

NEW APPARATUS, UPGRADES & METHODOLOGY

RISING (Research & Development Initiative for Scientific Innovation of New Generation Batteries) beamline

“Energy” and “environment” become more important for sustainable development in society. Novel developments in the environmental and energy technologies are expected in the next few decades. In a future “smart city”, the commodification and dissemination of natural energy into society, such as solar cells and wind power generation, the rejuvenation of infrastructure for transportation due to the commercial deployment of plug-in hybrid vehicles and electric vehicles, and the implementation of smart grid communication in the electrical network will be realized, which will bring us a completely different society. Rechargeable batteries are key components in all these technologies. In other words, a technical leap in rechargeable batteries will play a vital role in green innovation. A lithium-ion battery is typical of the rechargeable batteries.

Japan firstly commercialized lithium-ion batteries in 1990s. Japanese technologies and market share have dominated the world market until early 2000s. In the late 2000s, however, Korea and China have rapidly caught up in the market of compact size rechargeable batteries of portable devices and taken over the first place. In the next decades, Japanese technological predominance in the growing market for large-scale rechargeable batteries for plug-in hybrid vehicles and electric vehicles is being undetermined.

In these unpredictable circumstances, the Research & Development Initiative for Scientific Innovation of New Generation Batteries (RISING) project funded by NEDO (New Energy and Industrial Technology Development Organization) has been started in October 2009. This is the all-Japan project under the robust industry-government-academia collaboration. The final goal of this project is to take back the top share in the global market through the development of post-lithium-ion battery as well as further improvements in the performance of the existing lithium-ion batteries. The following three missions are being focused in the RISING project. They are (1) the innovation of lithium-ion batteries technologies through the strong cooperation among universities, industries and national institutes, (2) the development of truly innovative rechargeable batteries far surpassing the present lithium-ion batteries, and (3) the establishment of a new interdisciplinary community for rechargeable batteries. On the basis of the present project establishments, a new concept for innovative

batteries will be introduced and embodied, and also an energy density of 300 Wh/kg will be reached in a laboratory scale by 2015, which will be the obligatory first step in attaining rechargeable batteries with an energy density of 500 Wh/kg in 2030.

Through understanding of the properties in electrodes, electrolyte solutions, and especially the electrode/electrolyte interfaces of rechargeable batteries during battery reactions are indispensable. Thus, the research beamlines specialized for analyses of battery reactions are being built in the most advanced Japanese synchrotron research facility, SPring-8. Using the RISING beamline, we will explore why, under the policy of “Begin with the Basic” as the project leader Prof. Ogumi mentioned.

A typical lithium-ion battery consists of a negative electrode made of graphite, a positive electrode made of a lithium cobalt oxide, a separator diaphragm and an electrolyte containing lithium salt in an organic solvent. Theoretically, lithium ions are extracted from a layered oxide and intercalated into graphite during charge and reversely move from graphite to oxides during discharge. In a working battery, however, the negative and positive electrodes are composed of powders of active materials mixed with a small amount of binder and carbon powder as it is shown in Fig. 1. For example, lithium ions are extracted from graphite and move into the positive electrode through the separator in the discharge process. The migration time of lithium ions from the separator to the aluminum current collector in the positive electrode varies from 10 to 100 s. The time for the insertion of lithium ions into an active material that is controlled by the diffusion rate, a phase transition, and structural

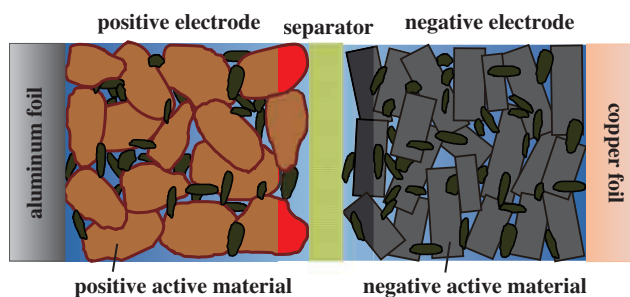


Fig. 1. Schematic drawing of the cross section of a pair of positive and negative electrodes in a commercial lithium-ion battery.

