

Coaxial TiN-CNT Composites as Effective Low Temperature Fuel Cell Electrocatalyst Supports

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Coaxial titanium nitride (TiN) coated carbon nanotubes (TiN-CNTs) were fabricated by a simple two-step procedure. These novel materials were utilized as Pt electrocatalyst support materials for the oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR). By effectively coupling the unique physicochemical properties of TiN and CNTs, improved performance in comparison to commercial Pt/C was observed, indicative of the favourable catalyst-support interactions provided.

Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) and more specifically, direct methanol fuel cells (DMFCs) are emerging on global markets as efficient energy conversion and storage technologies. Currently however, performance improvements and system cost reductions of these devices are required in order to render them commercially competitive and ensure their long term economic viability for production and sale. These advancements can be successfully realized by developing new electrocatalyst technologies used to facilitate the pertinent operational electrode reactions, namely the oxygen reduction reaction (ORR) (1-3) and the methanol oxidation reaction (MOR) (4, 5).

Traditionally, these catalysts are based on expensive platinum (Pt) materials, and suffer from poor electrocatalytic activity, stability and contaminant tolerance (6). Development of unique catalyst materials in order to improve the utilization and performance of Pt catalysts has been accomplished by either: i) modifying the Pt by alloying and/or nanostructure control (4, 7), or ii) developing unique catalyst support materials in order to effectively tailor the specific catalyst-support interactions (8-10). The latter is a favourable approach that many researchers have investigated, and particularly, titanium nitride (TiN) supports have recently been demonstrated capable of providing performance improvements for both the ORR (11) and MOR (12, 13), while also improving Pt tolerance to CO poisoning (12), a beneficial enhancement for MOR electrocatalysis considerations (4).

In the present study, unique coaxial TiN coated carbon nanotube (TiN-CNT) composites were developed as Pt nanoparticle supports. This approach effectively couples the beneficial properties of TiN, including favourable catalyst-support interactions and strong thermal, chemical and mechanical resistance; with the unique physical properties of CNTs, including high electronic conductivity, and a one-dimensional anisotropic morphology that can be arranged into porous, interconnected electrode architectures (14). Pt nanoparticle deposition was carried out by the modified ethylene glycol (EG) method, and the resulting composites were found to display

enhanced ORR and MOR capabilities in comparison with commercial, state of the art Pt/C catalyst.

Experimental techniques

Pt/TiN-CNT Synthesis

Commercial CNTs (Cheap Tubes Inc.) were used as the starting materials and functionalized by refluxing in 6M HNO₃ for 5 hours. Functionalized CNTs (50 mg) were then well dispersed in ethanol (60 mL) by ultrasonication for several hours and transferred to a magnetic stir plate. Titanium butoxide (500 uL) was added to the mixture and allowed to stir for 30 minutes, followed by the addition of DDI water (500 uL). Mixing was maintained for another 30 minutes, after which refluxing was carried out for 6 hours in order to deposit Ti precursors on the surface of the CNTs. After cooling, the products were collected by centrifugation, washed and calcined under an argon environment for 4 hours at 400 °C to form TiO₂ coated CNTs (15). Conversion of TiO₂ coating to TiN was achieved by heat treatment under ammonia at a temperature of 800 °C for 4 hours.

Pt nanoparticle deposition was carried out by the modified EG method. TiN-CNTs were ultrasonically dispersed in EG solvent, after which hexachloroplatinic acid hexahydrate salt dissolved in EG was slowly added to the mixture in order to achieve a Pt weight loading of 20 %. Mechanical mixing was maintained throughout the entire duration of the experiments, and the pH of the mixture was raised to 13 using a sodium hydroxide/EG solution. The solution was then heated to 140 °C under reflux conditions and maintained for 4 hours in order to facilitate Pt nanoparticle reduction and subsequent growth. After cooling, the pH of solution was adjusted to 5 using HCl and the sample was collected by filtration and thoroughly washed.

Physicochemical and Electrochemical Characterization

The morphology and structure of the materials developed in this work were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). X-ray diffraction (XRD) patterns were also obtained in order to investigate the crystalline structure of the developed materials.

