



## Review article

## Carbon-based catalysts for oxygen reduction reaction: A review on degradation mechanisms



Harsimranjit Singh <sup>a</sup>, Shiqiang Zhuang <sup>b</sup>, Benjamin Ingis <sup>a</sup>, Bharath Babu Nunna <sup>c</sup>,  
Eon Soo Lee <sup>a,\*</sup>

<sup>a</sup> Advanced Energy Systems and Microdevices Laboratory, Department of Mechanical and Industrial Engineering, New Jersey Institute of Technology, Newark, NJ, 07102, USA

<sup>b</sup> Jinan University, Xiamen, 361004, China

<sup>c</sup> Division of Engineering in Medicine, Department of Medicine, Brigham and Women's Hospital, Harvard Medical School, Harvard University, Cambridge, MA, 02139, United States

## ARTICLE INFO

## Article history:

Received 17 April 2019

Received in revised form

22 May 2019

Accepted 27 May 2019

Available online 28 May 2019

## ABSTRACT

This review focuses on the historic and recent progress of the stability of the carbon-based non-platinum-group metal (PGM) and metal-free catalysts for oxygen reduction reaction (ORR). It highlights the reported degradation mechanisms which are responsible for the instability issue. These mechanisms are (a) oxidative attack of the ORR intermediates, (b) demetalation of the metal-active site, (c) protonation followed by anionic adsorption, and (d) micropore flooding. For the metal-based catalysts, mechanisms (a) and (b) are the most commonly observed. From the review, it is known that the oxidative attack of ORR intermediates leads to the carbon oxidation, which can also result in the demetalation of the metal-active site. Additionally, the demetalation of the iron-based catalysts can also indirectly oxidize the carbon-support via Fenton reaction. The mechanisms (c) and (d) are sharply criticized. Finally, for the metal-free carbon-based catalysts, there is only a limited research available on the stability of these catalysts. Among the reported study, the mechanisms (a) and (c) can be responsible for the degradation of these catalysts. Therefore, it is recommended that more study should be focused on investigating the degradation parameters and mechanisms for metal-free catalysts.

© 2019 Elsevier Ltd. All rights reserved.

## Contents

|                                                                 |     |
|-----------------------------------------------------------------|-----|
| 1. Introduction .....                                           | 161 |
| 2. Theoretical understanding of oxygen reduction reaction ..... | 161 |
| 3. CARBON-BASED NON-PGM metal catalyst review .....             | 162 |
| 3.1. Oxidative attack of ORR intermediates .....                | 162 |
| 3.2. Demetalation .....                                         | 164 |
| 3.3. Protonation of active sites .....                          | 166 |
| 3.4. Micropore flooding .....                                   | 168 |
| 4. Carbon-based metal free catalysts review .....               | 169 |
| 5. Discussion .....                                             | 170 |
| 5.1. Carbon-based non-PGM metal catalysts .....                 | 170 |
| 5.2. Carbon-based metal-free catalysts .....                    | 171 |
| 6. Conclusion .....                                             | 172 |
| Conflicts of interest .....                                     | 173 |
| Acknowledgements .....                                          | 173 |
| References .....                                                | 173 |

\* Corresponding author. Department of Mechanical and Industrial Engineering, New Jersey Institute of Technology, 200 Central Avenue, Rm MEC 327, Newark, NJ07102-1982, USA.

E-mail address: [eonsoo.lee@njit.edu](mailto:eonsoo.lee@njit.edu) (E.S. Lee).

**Nomenclature**

|                |                                                |
|----------------|------------------------------------------------|
| AST            | Accelerated Stress Test                        |
| BOL            | Beginning Of Life                              |
| CV             | Cyclic Voltammogram                            |
| DEMS           | Differential Electrochemical Mass Spectrometry |
| DFT            | Density Functional Theory                      |
| DOE            | Department of Energy                           |
| E <sub>b</sub> | O <sub>2</sub> -binding energy                 |
| ESA            | Electrochemical Surface Area                   |
| EXAFS          | Extended X-ray Absorption Fine Structure       |
| FCTO           | Fuel Cell Technology Office                    |
| HOR            | Hydrogen Oxidation Reaction                    |
| ICP-MS         | Inductively Coupled Plasma Mass Spectrometry   |
| MEA            | Membrane Electrode Assembly                    |
| MOF            | Metal-Organic Framework                        |
| NAA            | Neutron Activation Analysis                    |
| N-G            | Nitrogen-doped Graphene                        |
| NHE            | Normal Hydrogen Electrode                      |
| OCV            | Open Circuit Voltage                           |
| ORR            | Oxygen Reduction Reaction                      |

|        |                                              |
|--------|----------------------------------------------|
| PEMFC  | Proton Exchange Membrane Fuel Cell           |
| PFSA   | Per-FluoroalkylSulfonic Acid                 |
| PGM    | Platinum Group Metal                         |
| ppm    | Parts Per Million                            |
| PSSA   | PolyStyreneSulfonic Acid                     |
| Pt/C   | Platinum on Carbon                           |
| RDE    | Rotating Disk Electrode                      |
| RH     | Relative Humidity                            |
| RHE    | Reference Hydrogen Electrode                 |
| ROS    | Reactive Oxygen Species                      |
| RRDE   | Rotating Ring Disk Electrode                 |
| SCE    | Saturated Calomel Electrode                  |
| SHE    | Standard Hydrogen Electrode                  |
| TEM    | Transmission Electron Microscopy             |
| TGA    | Thermogravimetric Analysis                   |
| TGA-MS | Thermogravimetric Analysis/Mass Spectrometry |
| TMPP   | Tetramethoxyphenylporphyrin                  |
| TOF    | Turnover Frequency                           |
| WF     | Work Function                                |
| XPS    | X-ray Photoelectron Spectroscopy             |

**1. Introduction**

Proton Exchange Membrane Fuel Cells (PEMFC) emerged as the solution to the increasing CO<sub>2</sub> emissions from the stationary and automotive applications of combustion of fossil fuels [1]. The PEMFCs use hydrogen fuel to convert chemical energy into electrical energy while producing water as a byproduct, making them one of the most environmentally benign energy conversion devices [2–4]. In a PEMFC, the hydrogen oxidation reaction (HOR) occurs at the anode where the hydrogen fuel is converted into protons and electrons, and an oxygen reduction reaction occurs (ORR) at the cathode which reduces the oxygen to form H<sub>2</sub>O [5,6]. The HOR is a kinetically faster reaction; therefore low catalyst loading is required on the anode. The ORR on the cathode is considerably sluggish; hence high catalyst loadings are required to enhance the reaction kinetics. Currently, industrial PEMFCs employ highly expensive Platinum Group Metal (PGM) catalysts for the ORR. The platinum is deposited as nanoparticles on the carbon support to maximize the surface area for the ORR [7]. These PGM catalysts add a major cost barrier which inhibits the commercialization of the PEMFC technology. Therefore, in the past decades, significant research was focused on developing a new class of carbon-based non-PGM catalysts with high ORR activity [7–14].

For simplicity, in this review the non-PGM catalysts are referred to both non-precious metal and metal-free catalysts. The carbon-based non-precious metal catalyst research includes the transition metals (M-N-C) based catalysts such as Fe-N-C or Co-N-C and metal-free catalysts include heteroatom doped-carbon catalysts such as N-C, B-C, S-C, etc. It is known that for practical applications, the non-PGM catalyst should exhibit volumetric activity >1/10 that of Pt/C catalysts. This volumetric activity results in a thicker catalyst layer as compared to the PGM catalysts; therefore it is highly desired in the non-PGM catalyst to have a high surface area and porosity for better mass transport properties during the ORR [7,10–15]. This improvement was made possible with new innovative materials and material synthesis approaches. Specifically, by introducing mesoporosity and high surface area in the non-PGM catalysts, many researchers have crossed the targeted activity [7,16]. Such materials include carbon nanotubes, multiwall carbon nanotubes, and metal-organic frameworks

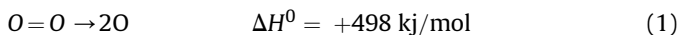
(MOF). In the past decade, both the transition metal-based and metal-free catalysts have crossed the volumetric activity and porous structure requirements for the ORR [7,9,10,16–18]. Nevertheless, these non-PGM catalysts cannot be implemented in the PEMFCs for commercial applications, due to their unacceptably low stability and durability in the operating conditions. The stability and durability of these catalysts is the retention of initial performance and activity over the required operational lifetime. Specifically, previous works refer to the stability and durability of the catalyst as the performance loss at constant current and performance loss during voltage cycling respectively [19]. The U.S Department of Energy Fuel Cell Technology Office (DOE-FCTO) currently targets PEMFC operational lifetimes of 60,000 h for the stationary applications and 5000 h for transportation applications [20]. While the PGM-based PEMFC has demonstrated thousands of hours of operation, current non-PGM PEMFC only operates for hundreds of hours [7].

In this review, we will provide a detailed understanding of the ORR which includes the different proposed reaction pathways for non-PGM catalysts. Following this, the reported degradation mechanisms for carbon-based non-PGM metal and metal-free catalysts are discussed extensively. These catalyst degradation mechanisms can be categorized on the atomic and meso/macro scales [21,22]. The atomic scale degradation includes the deactivation/modification of active sites during the ORR, and the meso/macro scale consists of the corrosion/oxidation of the carbon support, loss of the porosity by the ORR intermediates and polymer membrane degradation in the PEMFCs. Finally, discussion on the current status and understanding of the degradation mechanism is provided individually for carbon-based non-PGM metal and metal-free catalysts for developing inexpensive, state-of-the-art, active, and stable ORR catalysts.

**2. Theoretical understanding of oxygen reduction reaction**

The abundance of oxygen in the atmosphere makes it the most favorable oxidant for fuel cell cathodes. However, the high bond energy of the O<sub>2</sub> (498 kJ/mol) molecule makes it very stable and ORR an extremely sluggish reaction (equation (1)). To overcome this activation barrier and reduce oxygen to water in PEMFC, highly

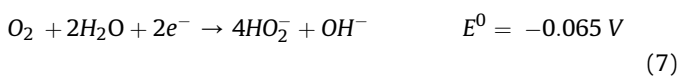
active cathode catalysts are desired.



**Acidic medium:** In general, oxygen can be reduced to water via two pathways; direct  $4e^-$  pathway which requires the transfer of  $4e^-$  and  $4H^+$  (equation (2)), or  $2+2e^-$  pathway, in which the oxygen is reduced to hydrogen peroxide, which can then reduce or disproportionate to water (equations (3)–(5)).



**Alkaline medium:** It is well known that the activation potential of the ORR depends upon pH values; therefore the ORR in the alkaline medium can be written differently (equations (6)–(9)).



The underlying reaction mechanism of the four-electron pathway on the active site of the catalysts is adsorption and dissociation of  $O_2$  molecule, followed by the OH formation and ultimately  $H_2O$  formation (equation (10)–(14)).



where \* is the catalyst active site. In the case of the two-electron pathway, several reactive intermediates are formed including OOH and  $H_2O_2$  (equations 15 and 16).



Furthermore, with the help of computational tools such as Density Functional Theory (DFT), researchers have reported two additional possible pathways for ORR [23–25]. The first step to initialize ORR through all the pathways is the chemisorption of the  $O_2$  molecule on the active site of the catalyst (equation (10)). After the chemisorption, the ORR can undergo (i)  $O_2$  dissociation, (ii) OOH dissociation, and (iii) HOOH dissociation to form  $H_2O$  molecule. The former method is already discussed above (equation (10)–(14)) and the latter pathways are shown in Table 1. In the

**Table 1**

Additional ORR mechanisms suggested with DFT.

| Dissociation of OOH                                | Dissociation of HOOH                                |
|----------------------------------------------------|-----------------------------------------------------|
| $O_2 + * \rightarrow O_2^* \quad (17)$             | $O_2 + * \rightarrow O_2^* \quad (22)$              |
| $O_2^* + (H^+ + e^-) \rightarrow OOH^* \quad (18)$ | $O_2^* + (H^+ + e^-) \rightarrow OOH^* \quad (23)$  |
| $OOH^* + * \rightarrow O^* + OH^* \quad (19)$      | $OOH^* + (H^+ + e^-) \rightarrow HOOH^* \quad (24)$ |
| $O^* + (H^+ + e^-) \rightarrow OH^* \quad (20)$    | $HOOH^* \rightarrow 2OH^* \quad (25)$               |
| $OH^* + (H^+ + e^-) \rightarrow H_2O^* \quad (21)$ | $OH^* + (H^+ + e^-) \rightarrow H_2O^* \quad (26)$  |

latter pathways, the  $O_2$  molecule associate to form OOH via protonation (equation 17–21), which can also follow the second protonation into HOOH (equation 22–26). Both of these mechanisms then undergo dissociations and protonations to form  $H_2O$ .

