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Review

A review of the stability and durability of non-precious metal catalysts for the oxygen reduction reaction in proton exchange membrane fuel cells



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HIGHLIGHTS

- Historical stability and durability data for NPMCs is critically analysed.
- The leading hypotheses for the observed instability of NPMCs are provided.
- Pathways towards mitigating the observed instability of NPMCs are discussed.

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ABSTRACT

A major hurdle to the widespread commercialization of proton exchange membrane fuel cells (PEMFCs) is the high loading of noble metal (Pt/Pt-alloy) catalyst at the cathode, which is necessary to facilitate the inherently sluggish oxygen reduction reaction (ORR). To eliminate the use of Pt/Pt-alloy catalysts at the cathode of PEMFCs and thus significantly reduce the cost, extensive research on non-precious metal catalysts (NPMCs) has been carried out over the past decade. Major advances in improving the ORR activity of NPMCs, particularly Fe- and Co-based NPMCs, have elevated these materials to a level at which they can start to be considered as potential alternatives to Pt/Pt-alloy catalysts. Unfortunately, the stability (performance loss following galvanostatic experiments) of these materials is currently unacceptably low and the durability (performance loss following of the metal site, (b) Oxidative attack by H_2O_2 , and (c) Protonation followed by possible anion adsorption of the active site. While (a) has largely been solved, further work is required to understand and prevent losses from (b) and/or (c). Thus, this review is focused on historical progress in (and possible future strategies for) improving the stability/durability of NPMCs.

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1. Introduction

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Globally, the majority (>85%) of the energy that is consumed by both stationary and automotive applications is produced through the combustion of fossil fuels [1]. Unfortunately, when fossil fuels are combusted in internal combustion engines (ICEs), a significant amount of by-products (pollution) such as NOx, SOx, and particulates are produced, which all have deleterious effects on the environment. Additionally, available fossil fuel reserves are highly centralized (~40% of the world's oil is located in the Middle East), which threatens the national security of many nations that rely on the import of fossil fuels to meet their energy demands. For these reasons, there has been an increasingly large interest in researching alternative energy systems.

Proton exchange membrane fuel cells (PEMFCs) have emerged as a leading candidate in the alternative energy industry. PEMFCs

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are electrochemical devices that efficiently convert chemical energy directly into electrical energy. Like a battery, PEMFCs consist of an anode, a cathode and an electrolyte (typically Nafion). At the anode, the fuel (typically H_2) is oxidized to form protons and electrons. At the cathode, oxygen is reduced to form H_2O . When H_2 and O_2 (from air) are used as the reactants, the only on-site product is pure H_2O , making PEMFCs far more environmentally friendly than ICEs. Additionally, PEMFCs may help to alleviate concerns over national security due to the many methods for generating H_2 (e.g. methanol or natural gas reforming, electrolysis of water, photocatalytic water splitting). In addition, many of these methods for generating H_2 can be combined with other renewable energy generation methods, such as wind and solar energy, to further increase the environmental benefits.

To accelerate the desired redox reactions occurring at both the anode and cathode of a PEMFC, a catalyst is required. Currently, the most active electrocatalyst towards both the hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) is Pt (and its alloys) [2]. In order to maximize surface area, the Pt is typically deposited as nanoparticles (2–6 nm) on a carbon support [3,4]. Unfortunately, even when deposited as nanoparticles, the high cost of Pt has been one of the major barriers to the widespread commercialization of PEMFCs [5,6]. While economies of scale may significantly reduce the price of manufacturing PEMFCs, Pt is a commodity and consequently, would likely only significantly increase in cost as PEMFC technology is scaled up. In addition to cost, Pt reserves (like fossil fuels) are highly centralized (90% are located in South Africa and Russia) [7] which again leads to national security concerns. For these reasons, there has been significant interest in developing non-precious metal catalysts (NPMCs) to help either reduce or completely eliminate the Pt in PEMFCs. Since the ORR is ~5 orders of magnitude slower than the HOR, the cathode of a PEMFC typically contains 80-90 % of the total Pt in the PEMFC [1,8,9]. Therefore, efforts towards synthesizing NPMCs have focused largely on developing Pt-free ORR catalysts (as opposed to HOR catalysts). There are many types of NPMCs, such as transition metal/ nitrogen/carbon (M/N/C) catalysts, with M = Fe or Co [1,5,8,10-21], transition metal oxides, nitrides and/or carbides [22-27], transition metal chalcogenides [28-32], carbon materials with unique nanostructures [33,34] and nitrogen (and/or boron)-doped carbon structures [27,35-49]. This review will specifically focus on transition metal/nitrogen/carbon (M/N/C) catalysts, with M = Fe or Co (the most promising NPMCs to date) and particularly on the current understanding of their stability/durability. For review of the other available NPMC materials, readers are referred elsewhere for detailed discussions [1,5,8,50-53]. However, for the remainder of this review, NPMC will refer specifically to metal/nitrogen/carbon (M/N/C with M = Fe or Co) catalysts.

The evolution of this class of NPMC began in 1964 when Jasinski reported a novel cobalt phtalocyanine catalyst which was capable of reducing oxygen in an alkaline environment [10]. Unfortunately, it was determined by other researchers that this type of metal-N₄ macrocycle was not stable in acidic environments [11]. A breakthrough in this field was made in the 1970s when it was discovered that heat treatment of the metal-N₄ macrocycles (supported on carbon) not only improved their activity towards the ORR, but also increased their stability when tested in acidic electrolytes [12,13]. Following this, the majority of the work on NPMC focused on pyrolysing metal-N₄ macrocycles supported on high surface area carbons [8]. The next breakthrough in this field was made in 1989, when Yeager's group synthesized a NPMC using simple organic/ inorganic precursors (polyacrylonitrile/Co(II) or Fe(II) acetate) which were pyrolysed on a high surface area carbon support [14]. This approach not only led to increased active site density, but also allowed for more flexibility in the design of NPMCs through choosing from the many potential precursors. However, despite these promising results, the ORR activities of these early NPMCs were extremely low, making them more of a scientific curiosity as opposed to a real alternative to Pt. In 2005, a detailed review by Gasteiger et al. highlighted the fact that even a free catalyst having <1/10 the volumetric activity of Pt/C could never be used for automotive applications due to the very tight volumetric constraints when designing an automobile [15]. Based on the best NPMC known to the authors at the time, it was concluded that achieving a volumetric activity of 1/10 that of Pt/C was improbable.

Fortunately, several breakthroughs since 2005 have led to significant advances in the activity of NPMCs. In fact, there are now numerous NPMCs demonstrating $\geq 1/10$ the volumetric activity of Pt/C [1,16,17]. As a result of these advances, recent work has shifted focus towards the optimization of the catalyst layer, as opposed to strictly focussing on ORR activity improvements. This has become a crucial area of work for NPMC researchers, since the much lower ORR activity of NPMCs versus Pt/C has necessitated much thicker cathode catalyst layers (~100 µm for NPMC versus ~12 µm for Pt/C [18]) and it has become widely known that thick catalyst layers result in mass transport limitations [54,55]. Specifically, it has been demonstrated that optimizing/controlling the porosity of the catalyst can have a significant impact on the performance of PEMFCs which utilize NPMCs at the cathode [18,56–58]. In fact, by introducing interconnected mesoporosity into the catalyst layer, Dodelet's group successfully synthesized a class of NPMCs that demonstrated a beginning of life performance comparable to that of a commercial Pt/C catalyst at current densities of <1 A/cm² when evaluated under 100% O₂ and fully humidified conditions [18].

The significant advances in NPMC activity over the past decade have thus propelled these catalysts beyond the realm of being purely a scientific curiosity, to their current status of potentially becoming a commercially viable option. However, despite the great advances in activity, these catalysts have shown remarkably poor stability and durability. For the purpose of this review, stability refers to the ability to maintain performance at constant current conditions while durability refers to the ability to maintain performance following a voltage cycling accelerated stress test (AST). In the literature, three main mechanisms of instability for NPMCs are generally proposed: 1) dissolution/leaching of the active metal site [59,60], 2) oxidative attack by H₂O₂ [61] (or the resulting free radicals) [62], and 3) protonation of the active site [63] or protonation of a N species neighbouring the active site followed by anion adsorption [64]. Regardless of the mechanism, state-of-the-art NPMCs have demonstrated very poor stability when tested in a membrane electrode assembly (MEA). Furthermore, stable NPMC performance during a constant potential hold at ~0.4 V for hundreds of hours has been considered a major achievement [65–67] despite the fact that real applications will require significantly increased operation times (5000 h for automotive, 80 000 h for stationary) [68]. Regarding the durability of NPMCs, recent reports have demonstrated promising results during potential cycling ASTs [56,67,69]. However, these potential cycling experiments have been extremely conservative, with the majority being carried out under a N₂ environment with upper potential limits constrained to <1.1 V. For real applications, particularly automotive, the cathode catalyst must remain stable during frequent potential excursions to >1.5 V during air—air start-up/shutdown [2,70,71].

This review highlights some of the major advances/observations related to the stability limitations of NPMCs since their discovery in 1964 [10]. Following this, a survey of the three most commonly reported mechanisms of instability (leaching of non-noble metal species, H₂O₂ oxidative attack, and protonation of the active site or protonation of a N species neighbouring the active site followed by anion adsorption) is provided. A critical review of the limited

durability data related to NPMCs is then given, followed by a short discussion on the cause of performance loss during voltage cycling. Finally, potential mitigation strategies are discussed, with a focus on each of the three main causes of instability.

