The strong development of lithium batteries used in portable devices and more recently for transportation and grid managing leads to a considerable amount of researches on materials and characterization of their properties.

In all systems used in commercialized batteries, reversible topotactical lithium intercalation reactions are involved. These reactions required simultaneous intercalation (deintercalation) of Li\(^+\) ions and electrons in the electrode materials. These processes concern the Solid State chemistry field (synthesis and characterization) and Solid State Electrochemistry (diffusion and electrochemical properties).

The cell voltage at the equilibrium is equal to the difference in Fermi level between the two electrode materials. This value is sensitive to all modifications occurring in the material involved in the intercalation reaction: (i) change in the material structure (Madelung contribution), (ii) cell parameter modifications, (iii) change in the band structure, (iv) band filling. The shape of the curve gives a direct image of the phase diagram. Moreover, thanks to the sensitivity of the voltage determination, it allows to detect very small changes in composition like the presence of vacancies in the framework structure, or structural defects. The electrochemical monitoring of the reaction allows to insert in a reproducible way 10\(^{-2}\) moles of Li\(^+\) in one hour or, in the opposite, 1 mole in one minute. At very low rate it is almost possible to intercalate almost “one electron per one electron” that allows to detect very small material modifications, whereas at very high rate it is possible to induce the formation of very metastable intermediates.

All reactions being performed in the vicinity of room temperature most of the material formed during the (de)intercalation process are metastable. Therefore, the electrochemical path allows synthesizing new materials or structures which cannot be synthesized by the classical Solid State synthesis methods. This is really a new way of research for Solid State chemistry.

To follow all these reactions and understand the mechanisms, all Solid State chemistry characterization techniques have to be considered. The most used are: (i) XRD with classical X-Ray sources or synchrotron radiation, (ii) neutron diffraction, (iii) electron microscopy, (iv) XAS, (v) MAS NMR spectroscopy, (vi) Mössbauer spectroscopy, (vii) Raman spectroscopy, etc…. One has also to mention the recent development of electron microscopy techniques in aberration corrected microscopes which allows to see the atomic columns and to detect the nature of the element on these columns (EELLS). This technique allow to detect the change occurring at the grain boundary during the electrochemical process, which is fundamental to understand the ageing mechanisms.

If all of these techniques are performed ex situ on materials removed from the cell after charge or discharge, some of them have been developed in specific cells for in situ (at the thermodynamic equilibrium) and in operando (in live) experiments during the cell cycling. They allow following the reaction at large scale (diffraction) or at the local scale (XAS, Mössbauer, Raman). In the case of diffraction phenomena the mechanism of the phase transitions can be characterized at various rates and give information on the competition between nucleation and growth processes.

For the last thirty years the Japanese research has been the cornerstone of the innovation for material discovery, material characterization and also of the industrial battery development. I have to emphasize the recent significant original developments either on synchrotron in operando experiments or on new electron microscopy techniques which have opened new ways of researches, which go beyond the battery field.