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Nitrogen-doped carbon nanofiber catalyst for ORR in PEM fuel cell stack: Performance, durability and market application aspects

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ARTICLE INFO

Article history:

Received 4 May 2016

Received in revised form

14 July 2016

Accepted 17 July 2016

Available online xxx

Keywords:

Noble metal-free catalysts

Nitrogen-doped carbon

Oxygen reduction reaction

PEM fuel cell

Cathode

Market application analysis

ABSTRACT

A noble metal-free catalyst based on N-doped carbon nanofibers supported on graphite (N-CNF/Fe) was employed for the oxygen reduction at the cathode of a Nafion PEMFC with a commercial Pt/C anode. Obtained performance in pure H₂ and O₂ indicated the presence of significant mass-transport limitations when utilizing catalyst loading between 1 and 10 mg cm⁻². Strategies to reduce the limitations were explored by optimization of the cathode ionomer content, catalyst loading and application technique. Pore-formers (Li₂CO₃, (NH₄)₂CO₃ and polystyrene microspheres) were utilized to improve the mass-transport within the layer. A maximum of 72 mW cm⁻² and 1400 A g⁻¹ or 300 W g⁻¹ at peak power was demonstrated. The catalyst was then applied to the cathode of a 10-cell fuel cell stack, and a 400-h durability test was conducted. The average cell voltage decay amounted to 162 μV h⁻¹. Finally, a market application analysis was conducted to illustrate the potential and challenges of replacing platinum as cathode catalyst. It was shown that even a near-complete elimination of the cathode catalyst cost by substitution of platinum with a carbon-based catalyst cannot produce a cost competitive product unless both the performance and the durability of the fuel cell with the new catalyst are very close to that of the state-of the art Pt-based system.

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Introduction

Proton-exchange membrane fuel cells (PEMFCs) have been in development for decades, but only recently started to penetrate

the real markets in such areas as automotive transport, distributed power generation and auxiliary power units [1]. Between 20 and 40% of the total PEMFC cost is the cost of Pt/C catalyst for oxygen reduction reaction (ORR) at the cathode [2,3]. So far, only Pt and platinum group metals (PGM) catalysts were

Abbreviations: N-CNF/Fe, N-doped carbon nanofibers grown from Fe particles on the surface of expanded graphite; N-C, nitrogen-doped carbon; FC, fuel cell; PEMFC, polymer electrolyte membrane fuel cell; MEA, membrane-electrode assembly; ORR, oxygen reduction reaction; PGM, platinum group metals; NCR, Nafion: catalyst ratio; GDL, gas diffusion layer; DMFC, direct methanol fuel cell; OCV, open circuit voltage; RRDE, rotating ring-disc electrode; TCO, total cost of ownership; CAPEX, capital expenses; OPEX, operational expenses; APU, auxiliary power unit; BoL, beginning-of-life; EoL, end-of-life.

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<http://dx.doi.org/10.1016/j.ijhydene.2016.07.137>

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successfully utilized in commercial PEMFC cathodes as no other material could demonstrate comparable ORR activity and durability in the acidic conditions of PEMFCs. However, platinum is listed by the European Commission as a critical raw material; its resources are limited and expected to be depleted by the end of the 21st century regardless of the introduction of fuel cell vehicles [4]. Therefore, it is important to find alternative and also cheaper catalysts. While non-PGM catalysts of different types have been attempted for some decades [5–7], a new type of catalytic materials – nitrogen-doped carbons (N-C) – has recently received a lot of attention [8–44]. Different synthesis routes for N-C materials have been implemented, although the majority of the methods use transition metals as precursors. Even though a multitude of active sites have been proposed for the N-C catalysts [45], it seems that the presence of transition metals during the synthesis procedure is important for achieving an active ORR catalyst in acidic medium [46–49]. Many synthesis methods are consequently based on the heat treatment of transition metal, nitrogen and carbon precursors, producing active sites involving that metal. A recent work also demonstrated a very active non-PGM catalyst with active sites devoid of any direct nitrogen coordination to a transition metal (iron) [50]. In our report the N-C catalysts obtained from metal precursors will therefore be denoted N-C/Me catalysts. N-C catalysts obtained from synthesis routes not involving any transition metal will be referred to as metal-free N-C catalysts [51]. A significant body of literature has been published to date reporting performance of N-C/Me and metal-free N-C catalysts inside fuel cell cathodes [13,15,50,52–70].

In this study, a novel non-PGM catalyst based on N-doped carbon nanofibers (N-CNF/Fe) was synthesized by decomposing ammonia and carbon monoxide over Fe nanoparticles supported on expanded graphite as described elsewhere [71]. This synthesis procedure is both easy scalable and economically competitive due to the use of a single-step CVD process, simple gaseous precursors and a highly conductive support material. In this article we report the performance and durability (400 h test) of the N-CNF/Fe catalyst for ORR in PEMFCs in both single cell and a 10-cell FC stack. The catalyst was applied to the cathodes of MEAs by conventional methods and at high loadings ($1\text{--}10\text{ mg cm}^{-2}$). In the second part of the article a market application analysis was performed to illustrate the impact of potential replacement of platinum as cathode catalyst in fuel cell systems, using an auxiliary power unit (APU) as an example.

