



Highly stable precious metal-free cathode catalyst for fuel cell application



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HIGHLIGHTS

- Highly stable PGM-free cathode catalysts are synthesized.
- Catalyst morphology influences activity and stability.
- FIB image analysis of catalyst layer is performed.
- Post-mortem failure analysis reveals stability.

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ABSTRACT

A platinum group metal-free (PGM-free) oxygen reduction reaction (ORR) catalyst engineered for stability has been synthesized using the sacrificial support method (SSM). This catalyst was comprehensively characterized by physicochemical analyses and tested for performance and durability in fuel cell membrane electrode assemblies (MEAs). This catalyst, belonging to the family of Fe-N-C materials, is easily scalable and can be manufactured in batches up to 200 g. The fuel cell durability tests were performed in a single cell configuration at realistic operating conditions of 0.65 V, 1.25 atm_{gauge} air, and 90% RH for 100 h. In-depth characterization of surface chemistry and morphology of the catalyst layer before and after durability tests were performed. The failure modes of the PGM-free electrodes were derived from structure-to-property correlations. It is suggested that under constant voltage operation, the performance loss results from degradation of the electrode pore structure, while under carbon corrosion accelerated test protocols the failure mode is catalyst corrosion.

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1. Introduction

The continued development of fuel cell technology has facilitated the beginning of true commercialization of the technology. To foster growth of fuel cells as a commercial product, increased economic viability is necessary. As production volume increases, production cost of many of the components will decrease. However, the cost of platinum-based catalysts accounts for approximately 40% of the current fuel cell cost and will not decrease with

increased production volume. The two primary approaches to reducing fuel cell cost are drastic reduction of Pt group metals (PGM) in the cathode, or completely replacing them with PGM-free catalysts. Several classes of PGM-free catalysts currently exist. The most promising of these for the oxygen reduction reaction (ORR) in the low-temperature proton exchange membrane (PEMFC) type of fuel cell is based on metal-nitrogen-carbon (M-N-C, where M = Fe, Ni, Co, and Mn) composites with metal-nitrogen active sites embedded in stacked carbon graphitic sheets [1–3]. The performance of some M-N-Cs has been recently reported to be on the order of 10–20% that of platinum catalysts, showing great potential. However, the durability data reported in the open literature reveals insufficient stability of this class of materials in real fuel cell tests [1,4–6]. Herein we report the first catalyst specifically developed

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for high stability that exhibits the necessary activity for a commercially viable PGM-free ORR catalyst in low-temperature PEMFCs.

The technology underlying the catalyst was invented by the University of New Mexico [4,7–10], scaled-up and modified by Pajarito Powder, LLC with characterization input from collaborators including Scott Calabrese Barton [7], Sanjeev Mukerjee [11,12], and Piotr Zelenay [13]. Catalysts based on this technology have been previously extensively characterized [10]. The sacrificial support method (SSM) used to synthesize this electrocatalyst from iron and nitrogen-carbon precursors results in an intrinsically PGM-free material. SSM synthesis produces material with multiple surface defects within a carbonaceous network and an internal network of connected pores with tunable size distribution. The key chemical features of these electrocatalysts that result in their high activity and excellent stability include: 1) the absence of free large iron/iron oxide particles, 2) the presence of graphite-protected iron and iron carbide species, and 3) the dominant iron species being atomically dispersed iron coordinated to nitrogen homogeneously distributed throughout the nitrogen-enriched carbon network. The formulations, processing and treatment conditions of catalyst layer were optimized for PEM membrane electrode assembly (MEA) performance for H₂/Air configuration and confirmed by desired physical-chemical properties. This paper presents the performance and characteristics of a PEMFC catalyst, which is the first PGM-free catalyst to demonstrate excellent stability for over 100 h at representative realistic operating conditions of 0.65 V, 1.25 atm_{gauge} air, and 90% relative humidity (RH). In addition, electrode chemical and three-dimensional morphological post-mortem analysis was used to identify the failure modes for the PGM-free electrode and MEA itself.

2. Experimental

The catalyst was synthesized using a modified version of the SSM as described in the literature [7,10,14,15]. The specific reagent formulation and processing procedure is proprietary technology developed by UNM and Pajarito Powder, LLC. MEAs (geometrical area: 5 and 50 cm²) were made from gas diffusion electrodes (GDEs) pressed with 211 Nafion[®] membrane using PTFE-impregnated glass-fiber sub-gaskets at 131 °C for 10 min (90 psi for 5 cm² and 70 psi for 50 cm² sized electrodes, respectively), then allowed to cool down under 1 psi pressure. Sub-gasket thickness for the anode was 150 μm and 250 μm for the cathode. The GDE was sprayed using a Sono-Tek Exacta-Coat automated spray system delivering 4 ml min⁻¹ ink through a 25 kHz ultrasonic nozzle onto an SGL 25BCE gas diffusion layer preheated to 65 °C. The ink was deposited at a rate of 40 μg cm⁻² per deposition pass, for a total of 3 mg_{catalyst} cm⁻² and 75 μm thick electrode. The inks were composed of 2:1 isopropyl alcohol:deionized water (v:v), catalyst, and D2021 Nafion[®] dispersion mixed to a ratio of 3.5 wt% solids. A 50 mL vessel containing the ink ingredients was placed in a water-cooled bath and mixed for 30 min using an IKA T-18 high shear mixer with the S18-19G dispersing element set at 18,000 RPM.

