



Activity and stability in proton exchange membrane fuel cells of iron-based cathode catalysts synthesized with addition of carbon fibers



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ABSTRACT

In this work, we report attempts to improve mass performance and durability of a catalyst prepared by ball milling a precursor consisting of a zinc-based zeolitic imidazolate framework (ZIF-8) mixed with 1,10-phenanthroline and ferrous acetate. The latter was then heat-treated at 1050 °C in argon to produce an oxygen reduction catalyst, identified as NC-Ar, for polymer electrolyte membrane fuel cells. Mass performance at 0.6 V of NC-Ar tested in either H₂/O₂ or H₂/Air remained unchanged after adding 26 wt% highly graphitized carbon fibers into its precursor, but its equivalent mass performance improved by 35% under these conditions. The catalyst produced after a heat-treatment at 1050 °C in argon of the carbon fiber-containing precursor is identified as NC-Ar (F90). The durability performance of NC-Ar (F90) over 100 h in H₂/Air is the same as that for NC-Ar. However, the durability performance of NC-Ar (F90) may be improved by performing a post-heat-treatment of NC-Ar (F90) with optimized temperature and duration. The best performing and most durable catalyst in this work is identified as NC-Ar (F90)+R985-1080 30 min. After 100 h in H₂/Air fuel cell operating at 80 °C and 2 bar absolute pressure, the latter produces about 0.5 A/cm² at 0.4 V (about 0.20 W/cm²), values that are higher than those (about 0.35 A/cm² at 0.4 V; or about 0.14 W/cm²) reported under similar experimental conditions (except for a higher absolute pressure of 2.8 bar) by Zelenay and collaborators (2011 [28]) for their most durable catalyst.

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1. Introduction

Fuel cells are clean and efficient electrical power generators that are contemplated to replace the internal combustion engine in future automobiles [1–3]. The production of electrical power by proton exchange membrane (PEM) fuel cells is based on two electrochemical half reactions: the oxidation of hydrogen (the fuel) at the anode and the reduction of oxygen present in air at the cathode. In order for PEM fuel cells to provide useful currents, catalysts are needed at both anode and cathode. So far these catalysts have always been based on platinum [4]. However, Pt is an industrial, precious and expensive metal of limited abundance. Furthermore, its price is sensitive to market fluctuation. Therefore, there is a strong incentive to lower the Pt content in PEM fuel cells or replace Pt with non-precious metal electrocatalysts [5,6]. This is possible at the cathode where the oxygen reduction reaction (ORR) is a slow reaction in the acidic condition of the proton exchange ionomer used as solid electrolyte in these fuel cells. ORR is indeed heavily

catalyzed at the cathode of H₂/Air or H₂/O₂ fuel cells, where about 90% of the total Pt content resides in all PEM fuel cells using Pt as electrocatalysts [7].

Among the various non-precious electrocatalysts that have been synthesized to perform the oxygen electroreduction in PEM fuel cells, Me/N/C catalysts, especially those that have been subjected to pyrolysis are among the most promising materials. Non-precious metal electrocatalysts for ORR may be obtained when a metal precursor, like an iron (or cobalt) salt or an iron (or cobalt) complex and a nitrogen precursor, like ammonia, acetonitrile, a nitrogen-containing polymer [polyacrylonitrile, polypyrrole, polyaniline, etc.] or a porphyrin are pyrolyzed at high temperature in the presence of a carbon support, like carbon black, activated carbon, milled graphite, carbon nanotubes, or graphene layers [4–6,8–10]. Very active Fe-based electrocatalysts for ORR have been reported by our group in 2009 [11]. In the latter work, it was shown that a catalyst loading of about 5 mg/cm², containing 90 μg Fe/cm², was able to produce the same current density in PEM fuel cell as a commercial cathode containing 400 μg Pt/cm² in the upper Tafel region. For current densities larger than 50 mA/cm², mass transport problems were observed and the polarization curve of the Fe-based cathode diverged significantly from that of the commercial Pt electrode. In

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2011, we solved most of the mass transport problem and reported that Fe-based electrocatalysts for ORR could also generate power densities similar to those generated by Pt-based catalysts in the useful potential range (0.6 V to open voltage circuit [OCV]) for fuel cells in automotive applications [12].

In the last few years, publications about Me/N/C electrocatalysts for ORR were mainly focused on activity and/or performance enhancement of the catalysts prepared by various synthesis procedures. Although these new catalysts showed improved activity and peak power density in H₂/O₂ fuel cell operation, they did not exceed the 0.91 W/cm² reported for the catalyst described in Ref. [12] ([13–26]). While the beginning-of-life activity and performance of many Me/N/C catalysts have been largely investigated, long-term durability performance, which is the last challenge to overcome for potential commercial applications, has been elusive.

Regarding the possible origin of the instability of these pyrolyzed catalysts, two publications are worth noting: one by Popov and collaborators [27] and the other by Zelenay and collaborators [28]. In their publication, Popov and collaborators describe the degradation mechanism of their nitrogen-modified carbon-based catalyst in PEM fuel cell. Their typical catalyst suffers from a fast initial degradation followed by a slower one over a 200 h long durability test in H₂/O₂ fuel cell at 75 °C. Their interpretation of the observed degradation is that a change of pyridinic N to NH⁺ possibly contributes to most of the performance loss during fuel cell operation. Water flooding in thick cathodes containing non-precious metal catalysts may also affect long term stability, while an H₂O₂ production from sub-four electron ORR, is apparently not a major cause of the poor stability of their cathode, because peroxide production for their catalyst is usually below 2%. On the other hand, Zelenay and collaborators report rather stable catalysts over nearly 700 h in H₂/Air fuel cell at 80 °C [28]. The current density of their best catalyst, derived from polyaniline (PANI), iron and cobalt, and identified as PANI-Fe-Co-C, decreased by only 18 μA/cm² per hour. The exact origin of the durability of this catalyst is not known, but the authors point to graphitization as a possible reason for improved stability. Although the latter catalyst showed a better durability than most other Me/N/C catalysts reported thus far, its peak power density was only 0.55 W/cm² in H₂/O₂ fuel cell at 80 °C. It therefore appears that active, well-performing and durable Me/N/C catalysts have not yet been achieved.