2. Review of stability

2.1. Observations

Instability in an acidic environment has plagued NPMCs since their discovery in the early 1960s [10-12]. While the stability of these catalysts has greatly improved in recent years, it is still not uncommon to have ~20% loss in performance during the first 2 h of operation [16,65,72]. In the early 1970s, Alt. et al. reported that NPMCs experience a rapid performance loss within the first few hours of operation, followed by a more gradual decline [12]. While specific data was not shown, it was stated that a loss of ~50 mV was observed within only a few hours, followed by a more gradual (but continuous) loss of ~5 mV/day, ultimately culminating in a complete loss of activity for some catalysts [12]. A definitive explanation for this loss in performance was not provided, but several hypotheses were suggested. For the Co-based NPMCs, Alt et al. attributed at least some of the loss in performance to oxidative cross-linking of the macrocycles. Additionally, it was found that for some of the Fe and Co-based NPMCs, the metal centres were slowly leached out when soaked in H₂SO₄, and the rate of metal leaching was greatly increased as the temperature was increased from room temperature to 80 °C. It was also suggested that H₂O₂ (generated during the ORR) may have oxidatively degraded the macrocycle, but no supporting evidence was provided.

In 1989 Gupta et al. [14] introduced a novel approach to synthesizing NPMCs that did not follow the traditional route of using metal-N₄ macrocycles. Unfortunately, despite their markedly different synthetic approach of pyrolysing comparatively simple organic/inorganic precursors (polyacrylonitrile/Co(II) or Fe(II) acetate) supported by a high surface area carbon, the same instability issues were observed. While long-term stability tests were not reported, it was stated that the catalysts were far less stable in acidic environments than alkaline environments. Since the solubility of Co is higher in acid than alkaline solutions, it was suggested that the greater instability in acidic environments may have been due to leaching of the metals.

The instability of NPMCs in acidic environments was again demonstrated in the work of Faubert et al. [73]. After heat treating Co and Fe-based tetraphenylporphyrins at temperatures from 100 to 1100 °C under Ar, both the activities and stabilities the catalysts were evaluated. Interestingly, it was observed that although the highest activity was achieved at heat treatments of ~700 °C, these catalysts showed the lowest stability. The best trade-off between activity and stability was observed for heat treatments at 900 °C. The impact of heat treatment on catalyst performance is shown in Fig. 1. While the Fe-based NPMCs prepared at heat treatments >900 °C showed reasonable stability during a 10 h hold at 0.5 V, none of the Co-based catalysts were stable.

Since stability was found to increase with increasing pyrolysis temperature, the authors relate the improved stability of the catalysts prepared at higher heat treatment temperatures to the formation of graphite sheets surrounding the metal centres. It was suggested that the graphite sheets form a protective layer between the metal and the acidic environment, thus preventing metal leaching. However, the authors could not definitively determine whether these graphite coated metal particles were active towards the ORR.

In a follow up study by the same group, a new synthesis approach was used with the ultimate goal of understanding

whether N, Fe, or both were necessary to form an active ORR catalyst [74]. In this work, ferrocene was used as a Fe precursor, with N introduced subsequently in the form of acetonitrile. Importantly, despite the very different synthetic route, the same rapid performance loss during MEA testing was observed (Fig. 2). It is clear in Fig. 2 that the greatest performance loss for the NPMC occurred within the first 2 h. Following this performance loss, the NPMC remained relatively stable. However, it should be noted that over the first 25 h the Pt/C catalyst actually improved in performance.

Due to the increasingly apparent problems surrounding the stability of NPMCs, a targeted study was performed in 2003 to investigate the effect of H_2O_2 (generated during the ORR) on the loss of performance for NPMCs [62]. The premise of this work was based on the observation that these catalysts appeared to have two active sites (FeN₄/C and FeN₂/C), and that the ratio of these two active sites may have impacted the percentage of H_2O_2 that was generated. The proposed structure of these two sites is given in Fig. 3.

Through the use of rotating ring disc electrochemistry (RRDE), the authors were able to demonstrate that the catalysts that possessed the highest ratio of FeN₂/C sites had the highest ORR activity, as well as the lowest percentage of H₂O₂ generation. The impact of H₂O₂ on these various catalysts was investigated through exposing them to a 5 vol % H₂O₂/1 M H₂SO₄ solution for 5 h. The results of this study (Fig. 4) clearly demonstrated that exposure to H₂O₂ can significantly decrease the ORR activity of these catalysts. Specifically, the voltage at which the maximum reduction current was observed at 0 rpm (Vpr) was found to decrease (increased overpotential) for every catalyst after being treated in the H₂O₂ solution. Selected catalysts in Fig. 4 that were also subjected to a purely 1 M H₂SO₄ solution (no H₂O₂) under similar conditions demonstrated no loss in activity, highlighting the role of H₂O₂ in the deactivation mechanism. In fact, for all catalysts, the overpotential at which V_{pr} was reached was shifted cathodically by 50–100 mV after treatment in H_2O_2 . It is important to note that these experiments were performed at room temperature. It would therefore be interesting to repeat a similar study at temperatures more relevant to PEMFCs (60–80 $^{\circ}$ C) where oxidation by H₂O₂ would likely proceed at an even faster rate. Additionally, the ratio of 2 e⁻ to 4 e⁻ pathways may have a temperature dependence, thus making a study at higher temperatures even more crucial.

Through performing a thorough study of their NPMCs, the authors were able to determine that the best predictor of instability in H₂O₂ solutions was the total Fe content (as opposed to the relative ratio of FeN₂/C:FeN₄/C sites). Specifically, NPMCs having a higher Fe content were generally more stable. The authors also measured the amount of Fe released from their catalysts after being treated in the H₂O₂ solutions, and were able to demonstrate a linear trend between the loss of Fe from the NPMCs and the loss in ORR activity. Finally, the catalyst showing the highest activity and stability I(2.0)FeTMPP was subjected to a 600 h 0.5 V potentiostatic stability test, with the beginning of life and end of life polarization curves shown in Fig. 5. Also shown in Fig. 5 is a pyrolysed perylene tetracarboxcylic dianhydride (p-PTCDA)-based MEA and a Pt-based MEA for comparison. The p-PTCDA catalyst possesses no Fe, and was found to have far less loss in performance versus the I(2.0)FeTMPPbased MEA. Following the durability test, neutron activation analysis (NAA) was used to analyse the membranes. The NAA results did not show any Fe in the membrane, and thus it was concluded that destruction of the NPMC active sites was solely responsible for the loss in performance, and that little or no membrane poisoning had occurred.

In the same year, Schulenburg et al. [61] examined the stability of a class of NPMCs formed through heat-treating carbon-



Fig. 1. Performance during potentiostatic holding at 0.5 V for (a) FeTPP/C and (b) CoTPP/C catalysts prepared at various heat treatment temperatures. Reprinted from Ref. [73]. Copyright (1996), with permission from Elsevier.



Fig. 2. Performance during potentiostatic holding at 0.5 V for (I) 2 wt. % Pt/C and (II) polyvinylferrocene-after acetonitrile treatment. Inset shows short term (<10 h) stability of the two catalysts. Reprinted from Ref. [74]. Copyright (1997), with permission from Elsevier.

supported iron(III) tetramethoxyphenylporphyrin chloride (FeTMPP-Cl). One of the primary goals of this work was to investigate whether acid or H_2O_2 is responsible for the greatly reduced performance of NPMCs during potentiostatic experiments. After being heat-treated for 1 h at 900 °C under Ar, the catalyst was subjected to a 100 h potentiostatic experiment at 0.7 V versus SHE while purging with O_2 (Fig. 6). As is generally observed by other researchers in this field [12,73,74], these authors reported a rapid loss in activity, followed by a much more gradual decrease. However, no discussion was provided as to why the majority of the activity loss was experienced within the first few hours.

Following this study, the FeTMPP-Cl catalyst was soaked in either a 0.5 M H_2SO_4 solution, or a 30 wt. % H_2O_2 solution, with the resulting activity of the acid or H_2O_2 treated FeTMPP-Cl catalysts shown in Fig. 7. Also shown in Fig. 7 is the activity of the untreated

catalyst before and after the 100 h potentiostatic hold at 0.7 V.

It is clearly evident in Fig. 7 that acid washing the FeTMPP-Cl catalyst had no impact on activity, whereas a significant decrease in activity was observed when treating the catalyst in H_2O_2 . It was therefore hypothesized that the majority of the activity loss following the 0.7 V potentiostatic hold was due to H_2O_2 that was formed as a by-product of the ORR. The fact that a much larger loss in activity was observed following the H_2O_2 treatment of the catalyst than the potentiostatic holding experiment was believed to be due to the much higher concentration of H_2O_2 during the H_2O_2 treatment versus the potentiostatic holding experiment (where H_2O_2 is only formed as a by-product during the ORR). The authors also found no change in the measured Tafel slope following the potentiostatic holding experiment, or the H_2O_2 treatment, leading them to conclude that the degradation was not correlated with a change in the rate determining step of the ORR.

Through Mössbauer spectroscopy, the authors were able to identify four distinct Fe species. The first was attributed to metallic iron, which was found to disappear following acid washing. The second was due to Fe₂O₃, and it remained after acid washing. The remaining two sites (called "component A" and "component B") were attributed to 4-fold (component A) or 6-fold (component B) Fe coordination sites. Since no change in activity was observed following the acid washing (Fig. 7), it was determined that metallic Fe is not active towards the ORR. While no direct evidence was given, the authors made the assumption that the Fe₂O₃ was also inactive. Therefore, the ORR activity of the FeTMPP-Cl catalyst was attributed to either component A or component B. The authors then demonstrated that, following the H₂O₂ treatment, component A was completely removed while component B remained, albeit at greatly reduced numbers, which accounted for the significantly reduced ORR activity of the FeTMPP-Cl catalyst.

Finally, it was stated early on in this work that, "...up to now no iron-based catalyst is known that is stable enough for practical application..." and that "Little is known about the processes that led to the degradation". It is interesting to note that a decade later, despite some advances in both the stability and the understanding of the mechanism of stability loss, these original statements are still true.



Fig. 3. Proposed structures of the FeN2/C [75] and FeN4/C [76] active sites. Ref [75] reprinted (adapted) with permission from Jaouen, F., S. Marcotte et al. Oxygen Reduction Catalysts for Polymer Electrolyte Fuel Cells from the Pyrolysis of Iron Acetate Adsorbed on Various Carbon Supports. The Journal of Physical Chemistry B. 2003 107 (6): 1376–1386. Copyright 2003 American Chemical Society. Ref [76] reprinted (adapted) with permission from Bouwkamp-Wijnoltz, A. L., W. Visscher et al. On Active-Site Heterogeneity in Pyrolyzed Carbon-Supported Iron Porphyrin Catalysts for the Electrochemical Reduction of Oxygen: An In Situ Mössbauer Study. The Journal of Physical Chemistry B. 2002 106 (50): 12993–13001. Copyright 2002 American Chemical Society.



