BL36XU Catalytic Reaction Dynamics for Fuel Cells

1. Introduction

BL36XU at SPring-8 is designed to solve problems in development of next-generation polymer electrode fuel cells (PEFCs). Its construction and advanced SR X-ray–based analysis systems for studying PEFCs were developed under a New Energy and Industrial Technology Development Organization (NEDO) program^[1]. Construction was completed in November 2012, and user operations began in January 2013. Additionally, simultaneous/sequential multi-analysis systems were made available to users in October 2016.

The performance of PEFC is highly sensitive to sample conditions such as humidity, temperature, gas pressure, and contamination of an MEA. Compared to measurements obtained at different points, simultaneous or sequential measurements using multi-analysis methods on a point fixed in the sample provides more reliable information than those obtained at different measurement points. Such measurements can effectively clarify the complex reactions occurring in a PEFC during operation^[2]. This report describes the quick operando ambient pressure HAXPES (AP-HAXPES) measurement system for PEFCs developed at BL36XU.

2. Quick operando ambient pressure HAXPES for reaction kinetic measurements of PEFCs

A real AP-HAXPES system equipped with a differential pumping system was developed in FY2017^[3]. The AP-HAXPES system has been used to investigate the electronic states of platinum nanoparticles on cathode electrocatalyst in PEFCs

under the various operating conditions ^[4].

In FY2019, a quick operando AP-HAXPES measurement system was designed and constructed to investigate the reaction kinetics in PEFCs under working conditions ^[5]. Figure 1 shows a schematic view of this system. To accumulate time-resolved spectra with sufficient signal-to-noise ratios, repeated cycles of the chemical reactions were conducted based on the time-tagged pump-andprobe method. The time-resolved AP-HAXPES measurements can be performed at typical pressures of 1×10^4 Pa $- 1 \times 10^5$ Pa with the maximum time resolution of ~200 ms. To avoid possible radiation damage on the sample due to prolonged intense Xray irradiation, the sample position can be varied continuously with a scanning speed of $\sim 20 \,\mu\text{m/min}$ along the vertical direction.



Fig. 1. Schematic of the quick near AP-HAXPES system ^[5].

Figure 2 shows time-resolved Pt $3d_{5/2}$ HAXPES at the cathode when the bias voltage suddenly changes between the cathode and anode (0.4 V \leftrightarrow 1.2 V) to evaluate the reaction rate constants in

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the changes of the Pt oxidation states. The system can investigate the oxidation and reduction kinetics of the cathode Pt electrode in PEFC at \sim 30 °C.



Fig. 2. Time dependence of Pt $3d_{5/2}$ HAXPES from the Pt/C cathode catalyst upon an abrupt step of the cathode–anode bias voltages between 0.4 V and 1.2 V ^[5].

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