



Performance analysis of a non-platinum group metal catalyst based on iron-aminoantipyrine for direct methanol fuel cells



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ABSTRACT

A highly active non-platinum group metals (non-PGMs) catalyst for oxygen reduction reaction (ORR) was synthesized by the sacrificial support method (SSM) developed at the University of New Mexico (UNM). SSM was modified in order to control hydrophobicity and morphology of transition metal–nitrogen–carbon material (M–N–C). As prepared catalyst was evaluated by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Brunauer–Emmett–Teller (BET) methods. Electrochemical activity towards ORR and tolerance to methanol poisoning of Fe–N–C catalyst were studied by rotating disk electrode (RDE). A performance analysis was carried out at the cathode of a direct methanol fuel cell (DMFC) comprising the variation of fuel concentration and temperature. A peak power density of about 50 W g^{-1} was recorded at 90°C in a wide range of methanol concentration (1–10 M). It was found that the non-PGM catalyst possesses an extraordinarily high tolerance to methanol crossover, with no significant decay of performance up to 10 M of alcohol concentration, making this material state-of-the-art in DMFC application. Chronoamperometric tests in DMFC at 90°C and 5 M methanol concentration (100 h) showed also a suitable stability.

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1. Introduction

Direct methanol fuel cells (DMFCs) are considered as an attractive alternative to batteries for portable applications and auxiliary power units mainly due to advantages of low temperature liquid-fueled fuel cells, such as high energy density of methanol as well as high energy efficiency [1–4].

One of the main drawbacks of DMFCs based on proton exchange membranes (PEMs) is the need of platinum group metals (PGMs) to achieve a practical performance at low temperature ($<100^\circ\text{C}$). At the moment, Pt at the cathode and PtRu at the anode are the benchmark formulations [5,6]. Despite the fact that in the last years the catalysts composition and structure have been optimized by different approaches resulting in improvement of fuel cell performance [7–10], the cost and scarce resources of Pt still hinder the commercialization of this kind of efficient energy conversion device [11]. One attractive idea is to substitute cathodic Pt/C catalyst with

recently developed highly performing non-platinum group metal (non-PGM) catalysts [12–16]. Among them, formulations based on transition metals M (where M = Fe, Co, etc.), nitrogen and carbon materials, abbreviated in literature as M–N–C, present great prospect for fuel cell application [17–24].

The development of mentioned above non-PGM catalysts was targeted on implementation into H_2/O_2 PEMFCs and only a few papers deal with utilization of M–N–Cs in DMFCs configuration. Up to date, some published results with different non-PGM formulations can be considered as promising, the difference in membrane-electrode assemblies (MEAs) fabrication, cell operating conditions and cells hardware does not allow directly comparing them. For instance, B. Piel et al. reported 45 mW cm^{-2} with a Co-based catalyst derived from tetramethoxyphenylporphyrin precursor with a loading of 2 mg cm^{-2} at the cathode, and 6 mg cm^{-2} of PtRu at the anode, operating at 70°C , 1.1 M methanol and pressurized air (2.04 atm) [25]. Y. Wei et al. obtained 58 mW cm^{-2} employing 10 mg cm^{-2} Fe catalyst supported on N-doped carbon aerogel at the cathode and 4 mg cm^{-2} PtRu at the anode, operating at 60°C with 2 M methanol and oxygen [26]. Y. Hu et al. have very recently reported a peak power of 21 mW cm^{-2} for a polyaniline-derived Fe–N–C doped with phosphorous, with 4 mg cm^{-2} at the

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cathode and 1.5 mg cm^{-2} PtRu at the anode, operating at 50°C , 2 M methanol and oxygen [27]. E. Negro et al. have recently reported Fe–N supported on graphitic carbon nano-networks with a loading of 2.5 mg cm^{-2} at the cathode, and 2.5 mg cm^{-2} PtRu at the anode, obtaining 15 mW cm^{-2} at 90°C with 2 M methanol and oxygen [28]. As a general observation, the decrease of catalyst loading results in lower performances; however, platinum content reduction or full elimination is mandatory towards cost-effective DMFC systems.

The main objective of the present work is to investigate the performance of PEM-DMFC based on a non-PGM cathode catalyst derived from pyrolysis of iron aminoantipyrine (Fe-AAPyr). In this class of catalysts, the covalent integration of Fe–N_x sites into π -conjugated carbon basal planes modifies the carbonaceous ligand capability of donating/withdrawing electrons, resulting in reasonably high oxygen reduction reaction (ORR) activity [29]. This catalyst has already been proven to be a perspective for the ORR in rotating disk characterization [30] and, more recently, very promising results have been obtained in the application at the cathode of alkaline direct methanol fuel cells [31]. Up to now, the performance of this class of non-PGM catalysts in PEM-based DMFCs has not been evaluated. Herein, the influence of cathode loading, cell operating temperature and methanol concentration on the electrochemical behavior has been investigated, employing a low PtRu loading at the anode in order to derive the performance for cost-effective and practical DMFC systems.

