

**Supporting Information for:**

***In-situ* Anomalous Small-Angle X-Ray Scattering Studies  
of Platinum Nanoparticle Fuel Cell Electrocatalyst  
Degradation**

James A. Gilbert<sup>1</sup>, Nancy N. Kariuki<sup>2</sup>, Ram Subbaraman<sup>2</sup>, A. Jeremy Kropf<sup>2</sup>, Matt C. Smith<sup>2</sup>,  
Edward F. Holby<sup>1†</sup>, Dane Morgan<sup>1</sup>, and Deborah J. Myers<sup>2</sup>

<sup>1</sup>Department of Materials Science and Engineering University of Wisconsin-Madison, Madison, WI 53706

<sup>2</sup>Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL 60439

## Discussion on Absolute Loss of Pt

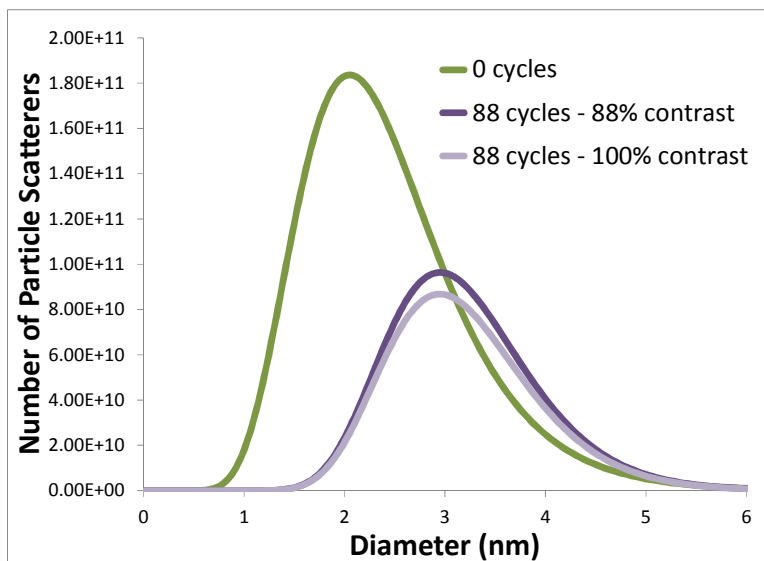
The absolute Pt loss rates are approximately two orders of magnitude higher ( $10^{-9}$  versus  $10^{-11}$  g/cm<sup>2</sup>-cycle) for the loss rates calculated from the ASAXS-determined change in PSDs when compared with the ICP-MS loss rates. It is believed that this discrepancy most likely originates from an inability to know the precise changes in the X-ray scattering contrast, used in the fitting of the intensity of the normalized ASAXS data, over the duration of each experiment. The scattering contrast is the difference in the scattering factors of the Pt nanoparticles and the background (everything else in the X-ray beam path). An overestimation of the contrast leads to an underestimation of the total volume of Pt, directly corresponding to an underestimation of the amount of Pt within the path of the X-ray beam. A decrease in the scattering contrast over the course of the ASAXS experiments would thus result in higher apparent Pt loss rates. It was found that a decrease of only about 12 to 15% in the scattering contrast over the duration of the experiments would be sufficient to account for the observed orders of magnitude difference in the Pt loss rates.

This decrease in contrast over the duration of the experiments could be a result of dissolution of Pt from the Pt particles into the surrounding perfluorosulfonic acid ionomer and/or electrolyte. Even the smallest amounts of Pt incorporated into the background scattering can have an effect on the scattering contrast because Pt has a significantly higher electron density than any of the other species in the scattering background. It was calculated that at an energy of 11.5 keV, approximately a 5% reduction in the scattering contrast could occur with binding of Pt to all the sulfonic acid groups in the ionomer and from the increase in electron density of the electrolyte at the concentrations of dissolved Pt determined from ICP-MS. This 5% reduction still does not completely account for the Pt loss rate discrepancies between the ASAXS and ICP-MS results. However, this analysis does show that large errors in the ASAXS-determination of the amount of Pt can result due to deviations in the background over the duration of the experiment if care is not taken to correctly account for the changes in scattering contrast.

Another possible source of a change in the contrast but whose impact wasn't specifically calculated is a build-up of oxide on the Pt nanoparticle surfaces with potential cycling. The ASAXS data was collected at a potential of 0.4V where Pt surfaces have been shown to be oxide-free.<sup>1,2</sup> However, it is possible that oxygen on the more stable surface sites (e.g., low-coordinated edge and corner sites) could still be adsorbed. This and other possible sources that could account for the contrast change are still being investigated as part of other *in-situ* ASAXS studies on electrocatalysts.

