Development of SPICA, New Dedicated Neutron Powder Diffractometer for Battery Studies

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Abstract. SPICA, a new special environment powder neutron diffractometer was built at BL09 in the Material and Life science Facility (MLF) of the Japan Proton Accelerator Research Complex (J-PARC). This is the first instrument dedicated solely to the study of next-generation batteries in J-PARC and is optimized for in situ measurements to clarify structural changes of materials in batteries. The basic design and instrumentation of SPICA have been completed. The highest $\Delta d/d$ resolution achieved at the commissioning stage was 0.09% at the back scattering bank of SPICA. The reliability of the diffraction data has achieved a sufficiently high level for the structural analysis of materials using the Rietveld method. The air scattering banks with the blades made of B$_4$C for in situ measurements also function very well.

1. Introduction
Mankind’s technology has been largely based on the use of energy since the industrial revolution. In modern society, batteries are the key technology for energy storage because most mobile devices such as miniaturized laptop computers and cellular phones are powered only by batteries with high power, large capacity and long cycle characteristics. [1,2] Such high performance power units are required not only for small devices, but also for electric vehicles (EVs) and hybrid electric vehicles (HEVs). The present lithium ion battery still has potential applications for these applications; however, it is gradually becoming insufficient to meet requirement. Therefore, it is necessary to push the envelope in the next-generation battery systems.

The reactions in typical batteries are not so complicated and can be described as charged ions that move between positive and negative electrodes through an electrolyte; the ions transfer in the electrodes and at the interfaces of the electrodes and electrolyte. However the relationship between the

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structure changes, ionic distributions in the electrodes and battery fading are still not clear. To improve present batteries toward the development of next-generation battery systems, it is necessary to make every effort to investigate the structural changes that occur at the electrodes and interfaces in an operational battery system. The neutron is a powerful probe to determine structural information regarding the locations of light elements such as hydrogen and lithium, especially in comparison with X-rays. Thus, an advantage of the neutron diffraction technique is the acquisition of more information on the location of light ions or the changes of atomic distribution in both electrodes and electrolyte materials.

The SPICA diffractometer has been newly installed in MLF/J-PARC. This diffractometer is optimized for in situ measurements to clarify the structural changes of battery materials at the atomic level. Neutrons have deep penetration, so that they enter deeply into a battery case and provide diffraction patterns of the electrode materials. Our approach with this diffractometer is to reveal the reactions in batteries and to determine factors of safety and degradation over long periods in practical battery systems.

In the present work, we have conducted design and installment of the diffractometer. Several neutron diffraction data were successfully collected using in situ techniques. Here, we discuss the basic characteristics of this new instrument and present a quick overview of its potential impact based on recent experimental results.

2. Instrument design for SPICA
To make in situ measurements of real batteries more fruitful, we need high $\Delta d/d$ resolution with wider d ranges to detect many phases during chemical reaction, high neutron intensity to know the specific reaction process in high speed charge/discharge, low background and large sample area to install big sample environment and a dedicated chemistry area to carry out long-term scheduled experiments with many sets of on-beam measurements and off-beam charge-discharge measurements. The instrumental design is started with the assumption that (1) the sample size is $20 \times 40$ mm$^2$ and (2) the $\Delta d/d$ resolution is under 0.08% at the back scattering bank.

SPICA is installed at BL09 in 1st experimental hall of MLF. The sample position is 52 m from the poisoned and decoupled moderator. The thin side of the poisoned moderator was selected. The neutron intensity on the thin side is weaker than that on the thick side; however, the thin side has an advantage of a symmetrical peak profile, which can be extracted the strain information from samples.

A focusing supermirror guide was required to increase the number of neutrons that reach the sample position. The elliptical guide with off-focusing in the vertical and horizontal planes is one of the candidates for focusing. After several elliptical guides designs were simulated using McStas [3], the final design of the supermirror guide, which has a gradually changed mirror coating from m=3 to 6 at the posterior half of the guide, was adopted.
The basic layout of the SPICA instrument is shown in Figure 1. The flight path is 52 m from the moderator to the sample position and 2 m from the sample position to the detectors. The T0 chopper rotates with a frequency of 25 Hz, which is the same as the repetition rate of the proton beam injection. The natural bandwidth of the instrument is 2.9 Å. Three single disc choppers are used for bandwidth selection to prevent frame overlaps and operated with 25/4 to 25/1 Hz repetition to select bandwidths. The minimum bandwidth is from 0.4 to 2.5 Å at 25 Hz repetition, and the maximum bandwidth is from 1.6 to 10.1 Å at 25/4 Hz repetition.

