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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 voltage cycling) remains uncertain. The three primary mechanisms of instability are: (a) Leaching of the metal site, (b) Oxidative attack by H<sub>2</sub>O<sub>2</sub>, 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

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 NO<sub>x</sub>, SO<sub>x</sub>, 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 phthalocyanine catalyst which was capable of reducing oxygen in an alkaline environment [10]. Unfortunately, it was determined by other researchers that this type of metal- $N_4$  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- $N_4$  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- $N_4$  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  $\mu m$  for NPMC versus ~12  $\mu m$  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/cm<sup>2</sup> when evaluated under 100%  $O_2$  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  $H_2O_2$  [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  $N_2$  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,  $H_2O_2$  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

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