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Complete List of Authors:	Yin, Xi; Los Alamos National Laboratory, Materials Physics and Applications Division Holby, Edward; Los Alamos National Laboratory, Sigma Division Zelenay, Piotr; Los Alamos National Laboratory, Materials Physics and Applications Division

Comment on "Non-PGM electrocatalysts for PEM fuel cells: effect of fluorination on the activity and stability of a highly active NC_Ar + NH_3 catalyst" by Gaixia Zhang, Xiaohua Yang, Marc Dubois, Michael Herraiz, Régis Chenitz, Michel Lefèvre, Mohamed Cherif, François Vidal, Vassili P. Glibin, Shuhui Sun and Jean-Pol Dodelet, *Energy Environ. Sci.*, 2019, **12**, 3015–3037, 10.1039/C9EE00867E.

Xi Yin[1], Edward F. Holby[2], Piotr Zelenay[1]*

[1]*Materials Physics and Applications Division, Los Alamos National Laboratory,*
Los Alamos, New Mexico 87545, USA
[2] *Sigma Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*

* Correspondence to zelenay@lanl.gov

Understanding the nature of active sites in platinum group metal-free (PGM-free) oxygen reduction reaction (ORR) electrocatalysts of the Fe-N-C type and their relatively rapid degradation during the fuel cell operation is critical for the further improvement of these electrocatalysts in energy conversion and storage. A variety of degradation mechanisms have been proposed in literature[1-4] but ongoing debate is fueled by experimental complications such as the presence of spectator Fe species, as well as the often incorrect application of proposed models and their resulting conclusions. A recent article by Zhang *et al*. published in *Energy & Environmental Science*[1] summarizes the effect of fluorination on the activity and durability of Fe-N-C fuel cell catalysts. This paper contains several essential misconceptions that weaken the validity of the conclusions drawn regarding degradation mechanisms. We feel it is important to point out what we believe to be mistakes made in this paper and make suggestions in order to help guide future studies on this topic. In particular, two main issues addressed here in detail are: (1) inclusion of non-kinetic effects in kinetic modeling and (2) inconsistencies in thermodynamics underpinning proposed degradation mechanisms.

(1) Inclusion of non-kinetic effects in kinetic modeling

Several models have been proposed to fit the experimentally determined current density decay profiles as a function of time.[1-3] The goal of such models is to gain insight into the underlying mechanism(s) responsible for the current density loss and to understand how different materials and environments affect the degradation to ultimately aid the development of strategies to mitigate Fe-N-C catalyst performance loss. As an example, we recently proposed single-parameter models based on first-order (exponential) and autocatalytic (logistic) decays for capturing the decrease of current density in the kinetic region.[2] The logistic decay model is referred to as "Los Alamos model" by Zhang *et al.*[1] In our original work, we intentionally selected a high fuel cell voltage of 0.84 V (equivalent to high potential of the cathode operation) to assure that the measured changes in current density are due to kinetic losses, *i.e.*, to assure that they can be directly tied to the losses in turnover frequency (TOF) and/or active site density (ASD). When applied to current density-time curves measured in this kinetic region, the single-parameter logistic decay model, indicative of autocatalytic degradation mechanisms, agreed significantly better with the experiment than the exponential decay model. A specific autocatalytic degradation mechanism, which involves generation of H_2O_2 at the active site through a two-electron process, was proposed to account for the activity loss.[2] H_2O_2 is a precursor for the formation of active radicals, hydroperoxyl in particular, that may be responsible for a decrease in TOF and/or ASD through attack on the active site. While the details of such an active site degradation mechanism need to be revealed in an independent study, the main finding of the single-parameter models proposed in Ref. 2 is that the autocatalytic degradation mechanism is much more consistent with the experimental data than the first-order degradation mechanism.