### 3. CARBON-BASED NON-PGM metal catalyst review

The M-N-C catalysts are considered the most promising candidates for eliminating the PGM catalysts from the electrochemical systems. However, the biggest conundrum of these catalysts is the nature and type of the active sites [26–28]. In these catalysts, the metal species as active sites can exist as atoms, particles, clusters, and carbides, but the most commonly reported are the  $MN_xCy$  moieties. In these moieties, the metal is coordinately bonded to the nitrogen atoms and embedded in the carbon matrix. Despite the type of active sites, these catalysts have been dangerously prone to degradation during the ORR. So far four degradation mechanisms have been reported: (i) oxidative attack of the ORR intermediates, (ii) demetalation of the metal species, (iii) protonation followed by anionic adsorption, and (iv) micropore flooding. Each of these mechanisms is explained in detail in the following sub-sections.

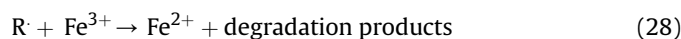
#### 3.1. Oxidative attack of ORR intermediates

Janiski et al. reported one of the earliest stability tests for his Cobalt-phthalocyanine catalyst [29]. Due to the low activity and  $2e^-$  selectivity ( $H_2O_2$  byproduct) of the non-PGM catalysts, the effect of the peroxide was investigated by adding 2.5 cc 30%  $H_2O_2$  to the electrolyte. However, no significant change was observed in the cathode voltage. But it was concluded that further experimentation was needed to understand the effect of the peroxide. Alt et al. studied the catalytic activity of  $N_4$  complexes and found the instability of phthalocyanine compared to tetraarylporphyrins when supported by active carbon or carbon black [30]. A rapid drop in the potential was observed within a few hours of operation, which was followed by a gradual decrease. Although there was no clear evidence presented to explain the performance loss, it was speculated that the C and N bridges are weakened by the oxidative attack of the oxygen or  $H_2O_2$  which degraded the molecule at its site.

To understand the effect of peroxide on the ORR activity of the non-PGM catalysts, several studies focused on the ex situ effect of  $H_2O_2$  [29,31–36]. In these studies, the catalysts were rigorously treated with peroxide prior to their electrochemical characterizations. Schulenburg et al. conducted three degradation tests, namely, peroxide treatment, acid treatment and long-term stability test for an iron-based catalysts to investigate the degradation mechanisms [31]. In the peroxide treatment test, 20 mg of acid washed FeTMP-Cl catalyst was treated with 30 ml of 30 wt%  $H_2O_2$  by continuous stirring for 100 h before collecting the residue catalyst. Similarly, in the acid treatment test, 25 mg of the catalyst was magnetically stirred in 30 ml of sulfuric acid for 100 h. For the stability test, a potentiostatic hold at 0.7 V Vs normal hydrogen electrode (NHE) was applied in 0.5 M sulfuric acid for 100 h. After the acid

treatment, the catalysts retained its catalytic activity. On the other hand, both the peroxide treatment and the stability test degraded the catalysts. A higher degradation of the catalysts was reported after the peroxide treatment than the stability test. This observation was explained with an argument based on the exposure of the catalysts to  $\text{H}_2\text{O}_2$ . In the peroxide treatment the catalyst was subjected to higher concentration of  $\text{H}_2\text{O}_2$  (30%) than the stability test (10–11% as ORR-byproduct). Therefore, it was speculated that the degradation mechanism was the oxidative attack of the  $\text{H}_2\text{O}_2$  on the N bounded to the metal active site (Fig. 1). However, it was found from the XPS data that the N1s binding energies were unchanged. Therefore it was hypothesized that the oxidized nitrogen atoms dissolved in the electrolyte but no further investigation was reported.

In the same year, Lefevre et al. observed similar performance loss phenomenon after the peroxide treatment to iron-based catalysts varied by Fe content and pyrolysis temperature [32]. The peroxide generation during the ORR was evaluated with RRDE measurements at room temperature, and the voltammograms were recorded in  $\text{H}_2\text{SO}_4$  (pH1) from 0.8 V to  $-0.3$  V Vs saturated calomel electrode (SCE). The peroxide treatment concentration was mimicked (5 h in  $\text{H}_2\text{SO}_4$  (pH1) + 5 vol%  $\text{H}_2\text{O}_2$ ) with that released near the catalyst during the ORR. In this study, the catalysts with electron transfer number ( $n$ ) > 3.9 measured less than 5%  $\text{H}_2\text{O}_2$  production. Moreover, from the peroxide treatment experiments, it was concluded that the catalytic activity of these catalysts was severely affected with even 5% of the peroxide generated during ORR. Additionally, the loss of the activity was also correlated with the Fe content. It was observed that the catalyst which was most affected with the peroxide treatment has the lowest Fe content. It was suggested that transition metal ions (specifically  $\text{Fe}^{2+}$ ) could act as Fenton's reagent and decompose  $\text{H}_2\text{O}_2$  into highly reactive hydroxyl ( $\cdot\text{OH}$ ) and hydroperoxy ( $\cdot\text{OOH}$ ) free radicals in an acidic medium which can be the cause of the instability of the iron-based non-PGM catalysts. Further research proposed the mechanism of free radical attack on the non-PGM catalyst by the following equations [33].



Gubler et al. have described in detail the formation, concentration and oxidative strength of the oxygen free radicals ( $\cdot\text{OH}$ ,  $\cdot\text{H}$ ,  $\cdot\text{OOH}$ ,  $\text{H}_2\text{O}_2$ ) while investigating the ionomer degradation [34]. The oxidative strength of these species was reported to be in order of  $\cdot\text{OH} > \cdot\text{H} > \cdot\text{OOH} > \text{H}_2\text{O}_2$ . In this study, it was claimed that the presence of Fe impurities resulted in a significant increase in the degradation of per-fluoroalkyl sulfonic acid (PFSA) and polystyrene

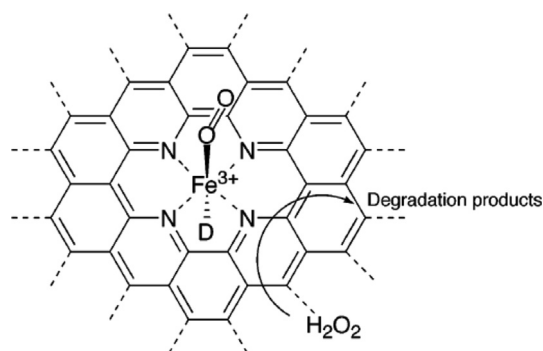


Fig. 1. Proposed hydrogen peroxide attack mechanism [31].

sulfonic acid (PSSA) ionomers. This observation was attributed to the increased concentration of  $\cdot\text{OH}$  radicals, which are formed by the decomposition of  $\text{H}_2\text{O}_2$  by the catalytic effect of  $\text{Fe}^{2+}$  (Fenton reaction). It was claimed that with Fe content greater than 40 ppm,  $\text{Fe}^{2+} + \text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{HO}\cdot + \text{H}_2\text{O}$  reaction becomes the dominant source of  $\cdot\text{OH}$  free radicals.

Recently, Goellner et al. also investigated the effect of  $\text{H}_2\text{O}_2$  on different M-N-C (M: Fe, Co, Cr) catalysts [35]. Like the previous studies, they also observed significant performance loss after the peroxide treatment; however, the peroxide effect differed depending on the type of metal. The adverse effect was most prominent in the case of  $\text{CrN}_x\text{C}_y$  followed by  $\text{FeN}_x\text{C}_y$  and then  $\text{CoN}_x\text{C}_y$  (Fig. 2). Direct evidence of the ORR free radicals (or reactive oxidative species) was provided by correlating the collection efficiency (remaining weight percentage of catalysts after ex-situ peroxide treatment) with fluoride concentration in the filtrate. It is known that the reactive oxygen species (ROS) can be quantified by fluoride concentration due to their attack on the Nafion membrane [34]. It was observed that at high concentration ( $2.10^{-2} \text{ mol mg}^{-1}$ ) treatment with peroxide, only 60% and 40% of the initial mass of Co-N-C and Cr-N-C was collected whereas no Fe-N-C catalyst was collected on the filtrate (Fig. 3). It was hypothesized that at this high concentration most of the Fe-N-C physical structure collapsed resulting in finer particles which passed through the filter. This provides evidence that the physical structure of Fe-N-C catalyst was most affected by peroxide treatment, which can be related to the ROS production via Fenton reaction. The extended X-ray absorption fine structure (EXAFS) and Fe Mössbauer spectroscopy analysis revealed that after the peroxide treatment most of the  $\text{FeN}_x\text{C}_y$  moieties were still present and have similar electronic structure and coordination chemistry as in the pristine catalyst, suggesting the high stability of the active sites. Since the Fe-based active sites remained stable after the peroxide

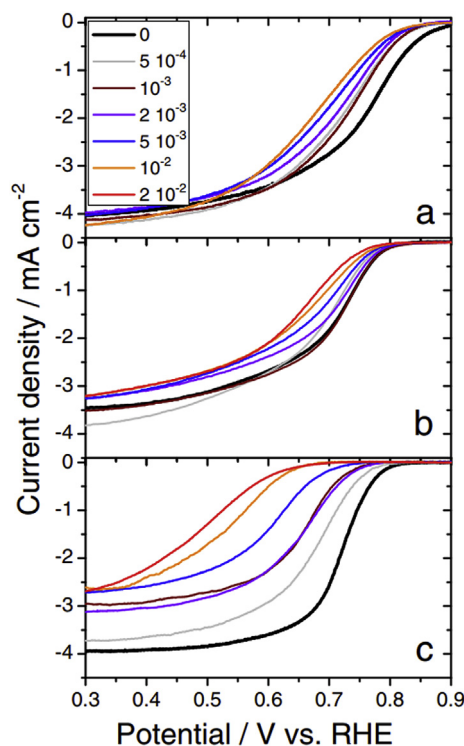
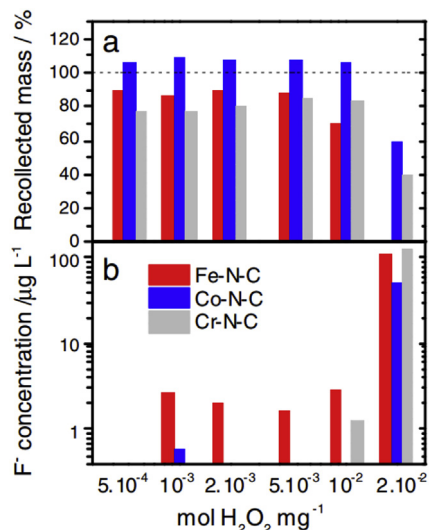


Fig. 2. Performance degradation of (a) Fe-N-C, (b) Co-N-C and, (c) Cr-N-C catalysts with different concentrations of  $\text{H}_2\text{O}_2$  (inset) [35]. (A colour version of this figure can be viewed online.)



**Fig. 3.** (a) Recollected mass of the catalysts at different amounts of H<sub>2</sub>O<sub>2</sub>, (b) Fluoride ions released by the Nafion membrane after H<sub>2</sub>O<sub>2</sub> treatment [35]. (A colour version of this figure can be viewed online.)

treatment, it was hypothesized that the decrease in the ORR activity was due to the oxidation of surface carbon, which resulted in the loss of surface conductivity and hence in reduced turnover frequency (TOF) of the FeN<sub>x</sub>C<sub>y</sub> moieties.

On further research by Choi et al., the N1s spectra, N and Fe content, pore size distribution, specific surface area, and bulk carbon structure of the peroxide treated Fe-N-C catalyst was found to be identical to the pristine catalyst [36]. However, the oxygen content increased from 5% to 10 at% after the peroxide treatment as revealed by the XPS. It was proposed that this increase in the oxygen content might be from the selective oxidation of the carbon support via Fenton reaction which was ultimately responsible for the lower ORR-TOF. To support this speculation, the degraded catalyst was subjected to an electrochemical reduction technique to clean the carbon support of these oxygen-functionalities. In doing so, a significant increase in the activity and selectivity of the catalysts was observed, which confirmed the role of H<sub>2</sub>O<sub>2</sub> and Fenton reaction in the degradation of the iron-based catalysts. Furthermore, to understand the effect of carbon oxidation on the TOF, DFT calculations were applied to evaluate the O<sub>2</sub>-binding energy (*E<sub>b</sub>*) and work function (WF). Fig. 4 illustrates the effect of epoxy and hydroxyl groups (that can be formed by Fenton reaction) on the WF and *E<sub>b</sub>* at different locations and numbers. The introduction of these electron-withdrawing oxygen groups (especially epoxy groups) elevated the work function due to the depletion of the  $\pi$ -electrons from the carbon support and weakened the *E<sub>b</sub>* which suggests that the FeN<sub>4</sub> centers on the graphene sheets are situated on the apex or the weak binding side of the activity vs binding energy volcano plot and thereby reducing the TOF.

