

Supplementary Material

In this work we made no particular effort to study the details of the white line intensity of the XANES. Our aim in Figure 3a is to show that the Pt local environment of the in-situ catalyst is metallic. This supplementary section summarizes effects that contribute to the white line intensities of the Pt L₃ edge XANES. In particular, these effects have to be taken into account while comparing the XANES of in-situ catalyst (solid grey line) with XANES of Pt foil (solid black line). The observed small reduction in the white line intensity for the in-situ catalyst can be attributed to:

1. Uncertainty due to normalization of x-ray absorption coefficient

Figure A1 shows variation of the normalized Pt L₃ XANES with beginning (E_{\min}) of the normalization range. The choice of normalization range affects the slope and position of the post-edge line. The resulting normalized spectra are somewhat attenuated as E_{\min} moves to higher energies. We expect that the observed reduction in the white line intensity of the in-situ catalyst (Figure 3a) is on the order of the uncertainty due to background subtraction as illustrated in Figure A1. Minimization of this error requires identical conditions for absorption of x-rays. However, this identity is rarely attained for samples of the same element having different properties such as thickness. For example, the absorption edge jump for the Pt foil standard is about 10 times greater than the one of the catalyst. Clearly, total x-ray absorption is different in these two cases which implies that optimal assignment of normalization range for data processing is not necessarily identical.

2. Repeatability of the in-situ x-ray absorption experiment

There are other factors contributing to the total x-ray absorption such as those related to the experimental arrangement. These factors are mostly reproducible from one experiment to another. However, there could be differences in catalyst coverage, fuel cell flow field, intensity of the incident x-rays, x-ray detector sensitivities and linearity, etc. Repeatability of the in-situ DMFC x-ray absorption experiment was reported in the previous work on JM PtRu.¹ Figure 2A adapted from that publication shows a minor difference in the Pt L₃ white line of the JM PtRu catalyst under in-situ conditions in two different experimental runs (red and orange lines). This variation is again on the same order of magnitude.

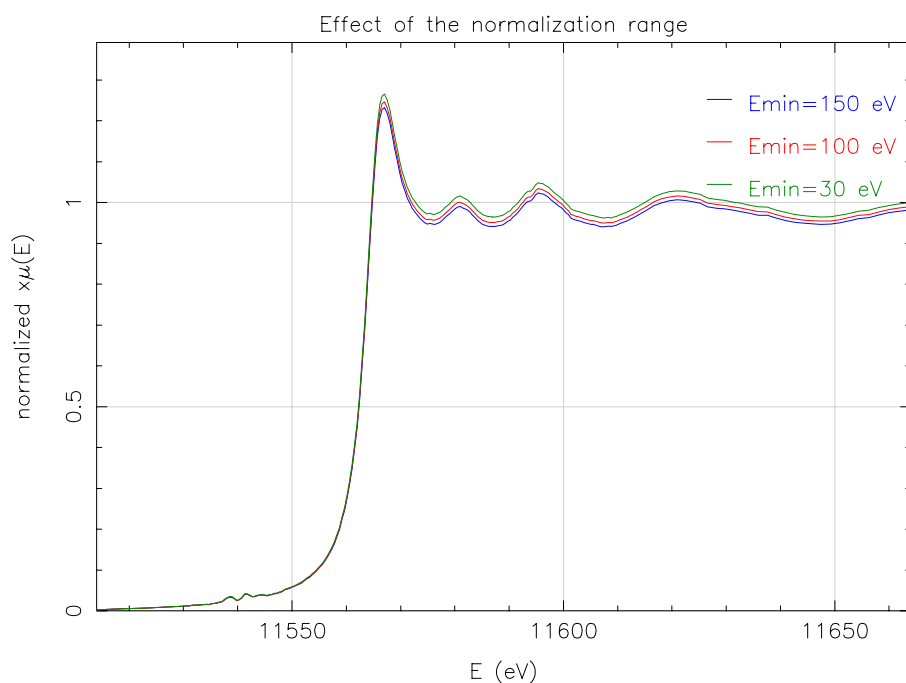


Figure A1. Variation of normalized SC PtRu Pt L₃ XANES with beginning of the normalization range (E_{\min}).

