrochemical surface area (ECSA) is measured from the area under the hydrogen adsorption/desorption peaks of CV curves after double-layer correction. For oxygen reduction reaction (ORR) experiments, the electrode was scanned from 0 to 1.0 V at 5mV/s in the electrolyte saturated with oxygen. All measurements were carried out at 60 °C.

As activities reported in the scientific literature even for pure platinum catalysts often vary by an order of magnitude in both rotating disk electrode experiments on polycrystalline Pt as well as in PEMFC testing of electrocatalysts,¹ Pt/TiN is compared with a commercial 20 wt% BASF Pt/C (average Pt particle size ~2 nm) electrocatalyst. The tests are performed under identical conditions on both the electrocatalysts using same amount of catalyst loading.

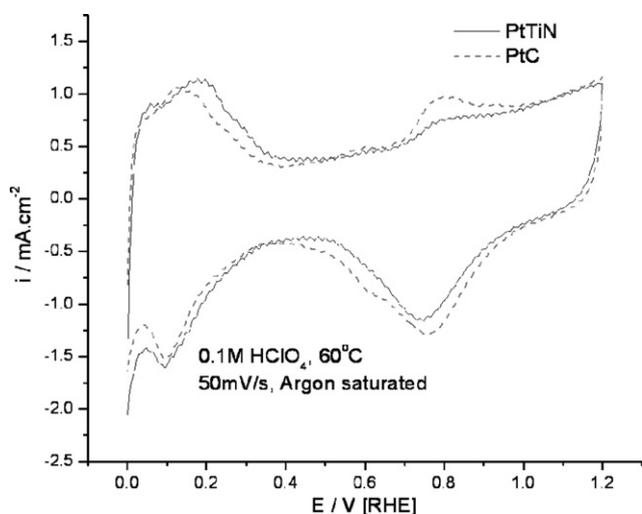


Fig. 3 Cyclic voltammograms of 20 wt% Pt/TiN and BASF 20 wt% Pt/C with a Pt loading of 20 $\mu\text{g}_{\text{Pt}}/\text{cm}^2$. Data recorded in argon saturated 0.1 M HClO₄ at 60 °C and 50 mV/s. Measurements are recorded after 20 cycles, to ensure the removal of any surface impurities on catalysts.

Table 1 Electrochemical surface area (ECSA), specific activities (i_s), and mass activities (i_m) of Pt/TiN and Pt/C determined from the CV and ORR determined at 50 mV s⁻¹ and 5 mV s⁻¹ respectively^a

	20 wt% Pt/C	20 wt% Pt/TiN
ECSA (m ² /g _{Pt})	68.7	75.6
Mass Activity (mA mg ⁻¹ _{Pt}), i_m		
0.9 V	6.2	16.4
0.8 V	90.6	294.2
0.7 V	586.2	1221.4
Specific Activity ($\mu\text{A cm}^{-2}$ _{Pt}), i_s		
0.9 V	9.1	21.7
0.8 V	131.8	389.2
0.7 V	853.3	1615.6

^a Catalysts were supported on glassy-carbon disk electrodes (for Pt-loadings of 20 $\mu\text{g}_{\text{Pt}}/\text{cm}^2$) and tested in 0.1 M HClO₄ at 60 °C.

The CV curve of Pt/TiN in Fig. 3 shows the usual voltammogram of Pt in acidic electrolytes and no additional current peak is seen, indicating that the TiN support is electrochemically inert and functions as a good electrical conductor in the potential region under PEMFC conditions. Pt/TiN also shows a similar peak intensity to Pt/C, between in the 0.05 V to 0.4 V region. It is also observed that a lower surface oxidation peak of Pt can be seen for Pt/TiN than for Pt/C at ~0.8 V. As can be seen in Table 1, the ECSA of Pt/TiN (derived from CV curves in Fig. 3) is higher than that of Pt/C for an equal amount of Pt loading. Considering the higher density of TiN (5.4 g cm⁻³)¹⁷ as compared to C (1.9 g cm⁻³),¹⁷ the C to Pt particles ratio per unit mass of electrocatalyst is 1:21 for 20 wt% Pt/C where as the ratio is 1:61 for 20 wt% Pt/TiN. Considering that the remaining things remain unchanged, there are more Pt nanoparticles supported on a single TiN particle than on a C particle. The TEM analysis indicated a minimal amount of unsupported Pt particles suggesting that most of the Pt particles are bound to the substrate. From the above points, it can be reasoned that more catalytically active

