Highly active and porous graphene encapsulating carbon nanotubes as a non-precious oxygen reduction electrocatalyst for hydrogen-air fuel cells

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**Abstract**

Heat treated iron-polyaniline-carbon – based non-precious metal catalysts represent a promising class of material to replace the platinum based ORR catalysts for PEMFC technologies. In the present research, we apply an ammonia treatment to tune the structure and activity of electrocatalysts derived from iron, polyaniline and carbon nanotubes (CNTs). By controlling the NH\(_3\) reaction conditions, we were able to tune the chemistry of nitrogen incorporation, including concentration and dopant type. The final catalyst had a robust morphology consisting of highly porous 2-D in-situ formed graphene-like structures that, along with the intermixed 1-D CNTs, were decorated with an abundance of nitrogen and iron species. The resultant surface chemistry led to impressive catalyst activity, with a half-wave potential of 0.81 V observed through half-cell testing and under H\(_2\)-air fuel cell testing, a current density of 77 mA cm\(^{-2}\) at 0.8 V was achieved, along with a maximum power density of 335 mW cm\(^{-2}\).

1. **Introduction**

Polymer electrolyte membrane fuel cells (PEMFCs) are highly promising clean energy devices considered as ideal alternatives to the conventional fossil fuel based technologies used in the automotive industry, telecommunications backup and materials handling [1–3]. Although the target markets exist, technical challenges relating to cost and durability must be addressed [4]. The major bottle-neck issues arise from the cathode where the oxygen reduction reaction (ORR) happens [5–10]. Currently the only technologically viable ORR catalysts are platinum-based. This is why developing new catalyst materials with higher performance, as well as providing cost drops is of great interest.

Non-precious metal catalysts (NPMCs) are attractive classes of materials to replace the platinum in conventional ORR catalysts. NPMCs are actively under development [6,7,11] and prepared via several synthetic approaches such as applying metal-organic framework precursors [12–14], the sacrificial support method [15–18], hydrothermal or solvothermal synthesis [19,20], pyrolyzing a carbon supported complex [21–25], and polymerization of nitrogen containing monomers [26–33]. These approaches, using a high temperature pyrolysis in the presence of iron and/or cobalt precursors, provide transition metal-nitrogen-carbon complexes (M-N-C) which are so far the most promising class of NPMCs.

In the present study, we apply and optimize an ammonia treatment to tune the chemistry of a catalyst derived from iron, PANI and carbon nanotubes (CNT). This approach results in improved performance, both in half cell and full cell conditions. NH\(_3\) contributes by enriching the N-dopant concentration, and by controlling the temperature we can tailor the particular identity of the nitrogen dopants to maximize catalytic activity. The overall synthesis process ultimately leads to in-situ graphitization of carbon, forming catalyst structures that consist of multilayer highly porous graphene morphologies encapsulating CNTs with an abundance of nitrogen and iron defects. This surface chemistry renders the catalyst highly active towards the ORR, coupled with the robustness of the graphene-like morphology.

2. **Materials and methods**

2.1. **Functionalized multi-walled carbon nanotubes**

Commercial carbon nanotubes with 30–50 nm diameters and 10–20 \(\mu\)m lengths were functionalized first by immersing 10.0 g of them in 400 ml of 70% nitric acid. The mixture was then refluxed at 85 °C for 8 h under vigorous agitation. Functionalized CNT (FCNT) were then filtered and washed with DDI water and dried in...
an oven overnight.

2.2. FeCl₃-PANI-FCNT polymerization

3 ml of aniline and 10 g FeCl₃ was added into 300 ml HCl at room temperature while continuously stirring throughout the entire process. Slowly, 5.0 g of (NH₄)₂ S₂O₈ (ammonium peroxysulfate, APS) was added as an oxidant to polymerize the aniline in the above solution. The mixture was rigorously stirred at room temperature for 3 h to allow fully polymerization of the aniline. After 3 h, a suspension of 400 mg FCNTs in DDI water was slowly pipetted into the polyaniline mixture. The final solution was rigorously stirred for 48 h. After this, the liquid was evaporated and the solid polymer (FeCl₃-PANI-FCNT) was collected.

