



Contents lists available at ScienceDirect

## Journal of Power Sources

journal homepage: [www.elsevier.com/locate/jpowsour](http://www.elsevier.com/locate/jpowsour)

## Effect of nitrogen post-doping on a commercial platinum–ruthenium/carbon anode catalyst



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### H I G H L I G H T S

- Commercial carbon-supported PtRu catalyst is post-doped with nitrogen.
- Nitrogen post-doping improves initial performance by more than 16%.
- Nitrogen-doped catalyst retains ~34% more surface area than unmodified catalyst.
- MEA with N-modified PtRu/C retains performance while unmodified PtRu/C loses ~33%.
- Post-doping improves performance of the best performing commercial catalysts.

### A R T I C L E I N F O

#### Article history:

Received 31 May 2013

Received in revised form

13 September 2013

Accepted 16 September 2013

Available online 2 October 2013

#### Keywords:

Electrocatalyst

Durability

Direct methanol fuel cell

Nitrogen doping

Carbon support

### A B S T R A C T

This work investigates the effects of after-the-fact chemical modification of a state-of-the-art commercial carbon-supported PtRu catalyst for direct methanol fuel cells (DMFCs). A commercial PtRu/C (JM HiSPEC-10000) catalyst is post-doped with nitrogen by ion-implantation, where “post-doped” denotes nitrogen doping after metal is carbon-supported. Composition and performance of the PtRu/C catalyst post-modified with nitrogen at several dosages are evaluated using X-ray photoelectron spectroscopy (XPS), rotating disk electrode (RDE), and membrane electrode assemblies (MEAs) for DMFC. Overall, implantation at high dosage results in 16% higher electrochemical surface area and enhances performance, specifically in the mass transfer region. Rotating disk electrode (RDE) results show that after 5000 cycles of accelerated durability testing to high potential, the modified catalyst retains 34% more electrochemical surface area (ECSA) than the unmodified catalyst. The benefits of nitrogen post-doping are further substantiated by DMFC durability studies (carried out for 425 h), where the MEA with the modified catalyst exhibits higher surface area and performance stability in comparison to the MEA with unmodified catalyst. These results demonstrate that post-doping of nitrogen in a commercial PtRu/C catalyst is an effective approach, capable of improving the performance of available best-in-class commercial catalysts.

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## 1. Introduction

Recent advancements in electrocatalysis and improvements in fuel cell components are bringing polymer electrolyte membrane fuel cells (PEMFCs) closer to commercial viability. However, further improvements in fuel cell durability, particularly through the mitigation of electrocatalyst degradation, are needed [1,2]. As a result, there is an increasing research activity aimed at developing a fundamental understanding of and improving catalyst utilization and stability. Among a variety of strategies for improving catalyst

performance, efforts focusing on modifying carbon support chemistries and optimizing low temperature catalyst–support interactions have recently led to significant improvements [3–5].

The genesis of interest in modified carbon support materials for PEMFCs and DMFCs originated in the mid-1990s, when it was hypothesized that changing the chemical structure of carbon through functionalization could lead to potential catalyst stability benefits due to tailored catalyst–support interactions [4]. Today, researchers have shown that a variety of heteroatoms, such as nitrogen [5–17], boron [15,16], phosphorus [16], sulfur [17], iodine [18], and fluorine [18] can effectively change the physical, chemical and electronic properties of carbon-based catalyst support materials in ways beneficial to their performance. Among many doping approaches, ion implantation shows particular promise as it is a scalable, semiconductor industry-adopted process that has been shown to be an effective route to incorporate dopants into carbon-based materials, including high-surface area supports [7,9,11,14,19].

The most widely studied heteroatom modifier is nitrogen because of its abundance, accessibility, low health risk, and promising results [7,20–23]. Noble-metal nanoparticle catalysts supported on nitrogen-modified carbon-based materials, when compared against unmodified supports, have shown improved dispersion, durability and catalytic activity for a variety of fuel-cell relevant electrochemical reactions, including the hydrogen oxidation reaction, the methanol oxidation reaction, and the oxygen reduction reaction [17,24–31]. More recently, theoretical DFT work and experimental studies conducted on model supports (highly oriented pyrolytic graphite; HOPG) have provided additional insight into the effect of nitrogen on nanoparticle catalyst durability [32–34]. These studies have identified the importance of nitrogen concentration and nitrogen defect clustering on overlying catalyst nanoparticle activity and durability. Typically, nitrogen-containing supports are not limited to one specific nitrogen functional group, but rather contain a wide spectrum of species, including nitrogen in graphitic, pyridinic, pyrrolic, and quaternary forms, as well as multi-nitrogen defects. Identifying which specific nitrogen groups are responsible for the observed enhancement in binding between catalyst and support is still a focus of considerable discussion. DFT analysis suggests that the effect of nitrogen on Pt and PtRu stability can be either beneficial or detrimental depending on the specific nitrogen functionality introduced into the carbon support, and for maximum beneficial effects it appears necessary to have a balance of graphitic, pyridinic and pyrrolic functionalities [33].

