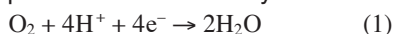


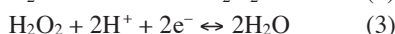
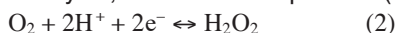
Observation of hydrogen superoxide adsorption during ORR on Pt/C catalyst in acidic solution via *in situ* high-energy resolution fluorescence detection X-ray absorption spectroscopy (HERFD-XAS)

The ultimate goal of our research was to develop a Pt-free polymer electrolyte fuel cell (PEFC). In the oxygen reduction reaction (ORR) at the cathode, it is generally understood that a direct four-electron reduction proceeds on a Pt catalyst, while a series of two-electron two-step reductions proceeds on a base metal or carbon-based catalyst. To obtain ideal reaction schemes and guidelines for catalyst design, we meticulously investigated the reaction pathway and adsorbed species on a Pt catalyst during the ORR process in an acidic environment by using high-energy resolution fluorescence detection X-ray absorption spectroscopy (HERFD-XAS) at SPRING-8 BL11XU [1-3].

Pt is used as an electrocatalyst in PEFCs owing to its high catalytic activity. Although the ORR scheme has long been studied, it remains to be completely elucidated. In the ORR of Pt in an acidic environment, a direct four-electron reduction reaction, as shown in Equation (1), is considered to proceed; however, hydrogen peroxide formation may also occur.



Several studies have sought to determine whether this is a reaction product with hydrogen that has passed through the polymer membrane from the anode or whether it is an intermediate species in a two-electron, two-step reduction reaction similar to that on non-Pt catalysts, as shown in Equations (2) and (3).



Molecular oxygen is an important ORR intermediate and has been studied using surface-enhanced infrared reflection and absorption spectroscopy (SEIRS) [4] and surface-enhanced Raman spectroscopy (SERS) [5]. However, these studies were limited to specimens such as Pt thin films and Pt single crystals.

We aimed to identify the species adsorbed on the surface of Pt nanoparticles under more realistic conditions by using a powdery carbon-supported polycrystalline Pt nanoparticle catalyst [1-3]. HERFD-XAS enhances energy resolution through the partial collection of fluorescent X-rays and enables the detailed analysis of the electronic structure of Pt and differentiation of the different adsorbed species on the surface of Pt nanoparticles. In addition, photon-in/photon-out spectroscopy using hard X-rays with high penetrating ability facilitate straightforward *in situ/operando* measurements in potentially controlled solutions.

HERFD-XAS experiments were performed at BL11XU (Fig. 1). The ink containing Pt/C catalyst (TEC10E50E: TTK) and ionomer (Nafion: DuPont) was sprayed onto 1 mm × 3 mm carbon paper (Pt loading of 0.75 mg/cm²) and placed on the GC electrode in the electrochemical half-cell. The incident X-rays were focused at an area of 2 mm × 0.1 mm.

For X-ray absorption spectroscopy (XAS) measurements, a potentiostat (Electrochemical Analyzer model 611E: ALS) was used to adjust the

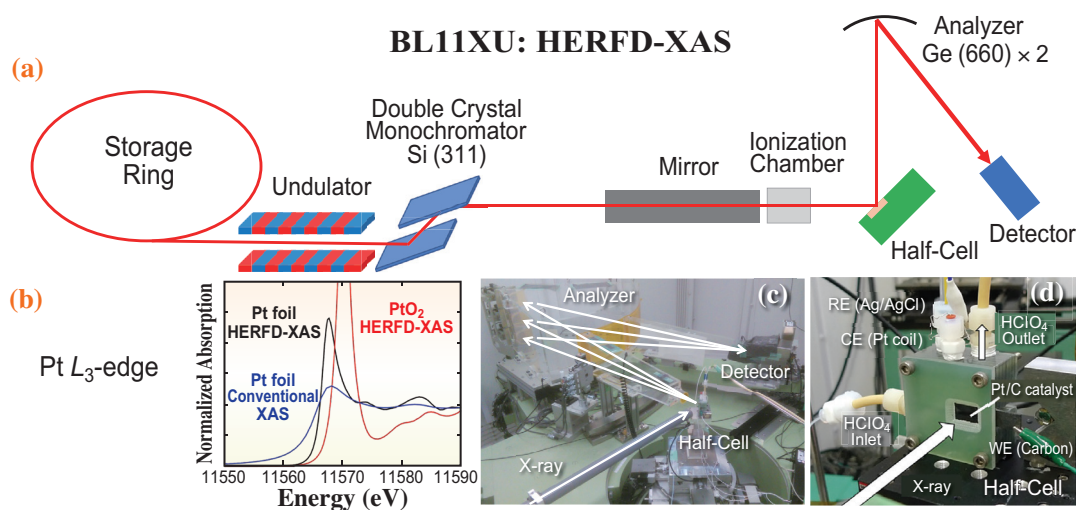


Fig. 1. HERFD-XAS system at BL11XU: (a) Schematic of optical system. (b) Effect of HERFD-XAS on the Pt L₃-edge XANES spectrum compared to the conventional XAS. (c) Incident and emission angles around electrochemical cell. (d) Electrochemical half-cell.