In their abstract, Zhang *et al.* state:

> *"It is shown that when the catalyst has active FeN_4 sites, it is the model proposed by INRS and using the superposition of two exponential decays that better fits the experimental decay, while the Los Alamos autocatalytic model is preferred when there are no Fe-based active sites in the catalyst or if the FeN_4 sites are poisoned (e.g., by fluorination as in this work)."*

We contend that it is not, in fact, a site-dependent activity loss mechanism that is responsible for Zhang *et al.*'s findings but instead that their interpretation is based on inadvertent inclusion of non-kinetic effects in the chosen data. They state, "*…Yin and Zelenay also recommend to only verify the models under low-current (high fuel cell voltage, i.e. > 0.7 V) conditions.*" This recommendation, as suggested above, is chosen such that only the regions of polarization plots where overpotentials are due to kinetic losses are considered in kinetic models of degradation. This is the region directly affected by TOF and/or ASD loss. Additional losses due to non-kinetic effects, including ohmic and mass transport losses, should not be part of a kinetic model as additional mechanisms unrelated to TOF/ASD are certain to affect the modeling outcomes. Based on this stated criteria, Zhang *et al.*'s choice of using current density data at a fixed 0.6 V cell voltage for all materials is only appropriate for certain low-activity materials (those with "*no Fe-based active sites*" and "*sites that are poisoned*") but not for others (catalysts with "active FeN_4 sites"). This conclusion is incorrect. Consideration of Zhang *et al.*'s Fig. 3 provides an ideal example of how their dataset explicitly includes both kinetic and non-kinetic contributions to overpotential. We took the liberty of replotting as accurately as possible the *iR*-free voltage data from Zhang's *et al.*'s Fig. 3 versus the logarithm of current density (**Figure 1** below) to determine in which cases fuel cell performance at 0.6 V of catalysts studied by Zhang *et al.* was kinetically controlled and in which cases it was not. The linear portions of these Tafel plots (exemplified by the added solid lines in **Figure 1**) represent the kinetically controlled regions for each catalyst and environment, wherein the catalyst (electrode) performance, once corrected for *iR*-losses, depends solely on electrocatalytic activity of the catalysts in oxygen reduction reaction (with anode losses assumed to be negligible thanks to the very high rate of hydrogen oxidation reaction at the Pt catalyst). Therefore, within these linear regions, ORR kinetics are the dominant contribution to overpotential. Beyond these linear regions, additional sources of overpotential such as mass transport start to contribute, often significantly, causing the deviation from the linearity observed in the curves of **Figure 1**. It is clear that at 0.6 V, the F20min-NC in (a) and the F2min-NC in (b) are in the linear, *i.e.*, kinetically controlled region and that the NC catalysts in (a) and (b) are in the non-linear regions. This simple Tafel test confirms that of the four cases depicted in **Figure 1**, the performance of NC catalyst at 0.6 V on both air and oxygen is not solely controlled by the ORR kinetics and thus not entirely dependent upon the active sites, their number and electrocatalytic activity. The contribution of non-kinetic effects to the measured currents is significant in these two cases, making them inadequate for kinetic modeling of active site degradation.

Not surprisingly given the results discussed above, Zhang *et al.* find that when tested at a higher cell voltage (consistent with the kinetic region) "*...the Logistic model of Los Alamos is able to fit the current decay curve of a catalyst like NC at 0.8 [V]"*. Thus, the statement in Zhang *et al.*'s abstract implying that the Los Alamos logistic model is not applicable to materials with FeN_4 sites has more to do with their inclusion of non-kinetic losses at 0.6 V in the higher activity materials than any issue intrinsic to the Los Alamos model. Furthermore, when considering cases where properly applied to kinetic data, Zhang, *et al.*, suggest the single-parameter Los Alamos model works well for capturing activity losses.

In contrast to the single-parameter Los Alamos models, the INRS double exponential-decay model uses four parameters. These additional parameters produce a model that is applicable to all current decay data recorded with NC catalyst in the voltage range from 0.8 V to 0.2 V (see Figs. 10D and S13 in Ref. 1, and Figs. 8 and S14-S19 in Ref. 3). Applicability of the INRS model to both kinetic and non-kinetic data implies its "over-parameterization", which renders a model of limited value in interpreting catalyst degradation mechanism. By definition, kinetic models should focus on the purely kinetic part of the catalyst decay curve, free of any non-kinetic complications. Only then can a model provide ambiguity-free insight into the catalyst degradation mechanism, typically reflected by a drop in the TOF and/or ASD values. As highlighted by the examples in Ref. 1 and **Figure 1**, the particular ranges of the kinetic region can be catalyst-dependent, something that must be considered when applying kinetic models of degradation.

