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Nitrogen and carbon doped titanium oxide as an alternative and durable electrocatalyst support in polymer electrolyte fuel cells



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HIGHLIGHTS

- Nitrogen and carbon doped TiO₂ is synthesized.
- Platinum is deposited on TiON support by a colloidal method.
- Pt/TiON-1 electrocatalysts show higher ORR activity.
- Pt on TiON-1 moiety show enhanced fuel cell performance.
- Stability of Pt/TiON-1 electrocatalyst is higher than Pt/C.

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ABSTRACT

Nitrogen and carbon doped titanium oxide as an alternative and ultra-stable support to platinum catalysts is prepared and its efficiency is determined by polymer electrolyte fuel cell. Nitrogen and carbon doped titanium oxide is prepared by varying the melamine ratio followed by calcination at 900 °C. Platinum nanoparticles are deposited onto doped and undoped titanium oxide by colloidal method. The doping effect, surface morphology, chemical oxidation state and metal/metal oxide interfacial contact are studied by X-ray diffraction, Raman spectroscopy, high resolution transmission electron microscopy and X-ray photo electron spectroscopy. The nitrogen and carbon doping changes both electronic and structural properties of titanium oxide resulting in enhanced oxygen reduction reaction activity. The platinum deposited on optimum level of nitrogen and carbon doped titanium oxide exhibits improved cell performance in relation to platinum on titanium oxide electrocatalysts. The effect of metal loading on cathode electrocatalyst is investigated by steady-state cell polarization. Accelerated durability test over 50,000 cycles for these electrocatalysts suggested the improved interaction between platinum and nitrogen and carbon doped titanium oxide, retaining the electrochemical surface area and oxygen reduction performance as comparable to platinum on carbon support.

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1. Introduction

The polymer electrolyte fuel cell (PEFC) is considered as an ideal energy conversion power source for mobile and stationary applications due to its high efficiency and being benign to the environment [1]. However, commercialization of PEFC is hindered by several issues such as high cost, low reliability and poor long-term durability, among which durability has been recently recognized as one of the central issues to be tackled [2]. Longevity of PEFC primarily hinges on the durability of the cathode and has been the focus of R & D activity over the last decade. The slow-kinetics of the oxygen

reduction reaction (ORR) at cathode and acidic nature of the membrane electrolyte limits the use to only noble metals like platinum (Pt) as electrocatalysts. Carbon is widely used as a supporting material for PEFCs because of its very high surface area and good electronic conductivity [3]. The carbon-support plays a significant role in determining the activity and durability of the catalysts. Indeed, support material has generated enormous interest in recent years because of their vital role in improving activity and stability of catalyst nanoparticles. Also an ensemble of reduction in precious metal loading with better catalyst utilization is possible using a suitable support thereby reducing the catalyst cost [4]. Ironically, significant oxidation of carbon support can be expected to decrease the performance of PEFC [5]. Besides, degradation of electrocatalysts is the main reason for the decline in fuel cell performance over time [6,7]. Therefore, long-term durability is as important as or even more important than the catalytic activity for electrocatalysts. There is

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a rapidly growing interest in the investigation of performance degradation of PEFCs and its components [2]. Most literature reports reveal that during PEFC operation, Pt nanoparticles either agglomerate or detach from carbon support, which results in electrochemical surface area (ECSA) decrement and PEFC performance loss [5,8].

In this aspect the research is advanced towards the exploration of new electrochemically stable non-carbon support to improve the performance and durability of electrocatalysts [9–11]. Titanium oxide (TiO₂) materials have received increasing attention as possible catalyst supports due to their inherent stability in electrochemical environment, beneficial interactions with metal catalysts and good proton conductivity [12–16]. Interestingly, Pt deposited on TiO₂ is reported to increase the long-time durability of PEFCs with comparable fuel cell performance to Pt/C, although the initial ECSA was observed to be lower [17,18]. This is due to the low electrical conductivity and surface area of TiO₂ which still remain as barrier for their application in fuel cells [12–14]. However, there have been considerable studies to modify TiO₂ structure or enhance its surface and structural properties to improve the ORR activity in fuel cells. For instance, doped version of TiO₂ is an interesting approach. Chevalier et al. reported Pt deposited on Nb–TiO₂ catalysts with improved ORR activity and stability [19]. Similarly, physical and chemical properties of TiO₂ can be tailored in various applications by substituting different atoms into the TiO₂ crystal structure to increase the variable valence state and structural flexibility that offers improved catalytic behaviour [20–28]. Interestingly, various research groups reported the changes in electronic and structural properties of TiO₂ by nitrogen and carbon (N & C) doping and functionalized carbon (C) on TiO₂ [21,22,24,29]. Owing to the high abundance, N & C doped TiO₂ has grown as one of the most interesting electrocatalyst which is appropriate for mass production [30,31]. The introduction of N or C into TiO₂ structure is more attractive because during growth process, the crystal structure has more dislocations with increased d-spacing resulting in more surface active sites. Besides, N and C doping into TiO₂ structure also leads to a large electron donor state near the Fermi level, improving the charge transfer properties [32,33]. In addition, depending on the synthesis procedure of N and C doped TiO₂, novel structures such as nanorods [21,23], nanowire TiO₂ [25], and spherical growths [24,30] with improved active sites can be prepared. These exceptional properties make TiO₂ more desirable as catalyst support for PEFCs replacing carbon.