The MEAs were loaded into the cell testing assembly (Fuel Cell Technologies Inc.) using single (5 cm²) or triple (50 cm²) serpentine pattern graphite flow plates. The cell hardware was assembled using 40 inch-lbs torque for 5 cm² and 50 inch-lbs for 50 cm² cells. The cell was allowed to come up to 80 °C under a feed of 200 sccm of 100% RH 1.5H₂/2.5Air and pressurized to a total of 1.70 atm_{gauge}. For the hold test, the load was applied potentiostatically to 0.65 V for 100 h at steady state, then reduced to 0.6 and 0.4 V to allow comparison to previous steady-hold tests in the literature. Polarization curves were measured sequentially at 1.25, 2.5, 1.25, 0.5, and 4.5 atm_{gauge} air with potentiostatic tests with 60 s potential holds

and the current at the end of the hold reported. Also, a fresh electrode was then subjected to a carbon corrosion accelerated test. The sample cell performance was measured in H₂/Air after 3 h of polarization tests as described above, then the cathode feed was switched to N₂. After 30 min of flushing, an external power supply (Kiethley 2400) applied 5000 cycles of triangular wave 1.0–1.5 V, 500 mV s⁻¹ linear sweeps. Air flow was resumed, and multiple polarization curves were measured. After 6 cycles performance stabilized and is reported.

Brunauer-Emmett Teller (BET) surface area (SA) measurements used a Micromeritics Gemini V system. The samples were degassed at 120 °C for 10+ h, and a 9 point analysis was used. Single and multipoint BET measurements for all samples were within 10% of each other, which is indistinguishable given the accepted accuracy of BET.

The pore size distribution (PSD) of the sprayed catalyst layer material was measured via mercury intrusion porosimetry (Micromeritics AutoPore IV 9500). A 3 mL penetrometer with a stem volume of 1.1 mL was loaded with 0.1 g of material. Mercury intrusion was measured over the pressure range of 0.1–30,000 psi. The pressure is related to a pore radius with the Washburn equation: $r_p = 2 \gamma \cos \theta / p_{measured}$ where the measured pressure ($p_{measured}$), contact angle (θ), and surface tension of mercury (γ), establish the pore radius (r_p). In this way the change in mercury volume from one pressure to another can be associated with intrusion into a certain pore size and a pore size distribution can be calculated.

Dynamic light scattering (DLS) measurement used a Microtrac Nanotrac 250 device. Pseudo-inks were prepared for DLS by mixing for 60 min in an IKA T-18 high shear mixer with S18-19G dispersing element at 18,000 RPM. The pseudo-ink consisted of 3.5 wt% solid catalyst in 50 mL of the same solvent composition as is used in the inks: 2:1 isopropyl alcohol:deionized water (v:v). The resulting pseudo-inks were diluted according to the instrument intensity requirements and measured at 3 aliquots.

Ashing tests were completed with 0.4–0.6 g of catalyst placed in a pre-weighed boat made of 309 stainless steel foil (boat weight ~1.0 g). The boat and catalyst were placed in a tube furnace (Lindberg TF55035A) with a 1" OD quartz tube liner with exhaust air pull. The furnace and sample were heated at 10 °C min⁻¹ until 800 °C, held for 10 min, and allowed to cool. The boat and remaining sample were weighed. The remaining materials were analyzed by SEM/EDS and XRD. Control tests show that the boats gain less than 10 mg after exposure to air, and none upon re-heating. Ashing tests were conducted in triplicate and averaged.

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was done by Green Analytical Laboratories (Durango, Colorado) using EPA6010B analysis method and EPA3050 digest method.

Scanning electron microscopy (SEM) was performed on a Hitachi S-5200 with 1.8 nm resolution at 1 kV and Oxford Scientific EDS. The samples were prepared by dropping a small amount of catalyst and ethanol slurry onto an aluminum sample holder block and allowed to dry. The analysis was performed at 1 kV and 5 μA. *High resolution transmission electron microscopy (HRTEM)* analysis was performed using a JEOL 2010F microscope with an accelerating voltage of 200 keV and a current of 190 μA.

2.1. X-ray photoelectron spectroscopy (XPS) analysis

The analysis was performed on pure catalyst powders, as well as on electrodes. Beginning of life (BOL) and end of life (EOL) MEAs were analyzed using a Kratos Axis DLD Ultra spectrometer using a monochromatic Al K α X-ray source, with emission voltage of 15 kV and emission current of 10 mA. High-resolution spectra for carbon, fluorine, oxygen, and nitrogen were acquired to study the

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