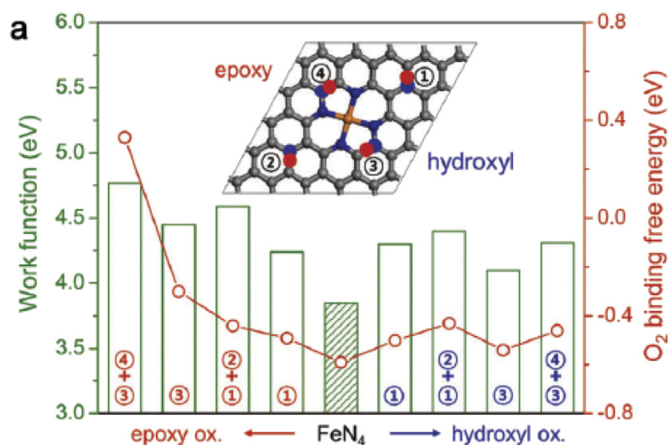
### 3.2. Demetalation

The nature of active sites of the metal-based non-PGM catalysts has been a point of contention in the ORR catalysts research community [26–28]. It is known that during their synthesis many transition metal-based structures are formed. While some of these structures are the active sites responsible for the ORR activity, others are only inactive bystanders [37–39]. Demetalation is a known factor for the performance loss by the loss of metal-active site in the metal-based non-PGM catalysts [39–47]. Several acid wash tests have reported that demetalation of the inactive

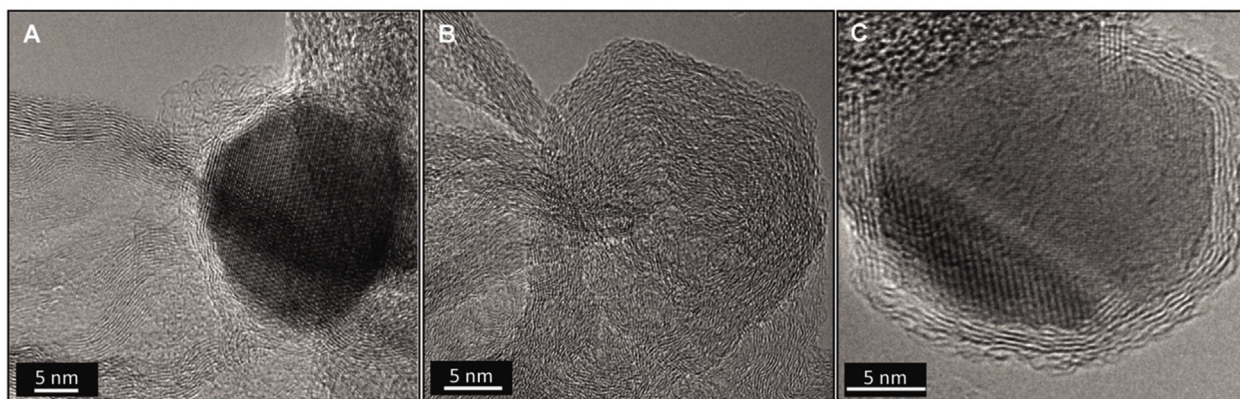
transition metal structures does not affect the activity of the non-PGM catalysts, however, these inactive metal species can be responsible for a variety of undesired effects on the PEMFC such as ionomer degradation due to Fenton reaction (as discussed in the peroxide mechanism section) [34]. But, in this discussion, we will only focus on the leaching/demetalation of the active sites resulting in the degradation of the non-PGM catalysts.

The leaching of metal active sites in correlation with performance loss was first reported by Gupta et al. [40]. In this study, a significant performance loss of the Co-based non-PGM catalyst was observed. It was speculated that the solubility of Co is higher in the acidic medium; therefore it is highly possible that the metal active sites leached out into the solution. Later, Lalande et al. and Fauber et al. investigated the effect of heat treatment on the activity and stability of the cobalt and iron based non-PGM catalysts [41,42]. The highest activity was observed in the heat treatment range of 500–700 °C and was ascribed to the N<sub>4</sub>-metal chelates. Contrary to the high activity, the most stable catalyst was synthesized at high-temperature pyrolysis (900–1000 °C). With the help of TEM images, a graphite sheet surrounding the metal centers was discovered, and it was proposed that these protective graphite sheets shield the metal active site from leaching out under the acidic conditions. Many researchers believe that the carbon protected metal particles cannot contribute to the surface catalysis [37,45,60]. However, it was reported in the study by Wu et al. that nitrogen functionalities are responsible for n-type carbon doping resulting in more disordered carbon structure and metal integration enhances ORR [43]. These protective graphite sheets can be seen in Fig. 5 [43].

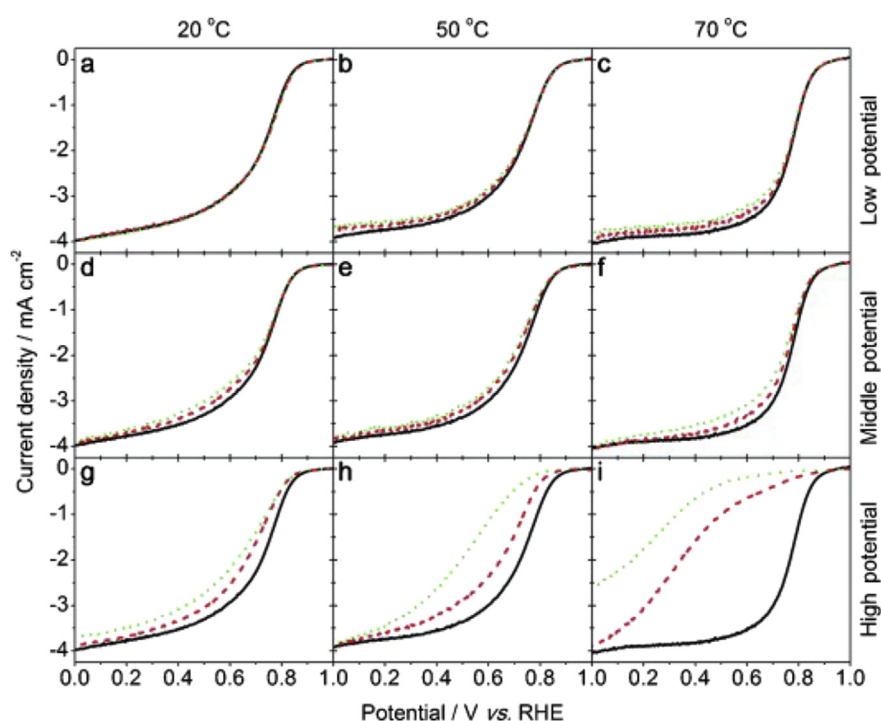
A detailed study on understanding the demetalation mechanism was conducted by Choi et al. [37]. In this study, Fe demetalation by cycling the potential in different potential range was investigated with the inductively coupled plasma mass spectrometry (ICP-MS) and differential electrochemical mass spectrometry (DEMS) methods. The potential was cycled between 0.1 and 0.4 V; 0.6–0.9 V and 1.2–1.5 V for 2000 and 5000 cycles and at 20 °C, 50 °C and 70 °C respectively (Fig. 6). It was concluded that Fe leaching is observed at potentials lower than 0.7 V Vs reference hydrogen electrode (RHE) and oxidation of the carbon support at potentials higher than 0.9 V Vs RHE. The Fe leaching did not result in any performance loss because of the leaching of only inactive Fe species. However, the carbon oxidation which was more severe at higher temperatures resulted in the destruction of the FeN<sub>x</sub>C<sub>y</sub>



**Fig. 4.** The effect of oxygen functionalities formed by surface oxidation on the work function and O<sub>2</sub>-binding energy (*E<sub>b</sub>*) of FeN<sub>4</sub> moiety. The position of the oxygen functionalities is represented by the numbers in the inset [36]. (A colour version of this figure can be viewed online.)



**Fig. 5.** The HRTEM image of (a) non-PGM metal catalyst embedded in graphitic nanoshells, (b) hollow nanoshells, and (c) onion-like nanoshells [43]. (A colour version of this figure can be viewed online.)



**Fig. 6.** ORR activity before (solid lines) and following potential cycling 2000 cycles (dashed lines) and 5000 cycles (dotted lines) at different temperatures of  $\text{FeN}_x\text{C}_y$  moieties in  $\text{O}_2$ -saturated 0.1 M  $\text{HClO}_4$ . (a–c) 0.1–0.4 V, (d–f) 0.6–0.9 V, (g–i) 1.2–1.5 V [37]. (A colour version of this figure can be viewed online.)

moieties and ultimately in the performance degradation. In the presence of catalytic environment/during operation, it has been reported that even after the preliminary acid treatment to remove inactive species, there is a possibility of Fe loss in the Fe-N-C catalysts. But this Fe removal can be the result of carbon oxidation by high overpotentials and/or oxidative attack of peroxide or simple demetalation in the acidic environment [31,32,37]. As discussed in the first paragraph of this section, the leaching of inactive Fe species does not affect the stability of the Fe-N-C catalysts but can be detrimental to the PEMFC system. In the follow-up study by Choi et al., the methods to remove the inactive iron species from the Fe-N-C catalysts were presented [44]. These methods include (i) synthesis of Fe-N-C catalyst without Fe particles, and (ii) post synthesis removal of exposed Fe particles by external potentiostat or an internal reducing agent ( $\text{SnCl}_2$ ).

Recently, Kumar et al. investigated the effect of different

transition metal species such as metal-coordinated with nitrogen, metal-carbides which are partially or entirely lodged in the graphene sheets/shells [45]. The group tested six metal-NC catalysts before and after the 10,000 cycles accelerated stress tests (AST), in which they varied the metal type (Co, Fe), metal content and heating mode. Specifically, atomically dispersed metal ion sites ( $\text{metal-N}_x\text{C}_y$ ) and metal nanoparticles embedded in carbon matrix ( $\text{metal@N-C}$ ) obtained by pyrolysis synthesis approach were tested. It was found that all the catalysts exhibited similar initial ORR activity, but the AST's revealed that the  $\text{metal-N}_x\text{C}_y$  catalysts lost 10–20% and  $\text{metal@N-C}$  lost 60–100% of initial activity. It is known that the cathode of the PEMFC can reach high potentials during the start-up and shut-down operation. Therefore, the start-up/shut-down of PEMFC was mimicked by cycling the potential at higher oxidation potentials (1.0 V – 1.5 V vs reference hydrogen electrode) in the RDE. The degraded catalysts were examined with Raman

spectroscopy and Energy-dispersive X-ray spectroscopy. It was concluded that the degradation of the catalysts in the AST's and start-up/shut-down was due to the demetalation of catalyst metal centers and carbon support corrosion respectively. This study provided evidence of higher stability of  $MN_xC_y$  moieties as compared to the carbon protected metallic species.

An extensive study to understand the degradation process of the Fe-N-C catalysts via demetalation was performed by Chenitz et al. [46]. Before this study, the peroxide attack, Fenton reaction, protonation followed by anion adsorption and micropore flooding mechanisms were considered to understand the initial rapid decay [51,53,54]. All of these mechanisms are discussed in the above and following sections. In this study, the specific demetalation of the  $FeN_4$  sites situated inside the micropores was proposed to be responsible for the initial fast degradation. The stability test was conducted by holding the potential at 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8 V V RHE with seven different MEAs in  $H_2$ /air fuel cell for 125 h. In the durability experiments, the potential was cycled between open circuit voltage (OCV)-0.2 V and the current density measurements were compared at individual potentials from 0.2 to 0.8 V. This test was carried on at two different cell temperatures, 25 °C and 80 °C. The stability data revealed that all the seven MEAs showed similar initial instability, indicating that the fast decay of the catalyst was independent of the potential it was held at. Moreover, the durability experiments revealed that the fast decay half-life ( $t_{1/2, \text{fast decay}}$ ) was almost similar at all the potentials and temperatures but the slow decay half-life ( $t_{1/2, \text{slow decay}}$ ) varied. The measured  $t_{1/2, \text{fast decay}}$  was  $138 \pm 55$  min and  $t_{1/2, \text{slow decay}}$  was minimum of  $\approx 2400$  min to infinity.

Following these observations, the adsorption-desorption isotherms were characterized, and the physical structure of the micropores was deduced to be interconnected open-ended slit-shaped. The average pore size for this non-PGM catalyst was reported to be 1.1 nm microporous and 3.5 nm mesoporous with  $85 \pm 5\%$  and  $15 \pm 5\%$  surface area respectively. Referring to the literature, it was assumed that despite the hydrophobic nature of the micropores, it was possible to transport water through these micropores due to the humidified air streaming on the cathode. This assumption was all the more important because the active sites of the Fe-N-C catalysts, i.e.  $FeN_4$  moieties resides in these micropores, and also, because the electro-oxidation of the carbon-support is possible in the presence of water at potentials  $>0.207$  V SHE. It was claimed that the carbon oxidation would result in the more hydrophilic nature of the micropores, and as a consequence will produce more interactions between the micropores and the flowing water. This phenomenon can reduce the water flux and transportation of the ORR relevant species such as  $O_2$  and protons through these micropores to the active sites making them inactive to ORR. In this case, the active sites will remain untouched, and the Mössbauer spectra of the degraded catalyst will be similar to the pristine catalyst. However, a significant decrease in the  $FeN_4$  sites was observed in the neutron activation analysis (NAA) and Mössbauer measurements of the catalysts subjected to different time scales of stability test. The current density loss co-related with the loss of  $FeN_4$  sites is shown in Fig. 7. It was proposed that the  $FeN_4$  sites were thermodynamically unstable in the open-ended micropores through which the Fe ions can flush out with the flowing water onto the MEA. Finally, it was concluded that the micropores which were responsible for the initial high activity of the non-PGM catalyst were also causing the initial fast decay via specific demetalation of the  $MN_4$  active sites.

