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Article

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Oxygen Reduction Reaction Causes
Iron Leaching from Fe-N-C Electrocatalysts

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Abstract

The electrochemical activity of modern Fe-N-C electrocatalysts in alkaline media is on par with that of platinum. For successful application in fuel cells, however, also high durability and longevity must be demonstrated. Currently, design and synthesis of simultaneously active and stable platinum group metal-free electrocatalysts is hindered by a limited understanding of Fe-N-C degradation, especially under operando conditions. In this work, using a gas diffusion electrode half-cell coupled with inductively coupled plasma mass spectrometry setup, Fe dissolution is studied under more realistic conditions, i.e. real catalyst layer and current densities up to 125 mA·cm\(^{-2}\). Varying the rate of oxygen reduction reaction, we show a remarkable correlation between Faradaic electrode charge and Fe dissolution. This finding is rationalized assuming that oxygen reduction and Fe dissolution reactions are interlinked, likely through a common intermediate formed during the Fe\(^{3+}/Fe^{2+}\) redox transitions in coordinated Fe cations. Moreover, such linear correlation allows an introduction and use of a simple metric (stability number). Hence, in the current work, a powerful tool for a more applied stability screening of different electrocatalysts is introduced, which allows on the one hand fast performance investigations under more realistic conditions, and on the other hand more advanced mechanistic understanding of Fe-N-C degradation in catalyst layers.

Keywords:

Fe-N-C, Oxygen Reduction Reaction, AEMFC, Fe dissolution, Fe\(^{3+}/Fe^{2+}\) redox transition
1. Introduction

On the way to a climate neutral hydrogen economy, energy efficient, durable and affordable fuel cells (FCs) are needed. While proton exchange membrane fuel cells (PEMFCs) have been commercialized, further development of this technology is hindered by its dependency on Pt as the main electrocatalyst material for both hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR). Therefore, research on finding highly active and stable platinum group metal (PGM)-free catalysts is booming as summarized in recent reviews. Among all identified PGM-free candidates, iron-nitrogen-doped carbon (Fe-N-C) is the most promising to catalyse the sluggish ORR. Recent studies have theoretically and experimentally demonstrated that Fe-N-C catalysts are more active and stable in alkaline than in acidic media. This indicates the unique possibility to use Fe-N-C as a relatively efficient, earth abundant and cheap cathode catalyst material in alternative anion exchange membrane fuel cell (AEMFCs) technology. Due to the recent ground-breaking developments in membrane science, AEMFCs demonstrate great potential for successful commercialization. With regards to durability and longevity, however, many open questions remain. In particular, understanding of Fe$^{x+}$ leaching and consequent implementation of mitigation strategies to its suppression are considered main challenges.

So far, four key Fe-N-C degradation mechanisms have been suggested to occur in parallel or series in acidic media, providing clues also to studies in alkaline electrolytes:

(i) *Carbon corrosion.* Corrosion of the carbon support leads to Fe demetallation and a drop in electron conductivity. It has been shown in various studies that this mechanism depends on temperature, electrochemical potential, and, as was demonstrated recently, on the presence or absence of O$_2$ in aqueous electrolytes.

(ii) *Reactive oxygen species (ROS).* Formed as intermediates or by-products of ORR, ROS have shown to cause Fe-N-C catalyst degradation in acidic conditions. ROS can
oxidize carbon support, resulting in a decrease of the ORR turnover frequency (TOF) of the existing Fe active sites. The presence, amount and effect of ROS have been reported to be dependent on the electrochemical potential, temperature, and ORR.\textsuperscript{10,20} In an alkaline environment the effect of ROS attack on catalyst degradation was shown to be minor.\textsuperscript{10,20}

(iii) \textbf{Agglomeration}. Agglomeration of active single atom FeN\textsubscript{4}C\textsubscript{12} sites to inactive ferric oxides Fe\textsubscript{2}O\textsubscript{3} was shown to be affected by temperature\textsuperscript{21} or exposure to air.\textsuperscript{22}

(iv) \textbf{Fe dissolution}. Direct Fe ions leaching from active sites is influenced by electrolyte pH,\textsuperscript{8} potential,\textsuperscript{15} temperature,\textsuperscript{15} chemical environment,\textsuperscript{8} and water-flux across the active sites within micropores.\textsuperscript{17}