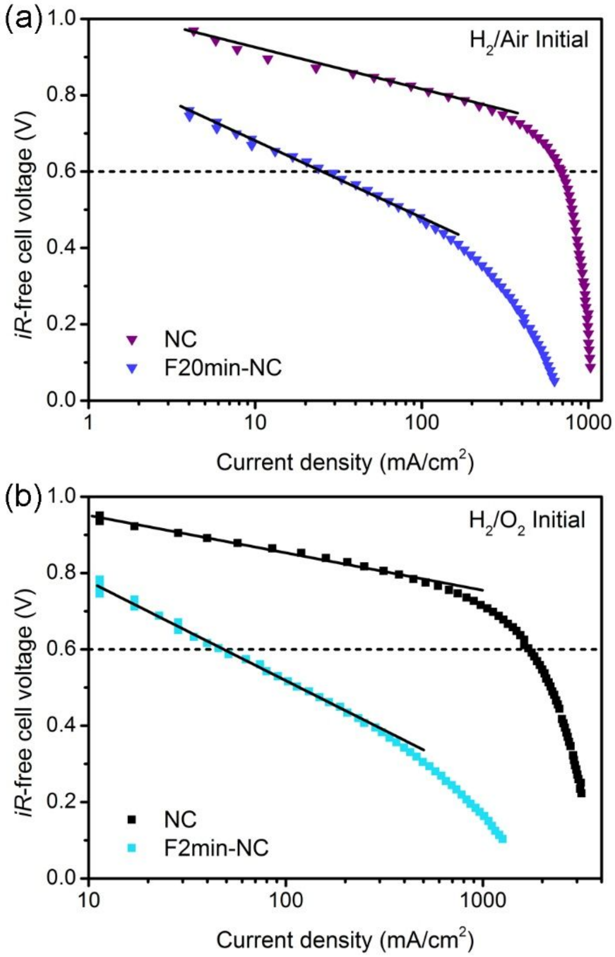

Figure 1. Zhang *et al.*'s[1] initial polarization curves at 80 °C in (a) H_2-air and (b) H_2-O_2 fuel cells recorded with NC catalyst and fluorinated NC catalysts (F2min-NC), showing *iR*-free cell voltage and current density in logarithmic scale (Tafel plots). A high-frequency resistance of 0.07 Ω cm^2 was used for the Nafion^{TM} 211 membrane when estimating *iR* loss. The solid sloped lines indicate

the kinetic controlled region of the curves. The position of linear fragments of the Tafel plots relative to 0.6 V (cell voltage chosen by Zhang *et al.*, marked with a dashed line) indicates that kinetic data is being used for the fluorinated catalyst but that additional sources of loss (*e.g.*, mass transport) affect the NC catalyst data.

(2) Inconsistencies in thermodynamics underpinning proposed degradation mechanisms

A key feature of the INRS interpretation[1] is that variations in concentration of dissolved Fe^{2+} dictate which active sites are stable over long time periods (attributed to mesopore-hosted sites) and which dissolve rapidly (attributed to micropore-hosted sites). By invoking Le Chatelier's principle, this work suggests that the local Fe^{2+} concentration stabilizes the micropore-hosted FeN_4 active sties. In their previous work,[3] the INRS group states "*Fe–*N_4*-like active sites are thermodynamically stable in stagnant acidic conditions*". This statement is based on a previously published INRS/University of Western Ontario (INRS/UWO) model[5] that does not explicitly contain Fe^{2+} concentration dependence but implicitly applies a 1 M Fe^{2+} concentration. This concentration is likely well above what is possible in an open fuel cell system where, as suggested in Zhang *et al.,*[1] Fe^{2+} will "*exit with excess water*" or diffuse to lower potential regions where the ions may plate out as metal or metal-compound particles.[6] In addition, we believe that the INRS/UWO dissolution enthalpy model (Eqn. 4 in Ref. 5) is missing one of the largest energetic contributions, the Fe cohesive energy. We outline this issue in detail below but believe the underlying assumption, that carbon hosted FeN_4 sites are stable in acid, is false without the addition of stabilizing ligands. Thus, it is our opinion that the interpretation of Le Chatelier's principle controlling two separate dissolution rates between non-ligated FeN_4 micro/mesopores does not accurately capture the full process of active-site-metal dissolution in PGM-free systems.