2.3. Catalyst synthesis

The catalyst precursors were first heat treated at 200 °C for 1 h under 70 ml min⁻¹ of argon (Ar), using a 30 °C min⁻¹ heating rate. The subsequent heat treatment for the resulting powder was done at 900 °C for 1 h using the same heating rate and Ar flow rate. The solid samples were then leached in 0.5 M sulfuric acid at 80–90 °C for 8 h to remove the inactive iron complexes as well as to introduce a porous morphology. As it can be seen from the nomenclature outlined in Table S1, after this leaching process, some catalysts were one step heat treated in ammonia at temperatures ranging from 900 °C to 1000 °C. Others were pyrolyzed at 900 °C in Ar for 3 h (Fe-P-C_Ar) to further improve the ORR activity and to remove surface functional groups. This is referred to as the conventional second heat treatment. After this step, ammonia treatment was done at temperature ranges from 800 °C to 1050 °C for 15 min and under a 300 ml min⁻¹ ammonia flow rate. These samples are designated Fe-P-C_Ar-NHxx in which the “xxx” is replaced with the NH₃ temperature (Table S1). A schematic of the catalyst synthesis is displayed in Fig. 1.

2.4. Physical characterization

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were utilized to investigate the nanostructured morphology of the fabricated electrocatalyst materials. The surface area of a material is very important in the development of new catalysts as a higher surface area usually suggests more exposed catalytic active sites to oxygen in ORR. Brunauer–Emmett–Teller (BET) was utilized to measure the surface area and the pore size of the catalyst materials. Raman spectroscopy was applied to study active sites in catalysts, as well as examine the effect of heat treatments on the material structures. The surface composition of catalysts was analyzed using X-ray photoelectron spectroscopy (XPS). Moreover, energy-dispersive X-ray spectroscopy (EDX) and electron energy-loss spectroscopy (EELS) were used to analyze the elements and their distribution in the catalyst materials.

2.5. Electrochemical characterizations

Half-cell rotating disk electrode (RDE) testing, a well-established method to evaluate the electrochemical performance of catalyst materials, was used to analyze the ORR taking place on the catalyst materials, whereby higher onset and half-wave potentials and increased current densities showed better activity toward ORR. In order to simulate the acidic circumstances encountered during PEMFC operation at the cathode, a 0.5 M H₂SO₄ solution was used as the electrolyte and saturated with oxygen during ORR testing. The working electrode was a glassy carbon disk (0.19635 cm²) which was coated uniformly by the catalyst ink to achieve a catalyst loading of 0.6 mg cm⁻². A graphite and Ag/AgCl electrode were utilized as the counter and reference electrodes, respectively. All potentials were converted to the reversible hydrogen electrode (RHE) scale for ease of analysis. In order to activate the catalyst, cyclic voltammetry (CV) was done under oxygen saturated electrolyte and scan rate of 50 mV s⁻¹. During ORR testing, the potential of the working electrode in oxygen saturated electrolyte was changed from ca. 1.0–0.0 V vs. RHE using linear staircase voltammetry (LSCV) with 30 mV amplitude and 30 s