### 3.3. Protonation of active sites

The initial rapid performance loss of the non-PGM catalysts is

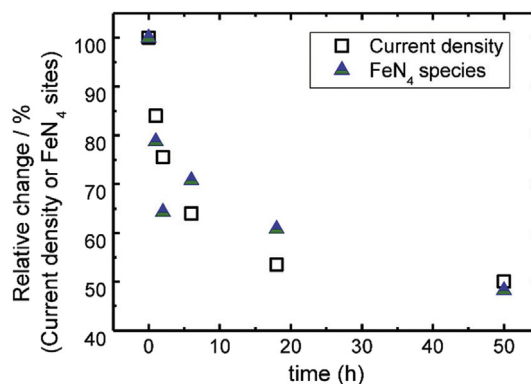


Fig. 7. Performance degradation of Fe/N/C catalysts due to the demetalation of the Fe species [46]. (A colour version of this figure can be viewed online.)

reported by several ORR catalysts research groups [30,41,46,48–55]. As discussed in the peroxide section, the first rapid decay was reported by Alt et al. [30]. Since then the stability study of the non-PGM catalysts is divided into understanding this initial drop occurring in a short time and the gradual decrease over a more extended period of time. Some researchers have attributed the sudden performance loss to the demetalation or protonation of the metal active site or to the protonation of N species coordinated with the metal center [30,49,51,53]. Other researches have claimed that the initial performance loss is not at all associated with the metal active site but with the flooding of the micropores resulting in the decreased transport of the ORR relevant species to the active site [53–55].

The instability of the non-PGM catalysts in the acidic conditions in contrast to the alkaline conditions has been reported in several studies [31,32,40,51,57]. In most of these studies, this instability was attributed to the leaching out of the 'metal active site' into the solution. However, Liu et al. reported instability of the nitrogen modified carbon composite (NMCC) catalyst in acidic medium [49]. It was hypothesized that the Fe or Co coordinated with nitrogen macrocycles ( $FeN_4$  or  $CoN_4$ ) were destroyed and converted to metallic species after the heat treatment at 800 °C in argon. With EXAFS and TEM techniques, it was proved that after the pyrolysis most of the  $CoN_x$  chelates were decomposed into Co metallic species and the resulting metallic species were covered in graphitic carbon. After the post-chemical treatment for metal removal, no surface Fe or Co species were observed in the XPS data. However, the acid leached catalysts had higher activity. It was claimed that instead of the metal- $N_4$  chelates, the nitrogen-functional groups (specifically pyridinic N and quaternary N) were responsible for the electrochemical activity and performance of the NMCC catalysts. Thus, disregarding the demetalation mechanism, it was believed that a different degradation mechanism was the cause for the instability that only occurs in the acidic conditions. In this study, two NMCC catalysts were synthesized, namely NMCC-800 and NMCC-1100 by pyrolysis in the argon atmosphere at 800 °C and 1100 °C respectively. The NMCC-800 exhibited high initial activity in both RDE and fuel cell tests, whereas the NMCC-1100 showed higher stability in the fuel cell test. The fuel cell stability test at a constant current density ( $200 \text{ mA cm}^{-2}$ ) revealed a performance loss of  $16.5 \text{ mV h}^{-1}$  in the first 2 h and  $0.99 \text{ mV h}^{-1}$  in following 150 h for the NMCC-800. However, the NMCC-1100 showed performance loss of only  $0.4 \text{ mV h}^{-1}$  in the first 10 h and  $0.07 \text{ mV h}^{-1}$  for the following 270 h operation. Since the active sites of the NMCC catalysts were believed to be the pyridinic and quaternary N, the difference in the stability of the two catalysts was explained through the relative content and nature of these active sites. The

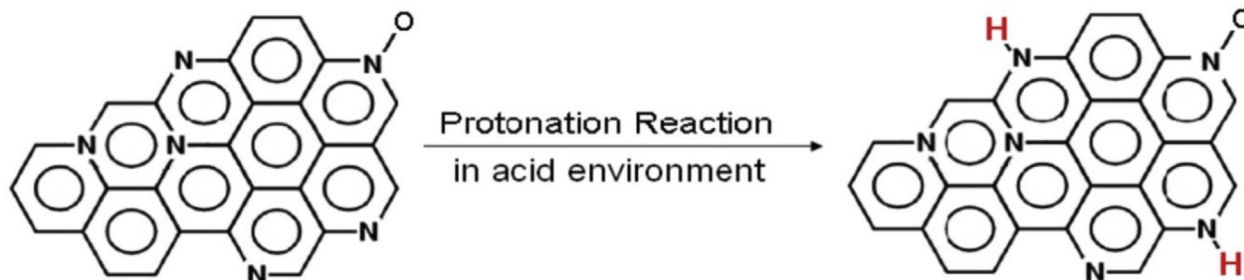


Fig. 8. Protonation mechanism of nitrogen-functional groups in 0.5 M  $\text{H}_2\text{SO}_4$  acidic medium [49]. (A colour version of this figure can be viewed online.)

N1s spectra of NMCC-800 had three peaks attributed to the pyridinic-N, quaternary-N, and pyridinic- $\text{N}^+-\text{O}^-$ , whereas for NMCC-1100 only two peaks quaternary-N and pyridinic were observed. It was argued that the two ORR active sites for NMCC-800 in contrast to only one ORR active site for NMCC-1100 were responsible for the high initial activity of the NMCC-800. However, for the stability, it was hypothesized that the lone pair on the pyridinic-N site (only in NMCC-800) could be protonated in the acidic environment, resulting in an inactive pyridinic-N-H site (no lone pair) leading to the rapid degradation of NMCC-800 catalyst. On the other hand, for NMCC-1100, the only active site was the quaternary-N, bonded with three carbon atoms it was believed to be resistant to the protonation mechanism due to the absence of extra electrons. The proposed protonation mechanism is shown in Fig. 8. A strong and valid argument was raised by Banham et al.<sup>2015</sup> for this mechanism which includes the comparison of RDE and MEA study [19]. It was argued that the higher availability and mobility of the protons in the RDE test could lead to rapid protonation; therefore the activities of both the NMCC catalysts should be similar. Along with this argument, no strong experimental evidence was provided which can prove this hypothesis.

Herranz et al. further investigated the protonation mechanism and made strong arguments with experimental support [51]. In this study, the Fe-based catalyst (Original catalyst) synthesized by pyrolysis in  $\text{NH}_3$  at  $950^\circ\text{C}$  was tested. To investigate the effect of peroxide degradation for the O catalyst, three potentiostatic hold stability tests were conducted, i.e., OCV under  $\text{H}_2/\text{O}_2$ , and 0.5 V for both  $\text{N}_2$  and  $\text{O}_2$  gases at the cathode. As expected, the  $\text{O}_2$  stability test of the O catalyst revealed 5 times higher performance degradation as compared to the  $\text{N}_2$  and OCV conditions. This decay was attributed to the peroxide attack on the catalyst. However, under the  $\text{N}_2$  condition, there was a significant performance loss which suggests that along with peroxide attack, the O catalyst was undergoing some other degradation which was independent of the ORR. To investigate this ORR independent mechanism, the O catalysts was acid washed (AW catalyst) in Ph1  $\text{H}_2\text{SO}_4$  for up to 100 h. The nitrogen binding/content and the specific surface area of the O catalyst were similar to the AW catalyst; however, the initial activity of the AW catalyst was only 1/20th of the O catalyst. The performance loss after the acid washing peaked in only 5 min of immersion with only a 30% loss of Fe in the solution. The AW catalyst was reheat treated (and named as RHT catalyst) at temperatures ranging from 200 to  $950^\circ\text{C}$  to observe any activity recovery. Interestingly, the RHT catalyst at  $300^\circ\text{C}$  recovered 50% of the performance. This observation suggested that there were two degradation mechanisms, one with recoverable activity decay (RAD) and second with non-recoverable activity decay. The XPS and TGA-MS characterization methods were used to understand the changes in the chemical bindings of AW and RHT catalysts. The XPS data revealed a new peak (bisulfate-type sulfur) in AW catalyst which disappeared in RHT catalyst. With the TGA-MS technique,

the removal of sulfur species was observed between  $200^\circ\text{C}$  and  $350^\circ\text{C}$ . Therefore, the formation and disappearance of this anion were co-related to the activity recovery. Moreover, the Mössbauer spectrum of the AW and RHT catalysts was similar, which suggests that  $\text{FeN}_4$  moieties were resistant to anion adsorption. Since the  $\text{FeN}_4$  moieties were not hosting the binding of the anion, therefore it was hypothesized the anionic adsorption at the basic N functionalities, which were formed by pyrolysis in  $\text{NH}_3$  on the surface of the catalyst. The exact reported mechanism is described as follows; initially, the pyridinic N sites those are located near the  $\text{FeN}_4$  moieties inside the micropores protonates and intend to transfer this proton to the  $\text{FeN}_4$  to complete the ORR. However, before transferring the proton, the anions present in the ionomer binds with protonated pyridinic N sites which neutralize the active site and thus decreasing the TOF of the catalyst. The neutralization mechanism is shown in Fig. 9. According to this mechanism, the active site of the Fe-based catalysts is the  $\text{FeN}_4\text{NH}^+$  site, however, several studies reported either  $\text{FeN}_4$  or the nitrogen functionalities as the active sites. This again adds to the ambiguity of the nature of the active site for the metal-based non-PGM catalysts.

In the follow-up study, Zhang et al. correlated the effect of neutralization mechanism on the rapid decay of the activity in the first 15 h [54]. In order to support the hypothesis that the neutralization mechanism was responsible for the initial degradation, it was clear that all the  $\text{FeN}_4\text{NH}^+$  active sites should be neutralized with the anions from the ionomer transferring inside the micropores within 15 h. Therefore, the ionomers long chained ionomers were substituted with shorter pendent chains such as Flemion and Aquivion. It was expected that these ionomers would transport more rapidly inside the micropore and neutralize the  $\text{FeN}_4\text{NH}^+$  sites faster than the longer pendent chained Nafion. But the decay rate was unchanged with these substitutions. Then a part of Nafion was replaced with tetrasulfonated hydrogen porphyrins

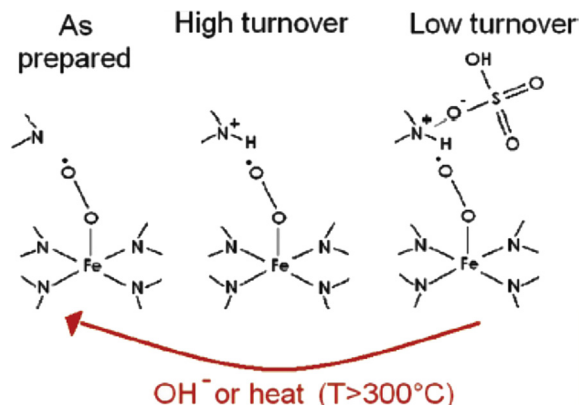


Fig. 9. Protonation followed by anion adsorption on the surface nitrogen groups formed by pyrolysis in  $\text{NH}_3$  [51]. (A colour version of this figure can be viewed online.)

consisting of bigger anionic molecules (larger than the micropore itself), to hinder the transport of anions inside the micropores and thus prevent the neutralization mechanism. However, the decay rate was still the same as with only Nafion. Therefore, it is still unsure that the protonation followed by anion adsorption (neutralization) hypothesis can be a viable degradation mechanism of the non-PGM catalysts.

### 3.4. Micropore flooding

Some of the best performing M-N-C catalysts are derived by integrating micro/meso porosity in the morphology [7,10–18]. Based on this technique, i.e. improved mass transport properties through these interconnected pores, Yang et al. synthesized a new catalyst by ball milling of ZIF-8 and chloroiron-tetramethoxyporphyrin (ClFeTMPP) labeled NC Por<sub>x</sub>-T Ar + NH<sub>3</sub>, where x is the Fe content, and T is the pyrolysis temperature [53]. The aim of this study was to investigate the effect of pyrolysis in Ar and NH<sub>3</sub> at high temperatures (850–1150 °C) on the durability of the catalyst. The catalyst with the highest activity was obtained with 0.8 wt% nominal Fe loading and 1050 °C (NC Por<sub>0.8</sub>–1050 Ar + NH<sub>3</sub>) in the H<sub>2</sub>/O<sub>2</sub> fuel cell. However, all the catalysts except NC Por<sub>0.8</sub>–1150 Ar + NH<sub>3</sub> showed similar instability during the chronoamperometry test at 0.6 V for 50 h. The Raman spectra and XPS analysis revealed that increasing the pyrolysis temperature, the graphitization of the carbon support increases along with a decrease in the heteroatom (O, N) content. It was proposed that on increasing the graphitization of the carbonaceous materials by increasing the pyrolysis temperature, the substantial decrease in the O and N functionalities drastically reduced the hydrophilicity of the carbon support and therefore reduced the possibility of the water flooding of the catalyst, which ultimately increased the durability of the catalyst synthesized at 1150 °C.