Continued understanding of these materials has also been provided by energy electron loss (EEL) spectral imaging, which has revealed a spatial correlation between the most stable nanoparticles and higher amounts of nitrogen in the carbon support [33,34]. Studies suggest that this correlation is likely due to both a reduction in nanoparticle dissolution and a reduction in nanoparticle agglomeration/coarsening facilitated by the dopant [23,26].

In our recent work, we have transitioned from the evaluation of model and high-surface area materials in half-cell configurations to membrane electrode assembly (MEA) single-cell fuel cell studies [35,36]. It has been demonstrated that a DMFC MEA employing an N-doped PtRu/C anode retained more electrochemically active anode surface area and sustained only half as much ruthenium cross-over as an MEA employing an otherwise identically synthesized undoped PtRu/C anode [36]. The DMFC performance of N-doped PtRu/C MEA was likewise better sustained compared to the undoped PtRu/C MEA after durability testing ( $5\times$  higher current density at 0.4 V after 625 h durability testing). Materials evaluated in these previous studies were doped with nitrogen prior to metal deposition. Therefore, the nitrogen dopants could be distributed

throughout carbon surface, both underneath and between the subsequently deposited catalyst nanoparticles.

The current work further examines the effects of nitrogen modification by studying the performance of a pre-existing state-of-the-art commercial catalyst implanted with nitrogen. In this case, nitrogen doping (via nitrogen ion implantation) is conducted on a commercial 60 wt% PtRu/C catalyst, consisting of PtRu nanoparticles already deposited onto a high surface area carbon support. Due to the shadowing effect caused by the pre-existence of the PtRu nanoparticles during the N-implantation process, the nitrogen heteroatom incorporation is expected only in regions of the carbon structure unshielded by PtRu nanoparticles. This work therefore helps to further advance fundamental understanding of the way in which nitrogen improves the stability of the nanoparticle catalysts while exploring a facile pathway for the enhancement of current industry leading products.

To assess the effects of post-doping on state-of-the-art carbon supported PtRu catalysts, unmodified and post-modified samples were characterized and compared using both RDE experiments and MEA tests. These studies demonstrate that after durability testing, the post-modified state-of-the-art commercial catalysts outperform the unmodified benchmark catalyst.

## 2. Experimental

### 2.1. Materials

The commercial anode catalyst used in these studies is nominally 60 wt% PtRu supported on carbon black (Johnson Matthey HiSpec<sup>®</sup> 10000). Specifically, the platinum weight loading is 39.39% and the ruthenium weight loading is 18.91%, as given by the company specifications for the specific lot used.

For the modification of samples with nitrogen, approximately 500 mg of PtRu/C catalyst was placed into a rotating sample holder (rotating wheel), and the chamber was evacuated to less than  $5 \times 10^{-6}$  Torr [37,38]. Prior to nitrogen ion implantation, powders were out-gassed by heating to above 180 °C for 15 min. Samples were then implanted with a 3 cm DC ion source (Veeco) at a pressure of  $1 \times 10^{-3}$  Torr ( $N_2$ ) at two different dosages by changing the beam current between 12 mA and 45 mA, while maintaining a constant discharge voltage (55 V) and acceleration voltage (100 V) for 60 min.

### 2.2. Characterization

Thermogravimetric analysis (TGA) was done using the TA Q600 (TA Instruments, New Castle, DE) by feeding 100 mL  $min^{-1}$  of synthetic air (80%  $N_2$ , 20%  $O_2$ ) with a heating rate of 5 °C  $min^{-1}$  to a temperature of 850 °C. The total metal content of the catalyst powders was determined based on the assumption that the final mass at 850 °C is composed of  $RuO_2$  and Pt. The Transmission Electron Microscopy (TEM) micrographs of undoped and post-modified PtRu/carbon were obtained on a Philips CM200 TEM. In addition to initial evaluation of catalyst powders, samples were also collected from the anode surface of the cycled MEA's.

XPS analysis was performed on a Kratos Nova X-ray photoelectron spectrometer using pass energies of 160 eV for the survey spectra and 20 eV for the high-resolution spectra of C 1s/Ru 3d, O 1s, N 1s, Ru 3p, and Pt 4f. Data processing was carried out using Casa XPS software and involved background subtraction, charge calibration, and curve fitting. A linear background was applied to O 1s and N 1s regions, while Shirley background was used for C 1s/Ru 3d, Pt 4f and Ru 3p regions. Charge referencing was done to the carbon peak at 284.8 eV. Consistent fitting parameters and constraints were applied to the C 1s/Ru 3d region to obtain the distribution of

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