While it is very likely that several degradation mechanisms are operative and the extent of each mechanism is different depending on the FC operational conditions, a comprehensive understanding of the stability of Fe-N-C catalysts is still lacking. For instance, the origin of the dissolved Fe species from Fe-N-C catalysts was found to be different in the various Fe-N-C stability studies.\textsuperscript{15-17,22} As an example, in scanning flow cell (SFC) experiments coupled to inductively coupled plasma mass spectroscopy (ICP-MS), Fe dissolution in an Ar-purged acidic electrolyte was assigned to leaching of inactive Fe sites.\textsuperscript{15,16} In contrast, for realistic cathodes in PEMFC tests, the decrease of ORR activity was correlated to a loss of FeN\textsubscript{4} active sites using ex-situ Mössbauer spectroscopy.\textsuperscript{17,22} This discrepancy illustrates that direct comparisons of the results from thin catalyst layers in aqueous model systems (AMS), e.g. rotating disk electrode (RDE) or SFC, and realistic cathodes in PEMFCs or AEMFCs are challenging, as highlighted in our recent review.\textsuperscript{23} Such differences may affect the intensity and the mechanisms of degradation significantly. A major discrepancy between AMS and real devices is the direct contact of the catalyst to gaseous O\textsubscript{2}, which cannot be easily realized in RDE or SFC. Moreover, even in AMS, the influence of O\textsubscript{2} on Fe-N-C stability is sporadically addressed as the stability
has traditionally been tested in de-aerated acidic environment. However, degradation of PGM-free materials can be significantly affected by the presence of O₂.¹⁸,²⁴ Thus, using online ICP-MS, Speck et al.²⁴ identified different dissolution mechanisms for MnOₓ in Ar- and O₂-purged alkaline media. On the one hand, Mn transient-dissolution occurs in both Ar and O₂ environment, which was attributed to the redox transitions of Mn. On the other hand, Mn total dissolution is drastically increased in O₂ environment. This was ascribed to the presence of ROS, such as HO₂⁻ generated during the ORR. A similar trend has been detected also for Fe-N-C catalysts degradation in acidic media. Combining RDE measurements with Raman spectroscopy, Kumar et al.¹⁸ showed that both deterioration of ORR activity and the extent of carbon corrosion are significantly more severe in O₂- compared to Ar-saturated electrolytes.

In order to bridge the gap between the fundamental and applied researches, gas diffusion electrode (GDE) half-cell setups have emerged as a tool to combine the advantages of AMS (three electrode setup, fast and comparable testing at standard operating conditions) and FCs (realistic catalyst layers and current densities) systems.²⁵-²⁹ In the current work, we use a GDE half-cell setup coupled with online ICP-MS (GDE-ICP-MS)³⁰ to systematically investigate the impact of O₂ atmosphere and a solid electrolyte interface on Fe demetallation in realistic Fe-N-C alkaline catalyst layers (CLs) at current densities up to 125 mA·cm⁻².

2. Results

In order to gain insights into the Fe-N-C demetallation in realistic alkaline CLs during ORR, Fe dissolution in Ar- and O₂-environments is compared during the application of similar potential steps. Figure 1 shows the effect of O₂ (or ORR) on the Fe dissolution at different potentials between 0.57 and 0.87 V_RHE. The novel GDE-ICP-MS setup allows detection of Fe dissolution at current densities up to -125 mA·cm⁻² (see Figure 1A), which is mainly limited by the highest alkaline electrolyte concentration that the ICP-MS can tolerate, i.e. 0.1 M. For
comparison: in AMS such as RDE only few mA cm\(^{-2}\) can be reached due to the solubility limit of O\(_2\) in used aqueous electrolytes.\(^{15,18,32}\)

**Figure 1.** Comparison of Fe-N-C demetallation between Ar- and O\(_2\)-saturated alkaline (0.1 M NaOH) environments before the accelerated stress test (AST), via gas diffusion electrode setup coupled to inductively coupled plasma mass spectrometry (GDE-ICP-MS). A: Current density profile. B: Potential profile. C-left axis (solid lines): Fe dissolution profile normalized to catalyst loading. C-right axis (dotted lines): Amount of dissolved Fe species at different potentials (V\(_{\text{RHE}}\)). The testing with O\(_2\) was using galvanostatic techniques and then the testing with Ar was programmed with potentiostatic techniques accordingly. More details of this experimental design can be found in section 3.4 of the supporting information (SI).