In the follow-up study, the Fe-based catalyst obtained from pyrolysis of a mixture of 1, 10 phenanthroline, iron acetate, and ZIF-8 showed two decay rates [54]. The initial performance loss was observed in the first 15 h and the second till the end of the chronoamperometry test at 0.6 V in the H<sub>2</sub>/O<sub>2</sub> fuel cell. The objective of this research was to provide evidence to the micropore flooding mechanism by disapproving the Fenton reaction degradation mechanism for the initial rapid performance loss. Assuming that the peroxide production in the acid electrolyte is proportional to the peroxide production in the PEMFC, the role of Fe ions in the degradation of the catalyst was investigated. Since the Fe-based catalysts are known to undergo Fenton reaction for Fe concentration >40 ppm, this study compared the durability of different catalysts with MOF only precursor, iron-salt precursor, and metal-free precursor. The iron concentration was examined by neutron activation analysis (NAA) technique. It was explained that even the catalysts synthesized with MOF only and metal-free precursors are bound to have some Fe impurities because it is common practice to use stainless steel vessels in the chemical industry. Therefore, significant effort was put to eliminate the Fe impurities and lower the Fe concentration from these samples. It was expected that the Fe-based or may be the MOF-based catalysts with Fe content 60,280 ppm and 1058 ppm respectively would undergo Fenton reaction and produce different concentrations of ORR intermediates. If these intermediates are responsible for the current decay in the first 15 h, all the mentioned catalysts will have different degradations because of the significant difference of the Fe content and ORR intermediate productions. As seen from Fig. 10, the normalized current decay curves for all the above samples are similar suggesting that the initial performance decay for these catalysts was independent of the oxidation of the catalysts by ORR intermediates.

This study claimed that the NC\_Ar + NH<sub>3</sub> (Fe-based) and

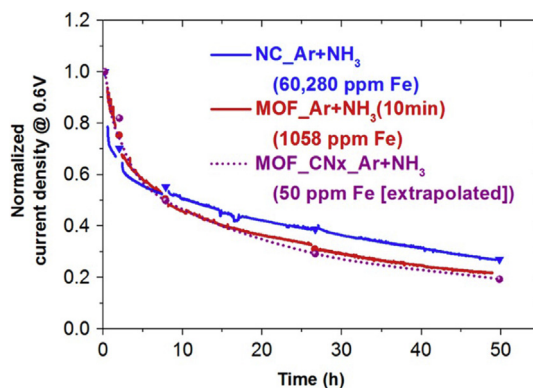
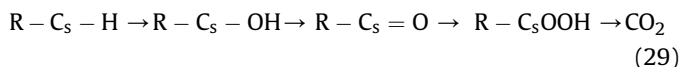


Fig. 10. Performance degradation of Fe-based, MOF-based and Fe-free samples [54]. (A colour version of this figure can be viewed online.)

MOF\_Ar + NH<sub>3</sub> (MOF-based) catalysts were initially hydrophobic in nature; however, the slow electro-oxidation of the carbon support resulted in the hydrophilic behavior of the catalysts. As the electro-oxidation of the carbon support is possible above 0.207 V Vs SHE (standard hydrogen electrode), the following mechanism for the oxidation of carbon was proposed:



where subscript 's' is the surface species. This study quantified the number of oxidized functionalities and compared with the number of surface carbon atoms per cm<sup>2</sup> found on the same catalyst. It was found that 58% and 38% of the surface carbon atoms gets oxidized to R-C<sub>s</sub>=O and R-C<sub>s</sub>OOH respectively, providing an indirect evidence for the electro-oxidation of the carbon support. Once oxidized these catalysts becomes hydrophilic in nature and remain filled with water throughout 15 h, resulting in a similar stability curves for all the catalysts.

It is essential to understand the difference between the micropore flooding mechanism and the catalyst layer flooding. The catalyst layer flooding mechanism chronicles in the non-PGM catalyst research [56–58]. Significant research has been focused on understanding and mitigating any performances losses through this mechanism. In this review, we are only targeting the degradation intrinsic to catalyst properties, not the PEMFC system.

Recently, Choi et al. designed specific experiments to investigate the possibility of the micropore flooding mechanism by synthesizing Fe-based catalysts with ample micropores [59]. For understanding the micropore flooding mechanism, two cases were assumed: (i) all the micropores are initially dry, but becomes wet during the operation, (ii) the micropores are initially partially wetted, but completely wet over time (Fig. 11). In this study, both of these cases were adequately defined and characterized.

Case 1 was assumed because Yang et al. and Zhang et al. claimed the initial beginning of life (BOL) hydrophobicity of the catalyst [53,54]. Since it was also assumed that the active sites were hosted in the micropores of the catalyst, Choi et al. claimed that this case was unlikely. It was explained that in this case there was no water in the micropores initially and also the ionomer cannot penetrate inside the micropores (dia < 2 nm) because of the larger diameter of the Nafion micelles (1–5 nm), there was no mode of proton transportation from the membrane to the active site, rendering the active sites in the micropores inactive to ORR and lower BOL activity. However, the BOL activity of these catalysts was exceptionally high. Additionally, with these ORR inactive sites, no additional water will be generated resulting in hydrophobic micropores

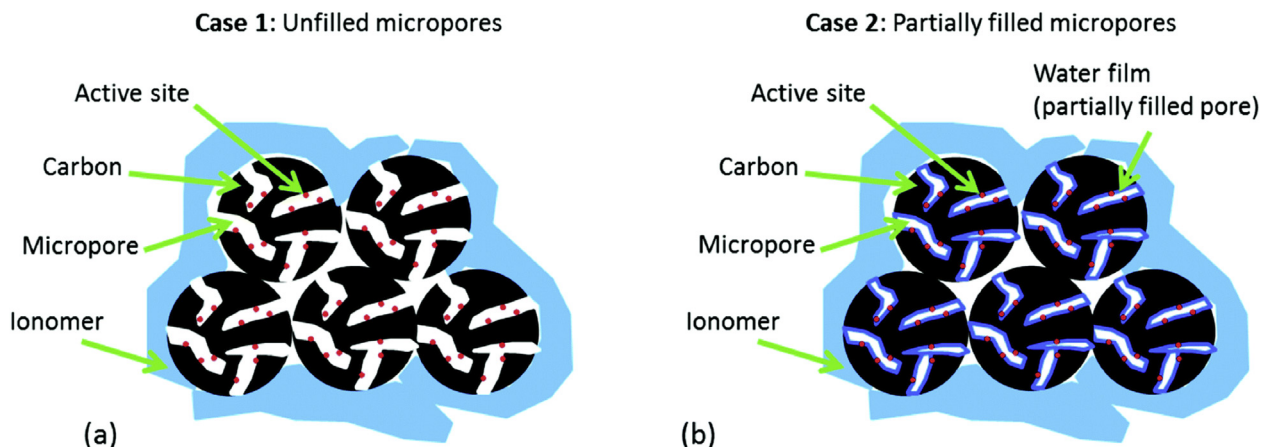


Fig. 11. The two cases assumed to investigate the viability of the micropore flooding mechanism [59]. (A colour version of this figure can be viewed online.)

throughout the operation, and the carbon support will be resistant to electrochemical oxidation without the presence of water. In case 2, it was assumed that there was already a thin water film inside the micropores. This water film aids in the transportation of the proton from the membrane to the active site for the ORR. This could lead to the generation of more water in the micropores, and during the fuel cell operation, this can result in the electrochemical oxidation of the carbon support making it more hydrophilic which can be the necessary evidence for the micropore flooding mechanism.

For characterizing these cases, the double layer capacitance measurements were evaluated. The double layer capacitance is related to the electrochemical surface area (ESA) with the following equation [30].

$$C = \frac{\epsilon \epsilon_0 A}{d} \quad (30)$$

where  $A$  is the electrochemical surface area,  $C$  is the capacitance,  $\epsilon$  is the dielectric constant and  $\epsilon_0$  is the permittivity. For case 1, the micropores are assumed to be completely dry; therefore any increase in the ESA due to the wetting will increase the double layer capacitance. For the case 2, only the double layer capacitance measurements cannot explain the micropore flooding mechanism, because the micropores were assumed to be partially/fully wet; therefore, there can be little to no change in the ESA and hence to the double layer current. To investigate the micropore flooding through this case, along with the double capacitance measurements, the polarization curves obtained under the  $O_2$  and air were compared.

To examine the initial wetting of the micropores, the effect of 60% and 100% RH on micropore flooding was evaluated by the cyclic voltammetry technique before and after polarization curves. There was no change in the double layer current before and after polarization curves. This shows that the micropores were partially or fully wet in the BOL and no more carbon surface was getting wet by the water generated during ORR. This observation rules out the possibility of case 1. Now if the micropore flooding mechanism was at the root of the initial performance decay, it could only be explained by assuming case 2 in which the catalyst was assumed to be partial wet at BOL. The stability tests were conducted by a potentiostatic hold at 0.4 V for 4 h, and two decay rates were observed. The CV curves were measured before and after the stability test at 60% and 100% RH. The results indicated an increase of 8% in the double layer capacitance current. This increase could be the result of full wetting of the micropores from partial wetting

condition at the BOL or the catalyst layer flooding. Considering the micropore flooding mechanism, this study compared the polarization curves under air and  $O_2$  to investigate the mass transport limitations. It was explained that if the performance loss resulted from the micropore flooding, mass transport limitations in the air could be observed much earlier than in  $O_2$ , but if the performance loss was due to the loss or deactivation of the active site, only kinetic losses could be observed. It was confirmed from the polarization curves that the catalyst primarily suffers from kinetic losses rather than mass transport losses even after the stability test (Fig. 12). Additionally, to disapprove the catalysts layer flooding mechanism, a dry-out experiment was performed after the stability test in which the cell was held at 80 °C for 5 h under  $N_2$ . There was no performance recovery after this test, providing convincing evidence that the catalyst layer flooding was not the degradation mechanism for this catalyst. The above observations state that the micropore flooding mechanism might not responsible for the initial performance decay and questions its feasibility [59,60].

#### 4. Carbon-based metal free catalysts review

The complexities of the Fenton reaction and demetalation degradation mechanisms made several researchers to completely eliminate metal particles from their non-PGM catalysts [31,61]. In this review, the metal-free non-PGM catalysts include the heteroatom-doped carbon-based catalysts such as nitrogen-doped graphene, boron-doped graphene, etc. For the metal-free non-PGM catalysts, the researchers have provided only limited information on stability. The reported stability studies were conducted in very mild conditions.

The first durability study for the metal-free ORR catalysts was reported by Qu et al. [62]. In this study, the catalyst nitrogen-doped graphene was synthesized by chemical vapor deposition of methane in the presence of  $NH_3$ . The durability of the catalyst was conducted by cycling the potential for 200,000 cycles in 0.1 M KOH solution saturated with air in the RDE setup. There was no decrease in the ORR current after cycling the potential. Although the number of cycles reported was exceptionally high, but the alkaline solution with the air-saturated environment was mild which has less significance in the actual PEMFC.

Yu et al. developed nitrogen-doped on single-walled carbon nanotubes [63]. The durability study was carried out in the RDE setup by cycling the potential for two days in 0.5 M  $H_2SO_4$  acidic medium. It was claimed the catalyst exhibited exceptional long-term stability when the catalyst showed no activity loss after the

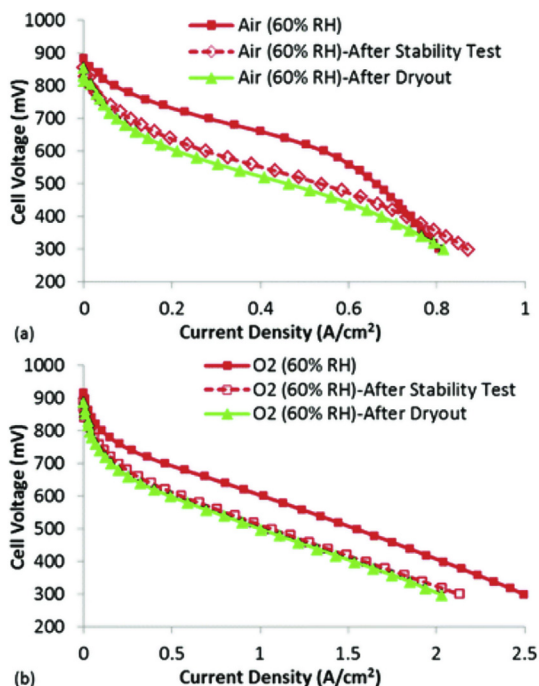


Fig. 12. Polarization curves in (a) air and (b)  $O_2$  environment at different RH [59]. (A colour version of this figure can be viewed online.)

stability test. The durability experimental conditions are slightly more severe than reported by Qu et al., but this protocol does not entirely define the durability of the catalyst in the  $H_2/O_2$  fuel cell. It is suggested to follow the guidelines laid out by the DOE-FCO for the most accurate representation of the stability and durability of the non-PGM and metal-free catalysts [20].

Li et al. published a research article on nitrogen-doped graphene with Quantum dots (N-GQD) [64]. In this research, the N-GQD catalyst was synthesized by the electrochemical process. The novel idea of creating more edge sites for easy doping of heteroatom has been reported in several studies. For the durability study, potential cycling experiment was conducted for 2 days in  $O_2$ -saturated 0.1 M KOH solution. The catalyst showed slight degradation; however, no degradation mechanism study was conducted or reported.