Electrochemical characterization was carried out by half-cell investigations using a CHI potentiostat and Pine rotator. Catalyst ink was prepared by mixing 4 mg of catalyst with 2 mL of an ethanol/DDI water mixture, upon which 20 uL was deposited onto the surface of a glass carbon rotating electrode. A Pt wire counter electrode and Ag/AgCl counter electrode were utilized for all testing. ORR activity was investigated by saturating 0.1 M HClO₄ electrolyte solution with oxygen and cycling the electrode potential at a scan rate of 10 mVs⁻¹. Background currents obtained under nitrogen saturation were removed in order to remove capacitive contributions. MOR activity was investigated using 1M methanol and 0.1 M HClO₄ electrolyte solution saturated with nitrogen. The electrode potential was cycled at a scan rate of 5 mVs⁻¹. Commercial state of the art Pt/C was tested in addition to Pt/TiN-CNT in order to provide performance comparison.

Results and Discussion

The successful fabrication of coaxial TiN-CNT was confirmed by TEM (Figure 1a), with then TiN coating being polycrystalline in nature with small amounts of CNT exposure observed. XRD patterns (Figure 1b) confirmed the hexagonal crystal structure of TiN, indicating the effectiveness of TiO_2 conversion to TiN by an ammonia heat treatment technique. Furthermore, the graphitic content of the CNTs was maintained throughout all fabrication techniques evidenced by the (002) plane diffraction observed at a 2 theta diffraction angle of ca. 26° .

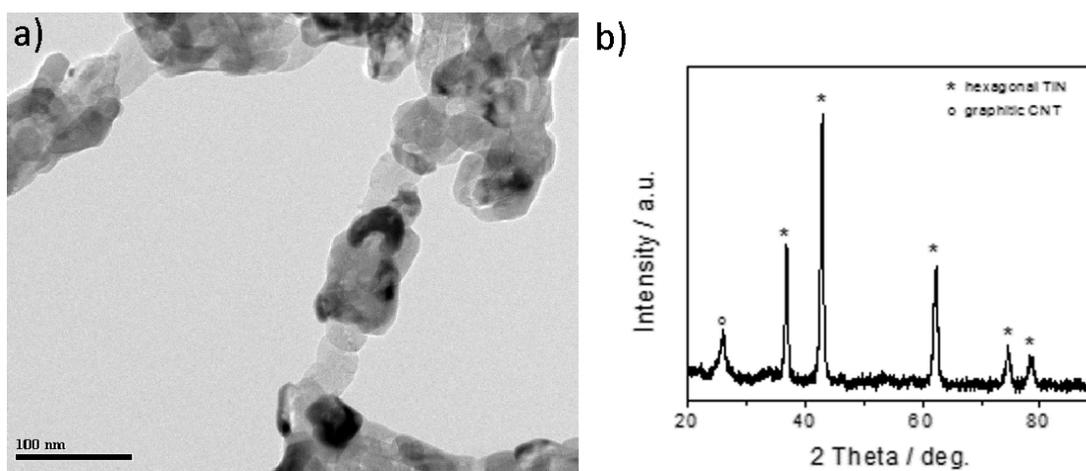


Figure 1. a) TEM image and b) XRD pattern of as synthesized TiN-CNTs.

TEM imaging was also used to confirm the successful deposition of Pt nanoparticles on the surface of TiN-CNTs (Figure 2). The effectiveness of the modified EG reduction method is evidenced by the well dispersed, relatively uniform Pt nanoparticles over the entire surface of the TiN-CNT composites. The average measured particle size was ca. 2.9 nm, with the majority of particles being in the 1-4 nm range.

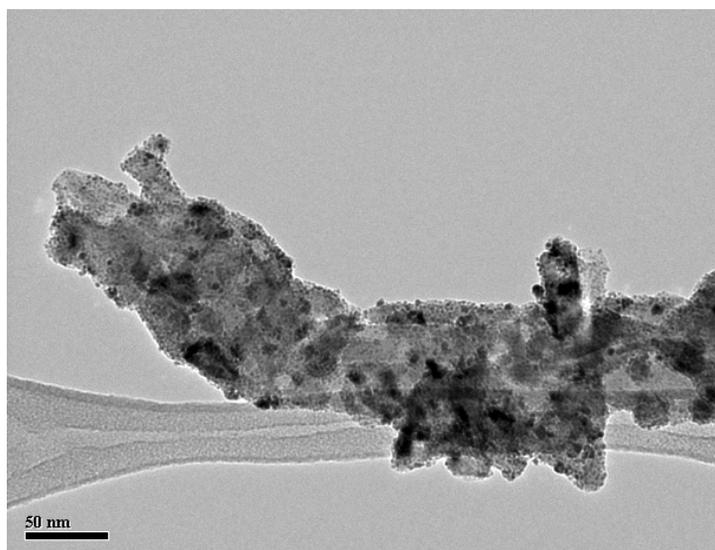


Figure 2. TEM image of Pt/TiN-CNT electrocatalyst.