![Fig. 1.](attachment:image.png)
period. For the half-cell durability test, the potential of the working electrode was cycled between 1.0 and 0.2 V vs. RHE at 50 mV s\(^{-1}\) in N\(_2\) saturated electrolyte. After different cycle numbers, ORR evaluation was performed with the conditions mentioned above. Rotating ring disk electrode (RRDE) testing was also used to measure selectivity of the catalysts towards the four-electron reduction of oxygen. The ring potential was set to 1.2 V vs. RHE to successfully oxidize any peroxide species reaching the ring electrode surface. For performance under PEMFC operating conditions, catalysts were tested at the fuel cell cathode, with a commercial Pt cloth gas-diffusion layer (0.5 mg cm\(^{-2}\) Pt) being used at the anode. Cathode ink was prepared using a mixture of 40 mg catalyst, 480 mg isopropanol, 480 mg DDI water, and 440 mg commercial Na\(_{fi}\)on solution (5 wt%). This way, the overall Na\(_{fi}\)on content in the dry catalyst ink was hold at 35 wt%. A dried Na\(_{fi}\)on 211 membrane (which was previously immersed in 0.5 M boiling sulfuric acid for 1 h and then in boiling DDI water for 1 h) was placed on the vacuum table. After sonication for 1 h, the ink was coated on the center of the membrane (5.0 cm\(^2\) area) by painting to reach a cathode catalyst loading of 4.0 mg cm\(^{-2}\). Membrane electrode assembly (MEA) was done as follow: The catalyst coated membrane (catalyst facing up) was placed on top of the anode and a commercial gas diffusion layer (GDL BC 25) was placed on top of the painted catalyst. The MEA was completed by hot pressing at 120 °C for 4 min using a pressure of 600 pounds for a 5 cm\(^2\) MEA. Fuel cell testing was carried out by flowing hydrogen to the anode at 200 standard cubic centimeters per minutes (sccm) and by flowing air or oxygen to cathode at 200 sccm. The cell temperature was held at 80 °C and the backpressure was set at 20 psig for both the anode and cathode side. Once the cell reached the appropriate potential, it was tested with an increment of 0.03 V point\(^{-1}\) and 20 s point\(^{-1}\).

3. Results and discussion

The initial phase of the current research was to study the effect of ammonia treatment temperature and heat treatment protocol. In order to optimize the heat treatment conditions, after acid leaching, some catalysts were first pyrolyzed in Ar at 900 °C for 3 h and then heat treated in ammonia at different temperatures. As benchmarks, after acid leaching, some samples were heat treated

![Fig. 2. SEM images of (a) FCNT (b) Fe-P-C_Ar and (c) Fe-P-C_Ar-NH900. (d) TEM image of Fe-P-C_Ar. (e) and (f) HRTEM images of Fe-P-C_Ar-NH900 at different magnifications. (g) BET surface area analysis and (h) pore size distribution of Fe-P-C_Ar and Fe-P-C_Ar-NH900.](image-url)
in only ammonia at varying temperatures. Sample nomenclature in Table S1 indicates sample heating environment and temperature. SEM images (Fig. 2a–c) shows the morphology of the FCNTs used as carbon supports and the resulting catalysts before and after ammonia treatment at 900 °C for 15 min. As it can be seen from the SEM images (Fig. 2b and c), the distribution of the carbon–nitrogen precursor (PANI) on the surface of the carbon support (FCNT) is uniform, and it seems that after NH3 treatment a large amount of porous structures are formed. The TEM image of Fe-P-C_Ar (Fig. 2d) in comparison to Fe-P-C_Ar-NH900 (Fig. 2e) also supports the notion of more porosity after the ammonia treatment. This was also confirmed from the BET results which are summarized in Fig. 2g and h. The rapid rise at low relative pressures (Fig. 2g) suggests the presence of micro-pores for both samples, while at high relative pressure, the lack of saturation indicates the formation of macro-pores that are present in higher amounts for the NH3 treated sample. Both of the Fe-P-C_Ar-NH900 and Fe-P-C_Ar catalysts show remarkably high specific surface area (higher for Fe-P-C_Ar-NH900) of ca. 1100 m² g⁻¹ and 1050 m² g⁻¹, respectively. Such high surface area is attractive from a mass transport perspective. This can effectively facilitate reactant access to catalytically active ORR sites, thereby improving electrode utilization and performance. In Fig. 2h, the pore size distribution clearly indicates the variety in the pore sizes from 2 nm to 200 nm. The extra macro-pores that were generated during ammonia treatment could decrease the diffusion length of oxygen molecules which has been reported helpful for improving the ORR performance [34]. TEM images (Fig. 2d–f) also shows formation of graphene like structures (red arrows) after pyrolysis. The in-situ formation of graphene like structures by using PANI is likely due to the similarity between graphene and the aromatic structures of PANI [26,27,29]. The high resolution TEM (HRTEM) image of Fe-P-C_Ar-NH900 indicates that the graphitic structures remained after ammonia treatment (Fig. 2f).