Materials and methods

N-CNF catalyst synthesis and characterisation

The noble-metal free N-CNF/Fe catalyst was prepared by a catalytic chemical vapour deposition method. Briefly, the N-CNFs were grown in a single-step process at $650\text{ }^\circ\text{C}$ from 20 wt. % Fe nanoparticles supported on expanded graphite by using a gas mixture of $\text{CO:NH}_3\text{:H}_2$ ($150:6.5:20\text{ mL min}^{-1}$). The physical properties of the N-CNF/Fe were characterized by N_2 adsorption measurements (Micromeritics TriStar II 3020), SEM imaging (Hitachi S-5500 S(T)EM) and XPS analysis (Kratos Axis Ultra DLD spectrometer, Al $K\alpha$ radiation). Detailed synthesis procedures and characterization are reported elsewhere [71].

MEA preparation

MEAs for single cell tests

Three iterations of cathodes have been prepared. Initially, both anode and cathode electrodes were prepared by a roll-printing method using propanediol solvent. The catalysts (HiSPEC4000 catalyst from AlfaAesar (Pt^{40}/C) on anodes and N-CNF/Fe catalyst on cathodes) were mixed with 5% Nafion solution in isopropanol (IonPower) to achieve the desired Nafion-to-catalyst ratio (NCR). On the anodes, a 0.32:1 Nafion-to-catalyst dry mass ratio (NCR ratio) was used in all tests, while for cathodes the NCR were 0.5:1, 1:1 and 2:1. Surfactant (polyvinylpyrrolidone, 18% to the mass of the catalyst) was used only for the anode to improve the ink stability. The propanediol solvent was then added, and the mixtures were sonicated by ultrasonic tip for 15–30 min to achieve uniform stable dispersions (catalytic ink). Afterwards, the catalytic ink was applied to the surface of a piece of gas diffusion layer (GDL) (SGL – Sigracet 24 BC) by hand using a mask and a Teflon roller to achieve the catalyst loading of approximately 1 mg cm^{-2} on the anodes (0.4 mg cm^{-2} Pt). The cathode catalyst loading varied between 0.3 and 10 mg cm^{-2} . GDLs with applied ink were subsequently dried in an oven at $100\text{ }^\circ\text{C}$ for 5 min to remove the solvent.

The second batch of cathodes was prepared by spraying. Here, isopropanol was used as solvent instead of propanediol, and the amount of solvent relative to catalyst was higher to achieve thinner catalytic ink. An airbrush (Iwata HP-C, nozzle 0.3 mm) was connected to the source of compressed air (2–3 bar), and the catalytic ink was manually sprayed over the surface of the GDL. NCR of 1:1 was used exclusively for this batch, while the catalyst loading varied between 0.36 and 2.32 mg cm^{-2} . The same roll-printed hydrogen electrodes as in all other tests were used in these MEAs.

Finally, the sprayed cathodes preparation method was modified by adding pore-forming agents: (a) Polystyrene latex microspheres $1\text{ }\mu\text{m}$ in diameter, (b) ammonium carbonate $(\text{NH}_4)_2\text{CO}_3$ and (c) lithium carbonate Li_2CO_3 , all purchased from Sigma Aldrich. All three pore-forming agents were added to the catalyst and ionomer mixture prior to sonication at the mass ratio of 1:1 to the catalyst. The removal of the pore-forming agents from the layers to produce pores was done by (a) soaking in toluene at room temperature for 48 h and subsequent drying in an oven at $130\text{ }^\circ\text{C}$ for 1 h, (b) heating in the oven at $130\text{ }^\circ\text{C}$ for 1 h and (c) soaking in 0.5 M sulphuric acid for 1.5 h followed by thorough rinsing in deionised water and drying in the oven at $130\text{ }^\circ\text{C}$ for 0.5 h.

Squares of approximately 6 cm^2 area were cut from all prepared GDLs with applied catalyst to form gas diffusion electrodes for single cell tests. Nafion N-212 (52 μm thick) membrane with a thermoplast border on both sides was used in all MEAs. Electrodes were laminated onto both sides of the membrane at 10 bar and $135\text{ }^\circ\text{C}$ for 10 min each.

MEAs for the fuel cell stack

A total of 11 large MEAs for the fuel cell stack (active area 75 cm^2) were produced utilizing the third iteration of cathodes with $(\text{NH}_4)_2\text{CO}_3$ pore former. First, the catalytic ink for both electrodes was prepared. For that, the catalyst was mixed in 50 mL vials with Nafion ionomer solution, ammonium carbonate (cathode only) and solvent (isopropanol for cathode

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