

ASAXS investigations of the stability of Pd-core, Pt-shell electrocatalysts for the ORR in PEMFCs

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Core-shell electrocatalysts are of interest for the oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFCs) as they have the potential to address two key concerns in development of these systems: the cost and the activity of the cathode catalyst. The traditionally used Pt-only carbon-supported nanoparticle catalysts are expensive and the slow kinetics of the ORR mean that relatively high metal loadings are required to achieve the desired performance [1]. Replacing the ‘unused’ core of the Pt nanoparticle with another metal tackles the cost issue and can have the reported added benefit of improving the activity for the ORR; however, the stability of these core-shell nanoparticles in the electrochemical environment is not well understood. [2,3]

A series of carbon-supported Pd-core, Pt-shell (referred to henceforth as Pt_{xML}/Pd/C, where x = 0.5, 1, 2 and 4 monolayers) have been prepared to investigate the role of shell thickness on the activity of such materials in the electrochemical environment. Ex situ characterisation using high resolution TEM, EXAFS and ASAXS (ASAXS measurements conducted on B1) of the as-prepared materials has confirmed the presence of a core-shell structure. To study the stability of the core-shell nanoparticles, catalyst electrodes were subjected to potential cycling in the oxide region between 0.6 and 1.0 V vs. RHE in 1 M H₂SO₄ at 80 °C, resulting in a loss of electrochemical surface area.

To investigate the structural changes causing this loss of electrochemical area, ex situ ASAXS data was collected on the cycled electrodes at the Pt L₃ and Pd K edges. Two distances (935 and 3635 mm) were used to obtain the desired *q*-range, with the data at each edge collected at three energies at regular *f* intervals below the absorption edge (Pt L₃ edge: E₁ = 11368 eV, E₂ = 11480 eV, E₃ = 11514 eV; Pd K edge: E₁ = 24123 eV, E₂ = 24258 eV, E₃ = 24305 eV.).

Figure 1 shows the total scattering profiles (left) obtained at the Pt L₃ edge of the cycled Pt_{1ML}/Pd/C sample, with the subtracted ASAXS (right) arising from the Pt in the sample. As seen in the ASAXS measurements on the as-prepared samples carried out previously, the low concentration of the Pt and Pd in the sample, combined with the strong background scattering of the support, meant that the ASAXS effect could not be seen on the full scale of the total scattering profile, however, subtraction of *I*_{E₃} from *I*_{E₁} gives a clear scattering profile. Plotting *I*_{E₁} - *I*_{E₂} and *I*_{E₂} - *I*_{E₃} resulted in overlaying curves, thus confirming the anomalous scattering of the samples.

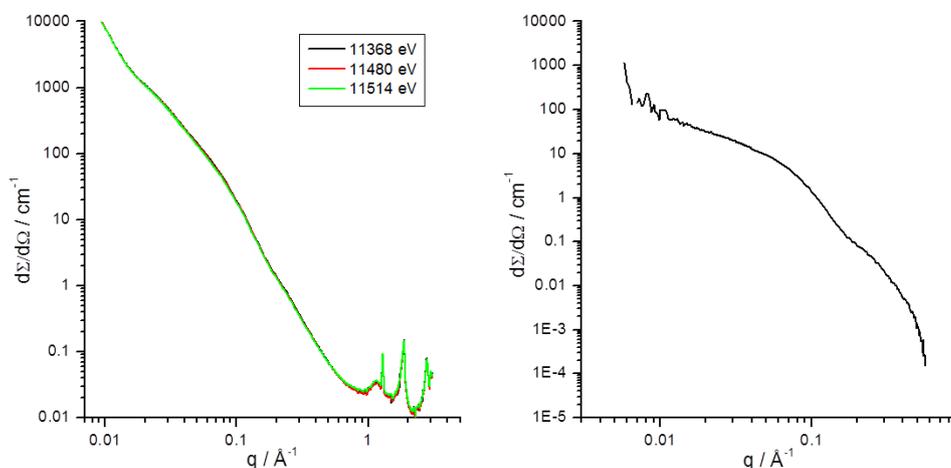


Figure 1: Total scattering and ASAXS of the cycled Pt_{1ML}/Pd sample at the Pt L₃ edge.

A comparison of the ASAXS curves of the fresh and cycled core-shell catalysts at the Pd K and Pt L₃ edges is shown in Figure 2. An increase in particle size is seen following the electrochemical ageing, with the additional formation of small Pt particles, however, the overall core-shell structure appears to be retained. This suggests that the loss of activity resulting from cycling in the oxide region arises from the increase in particle size rather than complete loss of the core-shell system.

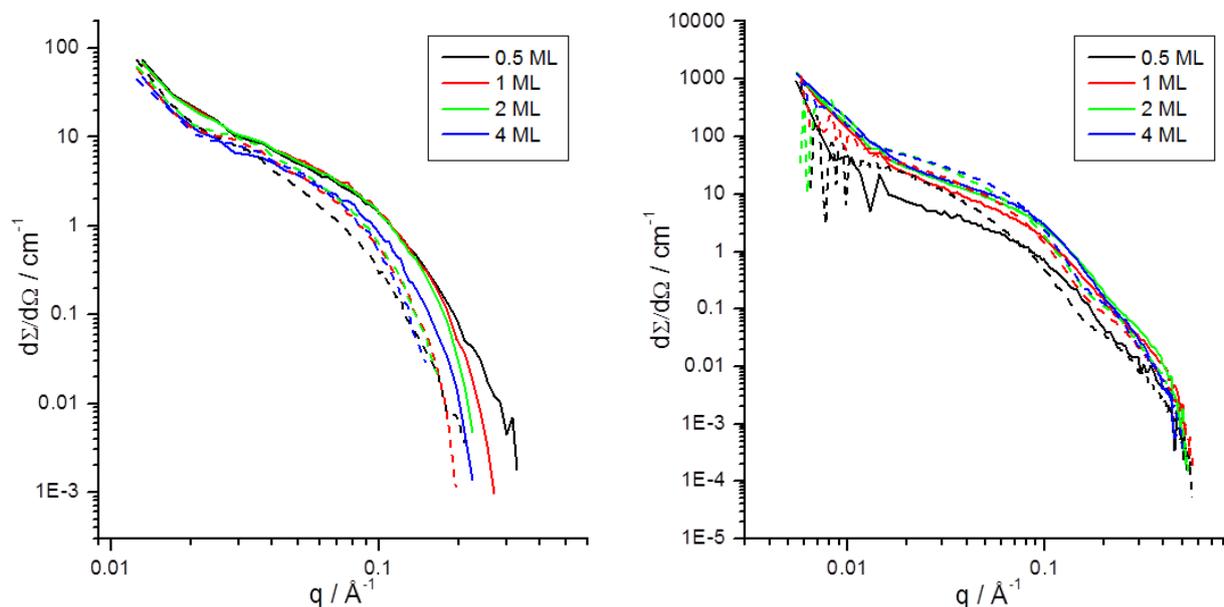


Figure 2: ASAXS of the fresh (solid line) and cycled (dashed line) core-shell electrocatalysts at the Pd K (left) and Pt L₃ (right) edges.

References

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