# The electrochemical oxidation of Pt nanocatalysts – an operando X-ray scattering study

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Pt nanoparticles are the state-of-the-art catalyst for proton exchange membrane fuel cells (PEMFCs), yet their long-term stability remains limited [1]. A major degradation pathway is metal dissolution, which predominantly occurs during transient oxide formation and reduction. While the surface oxide and its formation have been extensively studied on Pt single crystals using techniques such as high-energy surface X-ray diffraction, significantly less is known about the structure of the oxide formed on Pt nanoparticles [2–5].

Here, we investigate the oxidation of Pt nanoparticles under realistic conditions by combining quasi-simultaneous operando small-angle X-ray scattering (SAXS), X-ray diffraction (XRD), and total scattering with the pair distribution function (PDF) analysis in a custom-made operando electrochemical cell [6]. These complementary techniques allow us to follow the structural evolution across the multiple length scales of the nanoparticles during oxide formation. Together, SAXS, XRD, and PDF provide a comprehensive view of particle size, crystallinity, and changes in the local atomic order.

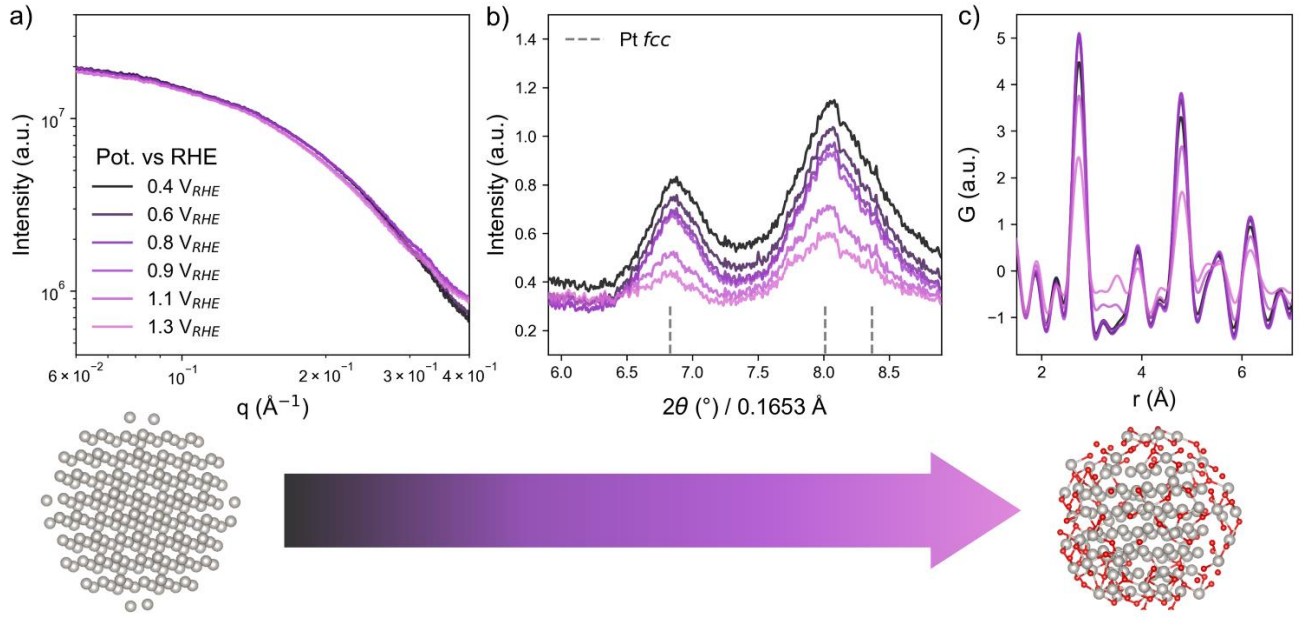



***Figure 1.*** *a) SAXS, b) XRD, and c) PDF of Pt nanocatalysts at different potential holds, revealing the transition from metallic to oxidized nanoparticles.*

By combining these techniques, we can fingerprint the structural motif of the oxide species forming on the Pt nanoparticle surface and track the thickness of the oxide layer (Figure 1). This multi-technique operando approach provides new insight into the structural evolution of Pt nanoparticles during electrochemical oxidation, representing an important step toward understanding degradation processes in fuel cell catalysts.

[1] D. A. Cullen, et al. Nature Energy (2021). 6 (5), 462-474.
[2] T. Fuchs, et al. Nature Catalysis (2020). 3, 754-761.
[3] T. Fuchs, et al. Angewandte Chemie International Edition (2023). 62, e202304293.
[4] C. A. Campos-Roldán, et al. Nature Communications (2025). 16, 936.
[5] S. Cherevko, N. Kulyk, K. J. J. Mayrhofer, Nano Energy (2016). 29, 275-298.
[6] G. K. H. Wiberg, R. K. Pittkowski, S. Punke, O. Aalling-Frederiksen, N. Schlegel, K. Jensen, M. Arenz, Chimia (2024). 78 (10), 682.