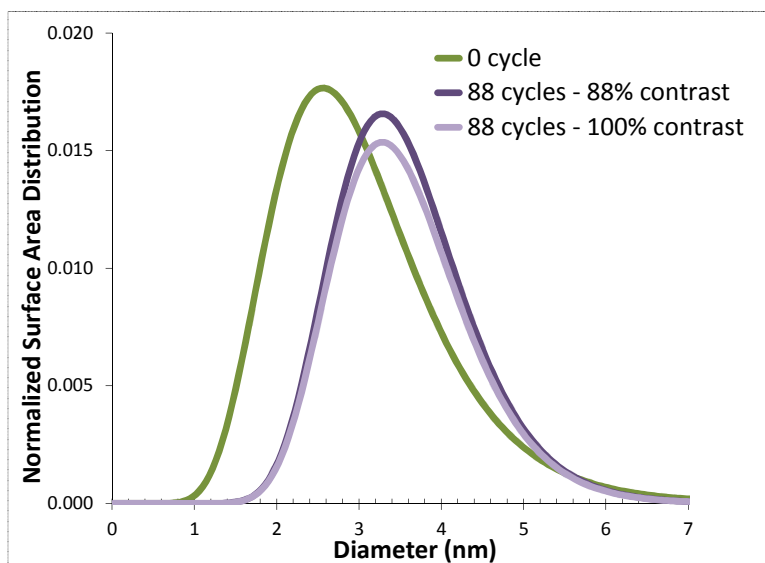
The discrepancy between the ASAXS and ICP-MS Pt loss rates only has a minimal impact on the results of this study. Figure S1 shows the small difference in the final PSDs when fitting the ASAXS data using the same contrast as used in fitting the initial PSD and using a contrast of 88% of that used in fitting the initial PSD for Square-1.1. The former represents the situation where there is no change in contrast during the potential cycling experiment and the latter represents the situation where a change in the contrast over the

duration of the experiment would be sufficient to adjust the ASAXS-determined Pt loss rate to match that measured through ICP-MS. This difference between fitting the data with the same contrast and fitting the data with a change in the contrast has no impact on the mean diameter results and trends and only results in a small change in the total number of scatterers, as shown in Fig. S1. This change in scatterer count would only minimally impact the critical diameter results (a reduction by  $\sim 0.1$  nm) and the GSA loss results (a reduction by 2 to 5%). Furthermore, because the contrast would be reduced over the duration of each of the experiments these errors would shift the values in the same direction leaving the relative trends between the experiments intact.



**Figure S1.** PSD of Square-1.1 before cycling (0 cycles) and the PSD after 88 cycles as fit from the ASAXS data using the same contrast as the initial PSD (100% contrast) and using a contrast of 88% of the initial contrast (88% contrast).

Figure S2 shows an analogous relatively small difference in the normalized GSAs between the different contrast values used in the ASAXS fitting as compared to the PSDs in Fig. S1 for Square-1.1. The 88<sup>th</sup> cycle of Square-1.1 was used in this analysis as it is the last cycle of one of the two experiments with the most observed degradation and it can be directly related to the measured Pt loss rate. Therefore, among all our experiments, this case represents a situation where the greatest reduction in contrast over the duration of the experiment was likely to occur.



**Figure S2.** GSA of Square-1.1 before cycling (0 cycles) and the PSD after 88 cycles as fit from the ASAXS data using the same contrast as the initial PSD (100% contrast) and using a contrast of 88% of the initial contrast (88% contrast).

In summary, Pt loss rates as determined through ASAXS and ICP-MS were found to differ by two orders of magnitude. This deviation can potentially be explained by a change in the scattering contrast between the Pt nanoparticles and the background over the duration of the potential cycling experiments. The change in scattering contrast was not available from the experimental data, resulting in an unknown trend of change over the duration of the experiments. Therefore, all reported results were obtained by using the initial contrast in all fitting of the ASAXS data. This leads to a small but systematic error in some of the results but leaves the overall trends and conclusions of these findings intact. Future studies will explore the source of the proposed change in scattering contrast.

## References

- 1) Imai, H.; Izumi, K.; Matsumoto, M.; Kubo, Y.; Kato, K.; Imai, Y. *Journal of the American Chemical Society* **2009**, *131*, 6293.
- 2) Teliska, M.; O'Grady, W. E.; Ramaker, D. E. *Journal of Physical Chemistry B* **2005**, *109*, 8076.