In the present work, we demonstrate that both electrochemical activity and stability of the N & C doped TiO₂ supported Pt catalyst can be greatly improved by preserving the optimum level of N & C doping on TiO₂ support. In-depth study of Pt on N & C doped TiO₂ electrocatalysts for real fuel cell system and long-time durability has not been studied previously in the literature to the best of our knowledge. In this investigation, we have used a hydrothermal method to prepare the TiO₂ support followed by doping nitrogen and carbon using melamine as a precursor. Finally, Pt is deposited on various amount of N & C doped TiO₂ (TiON) and undoped heat treated TiO₂ (HT-TiO₂) by colloidal method. The doping effect, structural defects, elemental mapping and composition, Pt nanoparticles dispersion, surface and chemical oxidation state were investigated by various characterization techniques. ORR activity of Pt on HT-TiO₂ and TiON electrocatalysts were studied by linear sweep voltammetry (LSV) using rotating disc electrode (RDE). Further, the implementation of Pt/HT-TiO₂ electrocatalysts in real fuel cell system was carried-out with varying metal loading. Its effect on both anode and cathode catalytic activity is also explored. Pt on optimum level of N & C doped TiO₂ exhibits improved fuel cell performance comparable to Pt/C. The accelerated durability test (ADT) for electrocatalysts was carried out by potential cycling between 0.6 and 1.2 V.

2. Experimental section

2.1. TiO₂ prepared by hydrothermal method

TiO₂ nanoparticles were synthesized by hydrothermal method. In brief, 8 ml of titanium isopropoxide (Merck, India) was added to 30 ml of ethanol solution followed by the addition of 10 ml of diluted acetic acid and stirred for 3 h. Finally, 30 ml of 0.5 M NaOH was added to above mixture and stirred for 1 h which was further transferred to autoclave and kept at 150 °C for 24 h. The white precipitate obtained was washed with de-ionized water (18 MΩ cm) followed by ethanol and dried at 80 °C for 12 h. Finally, 500 mg of as-synthesized TiO₂ was calcined at 900 °C for 1 h at nitrogen atmosphere. The heat treated sample was marked as HT-TiO₂. Nitrogen and carbon (N & C) doped TiO₂ (TiON 1:1) was prepared by mixing equal amount of as-synthesized TiO₂ and melamine (Acros Organics) together followed by heat treatment at 900 °C for 1 h at nitrogen atmosphere. Similarly different ratios of N & C doped TiO₂ such as TiON (1:2), TiON (1:4) and TiON (1:6) were prepared by varying the melamine ratio with respect to TiO₂. The above supports were marked as TiON-1, TiON-2, TiON-4 and TiON-6.

2.2. Platinum deposited on HT-TiO₂ electrocatalyst prepared by colloidal method

The platinum (Pt) deposited HT-TiO₂ electrocatalyst was prepared through colloidal method by using HT-TiO₂ and Na₆[Pt(SO₃)₄] as Pt precursor [34]. In brief, the required amount of HT-TiO₂ was dispersed in 200 ml de-ionized water followed by addition of required amount of Pt precursor (viz. Na₆[Pt(SO₃)₄] dissolved in 0.1 M H₂SO₄). Further, 150 ml of hydrogen peroxide was added dropwise with continuous stirring at 60 °C for 3 h. Finally, Pt/HT-TiO₂ electrocatalyst was obtained by the addition of formic acid with continuous stirring for 3 h at 80 °C. The resulting product obtained was washed repeatedly with de-ionized water and dried at 100 °C for 12 h. Similarly, Pt deposited on N & C doped TiO₂ (TiON) electrocatalysts were prepared using the above method. Pt deposited on as-synthesized HT-TiO₂, TiON-1, TiON-2, TiON-4 and TiON-6 is represented as Pt/HT-TiO₂, Pt/TiON-1, Pt/TiON-2, Pt/TiON-4 and Pt/TiON-6, respectively. Fig. 1S shows the flow chart of the preparation method and colour change at each stage (given in [Supplementary Information](#)). For comparison, 40 wt. % Pt/C (HISPEC 4100) procured from Alfa Aesar, US is taken as baseline.

2.3. Material characterization

Powder X-ray diffraction (XRD) studies were conducted using BRUKER-binary V3 powder diffractometer operating in reflection mode with Cu Kα radiation (λ = 1.5406 Å) at scan rate of 2° per minute. Raman spectra were recorded at 25 °C on Nanophoton Raman-11 spectrometer with 532 nm line of Nd-YAG laser. High resolution scanning electron microscopy (HR-SEM) images were obtained from Quanta 200 FEG instrument coupled with energy dispersive X-ray spectrometry (EDX) and parallel beam spectroscopy (PBS) for elemental analysis. High resolution transmission electron microscopy (HR-TEM) image were taken with a Techni G2 (model-TWIN, 300 kV field emission gun) microscope by FEI Company, Netherlands. The chemical oxidation state and chemical shift of the elements were determined by X-ray photoelectron spectroscopy (XPS) using omicron nanotechnology instrument, Germany.

2.4. Electrochemical characterization

Glassy carbon (GC) disk was used as working electrode along with saturated calomel electrode (SCE) and a Pt foil as reference and

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