BL12XU
(NSRRC ID)

BL12XU is one of two contact beamlines operated by the National Synchrotron Radiation Research Center (NSRRC), Taiwan. BL12XU has an undulator light source and two branches of the mainline and a sideline (Fig. 1). The mainline has been fully operational since 2001 and is used by many domestic and international scientists. It is mainly used for inelastic X-ray scattering (IXS) experiments. In the sideline, hard X-ray photoemission spectroscopy (HAXPES) is performed. Some adjustments and upgrades are still being made by the Max-Planck Institute for Chemical Physics of Solids (MPI-CPfS), but the HAXPES end station is open to general users.

1. Instrumentation

The following upgrades were made in FY2018.

1-1. High-pressure high-temperature (HP-HT) furnace for supercritical water

In an effort to realize an attosecond (10^{-18} s) time-resolution response function of supercritical water, IXS spectra must be collected over a wide range of energy and momentum transfers. We devised a furnace and a sample cell for IXS experiments with a wide scattering angle from 2° to 150° (Fig. 2). Initially an aluminum cell was used, but it had trouble at temperatures above 250 °C because aluminum rapidly becomes softer. However, we found that a sapphire cell annealed near its melting point has sufficient stiffness at high temperatures. Using a sapphire cell, we achieved conditions of 350 °C and 20 MPa this year. We are continuing to modify the cell to reach a temperature and pressure where supercritical water is available (370 °C and 22 MPa).

2. Experiments

In FY2018, we conducted 13 experiments of non-resonant IXS, 21 of resonant IXS (or resonant emission), and 9 of HAXPES. Representative examples are introduced below.

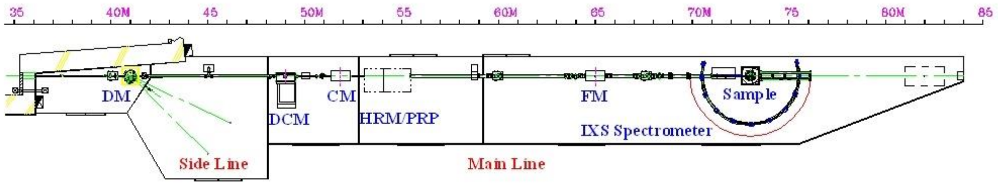

Fig. 1. Schematic diagram (top view) of BL12XU. DM is a diamond monochromator for the sideline, DCM a double crystal monochromator for the mainline, CM a collimating mirror, HRM a high resolution (channel cut) monochromator, PRP a phase retarding plate, FM a focusing mirror, and IXS an inelastic X-ray scattering spectrometer.