Fig. 4. Vpr of NPMCs (having different Fe contents) before (solid squares) and after (empty squares) treatment in 5 vol. % H₂O₂/1 M H₂SO₄ solution. The stars represent selected catalysts that were exposed to H₂SO₄ without H₂O₂ present. Reprinted from Ref. [62] Copyright (2003), with permission from Elsevier.

In 2006, a new class of NPMCs were reported by Zelenay et al. [66]. As opposed to the traditional approach of pyrolysing metal/ porphyrin composites, the authors directly loaded a Co-polypyrrole complex onto a Vulcan XC72 carbon black support (Co-PPy-C) without resorting to pyrolysis. The goal of this work was to form Co–N sites without destroying the original structure of the polypyrrole (as would occur during pyrolysis). X-ray absorption nearedge structure (XANES) spectroscopy was used to examine the chemical nature of the Co in the Co-PPy-C catalyst, revealing that



Fig. 5. Polarization curves for a Fe (2.0)FeTMPP-based MEA before and after 600 h at 0.5 V, a p-PTCDA-based MEA before and after 150 h at 0.5 V, and a Pt-based MEA at beginning of life. Reprinted from Ref. [62] Copyright (2003), with permission from Elsevier.

after conditioning, the majority of the Co was oxidized to Co^{2+} . The authors proposed that the Co^{2+} is stabilized in the Co-PPy-C catalyst through coordination with either N or O. While this catalyst did not demonstrate remarkable performance, it did not suffer from the same rapid loss in performance that has traditionally been associated with NPMCs. In fact, the Co-PPy-C catalyst showed very promising stability when used in a MEA and conditioned at 0.4 V for 100 h (Fig. 8).

While these results are promising, it remains unclear as to why this particular catalyst showed such improved stability in comparison to previously reported NPMCs. The authors attributed the high stability to the coordination of the Co^{2+} with either N or O. However, many other NPMCs have also show coordination of the metal centre with N or O, but have not demonstrated the same stability [62,77–79].

In an effort to gain a better understanding of why NPMCs suffer



Fig. 6. Potentiostatic hold (0.7 V vs. SHE) in 0.5 M H_2SO_4 for the FeTMPP-Cl catalyst [61]. Reprinted with permission from Schulenburg, H., S. Stankov et al. Catalysts for the Oxygen Reduction from Heat-Treated Iron (III) Tetramethoxyphenylporphyrin Chloride: Structure and Stability of Active Sites. The Journal of Physical Chemistry B. 2003 107 (34): 9034–9041. Copyright 2003 American Chemical Society.



Fig. 7. Potentiostatic hold (0.7 V vs. SHE) in 0.5 M H_2SO_4 for the FeTMPP-Cl catalyst [61]. Reprinted with permission from Schulenburg, H., S. Stankov et al. Catalysts for the Oxygen Reduction from Heat-Treated Iron (III) Tetramethoxyphenylporphyrin Chloride: Structure and Stability of Active Sites. The Journal of Physical Chemistry B. 2003 107 (34): 9034–9041. Copyright 2003 American Chemical Society.



Fig. 8. Stability of the Co-PPy-C-based fuel cell during a 100 h potentiostatic test at 0.4 V. Reprinted by permission from Macmillan Publishers Ltd: Nature [66]. Copyright 2006.

from such poor durability, Popov et al. [63] used X-ray photoelectron spectroscopy (XPS) to examine the correlation of performance with the stability of a Co–Fe–N chelate-based NPMC heat treated at either 800 (NMCC-800) or 1100 °C (NMCC-1100). Through rotating disc electrochemistry (RDE), it was shown that NMCC-800 was significantly more active than NMCC-1100 °C. However, in-situ MEA testing revealed that NMCC-800 was far less stable than NMCC-1100 (Fig. 9).

Through XPS analysis, the authors concluded that the N species in NMCC-800 were present as pyridinic-N (30%), graphitic-N (57%) and pyridinic-N-O (12%), while in NMCC-1100 there were only pyridinic-N-O (33%) and graphitic-N (66%) species present. It was stated that both pyridinic-N and graphitic-N are active towards the ORR, thus explaining the initial higher activity of NMCC-800 versus NMCC-1100. It was then hypothesized that subsequent protonation of the pyridinic-N in NMCC-800 during MEA testing renders this site inactive towards the ORR, thus explaining the rapid loss in activity for this catalyst. However, if this hypothesis were true, it is unclear why NMCC-800 demonstrates higher activity during the RDE test, where the concentration and mobility of H⁺ should be well in excess of that required to fully and rapidly protonate every available pyridinic-N site. If this did occur, then the RDE testing should have demonstrated very similar activity between NMCC-800 and NMCC-1100. Thus, the discrepancy between the RDE and MEA data seems to suggest that there may be more to the degradation mechanism than simply the protonation of the active site.

In 2009, Zeleney's group [36] performed a targeted study focused on elucidating the mechanism of performance loss for polyanaline (PANI) and polypyrrol (PPy)-based NPMCs. The NPMCs were prepared through in-situ polymerization of PANI or PPy supported on Ketjenblack or multi-walled carbon nanotubes (MWCNTs) in the presence of either Fe or Co, followed by heat treatment at 900 °C under N2 for 1 h. RDE was used to demonstrate that the PANI-based NPMCs showed improved ORR activity when compared to the PPy-based NPMCs, and had excellent selectivity towards the 4 e^- pathway (<1% H₂O₂ generated at 0.4 V versus RHE). In-situ MEA testing verified the improved performance of PANI-Fe-C when compared to PPy-Fe-C at low current densities (<0.3 A/cm²), but the PANI-Fe-C catalyst was found to suffer from increased mass transport losses at current densities >0.3 A/cm², which led to lower overall performance of PANI-Fe-C versus PPy-Fe-C at these higher current densities (Fig. 10 (a)).

Importantly, while the PPy-Fe-C-based catalyst showed higher BOL performance at 0.4 V, it suffered from very poor stability, decreasing to <50% of the initial performance after 100 h. The authors suggested that the poor stability of the PPy-Fe-C catalyst may have been due to differences in "the nature of the active ORR sites, water tolerance and/or other factors". It was also suggested that the PANI precursor resulted in a final structure that was more aromatic (versus PPy) and that this may help to explain the differences in durability. However, no conclusive evidence was provided/shown to strongly support these hypotheses.

Using the PANI precursor [36], the authors examined the effect of the transition metal, and demonstrated that a PANI-Fe₃Co–C composite had higher performance than PANI-Fe-C. Importantly, this composite NPMC also showed slightly improved stability in comparison to PANI-Fe-C over a 600 h potentiostatic experiment at 0.4 V. Additionally, it was shown that when carbon nanotubes (CNTs) were used in place of Ketjenblack, a further improvement in stability was observed. Since CNTs are highly graphitic, this improvement in stability was associated with the improved corrosion resistance of the CNT support when compared to Ketjenblack. However, it should be acknowledged that because the stability test was carried out at a constant voltage of 0.4 V, it is difficult to attribute the improved stability to the better corrosion resistance of CNT versus Ketjenblack since corrosion of carbon does not occur to a great extent at this voltage.

XPS was used to analyse the PANI-Fe-C catalyst during a 500 h potentiostatic experiment, which revealed a significant increase in the oxygen content of the catalyst at the end of the test. This



Fig. 9. Stability data for (a) NMCC-800 and (b) NMCC-1100 at a current density of 200 mA/cm² and a cathode loading of 2 mg/cm² [63]. Reproduced by permission of The Electrochemical Society.



Fig. 10. (a) Polarization plots for the PANI- and PPy-based MEAs and (b) stability data for the same MEAs. Cell temperature = 80 °C, cathode loading = 4 mg/cm² [36]. Reproduced by permission of The Electrochemical Society.

increased oxygen content was taken as evidence that the carbon and/or nitrogen functionalities had been oxidized. The XPS data was also used to correlate the evolution of N species during the potentiostatic experiment. Specifically, it was observed that the pyridinic N content (assumed to be responsible for the ORR activity of the catalyst) decreased significantly throughout the stability test. It was thus concluded that oxidation of the pyridinic N sites (presumably by H_2O_2) was primarily responsible for the instability of this catalyst. It is interesting to note that, while the mechanism proposed in this work is different from that of Popov's group [63], both groups were able to correlate the loss in activity to a decrease in the number of pyridinic N sites.

In 2011, a ground breaking discovery by Dodelet's group was published which demonstrated the highest ever reported volumetric activity for a NPMC [18]. The major breakthrough in this work was the ability to improve mass transport through the introduction of interconnected mesopores (diameter ~50 nm) into the catalyst layer, which resulted in an impressive volumetric activity of 230 A/cm³ at 0.8 V ($2.3 \times$ higher performance than their previous most active catalyst). Unfortunately, despite the incredible

advance in activity, this catalyst demonstrated extremely poor stability during a 0.5 V potentiostatic experiment (Fig. 11). It is clear that despite the initial high performance of this NPMC, it lost ~40% of its activity within the first 40 h.

The authors did not offer a hypothesis for why their catalyst had such low stability, but did acknowledge that a major improvement was required before this catalyst could ever be truly considered as an alternative to Pt-based catalysts for PEMC applications.

2.2. Mechanistic understanding

While there is consensus in the literature that NPMCs suffer from poor stability, there is presently no widely accepted mechanism for performance loss. This is not surprising given the vast number of synthetic approaches used, and the overall complexity of the final structure of NPMCs, which make it highly unlikely that any one single degradation mechanism dominates all NPMCs. However, a review of the literature shows three main degradation mechanisms are typically observed (or suggested): 1) leaching of the nonprecious metal catalyst, 2) attack by H_2O_2 (and/or free radicals), 3)



Fig. 11. Performance durability plot for the most active NPMC (blue curve, 1/20/80-Z8-1050-15 min), and a less active NPMC (purple curve, 1/20/80-Z8-1050-15 min). Reprinted by permission from Macmillan Publishers Ltd: Nature Communications [18]. Copyright 2011. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

protonation of the active site, or protonation of a N species neighbouring the active site, followed by anion adsorption.

