

## Simultaneous analytical system of electrochemical reaction rate and *operando* hard X-ray photoemission spectroscopy

Electrochemical technologies, such as for fuel cells, secondary batteries, photocatalysts, semiconductor systems, plating, corrosion protection, biochemistry, electrochemical sensors, metal refining, and electrolytic synthesis/polymerization, are the backbone of modern science and industry. To quantitatively understand the electrochemical reaction, the reaction rate must be accurately measured. For example, in the development of fuel cell catalysts, power generation can be estimated by quantitatively measuring the electrochemical reaction rate per unit area by supplying a reactant to a catalyst at a constant rate. The degradation of the catalyst can also be elucidated. In the development of anticorrosion materials, the effect of anticorrosion can be quantitatively understood by measuring the rate of corrosion.

For the analysis of the electrochemical reaction rate, a solution must be constantly supplied to the electrode surface, and material diffusion must be controlled to reproducibly and quantitatively measure the activity of electrode reactions or charge transfer processes. For this purpose, hydrodynamic voltammetry is used. An example of hydrodynamic voltammetry is the rotating disk electrode (RDE) method, where a disk electrode is placed in solution, and the current associated with the electrochemical reaction is measured while the electrode is rotated at a constant speed. The reactant is supplied to the surface of the electrode and carried outward along the surface by the rotation of the electrode, realizing a steady mass transport over the surface of the electrode. The setup of the RDE measurement is relatively simple, but maintaining the temperature and pressure is not always easy because the solution is usually placed in a container such as a flask. Furthermore, long-time measurement could be relatively difficult because of the decrease in the concentration of reactants and the increase in the concentration of products in the container. As another method of hydrodynamic voltammetry, the channel flow electrode (CFE) method has attracted attention in fields such as fuel cells, secondary batteries, metal corrosion, and surface treatment [1]. Figure 1 schematically shows a diagram of electrochemical measurement by the CFE method. A rectangular parallelepiped channel with a thickness of 1 mm or less is constructed in a cell made of an insulation resin. A conductive electrode, often used as a substrate of specimens, is embedded in the cell to make the walls of the electrode and the cell the same level. In the CFE method, instead of rotating the sample, the electrolyte solution is supplied in a laminar flow as Hagen-Poiseuille flow from the solution reservoir into the cell to the sample. In this way, the electrochemical reaction

rate is measured with the diffusion of the reactant being accurately controlled. Since the temperature and the concentration of reactants in solution are controlled in the solution reservoir, a steady-state reaction is easily reached, and the reproducibility is high. Usually, the CFE method can be suitably applicable to long-time measurements.

The electronic states of the electrode surface are closely related to the bonding of atoms and molecules, as well as to the reaction mechanisms, at the electrode surface. Therefore, data on the electronic state offer important information for the control of electrochemical reactions. The structures and electronic states of electrode surfaces during electrochemical reactions have been analyzed by infrared and Raman spectroscopies, probe spectroscopies, and X-ray photoelectron spectroscopy (XPS), for example. In recent years, synchrotron X-ray has been used, and the structures and electronic states have been actively studied by, for examples, X-ray diffraction, X-ray scattering, X-ray absorption spectroscopy, and photoemission spectroscopy (PES). The targets are also expanding to practical systems, such as nanoparticles used in fuel cell catalysts.

In the 1970s, hard X-ray photoemission spectroscopy (HAXPES) was reported, but at that time, the intensity of hard X-rays was still low. Around 2000, SPing-8 started to supply high-brilliance synchrotron hard X-rays concurrently with the improvement of photoelectron detectors. Since then, many studies of HAXPES using synchrotron X-rays have been reported [2]. In industry, HAXPES was first applied to semiconductors, but now, it is used in a wide range of fields including battery materials and catalysts. In addition, *in situ* and *operando* ambient-pressure XPS measurements on solid samples reacting with gases using soft, tender, and hard X-rays are reported. In some cases, even the liquid itself was measured. For *in situ* measurements on an electrode surface, a small container or a microcell enclosing an electrolyte solution was placed in ultrahigh vacuum (UHV), and the electronic states

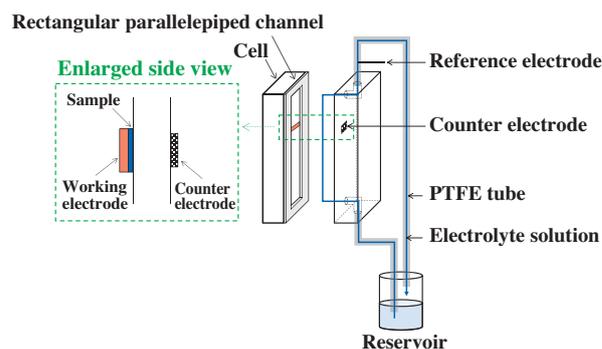


Fig. 1. Schematic illustration of the channel flow electrode method.