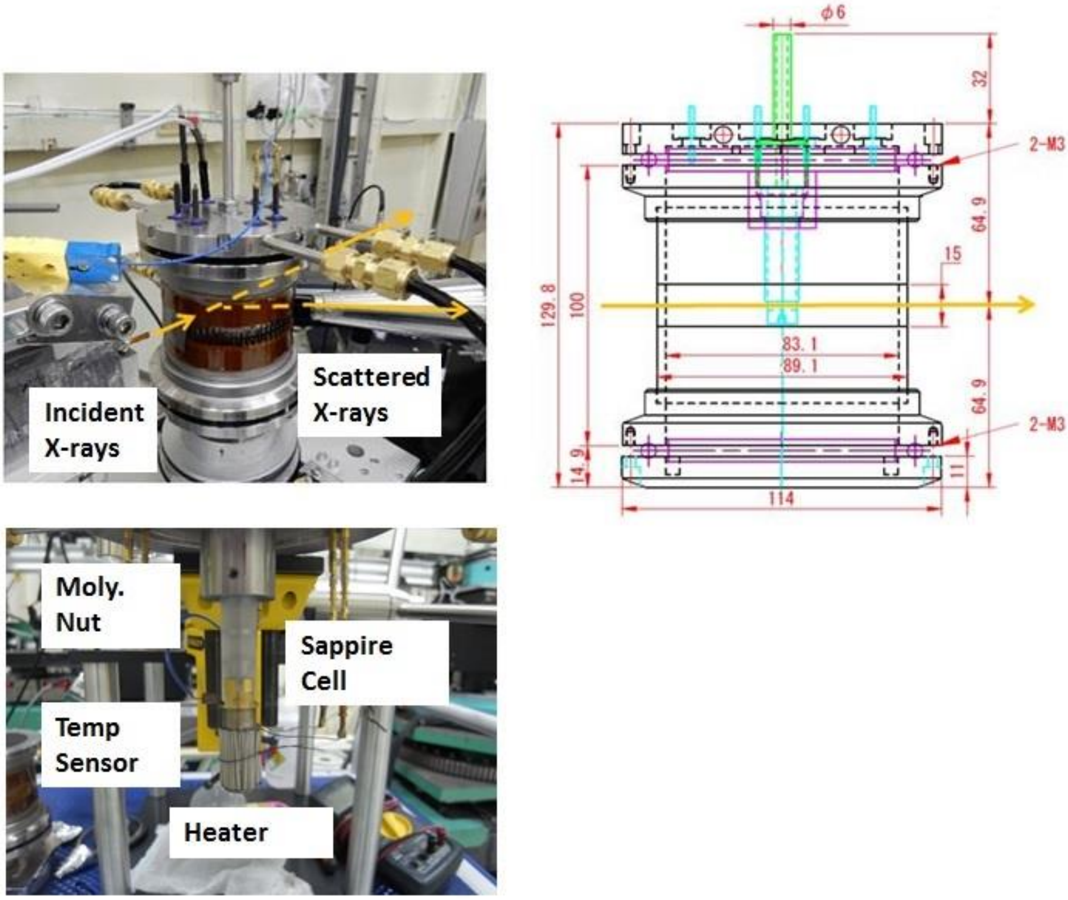

Fig. 2. Photos and drawing of the high-pressure high-temperature (HP-HT: up to 22 MPa, 370 °C) furnace to produce supercritical water. Inner cell seals HP-HT water. Wide opening covers a wide momentum range.

2-1. Identification of stabilizing high-valent active sites by *operando* high energy resolution fluorescence-detected X-ray absorption spectroscopy for high-efficiency water oxidation

Exploiting an advantage of the partial fluorescence technique (i.e., lifetime broadening suppression), S. F. Huang *et al.* identified faint pre-edge features on the tails of the main edges in Fe K-edge and Co K-edge in an Fe-doped Co spinel catalyst, which exhibits an outstanding intrinsic catalytic activity for the oxygen evolution reaction (OER). The catalytic reaction proceeds in the *d* orbitals of transition metal ions. They clarified the behaviors by investigating the pre-edge feature. *In situ* studies revealed that only a pre-edge feature in the Co K-edge evolves during the oxidation and reduction processes (Fig. 3). Hence, the catalytically active site is Co ions rather than doped Fe ions, which has been a controversial issue in the OER mechanism. Furthermore, they demonstrated that the expansion of the orbital overlap between Co ions and the electrolyte by doping Fe ions is the major factor for the enhanced overall catalytic activity. Stimulated by this successful example,

