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Assessing Utilization Boundaries for Pt-based Catalysts in an Operating PEMFC

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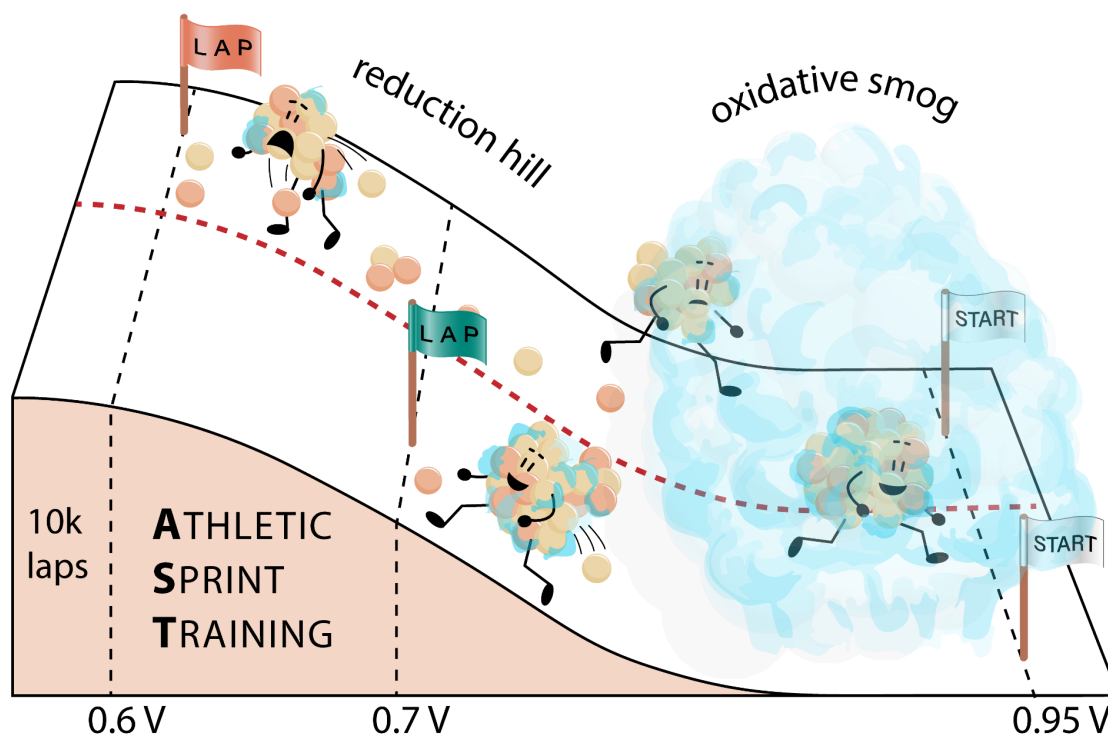
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Abstract

Octahedra (oh) PtNiX/C catalysts are notable cathode catalysts for proton-exchange membrane fuel cells due to their exceptional oxygen reduction reaction activity. Here, we investigate the degradation of oh-PtNiIr catalysts in fuel cell conditions using operando X-ray diffraction (XRD). Employing two accelerated stress tests with different lower potential limits and XRD-coupled cyclic voltammetry on benchmark Pt and oh-PtNiIr catalysts, we find that dissolution and degradation are proportional to the extent of reduction, independently of the catalyst's nature. Our method identifies the optimal potential range for Pt-based catalysts to minimize degradation without lengthy stress tests.

Keywords: PEMFC catalyst, degradation, voltage control, dissolution by reduction, operando X-ray diffraction, octahedra, Pt-alloys



A hydrogen economy is becoming integral to transitioning to a carbon-neutral future as we try to reduce our carbon footprint. Given the critical role of noble metals for Oxygen Reduction Reaction (ORR) catalysis, much research has been dedicated to improving the catalytic activity of Pt by modifying its electronic and structural properties via Pt alloying with transition metals (Co, Ni, Fe)^{1,2}. In 2007, Stamenkovic et al. identified the most active surface: Pt₃Ni(111), which led to the development of PtNi octahedra nanoparticles (NPs) with 10-fold mass and area-specific activity gain in the rotating disc electrode (RDE) configuration, due to maximizing the surface availability of PtNi(111) facets^{1,3,4}. However, transferring the activity measured in RDE experiments to a proton-exchange membrane fuel cell (PEMFC) and reaching stability targets remains a significant challenge for many of the highly active PtNi binary and ternary catalysts in the shape of nano-frames and octahedra⁴.

