BL08B2
(Hyogo BM)

1. Introduction

BL08B2, which is the Hyogo-prefectural beamline, is a hard X-ray beamline designed for industrial applications. BL08B2 supports X-ray absorption fine structure (XAFS), X-ray topography, Imaging/CT, X-ray diffraction (XRD), and small-angle X-ray scattering (SAXS) measurements, which are widely used in industry. In recent years, the development of new materials applicable to informatics technologies, so-called materials informatics, is actively performed to promote materials research. We support research and development in manufacturing through a coalition between synchrotron radiation measurements and informatics technologies.

Here, two studies are featured. As a proof-of-concept (PoC) study, the redox factor of lithium-ion batteries is discussed based on the feature selection from *in situ* XAFS/XRD dataset by informatics. Then an automatic measurement system for SAXS and XAFS is developed. This high-throughput system has already helped industrial users accumulate big data required for informatics applications.

2. Combination of XAFS/XRD and machine learning techniques for cathode materials

In situ XAFS/XRD is an excellent method to investigate changes in electronic and crystal structures during electrochemical cycling of battery materials. During this process, numerous datasets are obtained simultaneously, creating an enormous amount of data. However, data analysis and theoretical calculations in a timely manner are limiting factors. In FY2018, informatics was applied to feature selection as a PoC to demonstrate important factors related to the redox factor of lithium-ion batteries using machine learning. Important variables of spectral data from *in situ* XAFS/XRD were automatically selected by machine learning. The potential change in cathode materials ($Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$) was predicted by the selected features, demonstrating that these can be utilized to discuss factors affecting the redox mechanism of the cathode materials.

Figure 1 shows the experimental setup for *in situ* time-resolved XAFS and XRD measurements of cathode materials under charging. XAFS spectra can be either obtained in step-scanning or a continuous QEXAFS mode. XRD patterns are collected using a two-dimensional (2D) detector (PILATUS 100k). The Ni, Co, and Mn K-edge XAFS in the transmission mode and XRD measurements were carried out in an aluminum-laminated pouch-type cell.

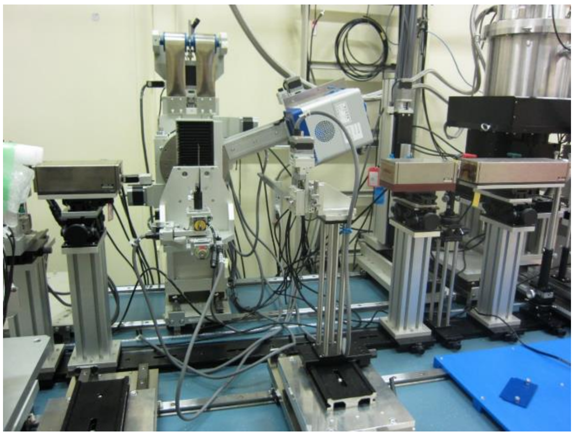

Fig. 1. *In situ* time-resolved XAFS and XRD measurement setup.

All of the obtained values by XAFS and XRD measurements were standardized prior to linear regression analysis. The open circuit potentials at x point in $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ were objective variables. The coefficient values of R^2 were determined by the 1:1 cross validation while the linear regression and ensemble learning methods were used for feature selection. As a typical example, Fig. 2 shows the actual and predicted potentials by LASSO. The predicted model from LASSO was determined by the actual potential, and has a high accuracy. It is well known that the major charge compensation at the metal site during charging is achieved by the oxidation of the Ni^{2+} ions, which agrees well with the results of our study using machine learning.

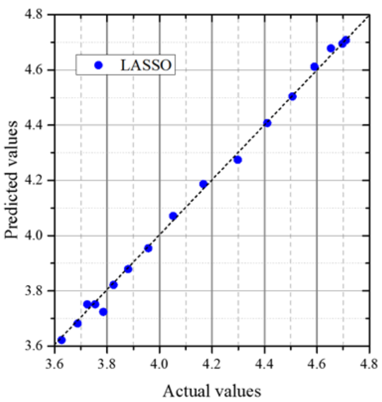

Fig. 2. Validation of the predicted and actual potentials.

