Newly Developed Soft X-ray High Energy Resolution Grating Spectrometer Opens Up the Door of Routine Analysis of Li by Electron Microscopes

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Key points
・ Distinguished wide energy range capable to analyze the Li K emission. The nominal low energy limit is 50 eV.
・ High energy resolution. The guaranteed energy resolution at the Fermi-edge of the Al-L emission of Al metal is 0.3 eV.
・ Ultimate sensitivity. Detection of a few tens of ppm of a light element including boron can be achieved.
・ Spectral mapping capability. Varied-line-spacing (VLS) grating and CCD detection camera are fixed during a measurement, and it enables the acquisition of an entire spectrum simultaneously for the respective grating.
・ Chemical state mapping function. A routine function for electron probe micro analyzers can be applied to provide chemical state mapping by courtesy of high-energy resolution feature.

Summary
Under an industry-academia joint seeds innovation project leaded by the Japan Science and Technology Agency (JST), JEOL, Tohoku University, Shimadzu Corporation, and the Japan Atomic Energy Agency succeeded to develop a soft X-ray high-resolution emission spectrometer specialized for electron microscopes by developing dedicated VLS gratings, and it allows the analysis of light elements including Li.

Background and development
From 2004 to 2007, the group of Prof. Masami Terauchi at Tohoku University developed a state of the art soft X-ray spectrometer that was attached to a general-purpose transmission electron microscope (TEM) under a project founded by the Ministry of Education, Culture, Sports, Science and Technology (MEXT). They successfully observed spectra the Al-L emission of Al metal with an outstanding high-energy resolution of 0.2 eV. As a result of this success, from 2008 to 2012 JST funded an industry-academia joint seeds innovation project (development stage) to develop a spectrometer which allows observing soft X-ray spectra across wider energy range taking advantages of the VLS gratings correcting aberrations. The gratings are optimized to be utilized as dispersive elements of soft X-ray high-energy resolution spectrometer that work with TEM systems as well as electron probe microanalyzer (EPMA) and scanning electron microscope (SEM). The newly released spectrometer is now commercially available for both the product lines of SEM and EPMA. The successive developments are going on to expand the accessible energy range and
applications to enhance the commercial adaptabilities.

By utilizing the VLS gratings as the dispersive elements, the movable portion in the spectrometer is eliminated. This allows the measurement of an entire spectrum for the elements of interest simultaneously as well as it makes it possible to acquire a full spectrum at each point while mapping (Fig. 1). The energy resolution of this spectrometer is more than one order of magnitude better than that of the traditional, wavelength dispersive spectrometer (WDS) attached to EPMA. The guaranteed energy resolution at the Fermi-edge of the Al-L emission of Al metal is 0.3 eV (Fig. 2). The nominal lowest energy of spectrometer is 50 eV. This allows the measurement of Li-K emissions (54 eV), which is not accessible with conventional WDS or energy dispersive spectrometer (EDS) (Fig. 3). These promising features of the soft X-ray spectrometer would play the leading roles to the development and characterization of Li-ion batteries. The charging and discharging of the Li+ ion in the Li-ion battery anode was observed by tracking the chemical changes (Fig. 4). Thanks to the high-energy resolution of the spectrometer, the characteristic X-ray spectra reveal spectral shapes that correspond to the chemical state of the elements (Fig. 5). By analyzing the variation appeared in the peak shapes of the spectra morphologically, it is possible assign the distribution of different chemical states of a single element, finally chemical state maps can be created (Fig. 6). In addition, the P/B ratio of this spectrometer is also much better than that of WDS or EDS, allowing for the detection and quantification of, for example, only a few tens of ppm boron or nitrogen in steel. Numerous examples of emission spectra for Li-K, Be-K, B-K, C-K, N-K, O-K, Mg-L, Al-L, Si-L, and P-L have been collected up to now. They predict that there are huge application fields ranging from metals to inorganics, including polymer materials, electronic materials, electronic devices, and batteries. This spectrometer would provide the insight that could not be obtained with either EDS or WDS. This spectrometer would contribute to the fundamental understanding of material properties and characteristics. The ability to perform routine chemical state analyses is also expected to make it useful for the practical development, evaluation, and testing of materials.

This commercial Soft X-ray Emission Spectrometer is produced by JEOL Ltd, in which a VLS grating is provided by Shimadzu Cooperation. It is planned to exhibit the released commercial Soft X-ray Emission Spectrometer (SXES) at the 5th International Rechargeable Battery Expo, Battery Japan (Feb 26 to 28, 2014, Tokyo Big Sight).

Refer to [Explanation of terminology] for the underlined words
Figure 1. Photograph of the newly released commercial soft X-ray spectrometer (SXES) attached to electron microscopes (left) and schematic diagram of simultaneous measurement of soft X-ray spectra by parallel detection (right).

Figure 2. The spectrum showing well-defined Fermi-edge of Al metal measured by SXES. The estimated energy resolution is better than 0.3 eV.
Figure 3. The emission spectra of Li-K (54eV). Samples are Li-metal (top) and LiF (bottom).
Observation of Li-K spectra in Li-ion battery anode

Fig. 4. Spectral maps of Li-ion battery anodes, corresponding to the respective charge conditions and energies.

**Si-L emission spectra**

Figure 5. Si-L emission spectra of SiC (left top), Si$_3$N$_4$ (left middle), SiO$_2$ (left bottom), and Si-wafer (right). Characteristic features of respective compounds are clearly observed.
Chemical state mapping using emission spectra of Al-L

Figure 6. Spectral mappings showing the difference of chemical states observed at a spectral shift of only 1 eV.
【Explanation of terminology】

◆ Fermi edge
At ground state, the electrons in a crystal occupy various energy levels. The highest energy level is called the Fermi level. A sharp upper boundary is produced in the X-ray spectrum, because no X-rays of a higher energy can be produced. This particular level is called the Fermi-edge, and is used to identify the chemical state of the element, traditionally through observation of the edge’s energy using photoelectron spectroscopy and electron energy-loss spectroscopy.

◆ Varied-line-spacing (VLS) grating
VLS grating having varied line spacing grooves makes it possible to correct aberrations in the spectral image. The grooves of the VLS grating are formed by recording the interference fringes of coherent laser beams having various wavefronts on the grating blank. Recently, The VLS gratings are widely used in monochromators of synchrotron radiation facilities and the emission spectrometers of plasma diagnostics, etc.

◆ General-purpose transmission electron microscope
A commercially available transmission electron microscope (TEM) using electrons accelerated with voltages of about 100 kV to 400 kV. By comparison, TEM systems that use accelerating voltages of 1000 kV or higher are called ultra high-voltage electron microscopes, and are in a separate class from the general-purpose instruments.

◆ Electron probe microanalyzer (EPMA)
An instrument used to determine the quantity and types of elements present in a part of a sample by exposing the sample to a beam of accelerated electrons and observing the characteristic X-rays emitted from the exposed region. It uses the wavelengths of the X-rays to determine the source element.

◆ Scanning electron microscope (SEM)
An instrument used to image the surface of a sample at high magnification. It scans the specimen surface with a narrow electron beam, detects the various electrons being emitted at each point illuminated by the beam, and creates an image of the area. The SEM consists of an electron optical system to generate and raster the electron, signal detectors, a specimen stage, monitors to display and record images, a recording system, a vacuum system to maintain a high vacuum environment in the microscope column and specimen chamber, and a control system to operate all these systems.

◆ P/B ratio
It is the ratio between the peak intensity (P) and the background signal intensity (B) of a spectrum.