In Figure 1A and 1B, the electrochemical protocol in Ar and O\(_2\) environment is displayed. In the presence of O\(_2\), -125 mA·cm\(^{-2}\) can be reached due to ORR at around 0.6 V\(_{\text{RHE}}\). In an Ar environment the current density is smaller than -1 mA·cm\(^{-2}\) at similar potentials. Under these electrochemical conditions, the Fe dissolution profiles (see Figure 1C, left axis, solid lines) show that significantly more Fe is dissolved in the presence of O\(_2\) than in the absence of O\(_2\). Overall, the total amount of Fe dissolved (see Figure 1C, right axis, dotted lines) in O\(_2\) is about one order of magnitude higher than that in Ar in the potential range between 0.8 – 0.6 V\(_{\text{RHE}}\). Also, at 0.87 V\(_{\text{RHE}}\) (the lowest applied ORR overpotential) the Fe dissolution is
already higher in O₂ than in Ar. Hence, it is clear that the amount of Fe dissolution would be hugely underestimated if the electrochemical testing is executed in an environment without O₂ as often done in AMS.8,15

In addition to the impact of the presence of O₂ or ORR, the following two characteristic features of Fe-N-C demetallation can be observed for both Ar and O₂ cases. Firstly, the Fe dissolution starts right when the cathodic current or potential steps are applied. After moving back to open circuit potential (OCP), also the dissolution drops immediately. In general, the amount of dissolved Fe species rises with increasing the ORR overpotential or/and current density. Additionally, the dissolution at the regularly repeated steps to similar potentials is almost constant (see Figure S1C in the supporting information (SI)), indicating that the order of the applied steps does not affect dissolution behaviour in the chosen protocol. Besides Fe dissolution, also the activity measured at low overpotentials does not drop over the whole protocol before the accelerated stress test (AST) (see Figure S1B).

To mimic fuel cell load cycles, we conducted AST between -0.05 and -125 mA·cm⁻² in O₂ environment, which correspond to 0.88 ± 0.03 and 0.56 ± 0.04 V_RHE, respectively. For comparison, AST in Ar was conducted in a similar potential range between 1.0 and 0.573 V_RHE. Also using this protocol, the total amount of dissolved Fe species during O₂-AST is almost one order of magnitude higher than that during Ar-AST (see Figure 2A).
Figure 2. Comparison of the quantitative results for the Fe dissolution in alkaline (0.1 M NaOH) during AST between Ar- and O₂-saturated environments. A: Amount of dissolved Fe species. B: Fe dissolution normalized to the applied charge.

Interestingly, despite the dramatically higher Fe dissolution during ORR compared to the one in Ar environment, the charge-normalized dissolution rates during ASTs in O₂ and Ar are similar (see Figure 2B). This implies that Fe dissolution in Fe-N-C could be associated with a charge-transfer-related process that commonly occurs in both Ar-AST and ORR. Detailed evaluation of the degradation mechanism can be found in the discussion section. To further validate this coherence, Fe dissolution in O₂ for different holding periods at -125 mA cm⁻² is compared in Figure S2. The results confirm that Fe dissolution is fairly constant when normalized to the applied charge. In contrast, when the same Fe dissolution data is normalized to the number of applied cycles, no correlation can be seen. Therefore, it is unlikely that solely the change of potential causes all the Fe dissolution. All these results imply that Fe dissolution in alkaline media is directly proportional to the applied current in the applied potential range, which will be discussed more in detail in the discussion section.

In oxygen evolution reaction (OER) research, the reciprocal of the charge-normalized dissolution, so-called S-number, has been well established as a metric for catalyst stability. Due to the correlation between applied charge and Fe dissolution, a similar concept can be applied here. The S-number of the studied commercial Fe-N-C would be around 10⁶. This
means that in the studied potential region between 0.57 and 0.87 \( V_{\text{RHE}} \), a Fe site can averagely undergo one million desired charge transfer reactions before it is dissolved. Accordingly, the average probability of losing a Fe atom at each charge transfer event is approximately \( 10^{-6} \). Further discussion on how applicable this value is for AEMFCs can be found in the section 2 in the SI. Although ORR is a complicated multi-step 4-electron-transfer reaction with several intermediate states,\(^{34,35}\) where the coordinated Fe cation could be variously unstable, the \( S \)-number could be a suitable quantification metric to study overall stability of Fe-N-C catalysts in various conditions and to compare different materials.