The detector system has been successfully installed (Figure 2). SPICA utilizes 1568 3He gas position sensitive detectors (PSDs) with 1/2 inch diameters and 0.60 m active length of a total 0.67 m. Eight detectors were assembled in one detector-component box. The detector-banks are formally grouped according to scattering angle; back scattering bank (175-150°), multi purpose bank including high angle (150-120°), 90° bank (120-60°), low angle bank (60-10°) and small angle bank (15-5°). The horizontal detector crates are arranged on a cylindrical locus from \(2\theta = 175\) to 5° and are located approximately 2 m from the sample position. The back scattering bank and multi purpose bank have two other up and down vertical crates (totally 3 crates) that cover the maximum elevation angle (+/-35°), because these banks are the main banks for high resolution and high intensity in situ measurements. At the low angle bank, there is just one extra down vertical crate that has a maximum elevation angle (-35°) to quickly collect low-\(Q\) data for long-range periodic structures. This detector-formation the collection of several diffraction data in a shorter time shot pulse by using multi-angle data with different wavelengths.

SPICA has a “sample vacuum chamber” with a diameter of 1m. The back scattering bank also has a “scattering vacuum chamber” located between the sample chamber and detectors. These chambers are basically filled with argon gas and evacuated for precise measurements. The sample vacuum chamber can be removed to set large special sample environments. The multi purpose bank has air scattering chambers installed with aluminum blades coated with B\(_4\)C resin as course collimators. The blades are spaced in view of each detector box. In the previous simulation study, the loss of neutrons in the air scattering chamber was approximately 6 - 11% in the wavelength range of 0.2 to 6.0 Å [4]. Among all detected neutrons, the ratio of air-scattered neutrons was suppressed to less than 1% with the blades. Therefore, the air scattering chamber is very reliable for in situ measurements because the SPICA instrument is capable of adapting to a large space for sample environments, in addition, the use of the removable sample vacuum chamber with very small loss of scattered neutrons.

![Design illustrations of SPICA instrument.](image)

**Figure 2.** Design illustrations of SPICA instrument. (a) 3He PSDs encircled equidistant from the sample position. The back scattering, 90° and low angle banks have not only the horizontal crate but also extra vertical crates. (b) The back scattering banks and incident neutron beam path can be evacuated. The multi-purpose banks have air scattering chamber with B\(_4\)C resin collimators.

### 3. Performance and recent data under commissioning

Several reference materials such as Si, CeO\(_2\), TiO\(_2\) provided by National Institute of Standards and Technology (NIST) were measured to confirm the reliability of the SPICA instrument. All diffraction
profiles indicated low background and good signal to noise ratios. A typical measurement time was 0.5hr for 0.5g of NIST Si powder at 25/3 Hz repetition. The best $\Delta d/d$ resolution using implosion diamond powder was recognized to be less than 0.09% at the stage of this commissioning. Figure 3 shows the Rietveld refinement of CeO$_2$ collected from the back scattering and 90º banks. The observed intensities are consistent with those calculated from the crystal model. Figure 4 shows a typical in situ measurement for a commercialized Li-ion battery using the air scattering chamber. The structural change of the material, which is dependent on the lithium content, was clearly observed. The lattice parameters for the anode and cathode materials as a function of the lithium content were extracted from the diffraction patterns. The structure refinements are in progress. These results promise that SPICA has the high potential of structure refinement for in situ measurement even using air scattering bank.

![Figure 3. Rietveld refinement pattern of NIST CeO$_2$ on SPICA. Observed (red +), calculated (solid light blue line) and difference (dark blue line) data are plotted. (a) Back scattering banks and (b) 90º banks (air scattering chambers).](image)

![Figure 4. Relationship between the discharge/charge time and the diffraction profile changes of materials in a 18650-type lithium battery.](image)

4. Conclusion
The SPICA instrument has been built to perform in situ measurements for battery studies. All components for experimental implementation using SPICA have been also been installed. After the basic commissioning, the structure refinements of NIST standard reference materials were successfully completed. Initial in situ experiments have also been conducted. The SPICA instrument was confirmed to provide good performance, low background, high reliability and high resolution.

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