Several challenges remain in transposing the phenomenal activity and durability reported in wet electrochemical cells of alloy catalysts to real devices. Octahedra (oh) NPs (5-8 nm) have a smaller electrochemical surface area (ECSA) than commercial 2-3 nm Pt catalysts, but at the same time, the rate constant for the ORR is at least 10 higher than Pt. Thus, octahedra must accommodate and withstand a larger current per nanoparticle at constant loading to produce the same overall current at a given voltage. As a result of the higher Turn Over Frequency (ToF) for the ORR, (oh) alloy NPs have higher water concentration in the vicinity of the catalyst. This can lead to local oxygen starvation due to inhibited oxygen diffusion to the NP surface. In addition, accommodating increased current density (per nanoparticle) requires a well-structured boundary that allows not only sufficient oxygen diffusion but also good proton and electron conductivity⁵.

Besides the problems described above, withstanding potential changes during PEMFC operation is perhaps the biggest challenge because the dissolution of nickel or platinum degrades the finely-tuned structure of oh-PtNi catalysts and thus lowers the catalytic activity. One way to stabilize the structure is to dope oh-PtNi with a small amount of additional metal such as Ir, Mo, or Rh^{6,7,8}. While this is a promising improvement, and the stability objectives are reached in the RDE configuration, performance in the membrane electrode assembly (MEA) configurations that meet the stability target following the DOE testing protocol has not been reported yet.

It is agreed that the stability is linked to the extent of Pt oxide growth and reduction, which leads to various degrees of dissolution and degradation. Up to now, much research has focused on the Pt oxidation-dissolution link. Many publications highlighted the influence of upper potential limit (UPL) in an accelerated stress test (AST), making clear that increasing the UPL increases the extent of oxidation and, in turn, the extent of dissolution^{9,10,11}. However, only a limited amount of research focused on the influence of lower potential limit (LPL)^{12,13,14}. By conducting a thorough flow cell experiment, Đukić et al. illustrated the importance of controlling the LPL to improve the PEMFC catalyst's lifetime, which they attributed to the reduction

kinetics of surface oxides¹⁵, but direct physical evidence is missing, and the actual mechanism between LPL and the stability of the catalyst in MEAs remains unknown. This is critical for the field because meeting the catalysts' activity and durability targets will enable large-scale commercial adoption of PEMFCs and the hydrogen economy.

In this work, we explore the dissolution mechanics of a PtNiIr/C octahedra catalyst (doped with $<1\%$ _{atomic} of Ir) and compare it with a reference commercial Pt/C catalyst. With a focus on LPL and reduction potentials, we investigate the linkage between the catalyst degradation and operational boundaries in 5 cm² PEMFC optimized for high-energy X-ray diffraction (XRD) measurement. The fast acquisition rate enabled by the high flux of EBS-ESRF allows tracking oxidation/reduction processes during the device operation with a high temporal resolution. We conclude that Pt and Ni dissolution is proportional not only to the extent of Pt oxidation but, interestingly, also to the extent of Pt reduction, which can depend on its kinetics.

For the experiments shown in this work, we use two types of catalyst-coated membranes (CCMs) prepared by Johnson Matthey (JM): (i) "Pt(JM)" benchmark CCM with Pt (volume weighted diameter is 2.9 nm as determined using XRD) on both cathode (0.187 mg_{Pt}/cm²) and anode (0.079 mg_{Pt}/cm²) that serves as reference material; (ii) "oh-PtNiIr" CCM with octahedra-shape (oh) PtNiIr (0.100 mg_{Pt}/cm² and 0.017 mg_{Ni}/cm²) (volume weighted diameter is 7.1 nm) at the cathode and Pt at the anode (0.079 mg_{Pt}/cm²). Loadings were measured at JM using X-ray fluorescence after spray-coating the Nafion[®]112 membrane.