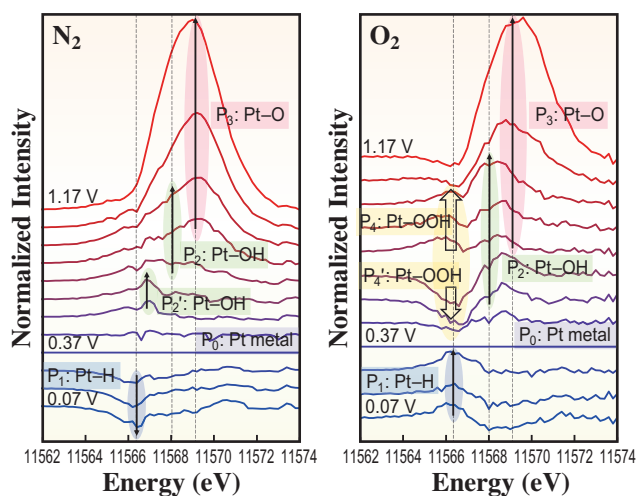


Fig. 2. Difference spectrum ($\Delta\mu$ analysis): $\Delta\mu$ compared to 0.37 V potential controlled in N_2 -saturated and O_2 -saturated 0.1 M of $HClO_4$ aqueous solution.

potential applied to the electrochemical cell between 0.07 V and 1.17 V (vs. RHE), in 12 steps at 0.1 V intervals, based on the Ag/AgCl reference electrode. To obtain accurate spectra, the sweep of cyclic voltammetry (CV) was repeated as a pretreatment until the catalyst surface was clean and the dissolved oxygen concentration in the electrolyte was stable. The effect of hysteresis due to the potential sweep direction was eliminated, and potential points in the negative direction were adopted each time.

Figure 2 shows the difference spectra ($\Delta\mu$) of the X-ray absorption near edge structure (XANES) at the Pt L_3 -edge from 1.17 V to 0.07 V in 0.1 V increments, referenced against 0.37 V. At approximately 0.37 V (P_0), the Pt surface transitioned into a metallic state without any adsorbates.

P_1 , P_2 , and P_3 peaks are commonly observed in both N_2 - and O_2 -saturated solutions. In contrast, the peaks of P_4 are observed only in O_2 -saturated solutions from 0.97 V to 0.47 V. Therefore, the P_4 peaks indicate the adsorbed species originating from the ORR reaction process.

The potentials at which the upward P_4 peaks appeared are in good agreement with the ORR onset potential; as the potential decreased, the intensity of P_3 decreased, and the intensity of P_4 increased. The appearance of this adsorbed species is in the early stage of the ORR, and it is regarded as an adsorbed species derived from the superoxide anion ($^*O_2^-$), which is a one-electron-reduced molecular-type oxygen. The generated superoxide anion is considered to undergo rapid protonation and exist as hydrogen superoxide (HO_2^*) owing to the abundance of H^+ in the acidic solution.

Furthermore, the downward peaks of P_4 indicate changes in the adsorption state, suggesting the possibility of further one-electron-reduced $H_2O_2^*$ adsorbed species. Subsequently, it undergoes a further two-electron reduction to form $^*OH^-$, which is also protonated and dissociates as water.

In summary, we sought to elucidate the ORR pathway from O_2 to H_2O on the surface of Pt nanoparticle electrocatalysts in an acidic environment. Direct four-electron reduction reactions are considered to occur on Pt catalyst. However, in this experiment, molecular-type oxygen-adsorbed species, such as hydrogen superoxide, were observed almost throughout the oxygen reduction reaction, including on the Pt catalyst (Fig. 3). The reaction scheme is the same as that in the case of non-Pt catalysts, and an intermediate state, wherein one electron is reduced at a time, was demonstrated. This implies that the activation energy barrier for breaking the O–O bonds is high.

Preventing the generation of hydrogen peroxide radicals (H_2O_2) during ORR is critical for component durability. The present HERFD-XAS study clearly demonstrated a new reaction pathway that prioritizes O–O bond cleavage, and the findings can provide guidance for future Pt-free catalyst designs for fuel cell cathodes, serving as a compass to navigate the uncharted waters of materials research.

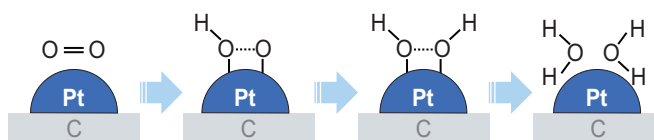


Fig. 3. Proposed adsorbed species during the ORR process on Pt/C catalyst in acidic solution.

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