

Supplementary Information

Particle Size Distribution Normalization:

Two types of PSD normalizations are considered in the text, normalized and mass normalized. In the normalized PSD case, the distribution is scaled such that the integral of the PSD function with respect to radius equals one ($\int_0^{\infty} PSD(r) dr = 1$). In the mass normalized case, the distribution is scaled such that the PSD yields the correct Pt mass on the support at that given time ($\int_0^{\infty} PSD(r) \frac{4}{3} \pi r^3 \rho_{Pt} dr = M_{Pt}$), where ρ_{Pt} is the density of Pt and M_{Pt} is the Pt total mass on the support). The normalized PSD is useful for viewing PSDs on the same scale while the mass normalized PSD is useful for assessing how much mass is on the support.

Concentration Profiles

The mechanisms of surface area loss can be further elucidated by directly observing the Pt concentration profiles in the electrolyte. Figure S1 shows representative Pt^{2+} concentration profiles with and without crossover H_2 from the PEMFC anode. Figure S1a shows a sloping concentration profile that goes to zero at the Pt sink. The slope implies that Pt^{2+} is being continually drawn away from the surface, which is consistent with the ESA loss being dominated by mass loss in the presence of crossover H_2 . Figure S1b shows nearly constant concentration profile with a concentration value almost four orders of magnitude higher than the concentration in the presence of H_2 . The higher concentration of Pt^{2+} close to the cathode surface is consistent with the ESA loss

being dominated by coarsening in the absence of crossover H_2 . It might seem that the much higher concentration of Pt in solution in the absence of H_2 would correspond greater amounts of Pt mass loss. However, the total Pt stored in the solution is much smaller than that precipitated by crossover H_2 at the Pt sink and much smaller than typical Pt loadings. For example, for the 5000h constant hold simulation described in Figure 4, the initial Pt loading of the cathode 0.4 mg. The total Pt in solution after aging in the absence of H_2 is 2×10^{-5} mg. In the presence of H_2 the total amount in solution after aging is 2×10^{-9} mg but the total amount precipitated at the Pt sink is 0.3 mg. Therefore, it is only through the Pt sink that a significant fraction of the Pt is removed from the support.

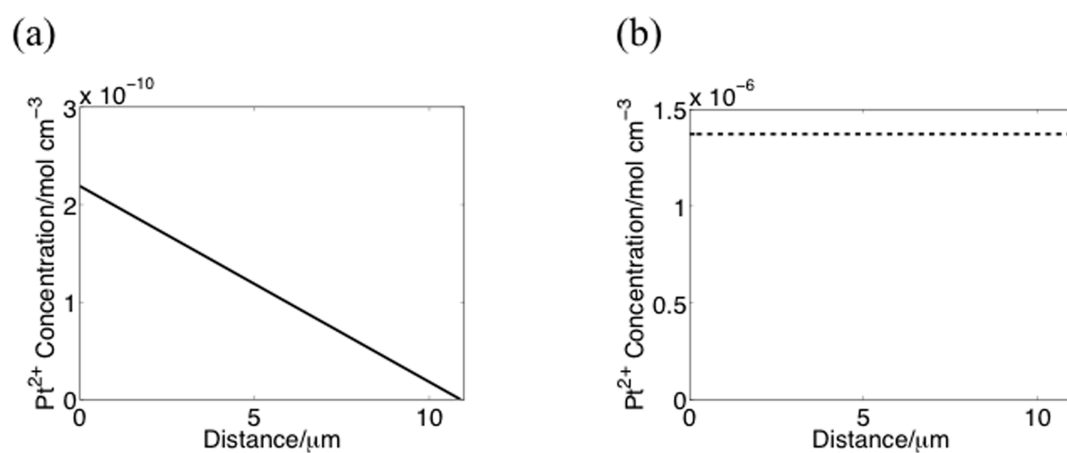


Figure S1. Concentration profiles after 5000 hrs. of 0.95V potential hold for **(a)** 2 nm distribution with crossover hydrogen **(b)** 2 nm distribution without crossover hydrogen. Note the vertical scales of the plots differ by roughly 4 orders of magnitude.