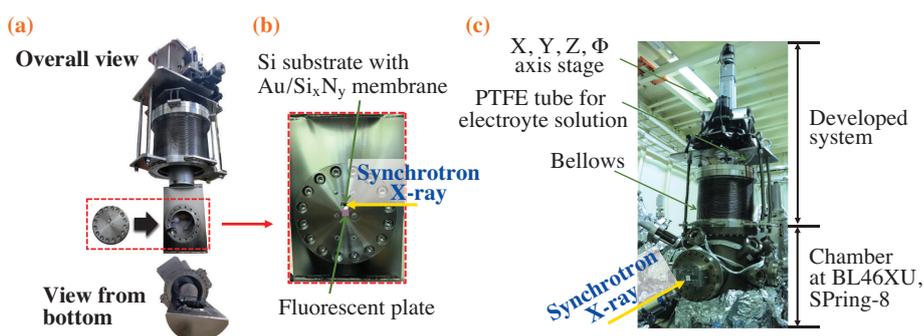


Fig. 2. Photographs of the constructed analytical system (a), the stainless flange (ICF152) with a Si substrate with a Au/Si<sub>x</sub>N<sub>y</sub> membrane (b), and the system installed in the UHV chamber at BL46XU (c). A fluorescent plate was attached to the stainless-steel flange to confirm the irradiation position of the synchrotron X-ray.

of electrodes during electrochemical reactions were measured by HAXPES [3]. For PES measurement during the electrochemical reactions, the solution, in most cases, was not continuously supplied from the outside to the electrochemical system.

We have developed an *operando* technique designed to measure the electronic state of an electrode immersed in electrolyte solution by HAXPES while measuring or even controlling the electrochemical reaction rate. Our system is expected to make a large contribution to the development of materials and to industrial processes [4].

Figure 2 shows photographs of the analytical system installed in the HAXPES chamber at SPring-8 BL46XU. For sample positioning by moving the lower part of the system for HAXPES measurements, the X, Y, Z, and  $\Phi$  stages were used with a positioning rod connecting the lower part of the chamber to the 4-axis stage. A flexible stainless-steel bellows between the positioning stages and the lower part of the chamber enabled sample movement. To simultaneously perform HAXPES measurements in ultrahigh vacuum while measuring the electrochemical reaction rate in solution under atmospheric pressure, a Si substrate was used with an ultrathin window of a 20-nm-thick Au/Si<sub>x</sub>N<sub>y</sub> membrane (15-nm-thick Si<sub>x</sub>N<sub>y</sub> coated with 5-nm-thick Au).

Figure 3(a) shows the chronoamperometry results obtained at 0.4 V. A cathodic current of approximately 8  $\mu$ A was observed, which is considered to be a reduction current due to a trace amount of oxygen contained in the solution as an impurity. The reaction rate was calculated to be 0.04 nmol·s<sup>-1</sup>. Figure 3(b) shows a Au3d<sub>5/2</sub> spectrum of HAXPES measured while measuring the current in Fig. 3(a). The blue circles and solid line were the experimental data and curve-fitting result, respectively, for the Au thin film electrode on the Si<sub>x</sub>N<sub>y</sub> membrane surface at 0.4 V in solution, while the green triangles and solid line were those of the metal Au in vacuum measured as a reference spectrum. The Au thin film electrode was observed to be in a metal state during this electrochemical measurement. In this way, we succeeded in developing an *operando* system designed for measuring the electronic state of a sample by HAXPES while measuring (or controlling) the electrochemical reaction rate under

Hagen-Poiseuille flow by the CFE method. This concept of simultaneous measurements can be expanded to different analytical methods. We are now working on *operando* small-angle X-ray scattering using a CFE cell [5].

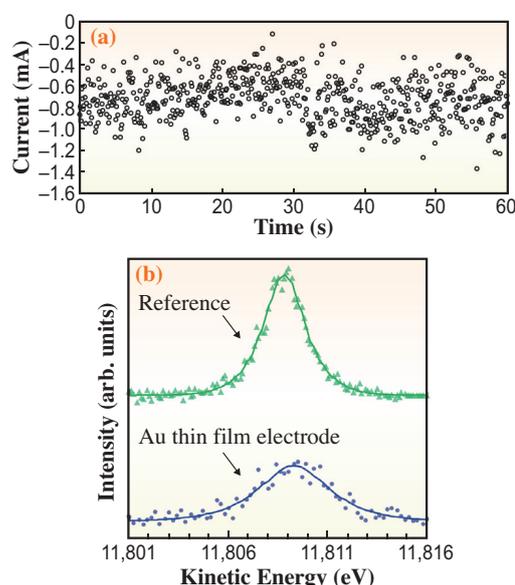


Fig. 3. (a) Chronoamperometry (flow rate = 25 cm<sup>3</sup>·s<sup>-1</sup>) measured at 0.4 V vs Ag/AgCl sat. KCl in 0.1 M HClO<sub>4</sub> at room temperature. (b) Au3d<sub>5/2</sub> HAXPES spectrum of Au thin film electrode measured during electrochemical reaction (blue circles for data and solid line for fitting). The horizontal axis indicates the kinetic energy of photoelectrons. The green triangles and solid line are of the spectrum of the reference metal Au. From all data, Shirley backgrounds were subtracted.

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