2.2.1. Leaching of the non-precious metal catalyst

The leaching of metals from NPMCs has been investigated for decades [14], and has led to some important conclusions regarding the active site in NPMCs. Specifically, the thermodynamic instability of Fe and Co (Fig. 12) in the PEMFC environment has led researchers to largely eliminate metallic Fe or Co as an active component in NPMCs [61,62,80].

It is currently believed that any metallic species remaining in the NPMC must therefore be surrounded by a protective graphite layer [67,83,84] that prevents the otherwise inevitable dissolution of the metallic species. While it is known that metallic species are readily dissolved, the remaining oxidized metal species appear to be very stable [53]. There are very few reports in the literature discussing the direct mechanism for dissolution of metal cations from NPMCs. However, one such mechanism was proposed by Baranton et al.



Fig. 13. Proposed mechanism of attack by H_2O_2 [61]. Reprinted with permission from Schulenburg, H., S. Stankov et al. Catalysts for the Oxygen Reduction from Heat-Treated Iron (III) Tetramethoxyphenylporphyrin Chloride: Structure and Stability of Active Sites. The Journal of Physical Chemistry B. 2003 107 (34): 9034–9041. Copyright 2003 American Chemical Society.

[85]. In this work, they synthesized an iron phthalocyanine (FePc) catalyst in which the active site was believed to be Fe coordinated to the nitrogen in the phthalocyanine macrocycle. The authors did not heat treat the catalyst, allowing the original structure of the FePc to be preserved, thus greatly simplifying interpretation of the active site/structure. Through the use of in-situ infrared reflectance spectroscopy, the authors were able to convincingly correlate the loss in activity of their catalyst with the substitution of the Fe sites by two protons, leading to H₂Pc (known to have low activity towards the ORR [86]) (Eq. (1)).

$$FePc + 2H^+ \rightarrow H_2Pc + Fe^{2+}$$
(1)

However, they noted that this activity loss was only observed when purging with O_2 , and that under Ar their catalyst was very stable. Therefore, they suggested that this mechanism must in some way be mediated by O_2 . Specifically, it was suggested that Fe^{2+} was oxidized to Fe^{3+} in the presence of O_2 , which reduced its ionic radius, thus making it less stable in the macrocycle. A similar explanation was also put forward by Merier et al. [87].



Fig. 12. Pourbaix diagrams for (a) Co (Reproduced from Ref. [81] with permission of The Royal Society of Chemistry) and (b) Fe [82] (Reprinted (adapted) with permission from Pesterfield, L. L., J. B. Maddox et al. Pourbaix (E–pH-M) Diagrams in Three Dimensions. Journal of Chemical Education. 2012 89 (7): 891–899. Copyright 2012 American Chemical Society.

While this work does support the possibility that metal cations can be leached from the active site, this does not appear to be a commonly observed mechanism of activity loss for heat treated catalysts, as previously discussed. The relatively good stability of cationic metal centres is generally believed to be due to the strong binding between the active metal site and the surrounding nitrogen species [14,61,66,88]. Without this strong coordination environment, the metal cations are not stable in acidic solutions, and the performance of the NPMC will rapidly decay due to the dissolution of metal species [89,90].

2.2.2. H₂O₂

Perhaps the most widely agreed upon mechanism for performance loss of NPMCs is oxidation of the carbon and/or active site by H_2O_2 , which is formed as a by-product of the ORR. In fact, this mode of degradation has been suspected since the early 1970s [12,61,64]. However, the exact mechanism by which H_2O_2 attacks NPMCs is still unclear. There are two main paths that can be considered: 1) direct oxidation by H_2O_2 [61], 2) H_2O_2 decomposition into aggressive hydroxyl free radicals, which then attack the NPMC [62]. It is important to distinguish between these two mechanisms in order to help guide any potential mitigation strategy. However, to date there is surprisingly little work in the literature focused on deconvoluting these two pathways.

2.2.2.1. Direct attack by H_2O_2 . The direct attack of NPMCs by H_2O_2 has been suggested by some authors [1,61,91–93]. A proposed mechanism for this attack was provided by Schulenburg et al. [61] In this work, it was suggested that the H_2O_2 can directly attack the N functionalities to which the metal centre is bound. This hypothesis expanded upon earlier work by the same group in which a similar attack mechanism was suggested [91] (Fig. 13).

It was hypothesized that the oxidized N species dissolve into the surrounding ionomer/electrolyte phase, thus explaining why the resulting oxidized N species are not detected. While some support for this hypothesis was obtained through Mossbauer spectroscopy, the details of this mechanism were left quite vague.

2.2.2.2. Indirect attack by H_2O_2 (formation of •OH radicals). It is well known that Fenton's reagents, such as Fe²⁺, promote the decomposition of H_2O_2 into highly reactive free radicals. This is a well understood mechanism in fuel cell membrane literature, where the resulting hydroxyl free radical (•OH), and to a much lesser extent the hydroperoxy radical (HOO•), are known to attack the membrane, ultimately resulting in catastrophic failure [94,95]. The relevant Fenton's reaction responsible for decomposition of H_2O_2 is given in Eq. (2) [95].

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + \bullet OH + H_2O$$
 (2)

While HOO• is also formed during the decomposition of H_2O_2 , it is significantly less reactive than •OH, and can essentially be ignored [94,96].

Importantly, it has been demonstrated that Co is not a powerful Fenton's catalyst [97,98]. In 2011, Gubler et al. [99] showed how comparing the relative redox potentials of metal cations can be used to predict their ability to act as Fenton's catalysts. Specifically, a metal cation is only expected to act as a Fenton's reagent if the redox couple for the specified cation is lower than that of the $H_2O_2/$ •OH redox couple. The relevant redox potentials for Co, Fe, and $H_2O_2/$ •OH are given in Eq. (3).

$$Co^{3+} + e^{-} \rightleftharpoons Co^{2+} \qquad E^{\circ} = 1.92 \text{ V} H_2O_2 + H^+ + e^{-} \rightleftharpoons \cdot OH + H_2O \qquad E^{\circ} = 0.88 \text{ V}$$
(3)
$$Fe^{3+} + e^{-} \rightleftharpoons Fe^{2+} \qquad E^{\circ} = 0.77 \text{ V}$$

From Eq. (3), it is clear that it is thermodynamically favourable for H_2O_2 to oxidize Fe²⁺, forming •OH in the process. However, it is very unfavourable for a similar reaction to occur with Co²⁺. Thus, this mechanism of oxidative attack (namely, the formation of aggressive free radicals due to H_2O_2 decomposition) is not expected to be of importance for Co-based NPMCs. This may help to explain why Co-based macrocycles are generally more stable than Fe-based macrocycles [100].

The possibility that hydroxyl free radicals are the main cause of peroxide-related degradation was suggested as early as 2003 by Dodelet's group [62]. In 2006, Dodelet expanded upon this hypothesis, and suggested the following mechanism for free radical attack on NPMCs [93]:

HO' + RH(active site or carbon support)
$$\rightarrow$$
 H₂O + R'
R' + Fe³⁺ \rightarrow Fe²⁺ + degradation products (4)

While this mode of catalyst degradation is still considered a strong possibility, little work has been performed to validate the mechanism [1,62,93,101].

2.2.3. Protonation/anion adsorption

2.2.3.1. Protonation of the active site. It has widely been observed that the most rapid performance loss is experienced within the first several hours of operation, followed by a more gradual decline in performance [63,72,73,84,102,103]. This suggests that there are two separate mechanisms of performance loss; one acting in a short time frame (<2 h), and one occurring over a longer time frame (>2 h) [104]. Additionally, it has been demonstrated that NPMCs are much more stable in alkaline than in acidic conditions [12,89,90,105]. This is generally observed even for NPMCs in which the metal centre is strongly coordinated to surrounding nitrogen species, and thus would be expected to be very stable in acidic media [64]. Therefore, both Popov's group [63,104,106,107] and Dodelet's group [64] have recently proposed that this initial rapid performance loss may be due to protonation of the active site (Popov's group), or protonation of a N species neighbouring the active site, which is then possibly followed by binding of anions (Dodelet's group), resulting in a loss in performance.

The protonation mechanism for performance loss was clearly described in 2009 by Liu et al. [63]. The hypothesis was that the lone pair of electrons on the pyridinic N could be protonated in the acidic PEMFC environment (Fig. 14). Once protonated, the pyridinic N was assumed to be inactive towards the ORR since it no longer possessed a lone pair of electrons to facilitate reductive oxygen adsorption.

This mechanism was used to account for the difference in stability (Fig. 9) observed between two NPMCs that were synthesized in the same way, but were heat treated at different temperatures. Specifically, it was shown (through XPS) that the NPMC heat treated at 800 °C (NMCC-800) had two ORR active sites (pyridinic N and graphitic N) while the NPMC heat treated at 1100 °C (NMCC-1100) had only one ORR active site (graphitic N). It was argued that since the graphitic N does not possess any lone pair electrons, it cannot be protonated and deactivated, explaining why NMCC-1100 has a higher degree of stability than NMCC-800 (Fig. 9). Additionally, it was suggested that the availability of two active sites in NMCC-800 explains the higher beginning of life (BOL) performance of this catalyst when compared to NMCC-1100.

Unfortunately, a significant concern regarding this hypothesis



Fig. 14. Proposed protonation mechanism showing how the pyridinic N becomes inactive towards the ORR [63]. Reproduced by permission of The Electrochemical Society.

arises when comparing the RDE and MEA data. If protonation of the active pyridinic sites is truly responsible for the rapid performance loss of NMCC-800, why was this not observed in the RDE experiment where both the mobility and availability of protons is certainly in excess of that in the MEA? Very rapid protonation of the catalyst layer during the RDE work would thus be expected, which according to the protonation hypothesis, should have resulted in both the NMCC-800 and NMCC-1100 catalysts showing very similar activities. However, this was not observed, and the significantly higher ORR activity of NMCC-800 than NMCC-1100 during the RDE experiment appears to invalidate this mechanism.