We find that the oh-PtNiIr catalyst incorporated in the CCM already has a different composition from the as-synthesized oh-PtNiIr powder: Energy Dispersive X-Ray (EDX) analysis (Figure S7) shows that the oh-PtNiIr powder has an atomic Pt:Ni ratio of 2.20, whereas the as-prepared oh-PtNiIr CCM has a ratio of 6.35. This suggests that the catalyst lost 57% of its Ni atomic content during the ink-making and printing. Such a high loss of transition metal alloying element has been observed and discussed previously in the work of Gatalo and Dubau^{16,17}. It has been pointed out that the CCM-making process, together with the activation potential cycling, can alter the catalyst morphology and composition to such an extent that the catalyst is no more the same material as synthesized, questioning the common approaches to catalyst activity testing using the RDE technique¹⁸. Our results provide further evidence that this is also the case for multimetallic oh-PtNiIr.

In contrast to compositional changes, the structural changes are less noticeable in the ink-making/printing step (transmission electron micrographs in Figure 1a,b). Qualitatively, the edges of octahedral nanoparticles are less pronounced in the catalyst coated on the membrane than in the catalyst powder, indicating that loss of the octahedral shape happened to some extent. Figure 1c shows the catalyst after

10k cycles of a standard (0.6 to 0.95) V accelerated stress test (AST). At the end of life (EOL), the atomic Pt:Ni ratio is 8.33, meaning 26% of Ni atomic content leaches out. Thus, two times more Ni content dissolved during the ink-making/printing procedure compared to the AST. It is clear that serious attention must be focused on adapting the ink-making/printing procedure to retain the composition of state-of-the-art multimetallic catalysts during the MEA preparation.

From Figure 1c, we can see that Ni dissolution itself is not the only degradation mechanism. Nanoparticles also aggregate, coalesce, ripen, and carbon support corrodes¹⁹.

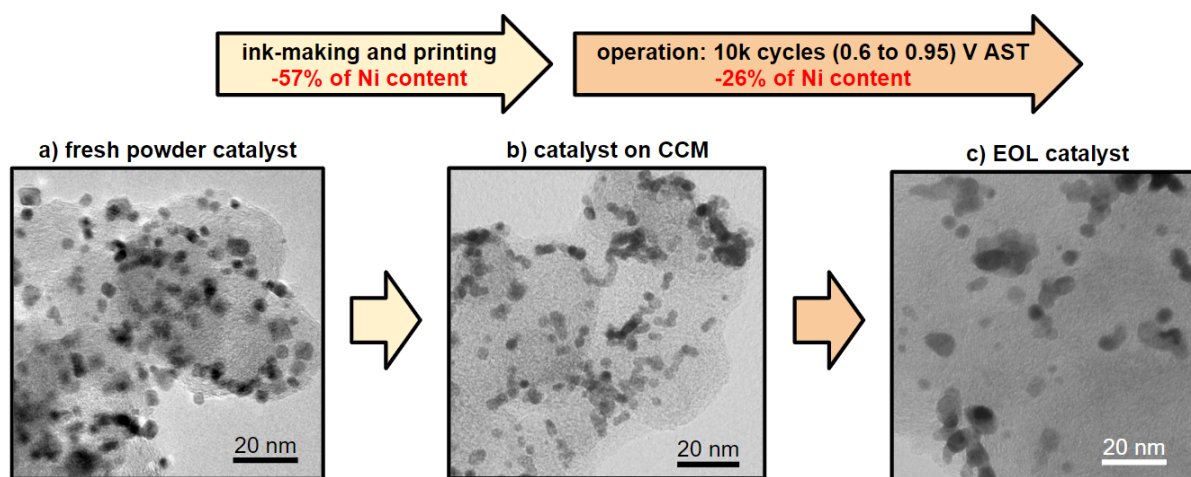


Figure 1: Transmission electron microscopy images of oh-PtNiIr catalyst at three stages: a) as-prepared powder, b) as-prepared CCM, and c) end-of-life catalyst after 10k cycles of (0.6 to 0.95) V AST. The ink-making/printing procedure leached out 57% of Ni content and made the edges of octahedra less pronounced. The AST leached out only 26% of Ni content but caused severe structural degradation.