To further approach more realistic AEMFC conditions, we additionally compare Fe dissolution in GDEs without and with a thin AEM attached in an \( \text{O}_2 \)-saturated environment. For Pt/C catalysts in acidic media, a significant stabilizing impact of Nafion membranes on the net Pt dissolution was recently observed.\(^{30}\) This effect was attributed to the impeded mass-transport of dissolved catalyst species through the membrane. However, for our AEM system, we cannot observe any significant impact of the AEM on the Fe dissolution (see Figure 3C and S3). The diverging effects of the Nafion membranes and the AEM can be attributed to the following differences between the two systems. Firstly, the thickness ratio of CL to the membrane in our AEM system is two to three orders of magnitude higher than that in the work mentioned above (see Table S1 and Figure S4). In our case, the doctor-blade coated AEM membrane is less than 1 \( \mu \text{m} \) thick, whereas in the literature membranes of 25 and 52 \( \mu \text{m} \) were used.\(^{30}\) Hence, the impacts of AEM on Fe-N-C demetallation in our study are diminished. Additionally, the varied physical properties of dissolved species and the membranes could contribute to the differing results.\(^7\) For future work, commercial AEMs with increased thickness should be used to reveal the impact of the transport of dissolved Fe species through the membrane on the total Fe dissolution. After the effect of different relevant conditions on Fe dissolution was examined, also the impact of catalyst dissolution on the catalyst activity should be compared (see Figure
First of all, when measuring ORR performance, no significant effect of the AEM on the initial activity (pristine) could be observed. Secondly, regardless of whether there is a membrane or not, similarly remarkable performance losses are detected after O$_2$-AST. Oppositely, no notable performance loss was observed after Ar-AST. Additionally, it is worth noted that, if compared to the state of the art literature values, the ORR performance of the used electrocatalyst is inferior. We attribute this discrepancy to the relatively low concentration of alkaline electrolyte, i.e. 0.1 M NaOH, which is the highest concentration that the on-line ICP-MS can tolerate.

**Figure 3.** A: The polarization curves of the Fe-N-C GDEs in the following five conditions. (i) Before any AST, and without the thin AEM (Pristine, black), (ii) Before any AST, and with the thin AEM (Pristine-M, grey), (iii) After Ar-AST, and without the thin AEM (After Ar-AST, blue), (iv) After O$_2$-AST, and without the thin AEM (After O$_2$-AST, red), and (v) After O$_2$-AST, and with the thin AEM (After O$_2$-M-AST, yellow). B & C: The relative losses of the power density at 0.6 V$_{RHE}$ (B) and the Fe content (C) over the Ar-AST, O$_2$-AST, or O$_2$-M-AST procedures. Note that the calculation of the loss of the Fe content is explained in the section 3.3 of the SI.

By comparing the relative loss of Fe sites (see Figure 3C) with the decrease of power density at 0.6 V$_{RHE}$ (see Figure 3B), derivations on how active the dissolved Fe species originally were, can be made. During Ar-AST, only negligible performance deterioration occurred, although still Fe dissolution was measured. This suggests that the detected Fe species were originally inactive or poorly active, which agrees with the results obtained by Choi et
al.\textsuperscript{15,16} from RDE and SFC-ICP-MS in acidic environment. However, during O\textsubscript{2}(-M)-AST, the power density at 0.6 $V_{\text{RHE}}$ decreased by more than 10\%, although less than 1\% of Fe species were dissolved. This indicates that during ORR, the detected Fe species were especially dissolved from the Fe active sites, which is consistent with the works of Chenitz et al.\textsuperscript{17} and Li et al.\textsuperscript{22}, using Mössbauer spectroscopy and PEMFCs running with $H_2$/air or O\textsubscript{2} at 80 °C. This comparison unveils the impact of O\textsubscript{2} or ORR on the origins of dissolved Fe from Fe-N-C in alkaline media, and helps explaining the existing discrepancy between observations from RDE and FC setups. With the presented data, some derivations on the degradation mechanism of Fe-N-C catalysts in realistic alkaline catalyst layers are made in the further course.