The Raman spectra of samples before and after ammonia treatment in Fig. 3a shows the asymmetric graphitic carbon resonance (G band) peak at ca. 1580 cm⁻¹ and defect carbon (D band) peak at ca. 1340 cm⁻¹. The lower D/G intensity ratio of the pyrolyzed Fe-P-C_Ar compared to that of the FCNT is probably due to more graphitic carbon species, which was likely arisen from in-situ formation of graphene structures during the high temperature pyrolysis of PANI in the presence of the transition metal. However, the lower D/G ratio after ammonia treatment (Fe-P-C_Ar-NH900) was likely due to the lower content of disordered carbon, which was due to the faster reaction between amorphous carbons (disordered carbons) with ammonia than the reaction between NH3 and graphitic carbon [10]. XPS C1s spectra of the catalysts (Fig. 3b) shows higher amounts of sp² bonded carbon (284.85 eV) [35] and

Fig. 3. (a) Raman spectra of FCNT, Fe-P-C_Ar and Fe-P-C_Ar-NH900, (b) C 1s, (c) N 1s spectra and (d) the corresponding nitrogen content and species distribution of Fe-P-C_Ar-NHxxx catalysts derived at different NH3 temperatures from 800 °C to 1000 °C.
a lower amount of oxidized carbon species (286.35 eV) [36,37] for the NH3-treated samples in comparison to Fe-P-C_Ar. For instance, the Fe-P-C_Ar-NH900 has 56.20 at% sp2 carbon and 11.69 at% oxidized carbon, compared to 52.02 at% sp2 carbon and 12.35 at% oxidized carbon for Fe-P-C_Ar. In agreement with Raman spectra, XPS indicates a higher degree of graphitization and reduced amount of defect structures for the NH3-treated sample. The higher amount of graphitic carbon could be due to an additional high temperature pyrolysis step (under NH3 atmosphere) in the presence of iron species. However, the amount of sp2 C=C decreases with increasing the NH3 temperature from 58.36 at% for Fe-P-C_Ar-NH800 down to 53.53 at% of sp2 carbon for Fe-P-C_Ar-NH1000. This finding suggests that the reaction between NH3 and graphitic carbon is facilitated at higher ammonia treatment temperatures, most likely due to the abundance of thermal energy to surpass the activation energy of the reaction. In Fig. S1a the XPS analysis also shows the existence of sulfur species mostly in the form of iron sulfide structure at 162.0 eV and carbon sulfide at 163.5 and 164.7 eV [38], with these dopant species arising from the APS that was used to initiate the polymerization of PANI. XPS N1s spectra of the catalysts derived at different NH3 heat treatment are also provided, in addition to the corresponding nitrogen content column plots in Fig. 3c and d, respectively. It can be seen that while the ammonia temperature has no significant effect on the pyrrolic N species quantity (400.2 eV), it does affect the amount of pyridinic (398.6 eV) and graphitic/quaternary nitrogen contents (401.5 eV). On the other hand, the binding energy that appears at 398.6 eV could also be a contribution of N–Fe bound and it is hard to distinguish between them [28]. From the XPS results, increasing the NH3 temperature from 800 °C to 1000 °C results in higher graphitic/quaternary nitrogen amounts in atomic percentage. Pyridinic N amount however shows increasing with temperature and a maximum at 900 °C (pyridinic N content of 0.96 at%) and then it decreases at higher temperatures. From the trends of XPS results, when comparing with the sample without any ammonia treatment (Fig. S1b), it appears that the NH3 treatment results in an increase in nitrogen content, accompanied by an increase in the relative concentration of pyridinic and graphitic nitrogen. While for Fe-P-C_Ar the amount of pyridinic and graphitic N were respectively 0.55 and 0.67 at%, they are correspondingly as high as 0.6–0.96 and 1.08–1.71 after ammonia treatment and doping. This trend is consistent with previous reports [18,39]. However, as these M-N-C systems are highly heterogeneous in nature, active site elucidation is very difficult and only recently have sophisticated in-situ synchrotron and Mossbauer techniques started to shed light on this important topic [39–41]. With regards to the active site density on these catalysts, the NH3 treatment etches some of the disordered carbon away that can allow for exposure of any ORR active sites that were buried. Additionally, the increased surface area and mesopore content could mean that the number of active sites accessible to oxygen molecules is significantly increased.