In laboratory conditions, catalyst degradation is typically studied by square-wave accelerated stress tests. U.S. DRIVE Fuel Cell Technical Team adopted the standard of cycling from (0.6 to 0.95) V with a 3 s dwell time at both lower potential limit and upper potential limit²⁰. This test mimics the dynamics of the typical FC operation with Pt dissolution and Ostwald ripening as preferential degradation pathways^{9, 21, 22}. Even though the mechanism of Pt degradation and dissolution as a function of upper potential limit is well known^{12, 23, 24}, the exact nature of the rather surprising linkage between LPL and Pt degradation is still unclear^{12, 13, 15, 16}.

To study the effects of lower potentials on the aging of oh-PtNiIr and Pt(JM) catalysts, we perform two square-wave ASTs with different LPLs: (0.6 to 0.95) V and (0.7 to 0.95) V, hereinafter referred to as 0.6 V LPL and 0.7 LPL AST, respectively. We use a custom-built 5 cm² fuel cell operating at 80 °C, at 80% relative humidity, and flowing H₂/O₂ at 200 sccm²⁵. Both Pt(JM) and oh-PtNiIr MEAs made from as-prepared CCMs with Sigracet 22BB gas diffusion layers were conditioned at constant current densities for approximately two hours (Figure S3). The ECSA,

specific activity, mass activity, and polarization curves are in the SI (Figure S5). Throughout the 10k cycles of each AST, we follow structural changes of the catalyst with XRD (Figure S6)²⁵. In general, we obtain three parameters from the XRD analysis: scale factor, lattice parameter, and crystallite size.

1. Scale factor, i.e., scattering intensity, corresponds to the total amount of scatterers. Thus, it can be used to track dissolution. Also, Martens et al. proposed that the scale factor decreases at oxidizing potentials due to the formation of an amorphous oxide layer on Pt NPs²⁴. On timescales where dissolution is negligible, scale factor is thus a direct indicator of the amorphous oxide growth/reduction onset.
2. Lattice parameter is a global measure of strain. In bimetallic systems, the changes can be caused by dissolution, following Vegard's law²⁶, or by the evolution of surface tension due to the field effect and adsorption phenomena²⁷. Changes in lattice parameter manifest as shifts in diffraction peak positions.
3. Crystallite size is the size of the coherently scattering domain. The size of the scattering domain does not change during aggregation, but it changes during coalescence and ripening. Thus, depending on the degradation process, one nanoparticle can be composed of a few such domains²⁸. Harsher degradation leads, in general, to a more pronounced crystallite size increase.

Figure 2a shows the evolution of crystallite sizes of Pt(JM) and oh-PtNiIr throughout 10k cycles with different LPLs. The 0.6 V LPL AST is significantly harsher as the crystallite size of the NPs increases throughout 10k cycles by 42% for Pt(JM) and 30% for oh-PtNiIr, whereas in the case of the 0.7 V LPL AST by only 17% for Pt(JM), and 10% for oh-PtNiIr, respectively. The degradation and ripening of NPs are the fastest at the beginning of the AST for both catalysts. In Figure 2b, we show the evolution of the lattice parameter of the oh-PtNiIr catalyst for 0.6 V LPL AST (diamonds) and 0.7 V LPL AST (stars). Nickel dissolution is substantial in the case of 0.6 V LPL AST as the lattice parameter increases from (3.8835 ± 0.0016) Å to (3.8943 ± 0.0004) Å, corresponding to a (27 ± 2) % loss of pre-AST Ni atomic content, which is well in line with the 26% loss of Ni measured by EDX. In contrast, in the case of the 0.7 V LPL AST, Ni loss was only (3 ± 2) % from the pre-AST Ni atomic content. These observations agree with the previously reported dependency of dissolution on LPL for Pt¹² and PtCo nanocatalysts¹⁶. Although the size increase for the oh-PtNiIr catalyst is still substantial even for 0.7 V LPL AST, its resistance to Ni dissolution is greatly improved. The positive effect of increasing the LPL on the degradation extent seems to be universal and independent of the catalyst's nature (particle size, composition, electrode loading, carbon support type, etc.), even though the details (potential limits, kinetics) will be likely different for each catalyst.