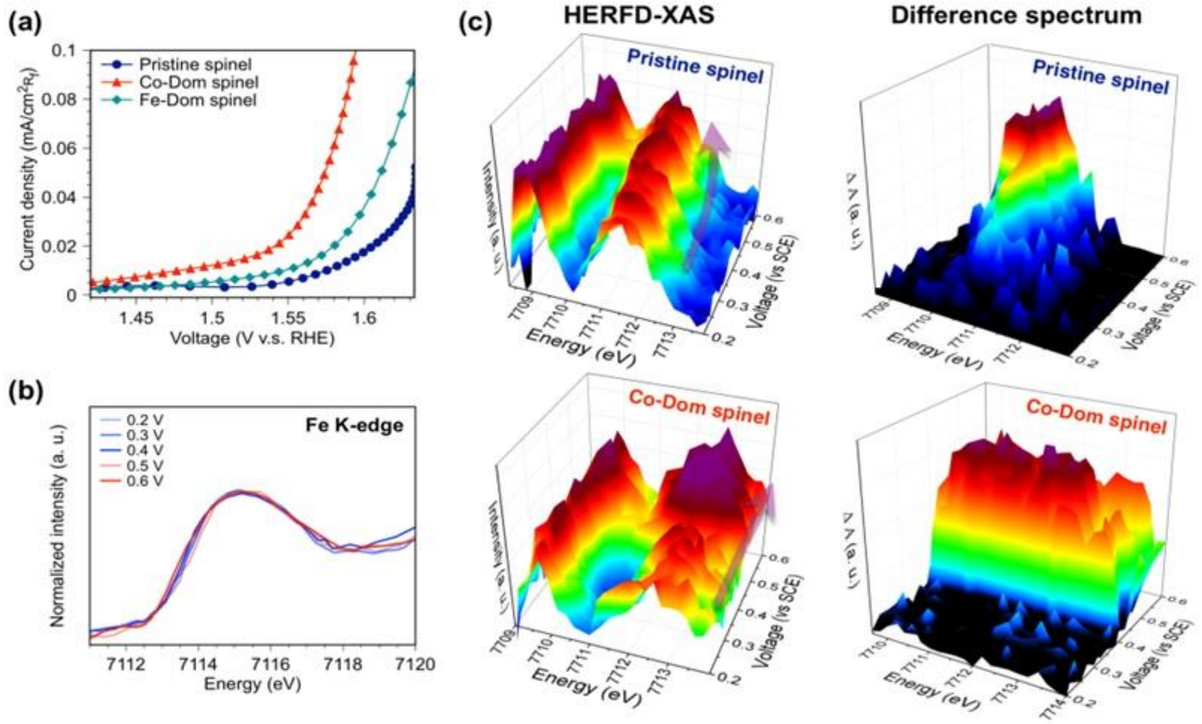

Fig. 3. (a) Catalytic activities of Fe-doped spinel. *Operando* PFY-XAS of (b) Fe K-edge for Co-dominated spinel and (c) Co K-edge for Fe-doped spinel. Changes in the electronic states as a function of the bias voltage are negligible for Fe ions but are apparent for Co ions, indicating a significant interaction between the electrolyte and Co ions [1].

this type of experiment is becoming more popular, and is being applied to research in Taiwan [1].

2-2. *c*-Axis dimer and its electronic breakup: insulator-to-metal transition in Ti_2O_3

Ti_2O_3 is a very interesting material, which shows an insulator-to-metal transition. Similar to V_2O_3, Ti_2O_3 also displays the corundum crystal structure, where the main feature contains two face-sharing transition metal $(TM)O_6$ clusters aligned as a dimer along the hexagonal *c*-axis. Unlike V_2O_3, Ti_2O_3 shows a gradual metal-to-insulator transition without a structure transition or magnetic ordering. The shorter distance of the Ti–Ti dimer of the Ti_2O_3 renders direct bonding *via* 3 dz^2 orbitals, which plays an important role in the insulator-to-metal transition. Using HAXPES on the valence band and Ti 2p core levels, C. F. Chen *et al.* found that the metal-to-insulator transition of Ti_2O_3 can be well explained by a Hubbard model in analogy to the ionization of hydrogen molecules $H^2 \rightarrow H^{2+}$. (Fig. 4) [2].

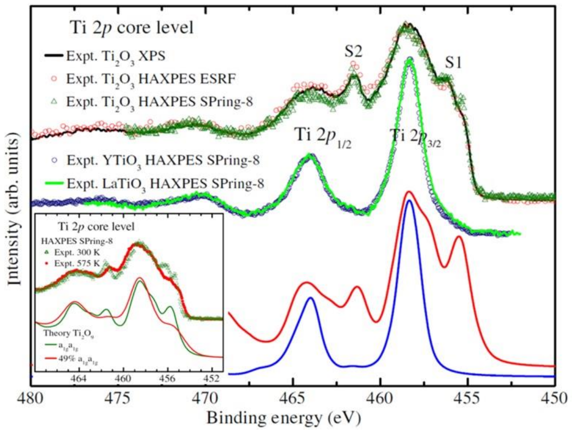

Fig. 4. Experimental Ti 2*p* core-level photoemission spectra of Ti_2O_3 taken at 300 K. References of $YTiO_3$ and $LaTiO_3$ were acquired at 300 K and 200 K, respectively. Theoretical configuration–interaction calculations using the TiO_6 and Ti_2O_9 clusters are also shown. Inset shows the temperature dependence of the Ti 2*p* core-level spectrum and the simulations using the Ti_2O_9 cluster [2].

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References:

[1] S.F. Hung et al., *J. Am. Chem. Soc.* **140**, 17263 (2018).

[2] C.-F. Chen et al., *Phys. Rev. X* **8**, 021004 (2018).