2.2.3.2. Protonation followed by anion adsorption. In 2011, a variation on the "protonation degradation" mechanism was proposed by Dodelet's group [64] While this mechanism also focuses on protonation of N groups, there are two important distinctions that make this mechanism different from that of Popov's group: 1) protonation occurs on ORR inactive N sites, 2) subsequent anion adsorption onto the protonated N sites is what ultimately deactivates the catalyst. The mechanism of this deactivation processes is summarized in Fig. 15.

Fig. 15 depicts how protonation of an inactive N site (located near the active metal centre) followed by subsequent anion adsorption onto the protonation N site, can lead to deactivation of the catalyst. To prove this hypothesis, Dodelet's group employed a rigorous series of tests on their NPMC.

The NPMCs used in this work were labelled as "O catalyst", "AW catalyst", and "RHT catalyst", referring to "original", "acid washed", and "re-heat treated", respectively. Through in-situ testing of the O catalyst, it was demonstrated that a 5 \times higher performance decay



Fig. 15. Proposed protonation/anion adsorption mechanism showing how NPMCs become deactivated due to anion adsorption [64]. Reprinted with permission from Herranz, J., F. Jaouen et al. Unveiling N-Protonation and Anion-Binding Effects on Fe/N/ C Catalysts for O₂ Reduction in Proton-Exchange-Membrane Fuel Cells. The Journal of Physical Chemistry B. 2011, 115 (32): 16087–16097.

was observed when holding the potential at 0.5 V with H_2/O_2 at the anode and cathode respectively, when compared to the same holding experiment but with N_2 at the cathode, or during open circuit voltage (OCV) conditions. The higher performance loss during the 0.5 V potentiostatic experiment under H_2/O_2 was expected, and was attributed to H_2O_2 . However, some performance loss still occurred under H_2/N_2 or OCP conditions, which could not be attributed to H_2O_2 (since very little Faradaic current is passed), thus suggesting an additional mechanism of degradation was taking place.

To investigate this performance loss further, the O catalyst was soaked in pH 1H₂SO₄ for 100 h. Interestingly, the ORR activity of the AW catalyst was found to be 1/20th that of the O catalyst. Furthermore, RDE work demonstrated that the activity of this catalyst had reached a minimum after only 5 min of immersion in the electrolyte, despite only 30% of the Fe leaching out during this time. Re-heating these catalysts to 300 °C resulted in a 50% recovery of their initial performance, suggesting that two mechanisms were at work, with one resulting in permanent performance loss and the other resulting in recoverable performance loss. Thermogravimetric analysis and mass spectroscopy demonstrated that the re-heating step primarily acted to remove HSO₄ anions from the surface of the NPMC, which were assumed to be responsible for the recoverable performance loss. Anion adsorption on the active site was ruled out based on Mossbauer spectroscopy, and a series of well-designed tests in various electrolytes. It was therefore determined that anion adsorption likely occurs on N functional groups, which are easily protonated at a pH ~1. As a final confirmation of this hypothesis, it was demonstrated that by washing the AW catalyst in NaOH, the performance was recovered to a similar level as re-heating the NPMC. Combined, this data provides strong evidence that anion adsorption is at least partially responsible for the decrease in ORR activity of some NPMCs.

3. Review of durability

3.1. Observations

Prior to 2009, very few publications discussed the cycling durability of NPMCs, with most authors preferring to show stability data (performance loss during potentiostatic experiments). However, as advances in NPMC research have brought the ORR activity of these catalysts to a more industrially relevant level, the requirement for durability during voltage cycling has attracted more attention. Thus, since 2009, there have been numerous reports [57,66,105,108,109,110], focussing on the cycling durability of NPMCs, with most authors reporting exceptional durability. However, as will be discussed, many of the voltage cycling experiments are extremely mild, and the majority of these experiments were carried out under N₂ environment, and are thus not likely to be representative of actual fuel cell conditions.

One of the earliest investigations on the cycling durability of NPMCs was performed by Coutanceau et al. [108] In this work, the authors investigated a metal tetra-sulfonated phthalocyanine

(MeTsPc)-based catalyst, with Me = Fe or Co. The MeTsPc was inserted into a polymer matrix (either polypyrrole (PPy) or polyaniline (PANI)) which was deposited onto a Au electrode. The resulting catalysts were labelled Au/polymer (either PPt or PANI)-MeTsPc. In order to evaluate the stability of their catalysts, the authors subjected the Au/PPy-CoTsPc and Au/PPy-FeTsPc catalyst to potential cycling from -0.15 to 0.85 V versus RHE, whilst continually monitoring their ORR activity. It was observed that both catalysts were highly unstable during potential cycling, with the Febased catalyst losing ~50% of its initial activity and the Co-based catalyst losing ~10% of its activity after only five cycles.

In 2010, Popov's group performed possibly the first targeted potential cycling accelerated stress test (AST) on a NPMC to determine the durability of their Co-Fe-N chelate-based NPMCs. The authors correctly noted that, until this date, there had been very little information available on the cycling stability of NPMC, and thus they did not have clear guidance as to what potential limits should be used. They chose potential limits of 0.8-1.2 V since this seemed to be a reasonable amalgamation of previously published guidelines for evaluating support durability (1.2 V potentiostatic experiments) and catalyst durability (cycling between 0.7 and 0.9 V) [105]. The cycling protocol was carried out in N₂ saturated 0.5 M H₂SO₄ or 0.1 M KOH electrolytes using a scan rate of 10 mV/s for up to 700 cycles. The loss in activity was evaluated by monitoring the increase in overpotential at a current density of 1.6 mA/cm² (roughly the half-wave potential) versus cycle number. In the acid electrolyte, rapid activity loss was observed within the first 100 cycles, followed by a much more gradual decrease in activity up to 700 cycles (Fig. 16 (a)). This initial rapid loss in activity, followed by a more gradual decrease, was consistent with what has previously been observed for potentiostatic experiments on NPMCs [63,72,73,84,102,103]. Interestingly, when the same cycling durability study was performed in 0.1 M KOH (Fig. 16 (b)), no loss in activity was observed after 700 cycles, again highlighting the enhanced stability/durability of these catalysts in alkaline conditions.

In the same year, Zelenay's group began investigating the cycling durability of their catalysts, which they had previous shown to have reasonably high stability [66]. Although some previous cycling durability work had been performed by this group, it consisted only of cyclic voltammetry in a N₂ purged environment [36]. In the first true durability study by this group, RDE and in-situ MEA cathode potential cycling from 0.6 to 1.0 V was performed, while



Fig. 17. Cycling durability of Fe-3PEI. Potential limits = 0.2-1.1 V vs. RHE, with a sweep rate of 50 mV/s. Reprinted from Ref. [57]. Copyright (2012), with permission from Elsevier.

monitoring ORR activity periodically throughout the test [67]. The authors demonstrated reasonable durability for this NPMC, which was believed to be at least partly due to the formation of graphene sheets which may help to reduce corrosion. However, with an upper potential limit of only 1 V, carbon corrosion is not expected to be a significant contributor to performance loss, particularly when Pt is not present in the catalyst layer [111]. Thus, it is difficult to attribute the observed durability entirely to the corrosion resistance of the support.

The cycling durability of the NPMCs prepared by Atanassov's group has also been investigated [57]. For this study, potential limits of 0.2–1.1 V versus RHE were used, with a sweep rate of 50 mV/s. In this work, the authors used the change in the half-wave potential as a measure of loss in activity. Much like Popov's group [105], they observed a large decrease in activity during the first 500 cycles, followed by a much more gradual activity loss (Fig. 17). However, it should again be stated that an upper potential limit of 1.1 V is not an aggressive AST for a NPMC. Unfortunately, there was



Fig. 16. Cycling durability of NPMC-900 in (a) 0.5 M H₂SO₄ and (b) 0.1 M KOH. Scan rate = 10 mV/s and potential limits = 0.7–0.9 V. Reprinted from Ref. [105]. Copyright (2010), with permission from Elsevier.

no further discussion/interpretation of the results on the durability of this NPMC catalyst.

A slightly more aggressive potential cycling AST was performed by Choi et al. [109] on a NPMC prepared using iron acetate, pyrimidine-2,4,5,6-tetramine sulphuric acid hydrate (PTAm) as the nitrogen source, and graphene as the carbon support. This AST consisted of potential cycling from 0 to 1.2 V at 50 mV/s. Since the graphene support was believed to impart corrosion resistance to the NPMC, an AST upper potential limit >1.0 V was a rational choice as it is high enough that carbon corrosion would be expected. For comparison, the same AST was performed on a commercial Pt/C catalyst. While the authors show that their NPMC had a higher durability than the Pt/C catalyst during their specific AST, this could have been partly due to the unexpected change in the limiting current that was observed for the Pt/C catalyst (but not the NPMC catalyst) following the AST. Obtaining cyclic voltammograms under N₂ would be helpful to clarify whether this unexpected change in the mass transport controlled region of the voltammogram was related to physical dislodgment of the catalyst.

Finally, recent work by Peng et al. [110] reported on a PANIbased NPMC having a graphene structure displaying a high degree of pyridinic-N and graphitic-N content. Cycling durability was evaluated between potential limits of 0.39-1.04 V versus RHE at a sweep rate of 10 mV/s. It was found that after 10 000 cycles, the activity in the kinetic region decreased by ~27%. The authors then highlighted the fact that at high overpotentials, their catalyst appeared to show less activity loss following the AST cycling than at low overpotentials (only 1.5% performance loss at 0.55 V versus RHE). However, it should be acknowledged that at 0.55 V versus RHE the ORR activity of the NPMC in this study is completely diffusion controlled, consequently, no loss in activity should/would be expected unless severe corrosion had occurred. As was previously stated, no carbon corrosion is expected under the very mild cycling protocol used in this study, thus making the small loss in performance at 0.55 V quite unremarkable.

