

Development of Electrochemical Flow-cell for Advanced in situ X-ray Investigations

J. Tillier, T. Binninger •, T. J. Schmidt •, O. Sereda

There is a clear need for high-efficiency and non-polluting energy conversion technologies for the automotive application. Therefore, an increasing interest to the Polymer Electrolyte Fuel Cells (PEFCs) has been seen over last 5 years. One critical issue facing the commercialization of PEFCs is the gradual decline in performance during operation, mainly caused by the loss of the Electro-Chemical Surface Area (ECSA) of the supported Platinum NanoParticles (Pt-NPs) at the cathode^[1]. The ECSA decrease of the cathodic catalyst can arise from different degradation mechanisms which take place simultaneously, especially during potential cycling. Only thanks to the in-situ analytical investigations the understanding of this phenomenon can be addressed in a proper way.

Electrochemical in situ Small Angle X-ray Scattering (in situ SAXS) offers the unique opportunity not only to observe the evolution of the Pt-NPs size distribution during an electrochemical degradation experiment, but also to simultaneously monitor the evolution of the absolute platinum mass content of the electrode. In situ SAXS experiments can be conveniently performed at synchrotron X-ray sources. The high photon flux from these radiation sources yields a very good scattering signal-to-noise ratio in a short acquisition time despite the strong X-ray absorption of the electrolyte layer in transmission geometry. Despite these advantages, in situ SAXS experiments at synchrotron facilities face the major drawback of highly restricted availability of beam time. Therefore, the laboratory equipment can play a key role in this regard. The multi-purpose laboratory X-ray diffractometers represent an attractive alternative to perform electrochemical in situ SAXS experiments due to their widespread availability. However, both the drastically reduced photon flux (10^{-9} of a typical synchrotron X-ray source) and the reduced flexibility at the sample stage of such systems impose major challenges to the engineering of a respective electrochemical in situ cell.

Here, we present the new designed electrochemical three-electrode flow-cell and the results obtained by in situ SAXS experiments on a laboratory diffractometer. The design was based on the same principles as the SAXS/XAS flow-cell for synchrotron facilities presented in Part I^[2]. However, the cell was adapted to the strong geometrical constraints defined by the sample holder and special configuration of the diffractometer (see Figure 1). An elongated electrode geometry was required in order to fully utilize the line-shaped X-ray beam of the device. Furthermore, the constant electrolyte flow prevented X-ray induced electrolyte degradation and heating. In this way, the system guaranteed constant experimental conditions even during long-term experiments.

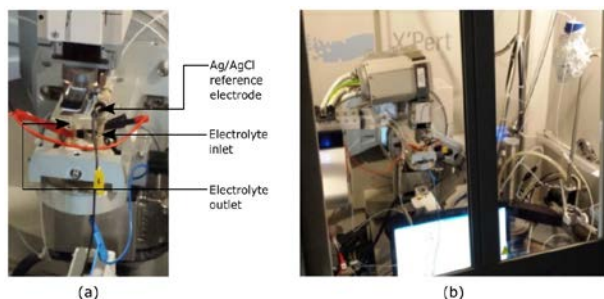


Figure 1: Pictures of the running in situ SAXS setup.

The raw SAXS curves $I_{scat}^{meas}(q)$ recorded during the in situ start/stop degradation study of the Pt-Vc 2 electrode are shown

in Figure 2 (left side). The Pt-NP-related scattering bumps shift to lower q -values with increasing number of degradation cycles. This behaviour is a clear signature of the growth of Pt-NPs due to Pt dissolution/re-deposition cycles (electrochemical Ostwald ripening) during potential cycling between 0.5 and 1.5 V_{RHE}.

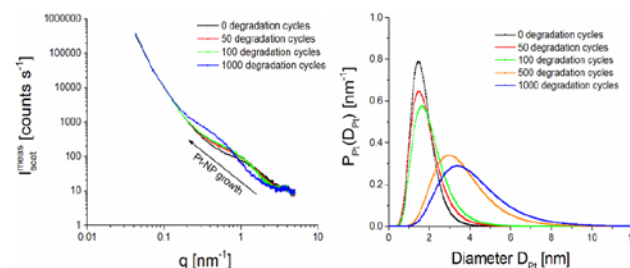


Figure 2: In situ degradation results of the Pt-Vc 2 electrode: raw data (left) and log-normal distributions for the diameter of Pt-NPs (right).

The Pt-NPs size distributions at different stages of the electrochemical protocol are depicted in Figure 2 (right side). As qualitatively already found from the analysis of the SAXS scattering curves, the size distributions demonstrate a particle growth with increasing number of degradation cycles. The distributions become broader and shift to larger particle sizes and the average diameter of the Pt-NPs increases from 1.8 nm in the initial state up to 4.2 nm after 1000 degradation cycles.

By performing the in situ investigations, the electrochemical degradation protocol has been established, which mimicked the corrosive conditions during PEFC start/stop events by potential cycles up to 1.5 V_{RHE}. An absolute normalization procedure for the SAXS data yielded net Pt differential scattering cross sections at various stages during the degradation cycling that could be analyzed not only for the Pt-NP size distribution, but also for the absolute number of Pt-NPs and the absolute Pt mass content of the nanoparticle phase. In this way, different degradation mechanisms could be distinguished. Carbon corrosion of the Vulcan support was qualitatively established in a separate experiment for a Pt-free Vulcan carbon electrode. The quantitative analysis of the Pt nanoparticle degradation revealed electrochemical Ostwald ripening as the dominant degradation mechanism for the Pt surface area. Thus, reducing Pt dissolution is the most important factor to prevent the degradation of catalyst performance under the start/stop potential cycling conditions.

Acknowledgments: this work was supported by CCEM Switzerland and Umicore AG & Co KG within the DuraCat project.

• Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

[1] Polymer Electrolyte Fuel Cell Durability, Springer (2009).

[2] Journal of the Electrochemical Society, 163 (10) H906-H912 (2016).