Zheng et al. reported a nanoporous graphitic- $C_3N_4$  on carbon catalyst for efficient ORR [65]. This study reported two durability studies, including the chronoamperometric response and potential cycling in  $O_2$ -saturated 0.1 M KOH solution. The chronoamperometry stability study reported 7.8% loss in the relative current after 45 h, and in potential cycling study, 10% cathodic current loss was observed after 10,000 cycles. The excellent stability of the catalyst was attributed to the homogeneous interactions of g- $C_3N_4$  with CMK-3 support. However, the cathodic current loss cannot be implied as insignificant, considering the catalyst was subjected to mild experimental conditions.

Wang et al. synthesized highly active boron and nitrogen-doped graphene (BCN) catalyst [66]. The high activity of this catalyst was attributed to the synergistic effect co-doped boron and nitrogen. The chronoamperometric stability study was conducted for BCN and Pt/C catalyst for 40,000 s in oxygen-saturated 0.1 M KOH solution. The BCN catalysts showed 10% degradation in the current in contrast to 55% of the Pt/C catalyst. Therefore, it was claimed that the BCN catalyst has highly stable active sites.

Choi et al. reported nitrogen-doped graphene/carbon nanotube (NGCA) catalyst for ORR in acid media [67]. The stability of the prepared catalysts was examined by chronoamperometric

measurement at 0.6 V for 10 h in a 0.1 M  $HClO_4$  solution with continuous  $O_2$  bubbling. After 10 h of operation, performance degradation of NGCA was –23.3%. The peroxide yield of the NGCA catalyst was measured to be 3%. Even though the NGCA catalyst produces a low percentage of peroxide, the stability of the catalysts was considerably low. However, no explanation for the degradation was presented, but the stability of the NGCA catalysts was compared with Pt/C catalysts, and it was claimed that the active sites of NGCA were more stable due to more graphitic nature of dual carbon supports.

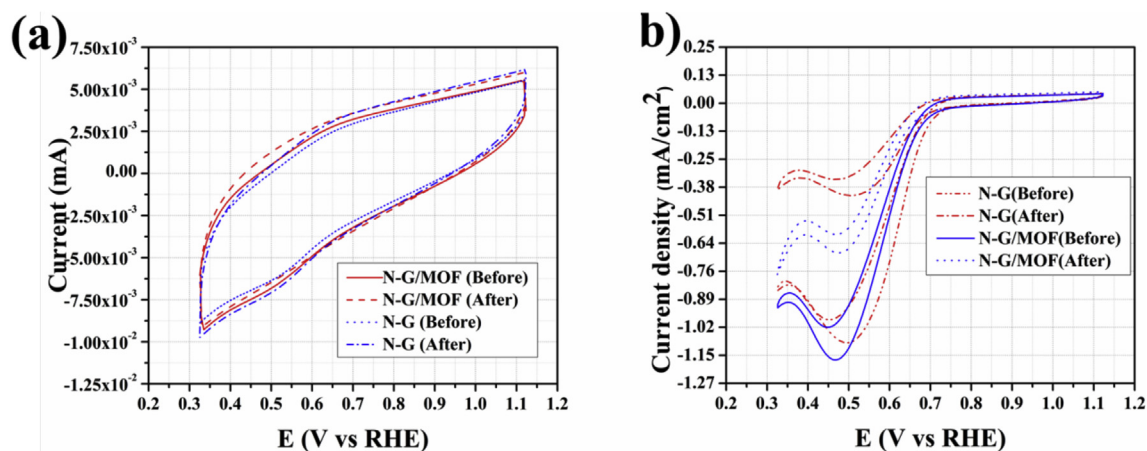
Most recently, Singh et al. has presented the potential cyclic durability study of the nitrogen-doped graphene (N-G) and metal-organic framework modified catalyst (N-G/MOF) in alkaline medium (Fig. 13) [68]. The N-G and N-G/MOF catalysts were synthesized with the mechano-chemical approach of ball milling [68–73]. The physical, chemical and electrochemical properties of these catalysts were iteratively optimized by controlling the grinding time and speed. The introduction of MOF particles in the N-G catalyst has enhanced the electrochemical performance due to increased microporosity and the chemical interactions of the N-G and MOF particles. Specifically, the durability experiments in  $O_2$  and  $N_2$ -saturated alkaline medium were conducted using RDE technique. The goal was to understand the durability of the catalysts with and without ORR. Both the catalysts exhibited remarkable durability in  $N_2$ -saturated environment, including when the potential was scanned at higher oxidation potentials (1.1–1.4 V Vs RHE). However, in the  $O_2$ -saturated electrolyte, both the catalysts showed significant degradation. This observation proves that the degradation of the catalysts was an ORR related phenomenon. Moreover, a gradual decay of current density was observed as opposed to the initial rapid decay of the metal-based non-PGM catalysts. It was anticipated that the degradation of these catalysts was due to the oxidative attack of the ORR intermediates.

## 5. Discussion

In order to replace the PGM catalysts from the PEMFCs, the non-PGM catalysts should exhibit both high activity and stability. Most of the non-PGM catalysts now have sufficient activity to actively reduce oxygen, but lack in respect to the stability. The stability limitation has hindered the commercialization of the non-PGM catalysts for both the stationary and transportation applications in PEMFCs. The stability research reported for the metal-based non-PGM catalysts has progressed significantly especially in recent years, on the other hand, metal-free non-PGM catalysts lacks much effort to understand and mitigate the degradation mechanisms.

### 5.1. Carbon-based non-PGM metal catalysts

From the review above, it is clear that the most commonly observed degradation mechanisms are the oxidative attack of the ORR intermediates and the demetalation of the active sites. Additionally, questions have been raised for the protonation (neutralization) and micropore flooding mechanisms. However, it should be acknowledged that these two mechanisms should not be disregarded entirely considering the experimental evidence and interpretation. The schematics for the degradation mechanisms are shown in Fig. 14. The non-PGM catalysts  $2e^-$  selectivity towards ORR results in the production of  $H_2O_2$ . This  $H_2O_2$  can attack the carbon support directly and/or indirectly through the decomposition of  $H_2O_2$  into more oxidative ROS via Fenton reaction. Both of these mechanisms can result in the oxidation of the carbon support. Some studies have reported the involatile carbon oxidation (producing  $R-C_5-O$ ,  $R-C_5=O$ , and  $R-C_5OOH$ ) while others have reported complete oxidation (producing CO and  $CO_2$ )



**Fig. 13.** Durability study of Nitrogen-doped Graphene and Nitrogen-doped graphene modified by MOF catalysts under (a)  $N_2$  and, (b)  $O_2$  saturated 0.1 M KOH before and after 2000 cycles [64]. (A colour version of this figure can be viewed online.)

[36,46,53,54]. The carbon oxidation can be responsible for increasing the hydrophilicity and blocking of the micropores, and thus lowering accessible active sites to the ORR [53–55]. Along with this, the carbon oxidation can modify the active site by weakening the  $O_2$ -binding energy [36]. The oxidized carbon can also lead to the demetalation of the active sites, which can lower the TOF by reducing the active site density. Furthermore, it has been demonstrated that the demetalation of the inactive metallic species is dependent on the applied potential, whereas the demetalation of the  $FeN_xC_y$  moieties is independent of the applied potential [46]. In any case, it is possible that the leached Fe species can participate in the Fenton reaction and further oxidize the carbon-support. Fig. 14(b) highlights the neutralization/protonation mechanism.

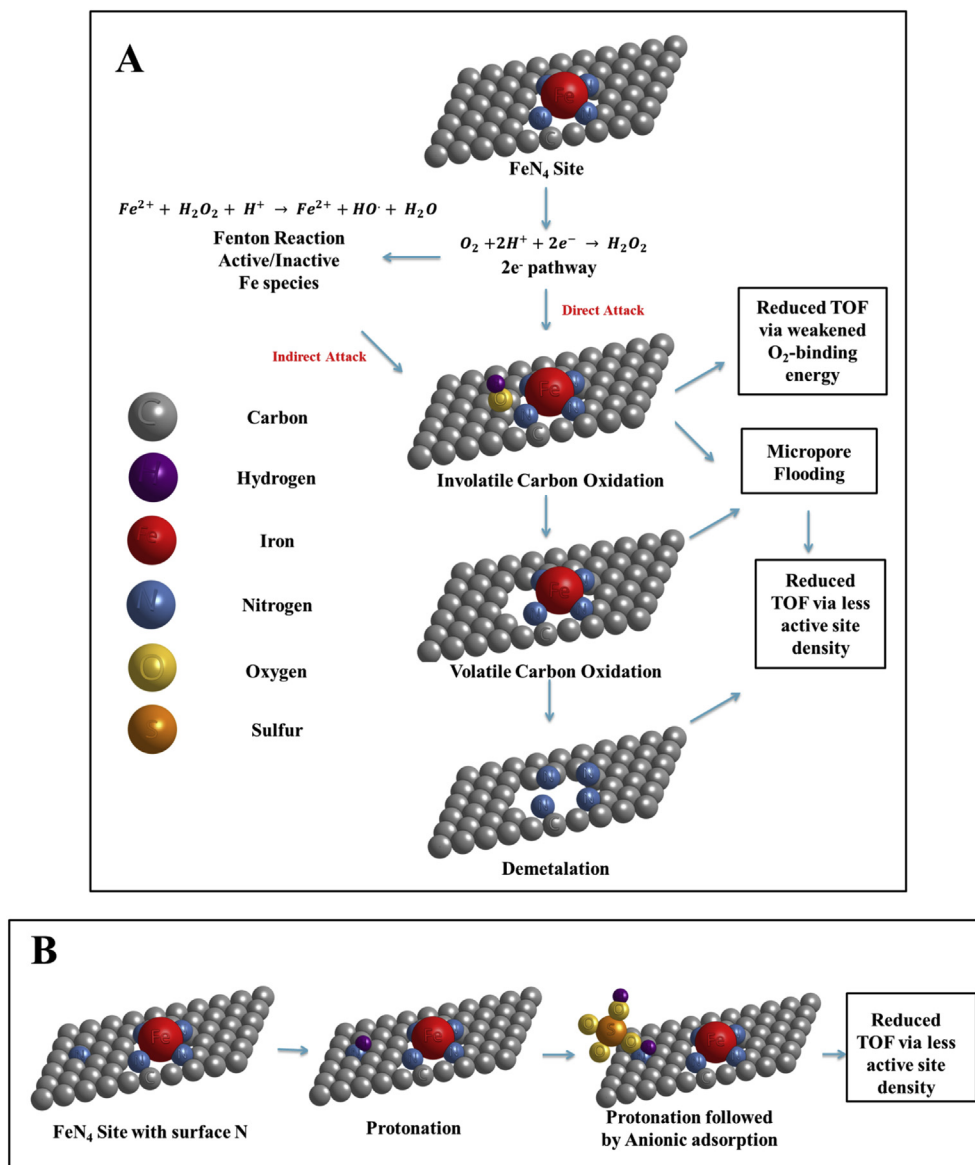
Since the early 2000s, significant effort has been focused on investigating the role of peroxide or ROS in the degradation of the non-PGM catalyst [29–36]. The exact mechanism through which these species degrade the catalyst is relatively clear, as most of the findings point to the oxidation of the carbon support. In general, the non-PGM catalysts generate a higher yield of peroxide than the PGM catalysts, which makes them more vulnerable to the chemical oxidation. The peroxide production in the non-PGM catalysts can be minimized by improving the  $4e^-$  selectivity of these catalysts. This can be achieved by the continuous improvement in the activity of the catalysts. Moreover, Fe-based non-PGM catalysts are more prone to the chemical oxidation due to the possibility of the Fenton reactions generating more ROS. It is reported that the Fe species in any form, whether active or inactive can undergo Fenton reaction. Along with chemical oxidation, the electrochemical oxidation of the carbon support is also possible above 0.207 V Vs SHE in the presence of water. During the start-up and shut-down of the PEMFCs, the potentials can reach as high as 1.5 V making the carbon-supports more susceptible to corrosion [74]. The three possible implications of the carbon oxidation near the active site via chemical and/or electrochemical method are (i) leaching of the active sites resulting in the demetalation degradation; (ii) weakening of the  $O_2$ -binding energy; (iii) increased hydrophilicity of the micropores resulting in the active site blocking. All of these mechanisms lead to a lower TOF of the non-PGM catalysts.

The activity and stability of the non-PGM metal catalysts are immensely dependent on the type of active site. As discussed above, non-PGM metal-active sites can exist as free metal atoms, particles, carbides and the most commonly observed  $MN_xC_y$  moieties. It is crucial to understand the type of active site in a catalyst before executing any stability study because several studies have

revealed the leaching of inactive by-standers metallic species which does not influence the stability of the catalyst. The leaching of metal active/inactive species is detrimental to both the catalysts performance (by lowering the active site density) and the fuel cell performance (by catalyzing the destruction of the ionomer). Therefore, it is recommended to acid wash the catalysts as a preparatory precaution for removing any unwanted metallic species before using them in PEMFCs. Except for  $MN_xC_y$  moieties, all the other types of active sites are expected to be embedded inside the protective graphite layers/shells; otherwise, they are extremely prone to the demetalation especially in the acidic environment of the PEMFC. The  $MN_xC_y$  moieties are reported to be more resistant to demetalation as compared to the other forms of the active site. Moreover, it has been demonstrated for extremely microporous catalysts that the active sites are situated inside the micropores of the catalysts. The initial high activity of the metal-based non-PGM catalysts is attributed to the increased mass transport of oxygen to the active sites in the micropores. However, the specific demetalation study also accounts these micropores for the lower stability of the non-PGM catalysts [46].