The INRS/UWO Fe dissolution model is presented in Ref. 5. In this model, the authors posit a dissolution reaction mechanism that includes dissolution of the Fe at the center of the proposed active site, becoming a dissolved 2+ ionic species. Subsequently, protons from the acidic environment bond to the cavity left by Fe dissolution. Combined, these are expressed as the reaction in **Equation 1** below (also Eqn. 1 in Ref. 5):

$$FeN_4[R]_s + 2H^+_{aq} \leftrightarrow Fe^{2+}_{aq} + H_2N_4[R]_s \qquad [1]$$

This approach is convenient in that the two reacting protons balance the charge of the ionic Fe product, meaning the reaction is independent of potential (no electrons as reactants/products), but no other rational is provided for why this should be the generalized dissolution reaction. This is particularly important given reports of potential-dependent Fe dissolution rates in similar systems.[7] Dissolution reaction free energies are broken into enthalpy, entropy, and heat capacity contributions, allowing for careful consideration of temperature impacts on the dissolution reaction.

The enthalpy model (Eqn. 4 in Ref. [5]) is shown in **Equation 2**:

$$\Delta_r H^0_{298} = \left[\Delta_f H^0_{298,Fe^{2+},aq} - 2 \times E_{N-H}\right] - \left[2 \times \Delta_f H^0_{298,H^+,aq} - 4 \times E_{Fe-N}\right] \qquad [2]$$

Here, binding energies of Fe-N and N-H, represented by *E* values, serve to quantify enthalpy changes for the bond-breaking contribution for Fe dissolution and bond-making contribution for H binding, respectively. To critically evaluate such a model, four enthalpy states of Fe must be considered, as shown in **Figure 2**. The $\Delta_f H^0_{298,Fe^{2+},aq}$ term, taken from Naumov *et al.*[8] gives the enthalpy difference between the Fe at its reference state (bulk α-Fe metal, Fe enthalpy state 1) and the Fe^{2+} ion at a 1 M concentration (Fe enthalpy state 2). The enthalpy of the $N_4[R]_s$ cavity left from dissolution can be added to both while still maintaining the relative enthalpy relationship which has been done to states 1 and 2 in **Figure 2** for consistency between states and mass conservation. The combined Fe-N binding energies, $4 \times E_{Fe-N}$, relate the enthalpy difference between Fe in $FeN_4[R]_s$ (Fe enthalpy state 3) and a free Fe atom with the resulting $N_4[R]_s$ cavity prior to protonation (Fe enthalpy state 4. A correct enthalpy model would give the enthalpy difference between the product (Fe^{2+} + $N_4[R]_s$ cavity) state 3 and the reaction ($FeN_4[R]_s$) state 2, as shown by the blue line in **Figure 2**. The INRS/UWO model gives the enthalpy change from state 3 to state 4 using the Fe-N bond breaking model, shown as a yellow line in **Figure 2**. State 4 is assumed based on the use of a Fox and Martin relation,[9] as well as the conventional use of the term binding energy. Transition from state 1 to state 2 is given using the reference dissolution enthalpy of Naumov *et al.,*[8] the red line in **Figure 2**. Clearly, for the complete reaction using these values, state 4 must be linked to state 1, which is the Fe cohesive enthalpy represented by the green line in **Figure 2.** This lack of cohesive enthalpy explains the anomalously low enthalpy changes predicted by the INRS/OWU model of plus/minus a few kJ/mol for all ligand-free FeN_4-like structures considered. A previous report of the Fe cohesive energy (dominated by enthalpy contribution)[10] gives a value of ~413 kJ/mol, several orders of magnitude bigger than the total calculated reaction enthalpy (lacking cohesive energy) reported in Ref. 5, Table IV. Using the $FeN_4C_{20}H_{12}$ structure and the INRS/UWO reaction of their Eqn. [10] as an example, the reported enthalpy change of the dissolution reaction is -1.0 kJ/mol and entropy change of -124.8 J/(mol K). At 298 K, the free energy change of the reaction is 36.2 kJ/mol, in agreement with the reported equilibrium constant of 4.5 10^{-7}. Thus, despite the favorable enthalpy for dissolution, the entropic contribution drives the free energy of reaction to be positive, effectively stabilizing the site from dissolution as explained in Ref. 5. Note that the enthalpy of dissolution for bulk Fe (the metallic phase most utilized in Pourbaix diagrams considerations) to Fe^{2+} is given as -92.5 kJ/mol in the INRS/UWO Table 1, suggesting the FeN_4-based sites are more stable than bulk metallic Fe. If the cohesive energy is added to the enthalpy, the -1.0 kJ/mol goes to *ca.* -414 kJ/mol and the additional entropy effects are no longer enough to stabilize the site at relevant temperatures, yielding a net thermodynamic driving force for Fe dissolution. This is true of all sites, ligated and non-ligated, and temperature ranges considered in the INRS/UWO work. Thus, this change in enthalpy is more than enough to alter the "*main conclusion of this work [...] that all evaluated Fe-based active or poisoned sites are chemically stable in [1 M] acid at both 298 and 353 K.*" [5]