3.2. Mechanism of performance loss during potential cycling

As there is limited data in the literature on the voltage cycling durability of NPMCs, it is not surprising that there is also limited information on the mechanism of activity loss during these ASTs. Some authors have attributed activity loss during voltage cycling to the same mechanisms as those proposed for the activity loss observed during potentiostatic experiments (e.g. leaching of the active site [69,108], protonation of the active site [105]), while others have not attempted to provide any explanation [57]. However, of the limited data available, most of the discussion centres around the degree of graphitization of the NPMC support [67,109,110]. This mechanism is supported by the observation that the carbon support appears to have a larger impact on durability than the catalyst itself, albeit during potentiostatic experiments at potentials above 1.0 V [36]. Initially, this explanation appears reasonable. Graphitic carbons are known to be more corrosion resistant than amorphous carbons, and carbon corrosion (Eq. (5)) is thermodynamically possible above 0.207 V versus SHE [112]. Thus, it sounds rational that using more graphitic carbon supports should result in improved durability during potential cycling experiments.

$$C + 2H_2O \rightleftharpoons CO_2 + 4H^+ + 4e^- \quad E^\circ = 0.207 \text{ V}$$
 (5)

However, as was discussed previously, the majority of researchers have used an upper potential limit of $\sim 1.0-1.1$ V during potential cycling experiments. In the absence of Pt (as is necessarily the case for NPMCs), little to no carbon corrosion will occur [111]. Thus, the fact that graphitic carbon supports (particularly graphene-based [109,110]) have demonstrated reasonable cycling durability during these relatively mild ASTs may not simply be due to a reduction in carbon corrosion, but may instead be providing a further clue into the true degradation mechanism.

3.3. What upper potential will a NPMC have to withstand?

A brief comment needs to be made regarding the cycling stability tests that have been performed in the literature to date. For Pt/C catalysts, potential cycling below 1.0 V has been used as a method to distinguish Pt degradation from the combined effect of Pt and C degradation [113]. This is because carbon corrosion does not readily occur below 1.0 V, but Pt dissolution can be greatly accelerated by continuous oxidation/reduction (e.g. cycling between 0.6 and 1.0 V). Importantly, Pt dissolution will occur under this voltage cycling protocol, regardless of whether the AST is performed under N₂ or O₂. However, since NPMCs do not contain Pt, potential cycling below 1.0 V under a N₂ environment may be of limited value since little to no degradation should be expected (assuming the degradation is related to carbon corrosion). In any real PEMFC application, voltage cycling between 0.6 and 1.0 V would only occur with air at the cathode, where the NPMC could be producing H₂O₂ and thus degradation would be expected. It can therefore be misleading (since the degradation mechanisms are completely different) and of little value (since this is not a realistic condition for a PEMFC product) to directly compare the stability of a Pt/C catalyst to a NPMC through cycling to an upper potential limit of only 1.0 V under a N₂ environment. However, comparing the RDE potential cycling ASTs up to 1 V obtained under O₂ with those obtained under N₂ may help to uncover the mechanism of performance loss for NPMCs. Since the rate of carbon corrosion would be the same (likely insignificant) under both O₂ and N₂ conditions, any differences in activity could be related to Faradaic processes/ products (e.g. H₂O₂), which can only occur in an O₂-saturated environment.

While it can be useful to compare the stability of NPMCs to Pt/C catalysts using these relatively mild potential cycling ASTs (provided the AST is performed under air), researchers should not consider equal or better durability of their NPMCs during these ASTs to mean that their NPMCs are more durable overall. For many applications, the fuel cell is subjected to many air-air start-up/ shutdown cycles. It is widely known that during air-air start-up and shutdown, the cathode can reach extremely high potentials (>1.5 V) [71,112,114]. These high potential excursions are extremely damaging to even the most durable, graphitic Pt/C catalysts, and any suitable PEMFC catalyst will likely have to withstand thousands of such cycles [113]. As there appears to be no work in the literature that looks at the cycling durability of NPMCs at potentials >1.2 V, it is difficult to say how they will survive this severe requirement. On one hand. Pt is known to catalyse carbon corrosion [111], and since NPMCs contain no Pt, they may show reasonable stability at these high potentials. However, the most active NPMCs are prepared using amorphous carbon supports [16,18], which will not likely withstand such high potentials. With this in mind, caution must be taken when declaring that a NPMC is more "durable" than traditional Pt/C catalysts, and until researchers demonstrate the tolerance of NPMCs to more aggressive upper potential limits, it remains unclear how durable these catalysts will truly be (although very recent work has suggested that FeNx and CoNx sites may be stable up to 1.5 V [115]).

4. Mitigation strategies for improving stability

While NPMCs have demonstrated reasonable durability during voltage cycling ASTs, significant advances in stability will be

required before they can be considered viable alternatives to Pt/C. Unfortunately, there is presently very little work in the literature that focuses on potential mitigation strategies for improving the poor stability that is ubiquitous among NPMCs. This is perhaps not surprising, as the first step to developing a well-planned mitigation strategy is to first clearly identify the root cause of instability, which is something that still appears somewhat controversial in the literature. Therefore, this section will be divided into potential mitigation strategies for each of the three most widely believed causes of poor stability: 1) leaching of the non-precious metal active site, 2) oxidative attack by H₂O₂, and 3) protonation and/or anion adsorption.

4.1. Leaching of the non-precious metal

This mechanism of instability has been widely known since NPMCs were first discovered, and is related to the thermodynamic instability of Fe and Co in the acidic, oxidizing environment of a PEMFC cathode. In early work, Gupta et al. [14] proposed that using an ionically conducting polymer (e.g. Nafion) as opposed to a liquid electrolyte (as was used in their study) could help to slow dissolution (the assumption being that ion diffusion through the polymer would be slower than through liquid). However, this is clearly not a viable strategy for two reasons. Firstly, this approach would only slow down dissolution, rather than preventing it. For many real PEMFC applications, where thousands of hours of operation are required, the catalyst would eventually leach out. Secondly, for Febased NPMCs. Fe^{2+} is known to be a Fenton's catalyst, and as such. will rapidly react with H_2O_2 to form aggressive free radicals [94,95]. Thus, the ionomer in the catalyst layer and membrane would eventually be destroyed. These issues were realized early on in NPMC research, and the current mitigation strategy is to acid wash the NPMCs prior to using them in the PEMFC. In this way, the majority of the unstable Fe species are removed prior to use as a cathode catalyst [79,102]. This strategy appears to be relatively successful, with the remaining Fe being quite stable (in acid) [61].

4.2. Oxidative attack by H_2O_2

While this mode of degradation appears to be the most widely accepted, there has been very little effort focussing on mitigation strategies. This may be in part due to the fact that the exact mechanism of H₂O₂ attack is still not widely known. However, two approaches have been discussed: (a) a synthetic route and (b) controlling catalyst layer thickness. Presently, research efforts have focused almost exclusively on approach (a), with researchers continually aiming at improving the selectivity of their catalysts towards the 4 e^- pathway. However, for NPMCs that generate <2% H₂O₂, significant performance loss is still observed [116]. Although the peroxide generation as measured by RRDE should not be taken as a physical property of a NPMC (due to the impact of catalyst loading on the measured peroxide generation [117]), this data does suggest that even NPMCs that generate a low percentage of peroxide will still suffer from degradation. This could either be interpreted as evidence that another mechanism is dominating performance loss (e.g. a protonation-based mechanism [63,64]), or evidence that even small concentrations of peroxide can lead to significant instability. For approach (b), it appears that thicker catalyst layers result in less measurable peroxide, since any peroxide that is generated has a higher chance of being further reduced to water. However, creating a thicker catalyst layer may itself not be a viable strategy, as thick layers result in diffusional limitations [54,55], and any H₂O₂ that is trapped in the catalyst layer may have a greater chance to undergo oxidative attack on the catalyst. Therefore, research efforts may have to shift to a joint strategy focussing on both a synthetic route and catalyst layer design.

4.3. Protonation followed by possible anion adsorption

This is certainly the most recently proposed mechanism of performance loss, and as such, it comes as no surprise that there is little to no discussion around possible mitigations. Additionally, the two protonation-based mechanisms (e.g. direct protonation of the active site, or protonation followed by anion adsorption of N sites neighbouring the active site) would likely require different mitigation strategies. It is hard to envision a mitigation strategy for eliminating direct protonation of the active site, since the large excess of protons in the extremely acidic PEMFC environment would likely overwhelm any "sacrificial" protonatable sites. However, for the anion adsorption model of performance loss, it is conceivable that tuning of the catalyst properties may prevent, or reduce, this form of activity loss. In fact, a similar mechanism of activity loss has been proposed for Pt-based catalysts, with a potential mitigation achieved through the strategic placement of the cyanide anion which was successful in blocking spectator anion adsorption while preserving ORR activity [118]. It is therefore conceivable that a similar approach could eventually be used to alleviate this specific form of NPMC instability, as was previously suggested by Dodelet et al. [64].