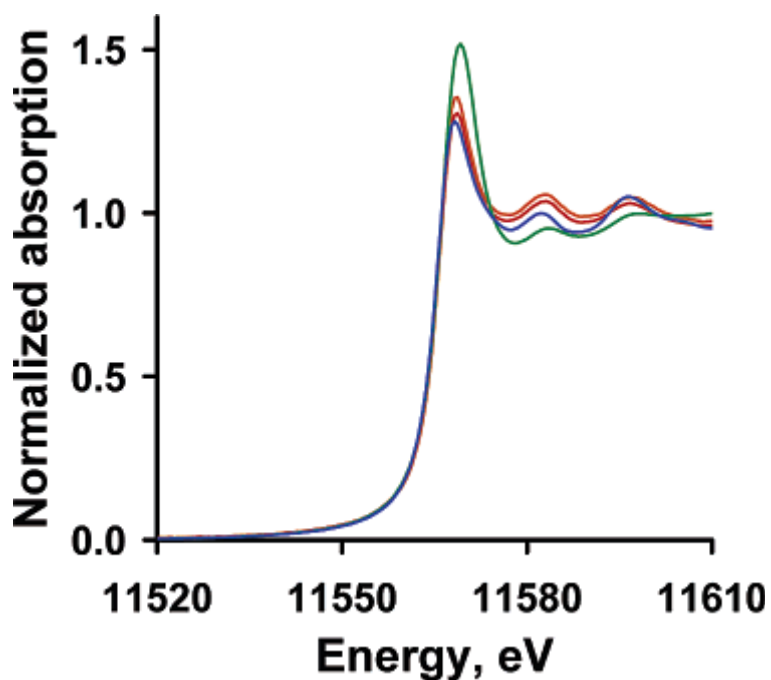


Figure A2. Pt L₃-edge XANES of JM PtRu catalyst: in-situ catalyst at 450 mV (red), in situ catalyst at 450 mV from another run (orange), as-received catalyst (green) and Pt foil (blue).

3. Size effect on the white line intensity

An increase in the white line intensity of a nanoparticle XANES vs XANES of bulk standard is usually attributed to partial oxidation due to high surface area and alloying effects. In our case Pt is fully reduced. Therefore, an increase in the white line intensity would indicate reduction in the d band population due to PtRu alloying.

A small reduction in the white line intensity for the SC PtRu catalyst in comparison to the Pt foil (black solid line) may also reflect the fact that electronic structure of the nanoparticles is different from the bulk. Bazin et al. emphasize a size effect on the white line intensity in addition to charge transfer such as due to PtRu alloying.^{2, 3} Although the size effect is shown to be significant only for very small clusters (less than 50 atoms), it is clear that surface morphology of a high dispersion catalyst can affect the white line intensity (i.e. the white line intensity is not necessarily a monotonic function of particle size). In fact, we observed a small reduction in the white line intensity of a pure Pt nanocatalyst in the reducing methanol environment vs. Pt foil.

In our previous work the effect of alloying was apparent from the observed increase in the Pt L₃ white line of JM PtRu catalyst in comparison to the Pt foil (Figure A2). The reduction in the white line intensity observed in this work may be due to the SC PtRu catalyst having much less Ru in the crystalline phase and a different surface morphology.

References:

1. S. Stoupin, E.-H. Chung, S. Chattopadhyay, C. U. Segre and E. S. Smotkin, *Journal of Physical Chemistry B*, 2006, 110, 9932-9938.
2. D. Bazin, D. Sayers, J. J. Rehr and C. Mottet, *J. Phys. Chem. B*, 1997, 101, 5332-5336.
3. D. C. Bazin, D. A. Sayers and J. J. Rehr, *J. Phys. Chem. B*, 1997, 101, 11040-11050.