## 5.2. Carbon-based metal-free catalysts

It can be inferred from the review, that most of the stability study of the metal-free carbon-based non-PGM catalysts attributed their high stability to the more stable carbon supports. Carbon oxidation is expected to be more prominent in lower activity ( $2e^-$  ORR pathway) catalysts which yield higher percentages of the  $H_2O_2$ . Additionally, the protonation mechanism was first explained on the nitrogen-functional groups, which are the active sites of the N-G catalysts [49]. This suggests that the protonation mechanism can also be culpable for the degradation of these catalysts. Furthermore, it has been demonstrated by Zhang et al. that the Fe impurity is very common since most of the chemicals are synthesized in stainless steel jars in the chemical industry [54]. Therefore, the possibility of Fe impurities leading to the decomposition of  $H_2O_2$  into ROS in metal-free catalysts cannot be ignored. Although a significant improvement is achieved in terms of the activity and performance of the metal-free carbon-based catalysts, stability studies are often excluded from the research articles. Only a few reported studies have demonstrated some stability experiments, but these experiments were either carried out in very mild conditions or without the explanation of the degradation of the catalysts.



**Fig. 14.** Schematic of (a) inter-relation of different degradation mechanisms (carbon-oxidation, demetalation, and Fenton reaction), (b) protonation mechanism resulting in lower turn-over frequency. (A colour version of this figure can be viewed online.)

## 6. Conclusion

The PEMFCs are the next generation of green and sustainable energy devices, which have the potential to solve the alarming crisis of CO<sub>2</sub> emissions generated by fossil fuels. The widespread commercialization of the PEMFCs is hindered by the prohibitive cost of the PGM-based ORR electrocatalysts. Although notable research is focused on lowering the PGM content from these devices, the ultimate goal of the PEMFC technology is to develop highly active and stable non-PGM catalysts. Over the decades, both the carbon-based non-PGM and metal-free catalysts have achieved remarkable breakthroughs in the catalytic activity by developing innovative synthesis methods and materials. However, the instability of these catalysts in the operating conditions has hampered their applications in the PEMFCs. In comparison to the activity research, stability research has often been excluded from the research articles. Several degradation mechanisms have been reported to investigate the cause of the instability of these catalysts.

These mechanisms include oxidative attack of ORR intermediates, demetalation, protonation/neutralization, and micropore flooding. Out of these mechanisms, the carbon oxidation by the ORR intermediates and demetalation are the most commonly observed degradation mechanisms. Moreover, the protonation/neutralization and micropore flooding mechanism are criticized.

The carbon oxidation mechanism can impact the stability of the ORR catalysts at both atomic and macro scales. At the atomic scale, it can lead to the removal of the active site from the carbon matrix (Demetalation), and at the macro scale, it can result in the loss of the structural conductivity through the loss of carbon atoms. In particular, the carbon oxidation mechanism has been correlated with the selective generation of H<sub>2</sub>O<sub>2</sub> by the non-PGM catalysts. It has been demonstrated that as little as 5% H<sub>2</sub>O<sub>2</sub> production can severely impact the stability of the non-PGM catalysts. Moreover, the Fe-based non-PGM catalysts can decompose the H<sub>2</sub>O<sub>2</sub> into ROS, which has even higher oxidative strength. Apart from this, the carbon oxidation is also possible at higher potentials. The

demetalation mechanism is one of the earliest reported degradation mechanism. Before investigating this mechanism, the nature of the metal active site should be well understood. The  $MN_xC_y$  moieties as the metal active sites are reported to be the most stable, with only a few studies reporting their demetalation. It is believed that these moieties reside in the micropores of the catalyst's structure, and are responsible for the high beginning of life (BOL) activity. A recent study has revealed the demetalation of these moieties is possible by the water flux through the open-ended slit-shaped micropores. Additionally, the leached Fe species can further oxidize the carbon support via Fenton reaction. Therefore, the carbon oxidation and demetalation mechanisms can degrade the catalyst independently or interdependently.

There are very few stability studies regarding metal-free non-PGM catalysts. Among the reported studies, carbon oxidation and protonation/neutralization are the reported degradation mechanisms. The tremendous advances in the catalytic activity of the non-PGM catalysts have made them excellent contenders for replacing the PGM catalysts. The instability issue of the non-PGM catalysts can be solved by understanding and development of mitigation strategies of the degradation mechanisms.

## Conflicts of interest

The authors declare no conflict of interest.

## Acknowledgements

The authors would like to thank the administrative support of the New Jersey Institute of Technology (NJIT). Also, we acknowledge the technological support from all the members of the Advanced Energy System and Microdevices (AESM) Laboratory in the department of Industrial and Mechanical Engineering at NJIT.

## References

- [1] V. Dorer, A. Weber, Energy and CO<sub>2</sub> emissions performance assessment of residential micro-cogeneration systems with dynamic whole-building simulation programs, *Energy Convers. Manag.* 50 (3) (2009) 648–657.
- [2] S. Sharma, B.G. Pollet, Support materials for PEMFC and DMFC electrocatalysts—a review, *J. Power Sources* 208 (2012) 96–119.
- [3] J. Zhang (Ed.), *PEM Fuel Cell Electrocatalysts and Catalyst Layers: Fundamentals and Applications*, Springer Science & Business Media, 2008.
- [4] R. Bashyam, P. Zelenay, A class of non-precious metal composite catalysts for fuel cells, in: *Materials for Sustainable Energy: A Collection of Peer-Reviewed Research and Review Articles from Nature, Publishing Group*, 2011, pp. 247–250.
- [5] B. Wang, Recent development of non-platinum catalysts for oxygen reduction reaction, *J. Power Sources* 152 (2005) 1–15.
- [6] Z. Chen, J.P. Dodelet, J. Zhang (Eds.), *Non-noble Metal Fuel Cell Catalysts*, John Wiley & Sons, 2014.
- [7] E. Proietti, F. Jaouen, M. Lefèvre, N. Larouche, J. Tian, J. Herranz, J.P. Dodelet, Iron-based cathode catalyst with enhanced power density in polymer electrolyte membrane fuel cells, *Nat. Commun.* 2 (2011) 416.
- [8] F. Jaouen, E. Proietti, M. Lefèvre, R. Chenitz, J.P. Dodelet, G. Wu, H.T. Chung, C.M. Johnston, P. Zelenay, Recent advances in non-precious metal catalysts for oxygen-reduction reaction in polymer electrolyte fuel cells, *Energy Environ. Sci.* 4 (1) (2011) 114–130.
- [9] H.T. Chung, C.M. Johnston, K. Artyushkova, M. Ferrandon, D.J. Myers, P. Zelenay, Cyanamide-derived non-precious metal catalyst for oxygen reduction, *Electrochem. Commun.* 12 (12) (2010) 1792–1795.
- [10] M. Lefèvre, E. Proietti, F. Jaouen, J.P. Dodelet, Iron-based catalysts with improved oxygen reduction activity in polymer electrolyte fuel cells, *Science* 324 (5923) (2009) 71–74.
- [11] F.T. Wagner, B. Lakshmanan, M.F. Mathias, *Electrochemistry and the future of the automobile*, *J. Phys. Chem. Lett.* 1 (14) (2010) 2204–2219.
- [12] X. Liu, L. Dai, Carbon-based metal-free catalysts, *Nature Rev. Mater.* 1 (1) (2016) 16064.
- [13] S. Yang, X. Feng, X. Wang, K. Müllen, Graphene-based carbon nitride nanosheets as efficient metal-free electrocatalysts for oxygen reduction reactions, *Angew. Chem.* 123 (23) (2011) 5451–5455.
- [14] S. Chen, J. Bi, Y. Zhao, L. Yang, C. Zhang, Y. Ma, Q. Wu, X. Wang, Z. Hu, Nitrogen-doped carbon nanocages as efficient metal-free electrocatalysts for oxygen reduction reaction, *Adv. Mater.* 24 (41) (2012) 5593–5597.
- [15] S. Chen, J. Bi, Y. Zhao, L. Yang, C. Zhang, Y. Ma, Q. Wu, X. Wang, Z. Hu, Nitrogen-doped carbon nanocages as efficient metal-free electrocatalysts for oxygen reduction reaction, *Adv. Mater.* 24 (41) (2012) 5593–5597.
- [16] X. Li, Y. Fang, X. Lin, M. Tian, X. An, Y. Fu, R. Li, J. Jin, J. Ma, MOF derived Co<sub>3</sub>O<sub>4</sub> nanoparticles embedded in N-doped mesoporous carbon layer/MWCNT hybrids: extraordinary bi-functional electrocatalysts for OER and ORR, *J. Mater. Chem.* 3 (33) (2015) 17392–17402.
- [17] I.A. Khan, Y. Qian, A. Badshah, M.A. Nadeem, D. Zhao, Highly porous carbon derived from MOF-5 as a support of ORR electrocatalysts for fuel cells, *ACS Appl. Mater. Interfaces* 8 (27) (2016) 17268–17275.
- [18] D. Yu, Q. Zhang, L. Dai, Highly efficient metal-free growth of nitrogen-doped single-walled carbon nanotubes on plasma-etched substrates for oxygen reduction, *J. Am. Chem. Soc.* 132 (43) (2010) 15127–15129.
- [19] D. Banham, S. Ye, K. Pei, J.I. Ozaki, T. Kishimoto, Y. Imashiro, A review of the stability and durability of non-precious metal catalysts for the oxygen reduction reaction in proton exchange membrane fuel cells, *J. Power Sources* 285 (2015) 334–348.
- [20] [https://www.energy.gov/sites/prod/files/2017/05/f34/fcto\\_myrrdd\\_fuel\\_cells.pdf](https://www.energy.gov/sites/prod/files/2017/05/f34/fcto_myrrdd_fuel_cells.pdf).
- [21] U. Martinez, S.K. Babu, E.F. Holby, P. Zelenay, Durability challenges and perspective in the development of PGM-free electrocatalysts for the oxygen reduction reaction, *Current Opinion in Electrochemistry* 9 (June 2018) 224–232.
- [22] U. Martinez, S. Komini Babu, E.F. Holby, H.T. Chung, X. Yin, P. Zelenay, Progress in the Development of Fe-Based PGM-Free Electrocatalysts for the Oxygen Reduction Reaction, *Adv. Mater.* (2019) 1806545.
- [23] L. Zhang, Z. Xia, Mechanisms of oxygen reduction reaction on nitrogen-doped graphene for fuel cells, *J. Phys. Chem. C* 115 (22) (2011) 11170–11176.
- [24] S. Kattel, G. Wang, Reaction pathway for oxygen reduction on FeN<sub>4</sub> embedded graphene, *J. Phys. Chem. Lett.* 5 (3) (2014) 452–456.
- [25] Z. Duan, G. Wang, A first principles study of oxygen reduction reaction on a Pt (111) surface modified by a subsurface transition metal M (M = Ni, Co, or Fe), *Phys. Chem. Chem. Phys.* 13 (45) (2011) 20178–20187.
- [26] H.T. Chung, D.A. Cullen, D. Higgins, B.T. Sneed, E.F. Holby, K.L. More, P. Zelenay, Direct atomic-level insight into the active sites of a high-performance PGM-free ORR catalyst, *Science* 357 (6350) (2017) 479–484.
- [27] A. Zitolo, V. Goellner, V. Armel, M.T. Sougrati, T. Mineva, L. Stievano, E. Fonda, F. Jaouen, Identification of catalytic sites for oxygen reduction in iron- and nitrogen-doped graphene materials, *Nat. Mater.* 14 (9) (2015) 937.
- [28] U.I. Kramm, J. Herranz, N. Larouche, T.M. Arruda, M. Lefèvre, F. Jaouen, P. Bogdanoff, S. Fiechter, I. Abs-Wurmbach, S. Mukerjee, J.P. Dodelet, Structure of the catalytic sites in Fe/N/C-catalysts for O<sub>2</sub>-reduction in PEM fuel cells, *Phys. Chem. Chem. Phys.* 14 (33) (2012) 11673–11688.
- [29] R. Jasinski, A new fuel cell cathode catalyst, *Nature* 201 (4925) (1964) 1212.
- [30] H. Alt, H. Binder, G. Sandstede, Mechanism of the electrocatalytic reduction of oxygen on metal chelates, *J. Catal.* 28 (1) (1973) 8–19.
- [31] H. Schulenburg, S. Stankov, V. Schünemann, J. Radnik, I. Dorbandt, S. Fiechter, P. Bogdanoff, H. Tributsch, Catalysts for the oxygen reduction from heat-treated iron (III) tetramethoxyphenylporphyrin chloride: structure and stability of active sites, *J. Phys. Chem. B* 107 (34) (2003) 9034–9041.
- [32] M. Lefèvre, J.P. Dodelet, Fe-based catalysts for the reduction of oxygen in polymer electrolyte membrane fuel cell conditions: determination of the amount of peroxide released during electroreduction and its influence on the stability of the catalysts, *Electrochim. Acta* 48 (19) (2003) 2749–2760.
- [33] J.P. Dodelet, Heat-treated non-precious metal-N<sub>4</sub> macrocycles and beyond, in: *N<sub>4</sub>-macrocyclic Metal Complexes: Oxygen Reduction in PEM Fuel Cell Conditions*, Springer Science+Business Media, Inc, 2006.
- [34] L. Gubler, S.M. Dockheer, W.H. Koppenol, Radical (HO•, H• and HOO•) formation and ionomer degradation in polymer electrolyte fuel cells, *J. Electrochem. Soc.* 158 (7) (2011) B755–B769.
- [35] V. Goellner, V. Armel, A. Zitolo, E. Fonda, F. Jaouen, Degradation by hydrogen peroxide of metal-nitrogen-carbon catalysts for oxygen reduction, *J. Electrochem. Soc.* 162 (6) (2015) H403–H414.
- [36] C.H. Choi, H.K. Lim, M.W. Chung, G. Chon, N.R. Sahraie, A. Altin, M.T. Sougrati, L. Stievano, H.S. Oh, E.S. Park, F. Luo, The Achilles' heel of iron-based catalysts during oxygen reduction in an acidic medium, *Energy Environ. Sci.* 11 (11) (2018) 3176–3182.
- [37] C.H. Choi, C. Baldizzone, J.P. Grote, A.K. Schuppert, F. Jaouen, K.J. Mayrhofer, Stability of Fe-N-C catalysts in acidic medium studied by operando spectroscopy, *Angew. Chem. Int. Ed.* 54 (43) (2015) 12753–12757.
- [38] J.L. Kneebone, S.L. Daifuku, J.A. Kehl, G. Wu, H.T. Chung, M.Y. Hu, E.E. Alp, K.L. More, P. Zelenay, E.F. Holby, M.L. Neidig, A combined probe-molecule, Mössbauer, nuclear resonance vibrational spectroscopy, and density functional theory approach for evaluation of potential iron active sites in an oxygen reduction reaction catalyst, *J. Phys. Chem. C* 121 (30) (2017) 16283–16290.
- [39] M. Ferrandon, X. Wang, A.J. Kropf, D.J. Myers, G. Wu, C.M. Johnston, P. Zelenay, Stability of iron species in heat-treated polyaniline-iron-carbon polymer electrolyte fuel cell cathode catalysts, *Electrochim. Acta* 110 (2013) 282–291.
- [40] S. Gupta, D. Tryk, I. Bae, W. Aldred, E. Yeager, Heat-treated polyacrylonitrile-based catalysts for oxygen electroreduction, *J. Appl. Electrochem.* 19 (1) (1989) 19–27.
- [41] G. Lalonde, R. Cote, G. Tamizhmani, D. Guay, J.P. Dodelet, L. Dignard-Bailey, L.T. Weng, P. Bertrand, Physical, chemical and electrochemical characterization of heat-treated tetracarboxylic cobalt phthalocyanine adsorbed on