The scanning transmission electron microscope (STEM) image shown in Fig. 4a and the corresponding EELS images shown in Fig. 4b–d outline the elemental distribution in this selected area of the catalyst. Considering that each pixel of the image represents an area of 4.0 nm × 4.0 nm, these images confirm that the iron, nitrogen and carbon species are very well dispersed throughout the FCNT and in-situ formed graphene structures. The uniform distribution can particularly be seen when looking at the superimposed images of Fe-N-C (Fig. 4e) and Fe-N elements (Fig. 4f). Such well-dispersed Fe species suggest that they can potentially coordinate with the nitrogen atoms to form Fe-N and Fe-N-C moieties, which are believed to be highly active for ORR [10,42]. However, sophisticated methods, including in-situ XAS or Mossbauer spectroscopy are needed to confirm these structures.

Fig. 4. (a) STEM image of Fe-P-C_Ar-NH900 and the corresponding EELS elemental mapping images for the selected spectrum area of (b) C, (c) N, (d) Fe, (e) superimposed Fe-N-C (light green, red, blue), and (f) superimposed Fe-N (light green, red) with each pixel represents an area of 4.0 nm × 4.0 nm.
The EELS spectrum and the element survey of the Fe-P-C_Ar-NH900 sample is displayed in Fig. S2 which shows the location of each element peak. As it can be seen from XRD patterns (Fig. S3), the peaks resulting from crystalline phases ($2\theta = 25.9^\circ$ and $43.2^\circ$) can be predominantly allocated to graphite crystalline structures while the peaks appearing at $2\theta = 30.8^\circ$, $33.5^\circ$, $46.8^\circ$ and $53.0^\circ$ are dominant formation of FeS species [28] which is in good agreement with the XPS S 2p spectra (Fig. S1a). EDX elemental mapping and line scanning were also applied to study the distribution of elements in the catalyst material in a larger scale. Line scanning EDX in Fig. S4a also supports the well-distributed nature of these elements along the FCNT and graphene sheets. Moreover, as can be seen in the STEM image of a different area of the same sample with lower magnification (Fig. S4b) and the corresponding EDX images (Fig. S4c–f), all of the elements were found to be homogenously distributed throughout the whole sample area and through all of the FCNT and in-situ formed graphene morphologies. The highly mesoporous morphology formed after NH$_3$ treatment, as well as extremely high surface area and the well dispersed Fe-N-C distribution are believed to be highly beneficial.

![Fig. 5. LSCV results for (a) catalysts derived from different synthesis protocols and (b) Fe-P-C_Ar-NHxx catalysts derived at different ammonia treatment temperatures. (c), (d) durability results for Fe-P-C_Ar-NH900. (e) Half-cell performance comparison of catalysts derived from CNT and carbon black, before and after ammonia treatment. All the polarization curves are performed in O$_2$ saturated 0.5 M sulfuric acid at 900 rpm rotational speed. (f) Fuel cell testing for Fe-P-C_Ar-NH900 (stars) and Fe-P-KJ_Ar-NH900 (squares) under H$_2$-air anode-cathode feeds. Fuel cell tests used 0.5 mg cm$^{-2}$ Pt at the anode.](image)
for the ORR performance [10].