2. Experimental

Materials preparation and physico-chemical characterization

Non-PGM Fe-AAPyr catalysts was synthesized by substantially modified sacrificial support method (SSM), developed at UNM [24,29,32,33]. Initially calculated amount of low surface area fumed silica (L90, Cab-O-Sil®, Cabot, surface area $\sim 90 \text{ m}^2 \text{ g}^{-1}$) was mixed with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma–Aldrich) and 4-Aminoantipyrine (AAPyr, Sigma–Aldrich) and in-house made carbon nanotubes (CNTs) [34]. Obtained mixture was subjected to dry mechanochemical treatment [35] by ball-milling in planetary ball mill at 400 rpm for 1 h. The finely homogenized mixture of precursors was pyrolyzed in inert atmosphere of Ultra High Purity (UHP) nitrogen at flow rate of 100 mL min^{-1} , 975°C and 45 min. Sacrificial support was removed by means of 25 wt% of HF for 48 h. Powder was washed with deionized water until neutral pH. In order to remove un-washed volatile silica compounds, a second treatment in ammonia atmosphere was carried out at 1000°C and 25 min. As obtained Fe-AAPyr catalyst was used in present study. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were obtained using Hitachi S-800 and JEOL 2010 EX instruments, respectively. Surface areas were measured by N₂ adsorption BET using a Micrometrics 2360 Gemini Analyzer. A four-point BET analysis was performed using a saturation pressure of 640 mm Hg.

Half-cell characterization

Electrochemical studies were carried out in a three-electrode cell at room temperature. 0.5 M H₂SO₄ was used as electrolyte, the reference electrode was a mercury/mercury sulfate (Hg|Hg₂SO₄, sat. K₂SO₄) electrode and a high surface Pt coiled wire was used as counter electrode. A rotating disk electrode (RDE) consisting of a thin film catalyst deposited on the glassy carbon disk (5 mm) was used as working electrode (WE). The catalytic layer was obtained following this recipe: first preparing 3 mg mL^{-1} ink by sonicating the catalyst in isopropyl alcohol/water (3/1, v/v) solution and

Nafion® (Ion Power, 5 wt%). Some drops of this ink were deposited onto the glassy carbon disk to reach the desired mass loading (0.6 mg cm^{-2} for the Fe-AAPyr catalyst, 15 wt% Nafion® according to previous works [29]). An Autolab potentiationstat/galvanostat was used to carry out the electrochemical experiments. Linear sweep voltammetry curves were carried out in the potentiostatic mode with a scan rate of 5 mVs^{-1} and at rotation rates from 100 rpm to 2500 rpm. The tolerance of the catalysts to the presence of methanol was evaluated by adding increasing aliquots of the alcohol to the base electrolyte, saturated with oxygen, for concentrations from 0.005 M to 2 M. The ORR response in the presence of methanol was evaluated at a rotation speed of 1600 rpm.

Fuel cell testing

Cathode electrodes were prepared by spraying a catalytic ink on a commercial hydrophobic gas diffusion layer (GDL-LT, E-TEK). The catalyst ink was prepared sonicating the catalyst in an isopropyl alcohol/water mixture (2/1, v/v) and Nafion® solution. The Nafion® content in the catalytic layer was 45 wt% [24]. Electrodes were prepared using the non-PGM catalyst (Fe-AAPyr) with loading values of 2.7 mg cm^{-2} and 7.4 mg cm^{-2} . For comparison purposes, a cathode based on commercial 40 wt% Pt/C (Johnson Matthey) was prepared following the same spraying procedure (1 mg Pt cm^{-2} , 33 wt% Nafion®) [36]. Anode electrodes based on PtRu black (Pt:Ru 1:1, Johnson Matthey) were prepared by doctor blade according to the procedure described in a previous report [37]. The catalytic layer was composed of 85 wt% catalyst and 15 wt% Nafion® ionomer, spread onto a commercial gas diffusion layer (GDL-HT, E-TEK). The noble metal (Pt+Ru) loading at the anode was 1 mg cm^{-2} in all membrane-electrode assemblies (MEAs).

MEAs were formed by a hot-pressing procedure at 130°C and 30 kgf cm^{-2} during 10 min, and subsequently installed in a 5 cm^2 fuel cell test fixture (Fuel Cell Tech., Inc.). A Nafion® 115 membrane ($\sim 130 \mu\text{m}$) was used as the solid electrolyte. In the various MEAs, the anode loading was maintained constant (PtRu black Johnson Matthey, $1 \text{ mg PtRu cm}^{-2}$) whereas the cathode loading was varied. The cell hardware was connected to a Fuel Cell Tech., Inc. test station. In case of single cell polarization experiments, aqueous methanol (from 1 M to 10 M) was pre-heated at the same temperature of the cell and fed to the anode chamber of the DMFC through a peristaltic pump; oxygen, pre-heated at the same temperature of the cell (100% relative humidity), was fed to the cathode. Reactant flow rates were 2 and 100 mL min^{-1} for methanol/water mixture and oxygen stream, respectively. The cell temperature was measured by a thermocouple embedded in the cathodic graphite plate, close to the MEA. Steady-state galvanostatic polarization experiments in DMFC were performed with an Agilent electronic load at various temperature and methanol concentration conditions. An Agilent milliohmeter operating at 1 kHz was used to determine the resistance of the cell. In order to evaluate the methanol cross-over, chromatographic analyses at the cathode exhaust were carried out and the CO₂ concentration was determined by quantification of the CO₂ peak area. The MEA based on the platinum cathode was used for this determination and complete oxidation of permeated methanol to CO₂ was assumed.

A 100 h chronoamperometric experiment at 0.3 V was carried out to evaluate the stability of the MEA based on the most performing non-PGM formulation (Fe-AAPyr 7.4). Cell conditions were 90°C , 5 M methanol fed to the anode and humidified O₂ fed to the cathode (2 and 100 mL min^{-1} respectively). The performance was evaluated by means of steady-state galvanostatic polarization curves under identical conditions to those reported above.

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