5. Conclusions

Significant advances, particularly in the past decade, have brought the activity of NPMCs to a stage where they are becoming industrially relevant. Unfortunately, NPMCs are widely observed to suffer from extremely poor stability, and cannot presently be considered as viable alternatives to Pt/C catalysts for PEMFCs. The mechanism for the poor stability of NPMCs is not known with certainty, but the main hypotheses are: 1) dissolution/leaching of the active metal site, 2) oxidative attack by H_2O_2 (or the resulting free radicals), and 3) protonation of the active site or protonation of a N species neighbouring the active site followed by anion adsorption. It should be noted that, due to the variety of synthetic approaches and designs, it is not possible (nor should it be expected) to clearly identify one single degradation mechanism for all NPMCs. A clear example of this is provided by comparing the data obtained by Schulenburg et al. [61], which showed no impact of acid washing their NPMC on its ORR activity, with that of Dodelet's group [64], which showed a decrease of $\sim 20 \times$ following acid washing of their NPMC. While NPMCs have demonstrated remarkably poor stability, they have shown promising durability during voltage cycling experiments. This may be due to the limited time spent in the potential region of 0.4–0.6 V, which is predominantly where H₂O₂ is generated. Based on the current state-of-theart NPMCs, future work clearly needs to shift focus towards finding mitigations for the poor stability of these catalysts, since their activity is now sufficiently high for many applications (particularly low power applications such as distributed generation and backup power). The primary mitigation strategy for preventing dissolution/ leaching has been to acid wash the NPMC prior to use in the PEMFC, and this strategy has been shown to be highly successful. Unfortunately, despite significant effort, much more limited success has been achieved in mitigating losses due to oxidative attack by H₂O₂ and/or protonation of the active site. It appears that these remaining challenges will have to be addressed through both a synthetic and rational catalyst layer design approach. Finally, moving forward, great care must be taken when designing accelerated stress tests (ASTs) to compare NPMCs to Pt/C catalysts. Without a proper understanding of the degradation mechanisms of

both NPMCs and Pt/C catalysts, and careful consideration of the real-life operating conditions of PEMFCs, poorly designed ASTs can lead to erroneous (and misleading) conclusions of the relative stability/durability of these two families of catalysts. However, if the necessary stability enhancements can be achieved, NPMCs could be instrumental in propelling PEMFCs from niche markets into widespread commercialization.

References

- F. Jaouen, E. Proietti, M. Lefevre, R. Chenitz, J.-P. Dodelet, G. Wu, H.T. Chung, C.M. Johnston, P. Zelenay, Energy Environ. Sci. 4 (2011) 114–130.
- [2] J. Zhang, PEM Fuel Cell Electrocatalysts and Catalyst Layers, Springer, 2008.
 [3] S.H. Joo, K. Kwon, D.J. You, C. Pak, H. Chang, J.M. Kim, Electrochim. Acta 54
- (2009) 5746–5753. [4] M. Debe, Nature 486 (2012) 43–51.
- [5] A.A. Gewirth, M.S. Thorum, Inorg. Chem. 49 (2010) 3557–3566.
- [6] J. Tollefson, Nat. News 464 (2010) 1262–1264.
- [7] M. Lefèvre, J.-P. Dodelet, ECS Trans. 45 (2012) 35-44.
- [8] D.C. Higgins, Z. Chen, Can. J. Chem. Eng. 91 (2013) 1881–1895.
- [9] F. Barbir, PEM Fuel Cells: Theory and Practice, Elsevier Academic Press, 2005.
 [10] R. Jasinski, Nature 201 (1964) 1212–1213.
- [11] C.W.B. Bezerra, L. Zhang, K. Lee, H. Liu, A.L.B. Marques, E.P. Marques, H. Wang, J. Zhang, Electrochim. Acta 53 (2008) 4937–4951.
- [12] H. Alt, H. Binder, G. Sandstede, J. Catal. 28 (1973) 8–19.
- [13] M.S. Horst Jahnke, Georg Zimmermann, Top. Curr. Chem. 61 (1976) 133-181.
- [14] S. Gupta, D. Tryk, I. Bae, W. Aldred, E. Yeager, J. Appl. Electrochem. 19 (1989) 19-27.
- [15] H.A. Gasteiger, S.S. Kocha, B. Sompalli, F.T. Wagner, Appl. Catal. B Environ. 56 (2005) 9–35.
- [16] M. Lefèvre, E. Proietti, F. Jaouen, J.-P. Dodelet, Science 324 (2009) 71-74.
- [17] H.T. Chung, C.M. Johnston, K. Artyushkova, M. Ferrandon, D.J. Myers, P. Zelenay, Electrochem. Commun. 12 (2010) 1792–1795.
- [18] F.J. Eric Proietti, Michel Lefèvre, Nicholas Larouche, Juan Tian, Juan Herranz, Jean-Pol Dodelet, Nat. Commun. 2 (2011).
- [19] M. Kobayashi, H. Niwa, M. Saito, Y. Harada, M. Oshima, H. Ofuchi, K. Terakura, T. Ikeda, Y. Koshigoe, J. Ozaki, S. Miyata, Electrochim. Acta 74 (2012) 254–259.
- [20] A.H.C. Sirk, S.A. Campbell, V.I. Birss, J. Electrochem. Soc. 155 (2008) B592–B601.
- [21] S. Gharaibeh, V. Birss, ECS Trans. 58 (2013) 1701-1712.
- [22] Y. Liu, A. Ishihara, S. Mitsushima, N. Kamiya, K.-I. Ota, J. Electrochem. Soc. 154 (2007) B664–B669.
- [23] J.Y. Kim, T.-K. Oh, Y. Shin, J. Bonnett, K.S. Weil, Int. J. Hydrog. Energy 36 (2011) 4557–4564.
- [24] J.-H. Kim, A. Ishihara, S. Mitsushima, N. Kamiya, K.-I. Ota, Electrochim. Acta 52 (2007) 2492–2497.
- [25] K. Lee, A. Ishihara, S. Mitsushima, N. Kamiya, K.-I. Ota, Electrochim. Acta 49 (2004) 3479–3485.
- [26] H. Zhong, H. Zhang, G. Liu, Y. Liang, J. Hu, B. Yi, Electrochem. Commun. 8 (2006) 707–712.
- [27] J. Ozaki, N. Kimura, T. Anahara, A. Ova, Carbon 45 (2007) 1847–1853.
- [28] H. Behret, H. Binder, G. Sandstede, Electrochim. Acta 20 (1975) 111–117.
- [29] D. Susac, L. Zhu, M. Teo, A. Sode, K.C. Wong, P.C. Wong, R.R. Parsons, D. Bizzotto, K.A.R. Mitchell, S.A. Campbell, J. Phys. Chem. C 111 (2007) 18715–18723.
- [30] E. Vayner, R.A. Sidik, A.B. Anderson, B.N. Popov, J. Phys. Chem. C 111 (2007) 10508–10513.
- [31] Y. Feng, T. He, N. Alonso-Vante, Chem. Mater. 20 (2007) 26–28.
- [32] K. Lee, L. Zhang, J. Zhang, Electrochem. Commun. 9 (2007) 1704–1708.
- [33] J. Ozaki, S. Tanifuji, A. Furuichi, K. Yabutsuka, Electrochim. Acta 55 (2010) 1864–1871.
- [34] N. Kannari, J. Ozaki, Carbon 50 (2012) 2941–2952.
- [35] S.M. Lyth, Y. Nabae, S. Moriya, S. Kuroki, M.-A. Kakimoto, J. Ozaki, S. Miyata, J. Phys. Chem. C 113 (2009) 20148–20151.
- [36] G. Wu, K. Artyushkova, M. Ferrandon, A.J. Kropf, D. Myers, P. Zelenay, ECS Trans. 25 (2009) 1299–1311.
- [37] H.R. Byon, J. Suntivich, E.J. Crumlin, Y. Shao-Horn, Phys. Chem. Chem. Phys. 13 (2011) 21437–21445.
- [38] K.R. Lee, K.U. Lee, J.W. Lee, B.T. Ahn, S.I. Woo, Electrochem. Commun. 12 (2010) 1052–1055.
- [39] Y. Li, W. Zhou, H. Wang, L. Xie, Y. Liang, F. Wei, J.-C. Idrobo, S.J. Pennycook, H. Dai, Nat. Nano 7 (2012) 394–400.
- [40] C.H. Choi, S.H. Park, S.I. Woo, ACS Nano 6 (2012) 7084–7091.
- [41] K. Gong, F. Du, Z. Xia, M. Durstock, L. Dai, Science 323 (2009) 760-764.
- [42] D. Higgins, Z. Chen, Z. Chen, Electrochim. Acta 56 (2011) 1570–1575.
- [43] D. Geng, H. Liu, Y. Chen, R. Li, X. Sun, S. Ye, S. Knights, J. Power Sources 196 (2011) 1795–1801.
- [44] D. Geng, Y. Chen, Y. Chen, Y. Li, R. Li, X. Sun, S. Ye, S. Knights, Energy Environ. Sci. 4 (2011) 760–764.
- [45] M. Chokai, M. Taniguchi, S. Moriya, K. Matsubayashi, T. Shinoda, Y. Nabae,