From the ORR polarization curves collected at 900 rpm (Fig. 5a and b), NH3 treatment improved the current densities, onset and half-wave (E1/2) potentials significantly. NH3 treatment induces formation of some types of heteroatom doping that are beneficial for ORR which could likely affect the catalytic performance by tuning the active sites via generating local heterogeneity in electron density. Moreover, the higher mesoporous and macroporous nanostructures of the NH3 treated catalyst (Fig. 2b–e and h) could facilitate the mass transport of oxygen into the catalyst layer and the removal of water molecules to the electrolyte. The effect of heat treatment protocol on ORR performance is shown in Fig. 5a. Samples which underwent a second pyrolysis in Ar before NH3 showed better performance compared to those which were directly heat treated in ammonia. The onset potential is however similar, which indicates that the nature of the active sites is likely similar. The key to the activity gains following this second pyrolysis mainly arise due to the acid leach. Any inactive inorganic metal species are removed through this procedure increasing the porosity and surface exposure of the catalyst. This second heat treatment then likely removes any residues remaining following the acid leaching procedure and increases the degree of graphitization. In Fig. 5b it can be seen that the catalyst derived at the NH3 temperature of 900 °C showed the best ORR performance (E1/2 of 0.81 V vs. RHE) compared to those synthesized at higher ammonia and temperatures. The obtained half-wave potential places this catalyst on par with some of the most active NPMCs reported to date [12,18]. With respect to the XPS results in Fig. 3c and d, the activity trends show that the pyridinic N content potentially plays an important contribution in the ORR activity, as the sample with the highest pyridinic N content (Fe–P–C–Ar-NH900 with pyridinic N content of 0.96 at%) and relatively high amount of graphic nitrogen, exhibited the best ORR activity. On the other hand, there was no clear similarity in trends between ORR activity and increase in the graphitic N content. Moreover, the possible contribution of sulfur species in ORR was studied and as benchmark, S-doped graphene (SG) was synthesized throughout high temperature pyrolysis of a sulfur precursor (benzyl disulfide) and graphene oxide at 900 °C in Ar. Also N-doped graphene (NG) was prepared via pyrolysis (similar to SG pyrolysis conditions) of polybenzimidazole in the absence of any metal precursor. When testing RDE in acid (Fig. S5), the SG shows a very low activity towards ORR, suggesting that S species do not contribute in ORR in acid. On the other hand, an obvious improvement in ORR activity was obtained when testing nitrogen doped catalysts, with a remarkable higher performance for Fe–P–C–Ar-NH900 compared to NG. The remarkable higher activity of Fe–P–C–Ar-NH900 catalyst, suggest that unlike S which does not contribute significantly in ORR in acid, Fe and N species likely involve in ORR activity.

The reaction between NH3 and carbon based materials includes the exchange of O2-containing groups with nitrogen-based species, accompanied with the etching of carbon by radicals formed during ammonia decomposition at high temperatures and therefore it is related to the NH3 treatment temperature [43]. When the ammonia temperature is above 900 °C, breakdown of the porous structures that were generated during overall previous pyrolysis steps could likely happen. A similar phenomenon was observed previously by another group, in which they showed that by increasing the NH3 temperature, the average mesoporous size decreased, pointing out the breaking down of the porous morphology [44]. Moreover, from the C 1s XPS results in Fig. 3b, it was observed that with increasing the NH3 temperature, higher amounts of sp2-graphitic carbon species undergo breakdown. The breakdown of graphitic carbon structures and the likeliness of porous morphologies decomposition could likely be the reasons for the lower ORR activity at ammonia treatment temperatures above 900 °C.

From RRDE results for Fe–P–C–Ar-NH900 and Fe–P–C–Ar (Fig. S6a and b), the number of electrons transferred per reduced oxygen molecule is measured to be 3.90 ± 0.05 at relatively high potentials (0.4–0.8 V vs. RHE), thereby showing a very good selectivity towards the four electron reaction. On the other hand, the peroxide yields for Fe–P–C–Ar in that high potential range can be as high as 10 ± 5%, it was much lower for Fe–P–C–Ar-NH900 (almost 5%) which indicates that after ammonia treatment, the selectivity to produce H2O during ORR increased meaningfully. The Fe–P–C–Ar-NH900 catalyst also shows relatively good durability behaviour (Fig. 5c and d). After 5000 cycles in N2, a 20 mV and a 45 mV potential loss toward ORR was observed in onset and half-wave potentials, respectively. RDE testing for Fe–P–C–Ar-NH900 exhibits improvement compared to the reference samples (Fe–P–KJ–Ar and Fe–P–KJ–Ar-NH900) which were synthesized using ketjen black instead of CNT as carbon support, under the optimized condition (similar to the synthesis conditions of Fe–P–C–Ar and Fe–P–C–Ar-NH900, respectively), in order to be used as benchmarks.