- carbon black as electrocatalyst for oxygen reduction in polymer electrolyte fuel cells, *Electrochim. Acta* 40 (16) (1995) 2635–2646.
- [42] G. Faubert, G. Lalande, R. Cote, D. Guay, J.P. Dodelet, L.T. Weng, P. Bertrand, G. Denes, Heat-treated iron and cobalt tetraphenylporphyrins adsorbed on carbon black: physical characterization and catalytic properties of these materials for the reduction of oxygen in polymer electrolyte fuel cells, *Electrochim. Acta* 41 (10) (1996) 1689–1701.
- [43] G. Wu, K.L. More, C.M. Johnston, P. Zelenay, High-performance electrocatalysts for oxygen reduction derived from polyaniline, iron, and cobalt, *Science* 332 (6028) (2011) 443–447.
- [44] C.H. Choi, C. Baldizzone, G. Polymeros, E. Pizzutillo, O. Kasian, A.K. Schuppert, N. Ranjbar Sahraie, M.T. Sougrati, K.J. Mayrhofer, F. Jaouen, Minimizing operando demetallation of Fe-NC electrocatalysts in acidic medium, *ACS Catal.* 6 (5) (2016) 3136–3146.
- [45] K. Kumar, P. Gairola, M. Lions, N. Ranjbar-Sahraie, M. Mermoux, L. Dubau, A. Zitolo, F. Jaouen, F. Maillard, Physical and chemical considerations for improving catalytic activity and stability of non-precious-metal oxygen reduction reaction catalysts, *ACS Catal.* 8 (12) (2018) 11264–11276.
- [46] R. Chenitz, U.I. Kramm, M. Lefèvre, V. Glibin, G. Zhang, S. Sun, J.P. Dodelet, A specific demetallation of Fe–N 4 catalytic sites in the micropores of NC<sub>Ar</sub>+NH<sub>3</sub> is at the origin of the initial activity loss of the highly active Fe/N/C catalyst used for the reduction of oxygen in PEM fuel cells, *Energy Environ. Sci.* 11 (2) (2018) 365–382.
- [47] K. Mamtani, U.S. Ozkan, Heteroatom-doped carbon nanostructures as oxygen reduction reaction catalysts in acidic media: an overview, *Catal. Lett.* 145 (1) (2015) 436–450.
- [48] J. Maruyama, I. Abe, Formation of platinum-free fuel cell cathode catalyst with highly developed nanospace by carbonizing catalase, *Chem. Mater.* 17 (18) (2005) 4660–4667.
- [49] G. Liu, X. Li, B. Popov, Stability study of nitrogen-modified carbon composite catalysts for oxygen reduction reaction in polymer electrolyte membrane fuel cells, *ECS Transactions* 25 (1) (2009) 1251–1259.
- [50] A. Garsuch, K. MacIntyre, X. Michaud, D.A. Stevens, J.R. Dahn, Fuel cell studies on a non-noble metal catalyst prepared by a template-assisted synthesis route, *J. Electrochem. Soc.* 155 (9) (2008) B953–B957.
- [51] J. Herranz, F. Jaouen, M. Lefevre, U.I. Kramm, E. Proietti, J.P. Dodelet, P. Bogdanoff, S. Fiechter, I. Abs-Wurmbach, P. Bertrand, T.M. Arruda, Unveiling N-protonation and anion-binding effects on Fe/N/C catalysts for O<sub>2</sub> reduction in proton-exchange-membrane fuel cells, *J. Phys. Chem. C* 115 (32) (2011) 16087–16097.
- [52] M. Busch, N.B. Halck, U.I. Kramm, S. Siahrostami, P. Krttil, J. Rossmeisl, Beyond the top of the volcano?—A unified approach to electrocatalytic oxygen reduction and oxygen evolution, *Nanomater. Energy* 29 (2016) 126–135.
- [53] L. Yang, N. Larouche, R. Chenitz, G. Zhang, M. Lefèvre, J.P. Dodelet, Activity, performance, and durability for the reduction of oxygen in PEM fuel cells, of Fe/N/C electrocatalysts obtained from the pyrolysis of metal-organic-framework and iron porphyrin precursors, *Electrochim. Acta* 159 (2015) 184–197.
- [54] G. Zhang, R. Chenitz, M. Lefèvre, S. Sun, J.P. Dodelet, Is iron involved in the lack of stability of Fe/N/C electrocatalysts used to reduce oxygen at the cathode of PEM fuel cells? *Nanomater. Energy* 29 (2016) 111–125.
- [55] L. Osmieri, R. Escudero-Cid, M. Armandi, A.H.M. Videla, J.L.G. Fierro, P. Ocón, S. Specchia, Fe-N/C catalysts for oxygen reduction reaction supported on different carbonaceous materials. Performance in acidic and alkaline direct alcohol fuel cells, *Appl. Catal. B Environ.* 205 (2017) 637–653.
- [56] I. Mayrhofer, F. Marone, M. Stampanoni, T.J. Schmidt, F.N. Büchi, Fast X-ray tomographic microscopy: investigating mechanisms of performance drop during freeze starts of polymer electrolyte fuel cells, *ChemElectroChem* 2 (10) (2015) 1551–1559.
- [57] J. Eller, J. Roth, F. Marone, M. Stampanoni, F.N. Büchi, Operando properties of gas diffusion layers: saturation and liquid permeability, *J. Electrochem. Soc.* 164 (2) (2017) F115–F126.
- [58] S.J. Normile, D.C. Sabarirajan, O. Calzada, V. De Andrade, X. Xiao, P. Mandal, D.Y. Parkinson, A. Serov, P. Atanassov, I.V. Zenyuk, Direct observations of liquid water formation at nano-and micro-scale in platinum group metal-free electrodes by operando X-ray computed tomography, *Materials today energy* 9 (2018) 187–197.
- [59] J.Y. Choi, L. Yang, T. Kishimoto, X. Fu, S. Ye, Z. Chen, D. Banham, Is the rapid initial performance loss of Fe/N/C non precious metal catalysts due to micropore flooding? *Energy Environ. Sci.* 10 (1) (2017) 296–305.
- [60] Y. Shao, J.P. Dodelet, G. Wu, P. Zelenay, PGM-Free Cathode Catalysts for PEM Fuel Cells: A Mini-Review on Stability Challenges, *Adv. Mater.* (2019) 1807615.
- [61] A.M.T.P. Van Der Putten, A. Elzing, W. Visscher, E. Barendrecht, Oxygen reduction on pyrolysed carbon-supported transition metal chelates, *J. Electroanal. Chem. Interfacial Electrochem.* 205 (1–2) (1986) 233–244.
- [62] L. Qu, Y. Liu, J.B. Baek, L. Dai, Nitrogen-doped graphene as efficient metal-free electrocatalyst for oxygen reduction in fuel cells, *ACS Nano* 4 (3) (2010) 1321–1326.
- [63] D. Yu, Q. Zhang, L. Dai, Highly efficient metal-free growth of nitrogen-doped single-walled carbon nanotubes on plasma-etched substrates for oxygen reduction, *J. Am. Chem. Soc.* 132 (43) (2010) 15127–15129.
- [64] Y. Li, Y. Zhao, H. Cheng, Y. Hu, G. Shi, L. Dai, L. Qu, Nitrogen-doped graphene quantum dots with oxygen-rich functional groups, *J. Am. Chem. Soc.* 134 (1) (2011) 15–18.
- [65] Y. Zheng, Y. Jiao, J. Chen, J. Liu, J. Liang, A. Du, W. Zhang, Z. Zhu, S.C. Smith, M. Jaroniec, G.Q. Lu, Nanoporous graphitic-C<sub>3</sub>N<sub>4</sub>@ carbon metal-free electrocatalysts for highly efficient oxygen reduction, *J. Am. Chem. Soc.* 133 (50) (2011) 20116–20119.
- [66] S. Wang, L. Zhang, Z. Xia, A. Roy, D.W. Chang, J.B. Baek, L. Dai, BCN graphene as efficient metal-free electrocatalyst for the oxygen reduction reaction, *Angew. Chem.* 124 (17) (2012) 4285–4288.
- [67] C.H. Choi, M.W. Chung, H.C. Kwon, J.H. Chung, S.I. Woo, Nitrogen-doped graphene/carbon nanotube self-assembly for efficient oxygen reduction reaction in acid media, *Appl. Catal. B Environ.* 144 (2014) 760–766.
- [68] H. Singh, S. Zhuang, B. Nunna, E. Lee, Thermal stability and potential cycling durability of nitrogen-doped graphene modified by metal-organic framework for oxygen reduction reactions, *Catalysts* 8 (12) (2018) 607.
- [69] S. Zhuang, E.S. Lee, L. Lei, B.B. Nunna, L. Kuang, W. Zhang, Synthesis of nitrogen-doped graphene catalyst by high energy wet ball milling for electrochemical systems, *Int. J. Energy Res.* 40 (2016) 2136–2149.
- [70] S. Zhuang, B.B. Nunna, J.A. Boscoboinik, E.S. Lee, Nitrogen-doped graphene catalysts: high energy wet ball milling synthesis and characterizations of functional groups and particle size variation with time and speed, *Int. J. Energy Res.* 41 (2017) 2535–2554.
- [71] S. Zhuang, B.B. Nunna, E.S. Lee, Metal organic framework-modified nitrogen-doped graphene oxygen reduction reaction catalyst synthesized by nanoscale high-energy wet ball-milling structural and electrochemical characterization, *MRS Commun* 8 (2018) 40–48.
- [72] Singh, H.; Zhuang, S.; Nunna, B.B.; Lee, E.S. Morphology and chemical structure of modified nitrogen-doped graphene for highly active oxygen reduction reactions. In *Proceedings of 48<sup>th</sup> Power Source Conference*, 14 June, 2018, (Denver, Colorado, U.S.A.).
- [73] S. Zhuang, H. Singh, B.B. Nunna, D. Mandal, J.A. Boscoboinik, E.S. Lee, Nitrogen-doped graphene-based catalyst with metal-reduced organic framework: chemical analysis and structure control, *Carbon* 139 (2018) 933–944.
- [74] J.P. Meyers, R.M. Darling, Model of carbon corrosion in PEM fuel cells, *J. Electrochem. Soc.* 153 (8) (2006) A1432–A1442.