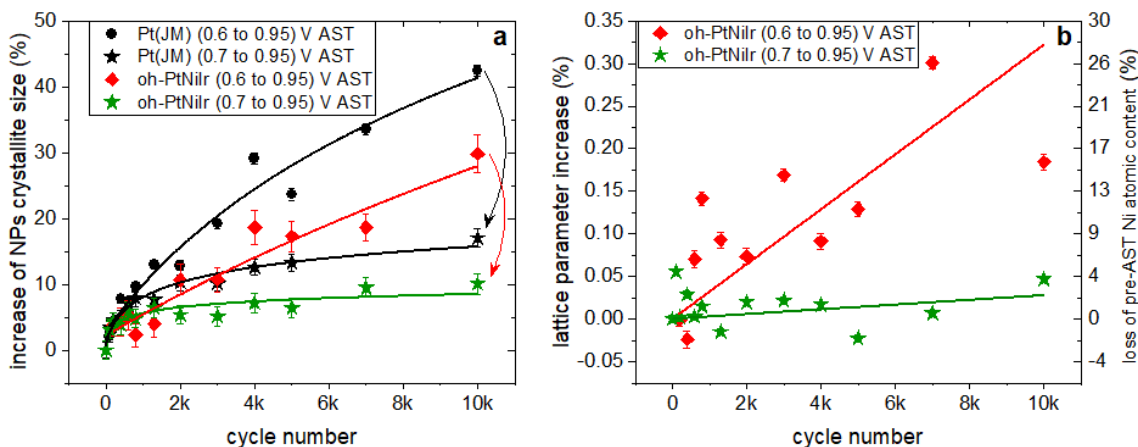


Figure 2: a) crystallite size evolution of Pt(JM) (black) and oh-PtNiIr (red/green) catalysts during 10k cycles of two square-wave ASTs. In the case of 0.6 V AST, Pt(JM) size increase is 42% and for oh-PtNiIr 30%, whereas in the case of 0.7 V AST, Pt(JM) size increase is 17% and for oh-PtNiIr 10%, lines of logarithmic function are provided to guide the reader through data points. b) lattice parameter evolution of oh-PtNiIr for 0.6 V and 0.7 V AST, a linear function was used to approximate the loss of Ni atomic content. Error bars correspond to the Rietveld fit uncertainty.

To build the connection between the LPL and dissolution mechanism, we follow the cyclic voltammetry (CV) at 50 mV/s with XRD over several cycles (XRD-CV). The top part of Figure 3 shows the evolution of scale factor (brown) for Pt(JM), while the bottom part shows the same for oh-PtNiIr. As the first CV cycle is clearly different from the subsequent ones due to impurity removal and reconstruction of the surface, only the second cycle is shown (Figure S4)¹⁸. For more details about the measurement protocol, see the experimental section in supporting information.

As expected, the Pt-O reduction region in the CV profiles is shifted towards higher potentials for the oh-PtNiIr compared to the Pt(JM) catalyst. This is a consequence of OH bond weakening, which is related to a d-band shift induced by alloying with a less noble metal. Similarly to Stamenkovic's work on single crystals, we see a negative shift of the H_{upd} region for the oh-PtNiIr catalyst with associated extension in the potential range of the double layer region with respect to Pt(JM)¹. However, assessing the actual reduction onsets just from the CV is complicated due to the convolution of multiple electrochemical processes happening on the electrode's surface (adsorption, place exchange). XRD-CV offers significant perspicuity, as the scale factor onsets directly corresponds to the place exchange, and the reversed process, causing the degradation and dissolution²⁴.

To unambiguously follow the growth of surface oxide, we start the anodic sweep at 0.05 V, where the catalyst is fully reduced (corresponding to scattering intensity of 1 a.u.). In general, the XRD scale factor follows the oxidation/reduction hysteresis

apparent in CV. It is constant up to the onset of the oxidation potential, after which it decreases until the reverse potential of 1.23 V. At the beginning of the cathodic sweep, the scale factor rests at its lowest value and starts increasing when the potential crosses the onset of the reduction potential. After passing a reduction region (highlighted in red in Figure 3), the scale factor returns close to its original value, as Pt dissolution is negligible in such a short experiment time. There is a slight slope between the end of the reduction region and 0.05 V in the cathodic sweep, pointing to the fact that the catalyst is not yet entirely reduced. A small number of catalytic sites, presumably highly oxophilic defects, are much harder to reduce, giving rise to this slope^{29,30}. Nevertheless, the reduction is ~97% complete at the end of the reduction region for both catalysts (Figure 3).