3. Discussion

The degradation of Fe-N-C proceeds through diverse mechanisms in different electrochemical potential ranges or pH environments.\textsuperscript{8,15,20} It has to be noted that the current work only allows derivations for the potential range between 1.0 and approximately 0.6 $V_{\text{RHE}}$ in alkaline media. This, however, corresponds well to a usual potential range of AEMFCs under load.\textsuperscript{36} Under the investigated conditions, Fe dissolution increases with decreasing potential. In contrast, carbon corrosion is expected to increase with potential.\textsuperscript{15,37} Therefore, carbon corrosion is not considered as the dominating degradation mechanism under the studied conditions. On the other hand, the main outcome of this work emphasizes that the Fe dissolution is directly proportional to the applied charge. In other words, Fe dissolution can be largely correlated to charge transfer events, which are part of the ORR catalytic cycle. This implies that the observed Fe dissolution may be attributed to the destabilization of Fe active sites at one or more step(s) during the ORR catalytic cycle, namely the adsorption of O\textsubscript{2} on Fe, the reduction of reaction intermediates and the $Fe^{3+}/Fe^{2+}$ redox transition.\textsuperscript{20,34,38-40} Those three steps and their potential impacts on Fe dissolution will be discussed below.
Firstly, according to density functional theory (DFT) calculations conducted by Aoyama et al.\textsuperscript{38}, the adsorption of O\textsubscript{2} molecules on Fe active sites can shift the Fe position from in-plane to out-of-plane. This leads to destabilization of the coordinated Fe cation and therefore pronounced dissolution. Although it is a study for an acidic condition, we could not rule out the possibility that a similar destabilizing effect due to this step is also occurring in alkaline media, as O\textsubscript{2} adsorption is a part of the ORR catalytic cycle in both environments.

Secondly, the Fe active sites could also be destabilized by ORR intermediates, mainly HO\textsuperscript{2−} (H\textsubscript{2}O\textsubscript{2}’s dominating form in alkaline) or ROS.\textsuperscript{34} The impact of H\textsubscript{2}O\textsubscript{2} on the stability of Fe-N-C in acidic media has been systematically studied.\textsuperscript{7,18-20,39} Choi et al.\textsuperscript{20} and Bae et al.\textsuperscript{10} performed H\textsubscript{2}O\textsubscript{2}−-treatment on Fe-N-C in acidic or alkaline media, and found notable declines of the ORR activity after H\textsubscript{2}O\textsubscript{2}−-treatments in acidic yet a negligible decrease after a H\textsubscript{2}O\textsubscript{2}− treatment in alkaline. This suggests that compared to H\textsubscript{2}O\textsubscript{2} in acidic, HO\textsuperscript{2−} is less harmful to Fe-N-C in alkaline environment, and thus its impact on the degradation process is potentially less pronounced. Indeed, a great discrepancy between the potential dependencies of the charge-normalized Fe dissolution detected in this work and the HO\textsuperscript{2−} faraday efficiency reported for a similar catalyst in a previous work,\textsuperscript{32} can be observed (see Figure 4). Yet, it has to be considered that the faradaic efficiency was determined in a rotating ring-disk electrode (RRDE) setup, where ORR is severely limited by the restricted mass transport of dissolved O\textsubscript{2} when the potential is below 0.8 V\textsubscript{RHE}. This could lead to deviations when the RRDE result is compared to the dissolution data from this work, gathered from GDE half-cell measurements, where those mass transport limitations do not play a significant role.\textsuperscript{25-28} Hence, the results point against a dominant impact of HO\textsuperscript{2−} or ROS on the stability of Fe-N-C in alkaline media and O\textsubscript{2} environment; however, with currently available data it cannot be conclusively excluded.
Thirdly, in a previous online dissolution study, the onsets of transition-metal dissolution in PGM-free catalysts (manganese oxide MnO$_x$) could be correlated to the corresponding redox transition potentials.$^{24}$ It was proposed that the reconstruction of the surface MnO$_x$ coordination during redox transitions could lead to the so-called transient-dissolution. Although the structures of MnO$_x$ and Fe-N-C are different and this demetallation mechanism has not been identified responsible for degradations of Fe-N-C catalysts yet, a similar concept could still be applied. Namely, the Fe$^{3+}$/Fe$^{2+}$ redox transition (see Equation (1) and (2) below) and its corresponding changes of coordination could result in transient instability of the coordinated Fe and thus potentially its dissolution.