ORR polarization curves for Pt/TiN-CNT and Pt/C are provided in Figure 3a. An improved ORR onset potential and current densities were observed for Pt/TiN-CNT, indicative of the favourable catalyst-support properties provided by these unique support materials. Moreover, higher current densities were obtained at lower electrode potentials (not shown), providing evidence of higher catalyst selectivity towards the overall 4 electron reduction mechanism to water. This is most likely due to the hindered release of peroxide intermediated from the carbon based supports due to TiN surface coverage.

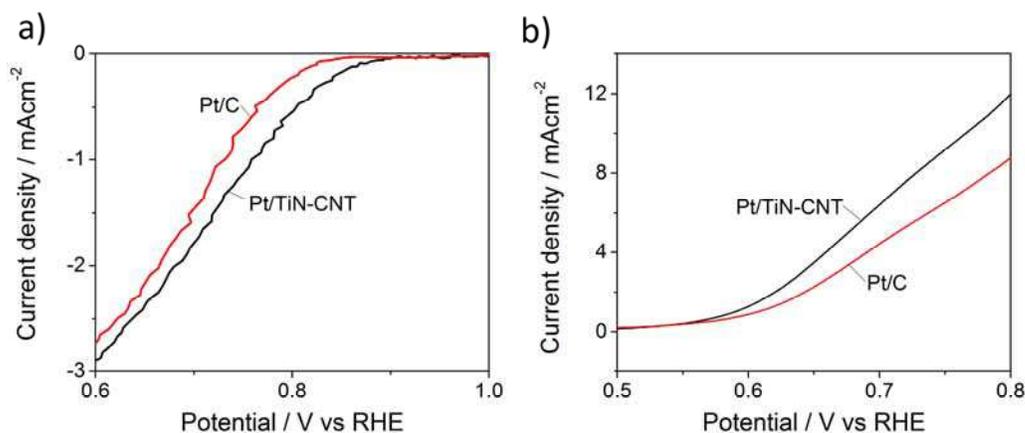


Figure 3. Pt/TiN-CNT and Pt/C a) ORR polarization curves carried out in oxygen saturated 0.1 M HClO₄ at a scan rate of 10 mVs⁻¹ and an electrode rotation rate of 900 rpm. b) MOR polarization curves obtained in nitrogen saturated 0.1 M HClO₄ containing 1 M methanol at a scan rate of 5 mVs⁻¹ and no electrode rotation.

MOR polarization curves are provided for both Pt/TiN-CNT and Pt/C in Figure 3b. Clearly, Pt/TiN-CNT provides enhanced MOR electrokinetics in comparison to state

of the art commercial Pt/C. Table 1 highlights results from the full range polarization curves obtained (not shown), where i_{\max} represents the maximum current density obtained in the forward potential scan direction, and i_f/i_b represents the ratio of the peak current density in the forward direction to the backward direction. The latter is a common evaluation of catalyst CO tolerance, where increased ratios represent hindered catalyst poisoning by CO intermediates (4). Pt/TiN-CNT demonstrated superior maximum peak current densities and CO tolerance in comparison to Pt/C, once again indicative of the improved catalyst-support interactions.

TABLE I. Maximum current density and i_f/i_b peak ratio for Pt/TiN-CNT and Pt/C from MOR evaluation.

Electrocatalyst	$i_{\max} / \text{mAcm}^{-2}$	i_f/i_b
Pt/TiN-CNT	22.9	1.22
Pt/C	15.8	1.12

Conclusions

Herein, the design and development of unique coaxial TiN coated CNTs is presented as electrocatalyst support materials for low temperature fuel cells. Uniform, well dispersed Pt nanoparticles were deposited on the surface using the modified EG method, and these Pt/TiN-CNT catalysts were found to display enhanced ORR and MOR activity in comparison with state of the art commercial Pt/C. Effectively coupling the unique physicochemical properties of TiN and CNTs clearly led to favourable catalyst-support interactions for low temperature fuel cells and may find application as replacements to traditional carbon based supports.

Acknowledgments

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