S. Kuroki, T. Hayakawa, M. Kakimoto, J. Ozaki, S. Miyata, J. Power Sources 195 (2010) 5947–5951.

- [46] J. Ozaki, K. Nozawa, K. Yamada, Y. Uchiyama, Y. Yoshimoto, A. Furuichi, T. Yokoyama, A. Oya, L.J. Brown, J.D. Cashion, J. Appl. Electrochem. 36 (2006) 239–247.
- [47] J. Ozaki, T. Anahara, N. Kimura, A. Oya, Carbon 44 (2006) 3358–3361.
- [48] J. Ozaki, T. Anahara, N. Kimura, C. Ida, A. Oya, B.B. Bokhonov, M.A. Korchagin, M. Sakashita, Tanso 228 (2007) 153.
- [49] J. Ozaki, S. Tanifuji, N. Kimura, A. Furuichi, A. Oya, Carbon 44 (2006) 1324–1326.
- [50] A. Ishihara, Y. Ohgi, K. Matsuzawa, S. Mitsushima, K.-I. Ota, Electrochim. Acta 55 (2010) 8005–8012.
- [51] Z. Chen, D. Higgins, A. Yu, L. Zhang, J. Zhang, Energy Environ. Sci. 4 (2011) 3167–3192.
- [52] A. Morozan, B. Jousselme, S. Palacin, Energy Environ. Sci. 4 (2011) 1238–1254.
- [53] R. Othman, A.L. Dicks, Z. Zhu, Int. J. Hydrog. Energy 37 (2012) 357–372.
- [54] M.L. Perry, J. Newman, E. Cairns, J. Electrochem. Soc. 145 (1998) 5–15.
- [55] D.W. Banham, J.N. Soderberg, V.I. Birss, J. Phys. Chem. C 113 (2009) 10103–10111.
- [56] A. Serov, M.H. Robson, B. Halevi, K. Artyushkova, P. Atanassov, Electrochem. Commun. 22 (2012) 53–56.
- [57] A. Serov, M.H. Robson, K. Artyushkova, P. Atanassov, Appl. Catal. B Environ. 127 (2012) 300–306.
- [58] H. Liu, Z. Shi, J. Zhang, L. Zhang, J. Zhang, J. Mater. Chem. 19 (2009) 468-470.
- [59] B. Wang, J. Power Sources 152 (2005) 1–15.
- [60] D. Deng, L. Yu, X. Chen, G. Wang, L. Jin, X. Pan, J. Deng, G. Sun, X. Bao, Angew. Chem. Int. Ed. 52 (2013) 371–375.
- [61] H. Schulenburg, S. Stankov, V. Schünemann, J. Radnik, I. Dorbandt, S. Fiechter, P. Bogdanoff, H. Tributsch, J. Phys. Chem. B 107 (2003) 9034–9041.
- [62] M. Lefèvre, J.-P. Dodelet, Electrochim. Acta 48 (2003) 2749–2760.
- [63] G. Liu, X. Li, B. Popov, ECS Trans. 25 (2009) 1251–1259.
- [64] J. Herranz, F. Jaouen, M. Lefèvre, U.I. Kramm, E. Proietti, J.-P. Dodelet, P. Bogdanoff, S. Fiechter, I. Abs-Wurmbach, P. Bertrand, T.M. Arruda, S. Mukerjee, J. Phys. Chem. C 115 (2011) 16087–16097.
- [65] N. Larouche, R. Chenitz, M. Lefèvre, E. Proietti, J.-P. Dodelet, Electrochim. Acta 115 (2014) 170–182.
- [66] R. Bashyam, P. Zelenay, Nature 443 (2006) 63-66.
- [67] G. Wu, K.L. More, C.M. Johnston, P. Zelenay, Science 332 (2011) 443–447.
- [68] Department of Energy, Technical Plan-fuel Cells, 2011.
- [69] H. Xiao, Z.-G. Shao, G. Zhang, Y. Gao, W. Lu, B. Yi, Carbon 57 (2013) 443-451.
- [70] U.S. DRIVE Partnership Fuel Cell Technical Team, 2010.
- [71] M.V.H. Lauritzen, Ping, Alan P. Young, Knights Shanna, Colbow Vesna, Beattie Paul, J. New Mater. Electrochem. Syst. 10 (2007) (2007) 143–145.
- [72] J. Maruyama, I. Abe, Chem. Mater. 17 (2005) 4660–4667.
 [73] G. Faubert, G. Lalande, R. Côté, D. Guay, J.P. Dodelet, L.T. Weng, P. Bertrand,
- G. Dénès, Electrochim. Acta 41 (1996) 1689–1701. [74] G. Lalande, R. Côté, D. Guay, J.P. Dodelet, L.T. Weng, P. Bertrand, Electrochim.
- Acta 42 (1997) 1379–1388.
- [75] F. Jaouen, S. Marcotte, J.P. Dodelet, G. Lindbergh, J. Phys. Chem. B 107 (2003) 1376–1386.
- [76] A.L. Bouwkamp-Wijnoltz, W. Visscher, J. van Veen, E. Boellaard, A. van der Kraan, S. Tang, J. Phys. Chem. B 106 (2002) 12993–13001.
- [77] M. Lefèvre, J.P. Dodelet, P. Bertrand, J. Phys. Chem. B 104 (2000) 11238–11247.
- [78] J.K. Dombrovskis, H.Y. Jeong, K. Fossum, O. Terasaki, A.E.C. Palmqvist, Chem. Mater. 25 (2013) 856–861.
 [79] T.E. Wood, Z. Tan, A.K. Schmoeckel, D. O'Neill, R. Atanasoski, J. Power Sources
- [75] Ha Young Li Han, Li and Schmerker, B. Schreid, R. Handberger, J. Forter Sources 178 (2008) 510–516.
 [80] A. Van Der Putten, A. Elzing, W. Visscher, E. Barendrecht, J. Electroanal. Chem.
- Interfacial Electrochem. 205 (1986) 233–244.
- [81] M. Varon, I. Ojea-Jimenez, J. Arbiol, L. Balcells, B. Martinez, V.F. Puntes, Nanoscale 5 (2013) 2429–2436.
- [82] L.L. Pesterfield, J.B. Maddox, M.S. Crocker, G.K. Schweitzer, J. Chem. Edu. 89 (2012) 891–899.
- [83] M. Manzoli, F. Boccuzzi, J. Power Sources 145 (2005) 161–168.
- [84] G. Lalande, R. Côté, G. Tamizhmani, D. Guay, J.P. Dodelet, L. Dignard-Bailey, LT. Weng, P. Bertrand, Electrochim. Acta 40 (1995) 2635–2646.
- [85] S. Baranton, C. Coutanceau, C. Roux, F. Hahn, J.M. Léger, J. Electroanal. Chem. 577 (2005) 223–234.
- [86] A. Biloul, P. Gouérec, M. Savy, G. Scarbeck, S. Besse, J. Riga, J. Appl. Electrochem. 26 (1996) 1139–1146.
- [87] H. Meier, U. Tschirwitz, E. Zimmerhackl, W. Albrecht, G. Zeitler, J. Phys. Chem. 81 (1977) 712–718.
- [88] P.H. Matter, L. Zhang, U.S. Ozkan, J. Catal. 239 (2006) 83–96.
- [89] C.Z. Deng, M.J. Dignam, J. Electrochem. Soc. 145 (1998) 3507-3512.
- [90] C.Z. Deng, M.J. Dignam, J. Electrochem. Soc. 145 (1998) 3513–3520.
- [91] M. Bron, S. Fiechter, P. Bogdanoff, H. Tributsch, Fuel Cells 2 (2002) 137–142.
 [92] V. Mazumder, M. Chi, K.L. More, S. Sun, J. Am. Chem. Soc. 132 (2010)
- 7848-7849.
- [93] J.P. Dodelet, Heat-treated Non-precious Metal-n4 Macrocycles and beyond, in: N4-macrocyclic Metal Complexes: Oxygen Reduction in PEM Fuel Cell Conditions, Springer Science+Business Media, Inc, 2006.
- [94] F.D. Coms, ECS Trans. 16 (2008) 235–255.
- [95] L. Gubler, S.M. Dockheer, W.H. Koppenol, J. Electrochem. Soc. 158 (2011)

B755-B769.

- [96] F.D. Coms, H. Liu, J.E. Owejan, ECS Trans. 16 (2008) 1735–1747.
- [97] T. Kinumoto, M. Inaba, Y. Nakayama, K. Ogata, R. Umebayashi, A. Tasaka, Y. Iriyama, T. Abe, Z. Ogumi, J. Power Sources 158 (2006) 1222–1228.
- [98] F. Jaouen, V. Goellner, M. Zaton, J. Roziere, Meeting Abstracts, MA2013-02, 2013, p. 1589.
- [99] L. Gubler, W.H. Koppenol, J. Electrochem. Soc. 159 (2011) B211-B218.
- [100] L. Zhang, J. Zhang, D.P. Wilkinson, H. Wang, J. Power Sources 156 (2006) 171-182
- [101] H. Meng, N. Larouche, M. Lefèvre, F. Jaouen, B. Stansfield, J.-P. Dodelet, Electrochim. Acta 55 (2010) 6450–6461.
- [102] E. Proietti, S. Ruggeri, J.-P. Dodelet, J. Electrochem. Soc. 155 (2008) B340-B348.
- [103] A. Garsuch, K. MacIntyre, X. Michaud, D.A. Stevens, J.R. Dahn, J. Electrochem. Soc. 155 (2008) B953-B957.
- [104] B.N. Popov, X. Li, G. Liu, J.-W. Lee, Int. J. Hydrog. Energy 36 (2011) 1794-1802
- [105] X. Li, G. Liu, B.N. Popov, J. Power Sources 195 (19) (2010) 6373-6378.
- [106] G. Liu, X. Li, P. Ganesan, B.N. Popov, Electrochim. Acta 55 (2010) 2853–2858.

- [107] G. Liu, X. Li, P. Ganesan, B.N. Popov, Appl. Catal. B Environ. 93 (2009) 156-165.
- [108] C. Coutanceau, A. El Hourch, P. Crouigneau, J.M. Leger, C. Lamy, Electrochim. Acta 40 (1995) 2739–2748.
- [109] J.-Y. Choi, D. Higgins, Z. Chen, J. Electrochem. Soc. 159 (2011) B86–B89.
 [110] Z.M. Hongliang Peng, Shijun Liao, Huagen Liang, Lijun Yang, Fan Luo,
- Huiyu Song, Yiliang Zhong, Bingqing Zhang, Sci, Reports 3 (2013). [111] L.M. Roen, C.H. Paik, T.D. Jarvi, Electrochem. Solid-State Lett. 7 (2004)
- A19-A22
- [112] J.P. Meyers, R.M. Darling, J. Electrochem. Soc. 153 (2006) A1432-A1442.
- [113] S. Zhang, X. Yuan, H. Wang, W. Mérida, H. Zhu, J. Shen, S. Wu, J. Zhang, Int. J. Hydrog. Energy 34 (2009) 388–404.
- [114] H. Tang, Z. Qi, M. Ramani, J.F. Elter, J. Power Sources 158 (2006) 1306–1312.
- [115] D.J.V. Goellner, F. Jaouen, in: 224th ECS Meeting, 2013.
- [115] D.J.V. Goellner, F. Jaouen, in: 224th ECS Meeting, 2013.
 [116] G. Liu, X. Li, J.-W. Lee, B.N. Popov, Catal. Sci. Technol. 1 (2011) 207–217.
 [117] A. Bonakdarpour, M. Lefevre, R. Yang, F. Jaouen, T. Dahn, J.-P. Dodelet, J.R. Dahn, Electrochem. Solid-State Lett. 11 (2008) B105–B108.
 [118] D. Strmcnik, M.A. Escudero-Escribano, K. Kodama, V.R. Stamenkovic,
- A. Cuesta, N.M. Markovic, Nat. Chem. 2 (2010) 880–885.