In this publication, we report the efforts made to investigate the effect of changes in the synthesis procedures on durability behavior over 100 h of operation, for one of our most active and well-performing catalysts. The original synthesis procedure of this catalyst was reported earlier [12]. Briefly, a mixture of a stable zinc-based zeolitic imidazolate framework (called ZIF-8 in the literature) was ball milled with 1,10-phenanthroline and ferrous acetate to produce a catalyst precursor that was then pyrolyzed at 1050 °C in Ar to obtain an initial catalyst identified as NC-Ar. NC-Ar may then be subjected to a second heat-treatment, this time in NH₃, at high temperature, producing a catalyst identified as NC-Ar + NH₃. To the best of our knowledge, the optimized version of the latter produced the highest beginning-of-life activity and peak power density for ORR in PEM fuel cell reported thus far. As far as its durability in H₂/Air fuel cell at 0.5 V over 100 h is concerned, NC-Ar + NH₃ exhibits an initial rapid degradation, followed by a slower one; a behavior similar to that described by Popov and collaborators. On the other hand, NC-Ar, which has only about half the beginning-of-life current density as NC-Ar + NH₃ under the same experimental conditions, degrades much more slowly. It is the degradation of NC-Ar that we have attempted to slow down in this work.

Our approach was to study the effect on the catalyst durability of adding carbon fibers in the catalyst precursor (before pyrolysis) or in the catalytic ink (after pyrolysis). All new catalysts of NC-Ar type were analyzed for their mass activity and their mass performance

in H₂/O₂ (the use of pure oxygen at the cathode exacerbates catalyst instability) and in H₂/Air fuel cells. N₂ isotherm measurements, TEM microscopy as well as XPS and neutron activation analysis were also used to characterize these alternatively synthesized catalysts. We will show that some of the procedures used to obtain the new catalysts may indeed improve their durability over 100 h in H₂/Air fuel cells, under operating conditions that are relevant for automotive applications (≥0.6 V, 80 °C, 2 bar absolute pressure).

2. Experimental

2.1. Synthesis of NC-Ar (F0), a NC-Ar catalyst without fibers (F0)

The method used to produce the NC-Ar (F0) catalyst is based on that described in Ref. [12]. Catalyst precursors (i.e. the mixture of various compounds to be subsequently pyrolyzed) were prepared by mixing 800 mg of MOF (ZIF-8, Basolite™ Z1200, Aldrich, produced by BASF), 200 mg of phenanthroline (1,10-phenanthroline, ≥99%, Aldrich) and 32 mg of iron acetate (Iron^{II} acetate, 95%, Aldrich) in 200 ml of 1:2 (by volume) solution of ethanol and deionized (DI) water, then drying the resulting slurry. To ensure the good homogeneity of the slurry, the MOF powder was first pre-dispersed by ultrasonic mixing in ethanol for 10 min before pouring it into the solution containing phenanthroline and iron acetate. Once completely dry, the powder was then placed in a hardened steel vial (ca. 65 cm³) with 20 chrome steel balls of 0.25 in. diameter. After purging the powder-filled vial under N₂, the vial was sealed and placed in a planetary ballmiller (FRITSCH Pulverisette 7) where it underwent 3 h of ball milling at 400 rpm. The resulting powder was then pyrolyzed for 1 h at 1050 °C under a constant flow of Ar. The resulting carbonized material was then manually ground using a mortar and pestle. The latter material was identified as: NC-Ar (F0) (F0 for no added fibers). This synthesis procedure yielded about 250 mg of catalyst powder (the typical mass loss during pyrolysis under Ar was roughly about 70%).

2.2. Synthesis of (NC-Ar (F_x), where x = 30, 60, 90, 120 or 200) catalysts with carbon fibers

To produce the catalysts with fibers, we simply added measured quantities of fibers in the slurry of the previously described synthesis. The fibers tested in this work were purchased from Pyrograf Products, Inc. (PR-19-XT-HHT, having 150 nm average diameter and a specific surface area of about 15–25 m²/g; their iron content was <100 ppm). The catalysts were prepared with the addition of 30, 60, 90, 120 or 200 mg of fibers and are identified as: NC-Ar (F30), NC-Ar (F60), . . . , NC-Ar (F200). Except for the addition of fibers and their pre-dispersion in ethanol, there was no other change to the synthesis procedure described above. The addition of fibers facilitated the handling of the catalyst precursors after the low-energy ball milling step, making them less electrostatic. The same temperature and time of pyrolysis were used for the catalyst with and without the fibers (1050 °C for 1 h under Ar). The mass loss of the fibers during pyrolysis under Ar was as assumed to be negligible, since these fibers are highly graphitized.

2.3. Synthesis of catalysts containing fibers only

Catalysts containing only fibers were produced by mixing 500 mg of fibers (PR-19-XT-HHT), 500 mg of phenanthroline (1,10-phenanthroline, ≥99%, Aldrich) and 32 mg of iron acetate (Iron^{II} acetate, 95%, Aldrich) in a 200 ml 1:2 solution (by volume) of ethanol and deionized (DI) water, then drying the slurry. The dry powder was then placed in a hardened steel vial (ca. 65 cm³) with 20 chrome steel balls of 0.25 in. diameter. After purging the powder-filled vial under N₂, the vial was sealed and placed in a

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