Further, there is a slight difference between both oxidation and reduction onsets for Pt(JM), but no difference is observed for oh-PtNiIr within the 0.02 V resolution limit. Note that for the Pt catalyst, Martens et al. showed the dependence of the hysteresis width on a scan rate caused by slow reduction kinetics²⁴. The oh-PtNiIr catalyst shows no scan rate dependence confirming its fast redox kinetics (see Figures S1 and S2 for more details). The discussion of the influence of catalyst parameters, such as particle size, shape, carbon type, loading, etc., on the observed profiles is in the SI. It is important to note that all the parameters have an impact on the lifetime durability of the device. Nevertheless, the important conclusion drawn from this work is that the catalyst degradation is much more affected by the extent of Pt reduction in comparison to the particle size, shape, alloying, carbon type, etc.

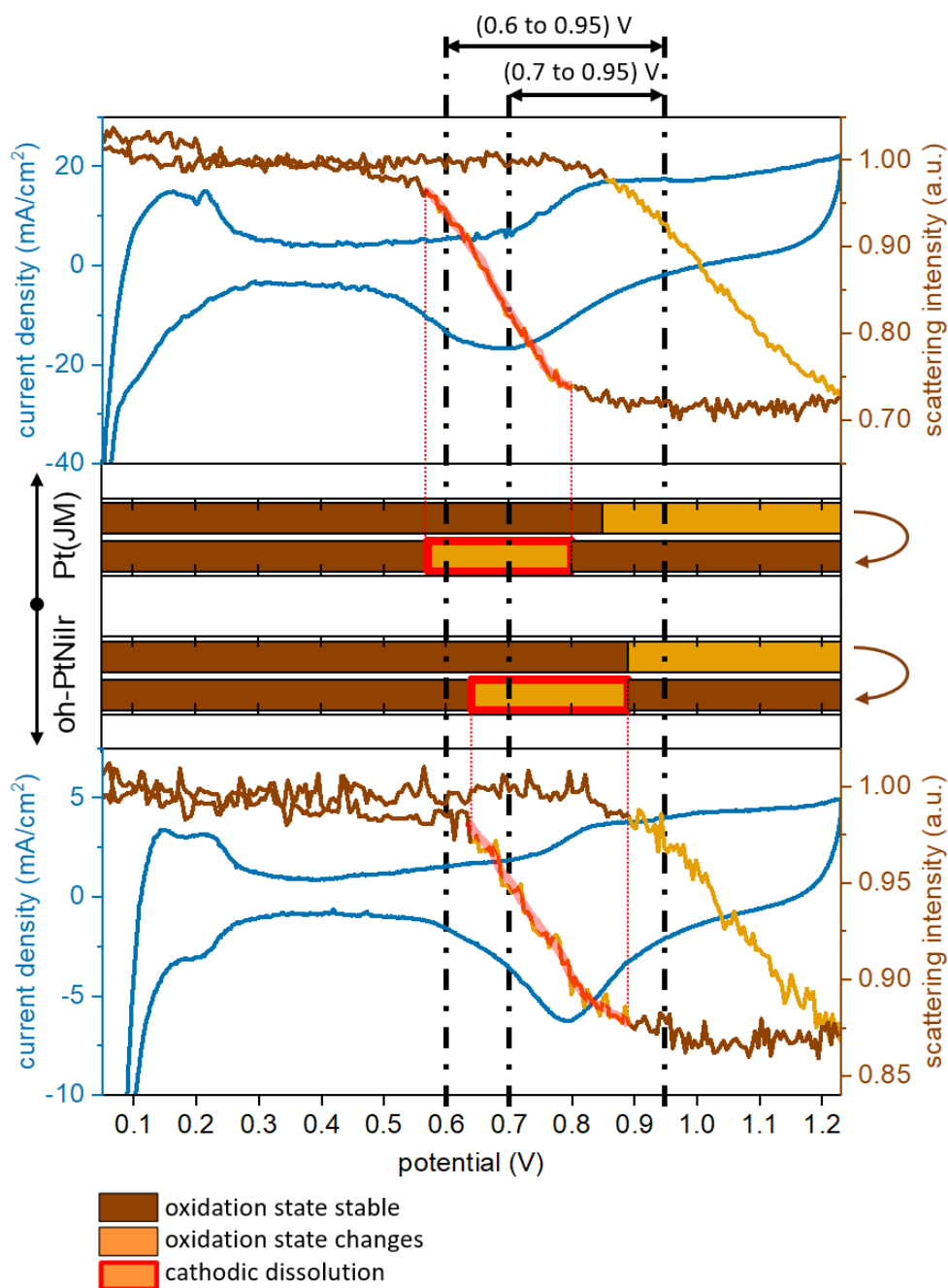


Figure 3. X-ray diffraction coupled with cyclic voltammetry. Scale factor (brown) was obtained from XRD during CV with a 50 mV/s scan rate. The upper half shows the results from Pt(JM) and the lower part from the oh-PtNiIr. The cathodic dissolution region is highlighted by a red curve that extends into a simplified diagram where the same region is highlighted by a red box. Black vertical dash-dot lines mark the potential boundaries of two types of ASTs.

Finally, we connect the degradation data from ASTs with the oxidation/reduction dynamics shown in XRD-CV. Setting the LPL to 0.6 V during AST results in a fully reduced oh-PtNiIr catalyst (the scattering intensity in XRD-CV reaches its fully reduced value), while at 0.7 V LPL, the reduction is only partial for both Pt(JM) and

oh-PtNiIr. Given that the 0.7 V LPL AST results in much less degradation, the dissolution amount must be proportional to both the degree of oxidation and the degree of reduction and it is independent of the catalyst's nature. This result also implies that the oxophilic sites that are more difficult to reduce (likely the uncoordinated sites) are stable in the oxide form but prone to dissolution once reduced. Therefore, one of the strategies to limit the dissolution is to keep those vulnerable sites permanently oxidized, e.g., by altering their electronic structure by ternary/quaternary metal doping or by increasing the LPL.