\[
N_4Fe^{2+} \cdots O_aH_b \rightarrow N_4Fe^{3+} \cdots O_aH_b^- \quad (1)
\]

\[
N_4Fe^{3+} \cdots O_cH_d + e^- \rightarrow N_4Fe^{2+} \cdots O_cH_d \quad (2)
\]

From the Fe dissolution data during ORR, any destabilizing step during the ORR catalytic cycle could be suspected to be responsible for the Fe demetallation in Fe-N-C. However, more insights may be gained from the surprisingly similar values of the charge-normalized Fe dissolution during O$_2$-AST and Ar-AST (see Figure 2B). This implies that the key destabilizing factor to the Fe dissolution in Fe-N-C could be one that is related to charge transfer events and also occurs in both O$_2$-AST and Ar-AST. Among the three above mentioned
destabilizing factors during ORR, only Fe$^{3+}$/Fe$^{2+}$ redox transitions also take place during Ar-AST as can be seen from the cyclic voltammograms in Ar environment (see Figure S5). Indeed, the correlation between Fe$^{3+}$/Fe$^{2+}$ redox transition and the stability of Fe active sites in the absence of O$_2$ could be supported by the findings revealed by Li et al.$^{22}$ They reported that the Fe active sites that undergo reversible Fe$^{3+}$/Fe$^{2+}$ redox transitions due to potential switches between 0.2 and 0.8 V$_{RHE}$ (FeN$_4$C$_{12}$) are less stable than those where the charge of Fe ions (2+) is constant and independent of the potential switches (FeN$_4$C$_{10}$). This supports the idea that the coordinated Fe could be less stable during its redox transitions even in the absence of O$_2$.

Based on this correlation between Fe$^{3+}$/Fe$^{2+}$ redox transition and Fe dissolution, we propose that Fe demetallation of the investigated Fe-N-C catalyst in alkaline media can be attributed to the instability of the coordinated Fe during the redox transition. This hypothesis can also explain the different amounts and varied origins of the dissolved Fe species in the absence and presence of ORR: On the one hand, the Fe redox transition in a de-aerated electrolyte would only be triggered by the change of electrochemical potential, occurring only twice in each AST cycle. Also, the transitioned Fe species do not necessarily have high activity. On the other hand, in the presence of O$_2$, the active Fe sites continuously undergo redox transitions when catalysing ORR in the first half of each AST cycle. Moreover, the more active the Fe site is, the more frequent it undergoes the redox transition. Therefore, the Fe dissolution from the active sites during O$_2$-AST is more significant than that during Ar-AST.

4. Conclusions and Outlook

In the present work, Fe demetallation in alkaline Fe-N-C CLs is studied at realistic conditions, such as O$_2$ environment, elevated current densities, and a thin AEM on the CL. We show that Fe dissolution is significantly enhanced in O$_2$ environment compared to Ar. Additionally, Fe dissolution is shown to be directly proportional to the applied charge. By
comparing activity data with Fe dissolution, we can derive that Fe dissolution in Ar mainly happens at inactive sites, whereas during ORR significantly more Fe active sites are dissolved. Moreover, we discovered strong correlations between the Fe dissolution and the Fe$^{3+}$/Fe$^{2+}$ redox transition in the presence and absence of ORR in the studied potential range, $1.0 – 0.57 \text{ V}_{\text{RHE}}$. This leads to our hypothesis that the instability of the coordinated Fe during the redox transitions could be highly responsible for the Fe demetallation in Fe-N-C catalysts in alkaline media. This hypothesis could help rationalizing the different scales and origins of the Fe dissolution in the presence and absence of ORR. For future work, differently synthesized Fe-N-C catalysts in different potential regions should be evaluated. The Fe dissolution data should be accompanied by ex-situ spectroscopic techniques, such as Mössbauer and Raman spectroscopies, to rationalize the structure-stability relationship of Fe-N-C catalysts. Based on that, special strategies for improving the stability of Fe-N-C catalysts for AEMFCs need to be developed, since the dominant degradation mechanism of Fe-N-C catalysts might be different in alkaline compared to acidic environment.