3. Automatic measurement system

For high-throughput data collection toward informatics applications, an automatic measurement system was developed. This system contains auto-optics, sample changer robot, and user-friendly control software programmed by LabVIEW for SAXS and XAFS.

Auto-optics is the fully automatic adjustment function of optics. Users only need to select the desired absorption edge from the element periodic table on the graphical user interface (GUI), then the monochromator, mirror, slits, optical stages and energy calibration will be adjusted within 30 min.

The sample changer robot can automatically measure up to 80 samples of SAXS or XAFS. Samples can be in the form of films, plates, tablets, or capillaries. Each sample is mounted in a sample holder of a 35-mm film slide. A robot arm with a pneumatic chuck exchanges the sample holders. The robot arm can rotate the sample holder by 45 degrees for transmission- and fluorescence-XAFS measurements. Figure 3 shows the sample changer robot during a SAXS/WAXS measurement.

The sample changer robot performs automatic measurements in three steps. (1) The sample is picked up from a sample cassette and moved to the front of the CCD camera. (2) The center or selected position of the sample is adjusted by a vision system. (3) The sample is moved to the measurement position. After the measurement, the sample is returned to the sample cassette. Then the next sample is picked up. This procedure is repeated until all samples in a batch are measured.

Fig. 3. Sample changer robot at BL08B2. Sample is shown in the beam position.

The sample changer is controlled by auto measurement software equipped with GUI. The experimental conditions can be inputted using a dedicated format with an Excel spreadsheet. Using the sample changer robot, the single-cycle measurement time is reduced to 1 min for the SAXS or QXAFS, including changing and measuring the sample. A batch measurement with up to 80 samples can be completed within 2 h. The startup and adjustment time for the sample changer robot is only 1.5 h. Hence, it is convenient for users to operate during their beamtime.

4. Beamline statistical data

Almost all BL08B2 users are from the manufacturing industry. In FY2018, users represented more than 20 manufacturing companies inside and outside the Hyogo prefecture. The main fields were semi-conductors, batteries, automobiles,and material food. Figure 4 shows the distributions by industry and measurement method. Users are interested in high-resolution, real-space imaging techniques such as CT, which allows direct and efficient imaging of structures. For decades, these techniques have realized direct visualization of structures in materials.

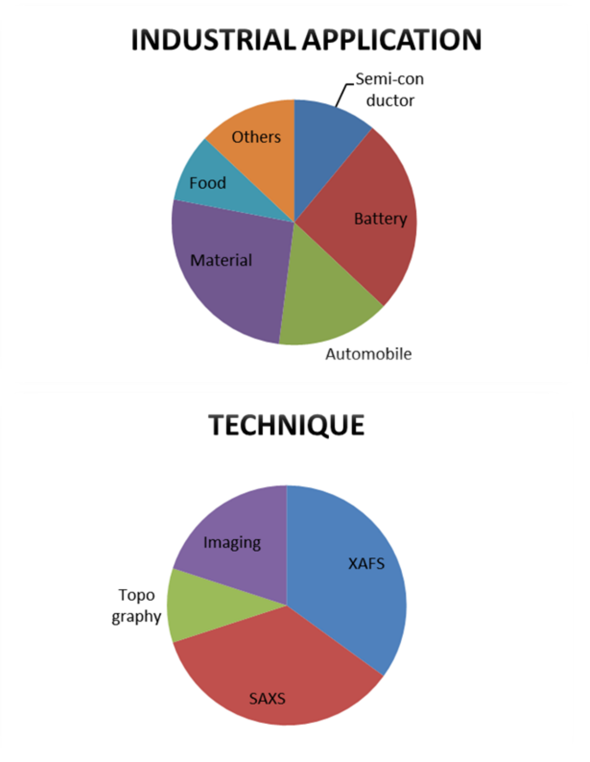

Fig. 4. Distribution by industrial application and measurement method.

5. Conclusions

As shown in this report, important features of the redox factor during a charging process of Li-ion batteries can be discussed by machine learning based on X-ray analysis data from *in situ* XAFS/XRD measurements. To collect data efficiently, an automatic system for XAFS and SAXS measurement is developed and successfully tested.

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