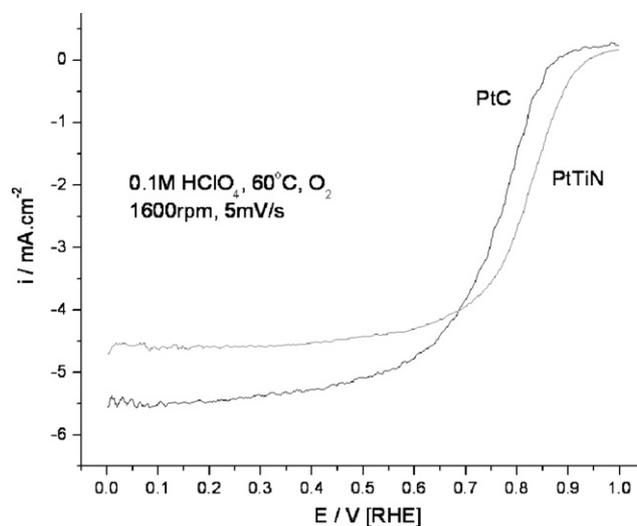


Fig. 4 Oxygen reduction current densities on 20 wt% Pt/TiN and BASF 20 wt% Pt/C (Pt loading in both cases: 20 $\mu\text{g}_{\text{Pt}}/\text{cm}^2$) on a glassy-carbon electrode at 1600 rpm in O₂ saturated 0.1 M HClO₄ at 60 °C (5 mV/s, anodic scan).

platinum sites are present in Pt/TiN resulting in higher ECSA. The TEM images (ESI†) of Pt/TiN also show the high Pt particle density on TiN supports. As shown in Fig. 4, the Pt/TiN shows a higher reduction current i.e. an excellent activity for oxygen reduction in comparison with carbon supported catalyst. Accordingly, the improved activity and ECSA of Pt/TiN in the electrochemical half cell may be attributed to the superior dispersion of Pt nanoparticles on TiN nanoparticle supports.

Table 1 compares the mass and specific activities of Pt/TiN and Pt/C drawn from CV and ORR plots of Fig. 3 and 4. It can be seen that Pt/TiN exceeds Pt/C at different potentials by a factor of 2, both in terms of mass and specific activities. These experiments were found to be repeatable for electrochemical measurements of 20 wt% Pt/TiN and 20 wt% Pt/C electrocatalysts and also reproducible for multiple batches of Pt/TiN prepared using the polyol process.

Though the reasoning behind the higher performance of Pt/TiN is being investigated, we speculate that a metal-support interaction observed in catalytic reactions,^{18,19} in this case, between the platinum catalyst and the titanium nitride support could also be a cause of an improved catalytic activity.

As literature shows that the electrocatalytic activities of the catalyst particles are influenced by the support material,^{18–20} TiN is playing a crucial role along with being a conductive support in our case and possibly aiding the catalysis through “electrochemical promotion”. Further research is being performed to understand TiN as a catalyst support and its durability properties are also being evaluated.

X-Ray diffraction and X-ray photoelectron spectroscopy (XPS) results (ESI†) showed the presence of a oxygen-rich layer on the surface of non-platinized and platinized TiN nanoparticles. The high surface oxygen content is due to a thin oxide/oxy-nitride layer (of a few nm thickness) that is formed on the TiN surface⁸ due to its oxidation from exposure to oxygen and/or moisture in air. Though the oxide layer has an affect on the electrical conductivity at the TiN surface, the CV and ORR of Pt/TiN in Fig. 3 and 4 respectively, did not indicate a poorly conducting catalyst support. This leads to a possibility that the oxide layer may be aiding the oxidation process thereby getting reduced to TiN as suggested by Musthafa¹² and Giner.¹³ Surface analysis and electrochemical techniques are being used to study the above phenomenon.

In summary, here we have demonstrated a platinum/titanium nitride electrocatalyst from a new class of (noble metal/metal alloy/

(transition metal nitride and carbide) materials, synthesized via a polyol process. As shown with the Pt/TiN, such electrocatalysts show higher electrochemical performance under PEMFC conditions. This therefore opens up the possibility of making a variety of Pt-based alloys like Pt–Ru, Pt–Au and Pt–Fe with this class of transition metal-nitride or -carbide materials for use as electrocatalysts for the PEMFC.

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