# Development of an *Operando* XRD PEMWE Cell for Correlating Catalyst Structure and Performance

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In proton exchange membrane water electrolysers (PEMWE), the catalyst materials play a crucial role in enhancing the efficiency of hydrogen production by facilitating electrochemical reactions at anode and cathode. In particular, iridium- and ruthenium-based anode catalysts undergo significant structural changes under operating conditions. In addition to widely reported crystallite growth and particle dissolution [1], also other structure-related processes occur. For instance, the rapid decrease in performance of initially highly active amorphous $IrO_x$ is associated with partial crystallization to the rutile $IrO_2$ phase [2]. Such degradation processes are not necessarily detectable by cell tests alone, as they may be masked by effects such as membrane thinning and the resulting increase in proton conductivity [3]. Even time- and resource-intensive post-mortem analyses fail to capture the dynamic evolution of these processes and their direct correlation with electrochemical performance.

To enable an analysis of catalyst particles during the PEMWE operation, an *operando* X-ray diffraction (XRD) cell is constructed. The concept is based on reflection-mode XRD measurements using a Mo-X-ray source, allowing high penetration depths. The cell design addresses the issue of insufficient contact pressure beneath the X-ray window, as commonly used materials are either not sufficiently rigid (*e.g.* Kapton®) or too brittle (e.g. Be). Due to the low incidence angle of the X-ray beam, there is a significant offset between the beam entrance point and the probed region on the catalyst-coated membrane (CCM). This is taken into advantage with an input and an output Kapton® window, separated by a supporting structure ensuring the contact pressure to the CCM region below. The X-ray beam enters the cell through the cathode side and must pass through the carbon paper (Toray®) gas diffusion layer to reach the CCM. Due to the low X-ray absorption of carbon, the horizontal offset can be adjusted *via* the thickness of the carbon paper with minimal intensity loss. The geometry is designed such that a line-focused X-ray beam is diffracted at the catalyst layers directly beneath the supporting structure. Pressure-sensitive films confirm sufficient contact pressure in this region. The setup of the operando PEMWE cell was designed to resemble an industrial electrolyser cell to ensure the relevance of the obtained results at larger scales too. The cell body is made of glass-fiber-reinforced high-performance polymer (Rigid 10k) to ensure the necessary contact pressure between the cell components. Inside the XRD housing a water supply is implemented with a preheating cell to ensure *operando* PEMWE with temperatures up to 80° Celsius. Automated water and power supply allow long-term operando XRD measurements exceeding 500 h.

Initial tests of the *operando* PEMWE cell demonstrate the appearance of characteristic diffraction peaks of catalyst materials. These signals are sufficient to determine crystallite size, particle dissolution, and potential phase transformations *via* Rietveld refinement. The versatility of the cell is explored in several applications. The cell is used to investigate the reduction of $IrO_2$ to metallic Iridium at low cell voltages [2]. *Operando* observations of this process allow the determination of the threshold voltage and the rate of the reduction process. These findings can be used to establish guidelines for minimum protective voltages. In addition, the cell is applied to study amorphous $IrO_x$ as anode catalyst. The unfavorable crystallization to the rutile $IrO_2$ structure is investigated under different operating protocols and *operando* XRD can reveal which conditions particularly promote this crystallization. These investigations contribute to a deeper understanding of catalyst degradation mechanisms and support the development of more stable and efficient PEMWE catalysts.

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