In order to evaluate the Fe–P–C–Ar-NH900 catalyst under PEMFC operating conditions, they were integrated as cathodes into a single cell MEA. Although H2–O2 performance provides a gauge of intrinsic catalyst layer activity, testing under H2–air conditions should be provided as evaluation under practical operative conditions. When applying air as the cathode reactant (Fig. 5f), the MEA showed current densities of 77 mA cm−2 at 0.8 V and 537 mA cm−2 at 0.6 V, in addition to a maximum power density of 335 mW cm−2 with a clear improvement in comparison to the reference sample (Fe–P–KJ–Ar-NH900). From SEM images in Fig. S7a and b, in comparison to Fe–P–C–Ar-NH900, Fe–P–KJ–Ar-NH900 has less macro pores which could likely limits diffusion of the feed into the catalyst bulk towards the active sites and this could be the reason for better performance of Fe–P–C–Ar-NH900 at higher current densities which is the mass transport control region. To the best of our knowledge, the obtained power densities and IR-free current densities in an H2–air fuel cell for Fe–P–C–Ar-NH900 are the best results reported to date in the literatures for a NPMC electrode. The electrocatalyst morphology, with its high surface area of ca. 1100 m2 g−1 and variety of pores ranging in size from 2 nm to 200 nm, is the likely cause of the high H2–air performance. This catalyst structure is conducive to mass transport through the catalyst layer, a factor that is increasingly important when using air as the reactant feed. Clearly the tuned chemical modification and porous catalyst morphology render Fe–P–C–Ar-NH900 an attractive non-precious ORR catalyst for PEMFCs, based on half-cell and fuel cell performance evaluations.

4. Conclusion

An NH3 treatment was applied and optimized to tune the activity and improve the PEMFC performance of ORR catalysts derived from iron, PANI and CNT. NH3 contributed by enriching the N-dopant concentration, while careful choice of the temperature had an impact on nitrogen dopant identity and ORR activity. The final catalyst consisted of in-situ formed graphene-like structures that had well-distributed nitrogen and iron defects. The catalyst derived under the optimized condition (F–P–C–Ar-NH900) exhibited high catalyst activity, including an E1/2 of 0.81 V vs RHE through RDE testing. MEA performance under H2–air conditions that are application friendly, current densities of 77 mA cm−2 at 0.8 V and 537 mA cm−2 at 0.6 V were achieved. Furthermore, a maximum power density of 335 mW cm−2 at 0.6 V was observed. To the best of our knowledge, this is the best H2–air performance shown to date for a Pt-free cathode. This catalyst also showed a
very good selectivity towards the four electron reaction with the number of electrons transferred per reduced oxygen molecule was calculated to be 3.90 by RDRE. These electrochemical evaluations indicate that the chemical modification of Fe–PANI–CNT catalyst by NH3 results in a highly promising Pt-free PEMFC ORR electrocatalyst.

Acknowledgements

This work was supported by the University of Waterloo and the Waterloo Institute for Nanotechnology. TEM imaging was carried out at the Canadian Center for Electron Microscopy (CCEM) located at McMaster University. This research was conducted as part of the Catalysis Research for Polymer Electrolyte Fuel Cells (CaRPFC) Network administered from Simon Fraser University and supported by Automotive Partnership Canada (APC) Grant no. APCP-417858–11 through the Natural Sciences and Engineering Research Council of Canada (NSERC).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2016.05.035.

References

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