

BL28XU

Advanced Batteries

1. Introduction

BL28XU is managed and operated by Kyoto University to realize technological innovations in rechargeable batteries. It was renamed “Advanced Batteries” from “RISING2” in FY2021. The RISING2 project ran from FY2016 to FY2020 as a contract research project of the New Energy and Industrial Technology Development Organization (NEDO) to promote technology development for practical uses of storage batteries. The project exclusively used the beamline for this purpose. In FY2021, the RISING3 project was launched as a successor to RISING2. The project focuses on two types of post-lithium-ion battery (LIB) system: (1) fluoride batteries, which show great potential in terms of both energy density and safety, are based on highly original technologies developed in Japan, and (2) zinc-anode batteries, which offer significant safety advantages and cost benefits. Since FY2021, the RISING3 project has used the majority of the beamtime of BL28XU for the research and development of these battery systems.

The main subjects of the RISING3 project that are being investigated in the beamline are as follows: (1) the elucidation of reaction distribution generation factors, (2) the analysis of active material reactions and nonequilibrium behaviors, (3) the elucidation of electrode/electrolyte interface phenomena, (4) the elucidation of the formation mechanism of random materials such as an electrolytic solution and electrolytes at the electrode interface, and (5) the elucidation of thermodynamic or physical instability phenomena inside the storage batteries. Measurement techniques for in situ

observations of the reaction inside storage batteries via X-ray diffraction (XRD), confocal X-ray diffraction, X-ray absorption spectroscopy (XAS), and hard X-ray photoelectron spectroscopy (HAXPES) have been mainly employed for this purpose.

2. Development of grazing-angle XAS/XRD measurement system

Thin-film electrodes have the advantage of being effective in the evaluation of electrochemical behavior at low temperatures and the analysis of electrode reaction mechanisms. XRD and partial fluorescence yield XAS (PYD-XAS) using grazing-incidence X-rays are promising analytical techniques for thin-film electrodes, as they enable surface-sensitive measurements of crystal structure and electronic states, respectively. Therefore, we have built a system optimized for operando measurements of thin-film electrodes.

Generally, thin-film batteries are highly reactive and cannot be exposed to air. Therefore, we designed an enclosure for thin-film batteries. The sample is fixed to the enclosure in a glove box filled with argon gas. The enclosure is then moved onto the diffractometer and evacuated. Cables for charging and discharging are connected to the potentiostat via feedthroughs. The enclosure is equipped with a heater and a thermocouple, enabling external temperature control via the feedthrough.

The thin-film sample is positioned vertically in the enclosure, and the incident X-ray undergoes total reflection in the horizontal plane by controlling

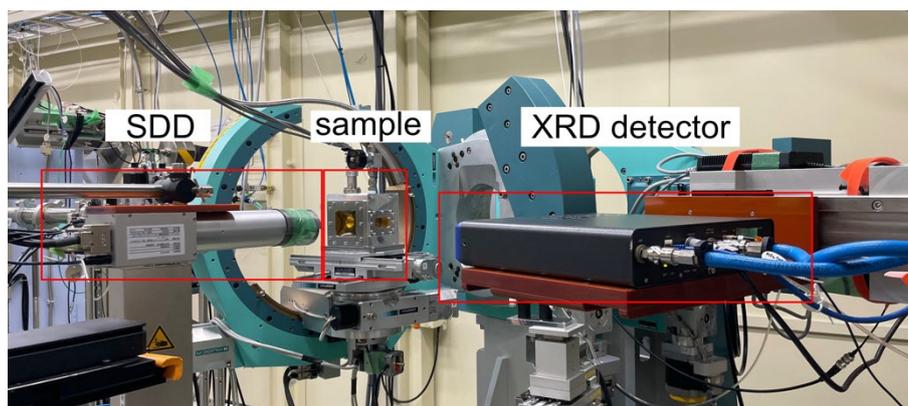


Fig. 1. Grazing-angle XAS/XRD measurement system

the φ -axis (rotation around the vertical direction) of the multi-axis diffractometer. The enclosure has large Kapton windows located on the downstream face and side, leading diffracted light and fluorescent light to the XRD and XAS detectors, respectively. A two-dimensional detector mounted on the diffractometer arm allows for rapid XRD measurements. The window size limits the 2θ angle range to approximately $10\text{--}30^\circ$. The polarization characteristics of the undulator light source cause intensity attenuation approaching 90° , which can be compensated by software. PYD-XAS can be performed with high sensitivity using a multi-element silicon drift detector (SDD) positioned at $2\theta=90^\circ$, where elastic scattering weakens.

While XRD and XAS typically use different incident photon energies, the compact channel-cut monochromator at BL28XU enables rapid switching between XRD and XAS. This allows combinational XRD/XAS measurements with high temporal resolution.

This system was employed to investigate the defluorination/fluorination mechanism of an FeF_x thin-film electrode, which is a cathode material of a fluoride-ion battery whose electrochemical properties and reaction mechanism remain largely

unexplored. The XAS measurements revealed that the reversible discharge/charge of the FeF_x cathode at room temperature was due to defluorination/fluorination between FeF_3 , FeF_2 , and $\text{Fe}^{[1]}$.

Acknowledgments

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