Such knowledge has a direct implication for the operation of a fuel cell, especially involving high-active shape-controlled platinum alloys. Their activity is strongly bound to a specific crystal structure, and the extent of surface restructuring during the reduction will affect this activity to a larger extent than other catalysts. In general, if we want to preserve high performance, we must carefully select the operational boundaries and limit both the lower and higher potential boundaries regardless of the catalyst type. In the automotive industry, where multimetallic catalysts will be used to lower the stack's cost, the loss in power density at higher LPL can be compensated by a more active catalyst and, thus, significantly higher current densities at lower overpotentials. Moreover, operating at higher LPLs increases FC efficiency.

In conclusion, we have shown the practicality of the XRD-CV technique to explain the degradation behavior and provided further important insight into catalyst degradation mechanisms in the operational PEMFC. We have found specific onsets of a key crystallographic parameter (scale) associated with the oxidation, reduction, and degradation of two types of catalysts. By employing two AST with different lower potential limits (0.6 to 0.95) V and (0.7 to 0.95) V, we showed a strong dependence of catalyst degradation on the lower potential limit for oh-PtNiIr and confirmed this dependence for Pt/C.


Combining these two results, we conclude that the extent of degradation is proportional not only to the degree of oxidation but also to the degree of reduction within a cycle, independently of the catalyst's nature. While other approaches (e.g., tuning of the surface composition and electronic structure) to improve stability and retain activity are important and effective at the RDE level, they are not enough, and an operational boundary has to be set on both lower and higher potential limits. Once the activity enhancement is transferred from a lab to the device, this approach will work best for automotive applications where a multimetallic catalyst reduces the stack's price, the increased exchange current density does not reduce the power density, and operation at higher voltages increases FC efficiency. We think that limiting LPL is a crucial step for implementing alloyed catalysts into PEMFCs and FC automotive as such. Moreover, the presented methodology can be further developed to serve as a benchmark measurement to explore the operation boundaries for all kinds of Pt-based catalysts.

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Notes

The authors declare no competing financial interest.

Supporting information

oh-PtNiIr faster kinetics and microstrain, the effect of catalyst parameters on observed trends scattering intensity and microstrain, experimental section, raw data references

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