The Kyoto University RISING beamline (BL28XU)

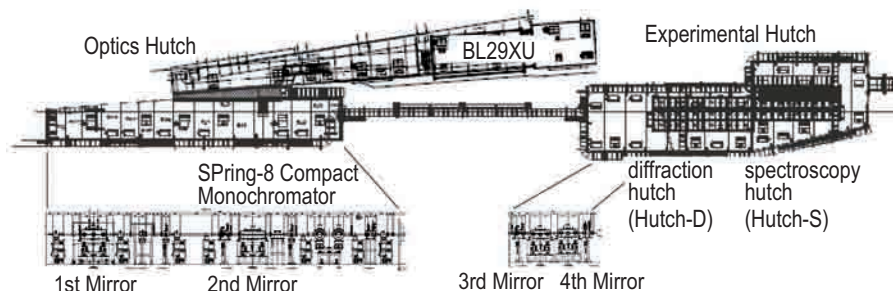


Fig. 2. Floor plan of the RISING beam line (BL28XU) in the SPring-8 experimental hall.

relaxation during lithiation and delithiation, ranges from 10 ms to 1 s. In addition, the migration time through the interface layer between the active material and the electrolyte ranges from 100 μ s to 1 ms. Namely, because of this distinctive structure of composite electrodes, the total battery reaction in the composite electrodes in commercial batteries is composed of various elementary reaction processes with different time constants, which induces a time-dependent reaction distribution in a limited space of 100 μ m between the two electrodes. This reaction heterogeneity during battery charge/discharge cycles will be thoroughly investigated by special time-resolved experimental techniques for the innovation of the battery performance and the improvement of the cyclic degradation.

Quasi-monochromatic synchrotron beams are obtained from the tapered in-vacuum undulator in the RISING beamline. This beamline consists of one optics hutch and two experimental hutches, as shown in Fig. 2. By using the four mirrors installed for horizontal and vertical focusing processes, and a cut-off of higher harmonics, about 10 to 100 μ m² focused and very low divergent beams are obtained at the sample in the lower experimental hutch. Either quasi-monochromatic or monochromatic beams from 5 to 30 keV are chosen by the SPring-8 compact monochromator with a Si 111 channel-cut crystal, which is located at the lower side of the second mirror in the optics hutch. In the upper experimental hutch, mainly time-resolved diffraction experiments are carried out during battery reactions. In these diffraction experiments, the anomalous X-ray scattering phenomena will be especially utilized for element- and valence-selective diffraction measurements. Furthermore, the grazing incident X-ray scattering method will also be adopted in order to analyze the structural change at the active material and electrolyte interface during the reaction in a film model battery. In the lower experimental hutch, the spectroscopy experiments by time-resolved XAFS and hard X-ray

photoemission spectroscopy (HPES) measurements are carried out. In addition to the conventional time-resolved XAFS measurements, the quick XAFS, the dispersive XAFS, and the time- and space-resolved XAFS with submicron focused beams by a Kirkpatrick-Baez (KB) mirror will be planned in this spectroscopy hutch. By combining these diffraction and spectroscopy measurements with various measurement times and probe sizes in Fig. 3, we will study complex phenomena in model batteries and commercial ones.

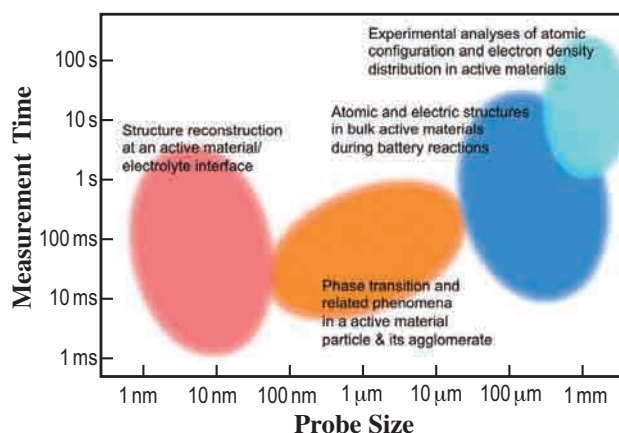


Fig. 3. Mapping of various phenomena in battery materials projected on a graph of measurement times and probe sizes used in the RISING beamline.

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