5. Experimental

5.1 Electrode manufacturing

The alkaline Fe-N-C catalyst layer (CL) was fabricated on a gas diffusion media including a microporous layer (H23C8, Freudenberg, 4x4 cm², 218 ± 5 μm). The CL was composed of 70 ± 0.3 wt% commercial Fe-N-C catalyst (PMF-011904, Pajarito Powder) and 30 ± 0.3 wt% commercial ionomer (Aemion™ HNN5-00-X, Ionomr). The anion exchange membrane (AEM) comprised solely of this ionomer. More details of the sample preparation can be found in section 3.1 of the SI. The loading of the CL is determined to be 1.35 ± 0.05 mg·cm$^{-2}$. The thicknesses of the CL and AEM are 47.5 ± 5.2 μm and 0.5 ± 0.2 μm, respectively, measured from images (see Figure S4 and Table S1) taken via cross-sectional
imaging with a focused ion beam scanning electron microscopy (Crossbeam 540 FIB-SEM, Zeiss). More detailed information on the procedure can be found in section 3.2 of the SI.

5.2 GDE-ICP-MS measurements

The GDE-ICP-MS setup and methodology have been introduced in our previous work. Also, Scheme S1 demonstrates the concept of the setup. To detect $^{56}$Fe species, ICP-MS (Perkin Elmer, NexION 350) was operated in dynamic reaction cell (DRC) mode using CH$_4$ (5.5, Air Liquide) and with 100 μg·L$^{-1}$ of Ge ((NH$_4$)$_2$GeF$_6$, Merck Centripur) in 1 wt% HNO$_3$ (Suprapur®, Merck) as the internal standard. A four-point calibration was carried out with a blank and three standard Fe solutions (0, 1, 5, 25 μg·Fe·L$^{-1}$) every day before measurements. For the standard solutions, the Merck Centripur ICP standard (Fe(NO$_3$)$_3$, 1000 mg·L$^{-1}$, in 2–3% HNO$_3$) was first diluted 100 times with 1 wt% HNO$_3$(aq), and then further diluted to the aimed concentrations with a 0.1 M NaOH electrolyte (Merck Suprapure). More details can be found in section 3.3 of the SI.

The electrochemical measurements were performed in 0.1 M NaOH in a GDE half-cell. The impact of (i) gas supplied to the back of the GDE (Ar vs. O$_2$, 50 ml·min$^{-1}$) and (ii) the CL | electrolyte interface (AEM vs. no AEM) have been investigated. The measurements with O$_2$ were conducted with galvanostatic techniques; the ones with Ar were with corresponding potentiostatic techniques, imitating the potentials reached during ORR in the presence of O$_2$. The electrochemical protocol consists of three parts, (i) an activity test, (ii) an accelerated stress test (AST), and finally (iii) a repeated activity test. (see Scheme 1). A detailed explanation of this experimental design can be found in section 3.4 of the SI. Each set of experiments was performed at least twice to show the result's reproducibility.
Scheme 1. Electrochemical protocol consisting of an activity test, an AST and a repeated activity test after the AST.

All data is presented with respect to reversible hydrogen electrode (RHE) reference and 100 % iR-corrected. The reference electrode (RE, Ag/AgCl Metrohm) potential vs. RHE was calibrated on every measurement day ($E_{Ag/AgCl} = 0.944 \pm 0.0115 \text{ V}_{RHE}$). For potentiostatic measurements (Ar environment), the potential was 80 % in-situ iR-compensated and 20 % post iR-corrected. The uncompensated resistance ($R_u$) was determined via electrochemical impedance spectroscopy (EIS) at open circuit potential (OCP). For galvanostatic measurements ($O_2$), the data was 100 % post iR-corrected. The $R_u$ was measured via EIS at each current step, as proposed previously.\textsuperscript{27,28} In all experiments, the electrolyte was always purged with 50 ml·min$^{-1}$ Ar.

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