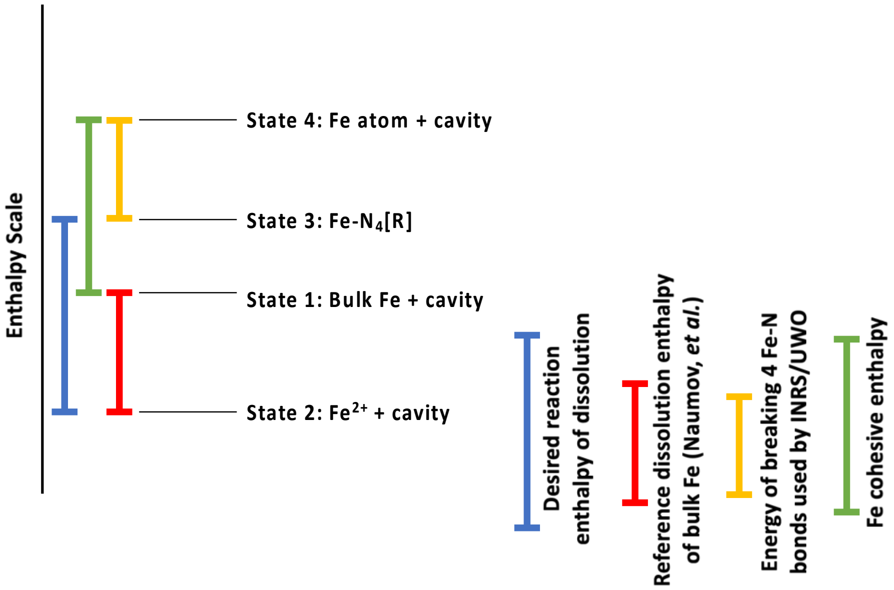

Figure 2. Proposed enthalpy relations between four Fe states relevant to dissolution models.

While Le Chatelier's principle is invoked in Ref. 1 to describe why some sites are stable and others are not, this explanation is no longer consistent if Fe-sites are not stable, even at very high ionic concentrations. Why then is the loss of ORR activity not exceedingly rapid, causing near instant activity decay? We hypothesize that a ligation effect prevents the rapid dissolution of FeN_4-like sites at fuel cell cathode-relevant pH and potentials. Previous work has shown that spontaneous ligation is important for producing active sites with high ORR activities.[11-13] A DFT-based model, which extends well-established methods for Pourbaix diagram generation[14] to FeN_4 structures and includes potential-dependent dissolution reactions provides further insight and justification for this ligation hypothesis, suggesting that OH ligation does in fact stabilize FeN_4-based sites against dissolution at low pH.[15] In agreement with the above analysis, using the INRS/UWO model when corrected for cohesive energy, this approach also shows that FeN_4 readily dissolves in acid, even at the unrealistically high Fe^{2+} concentration of *ca.* 1 M implicitly considered in Ref. 5. Ligated FeN_4 sites, however, are shown to be stable over a wide range of fuel-cell-relevant pH values, potentials, and Fe^{2+} concentrations.

In summary, we believe that several previous studies, including the one by Zhang *et al.*[1] commented on here, have made the following errors in their mechanistic models:

- applying non-kinetic data to kinetic models;
- overparameterizing models in order to fit with non-kinetic data and therefore misinterpreting the degradation mechanisms;
- incorrectly referencing thermodynamic models leading to what we calculate to be an incorrect assumption that bare FeN_4 sites are stable in acid media at temperatures and ionic concentrations (Fe^{2+} and H^+) relevant for fuel cell and rotating ring-disk electrode experiments.

As the field of PGM-free electrocatalysts matures, it is important to directly address stability issues and while we applaud the focus area of research by Zhang *et al.*,[1] we would also like to highlight the complexity of kinetic modeling of degradation processes and the importance of both clarity and proper model application to current and future researchers. Errors made now can perpetuate and lead to incorrect underlying assumptions which in turn can divert the entire field of research. We hope that the community finds these points to be constructive in guiding future active-site durability studies.

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