

Nanoscale Observation of the Interface of an Operating Lithium Ion Battery

The research group at Research & Development Initiative for Scientific Innovation of New Generation Batteries (RISING) Project of NEDO at Kyoto University, Japan, conducted a study on the behavior of an operating lithium ion battery, and succeeded in the world's first in-situ observation of the outermost surface of the electrode, elucidating the initial degradation process of the storage cell.

As one of the major factors leading to the degradation of a lithium ion battery, a reaction barrier is known to exist in the electrode-electrolyte interface, hindering the free passage of lithium ions. An effective measure to reduce the barrier is an integral part for future development, which requires in-situ observation of the interface while the battery is operating. The lack of practical techniques, however, has hindered nanoscale observation of the interface at work. The development of a proper analysis technique has strongly been desired.

In this research, an experiment system is constructed in search of gaining information on the nanoscale behavior taking place at the interface during the charging/discharging process, wherein X-ray absorption spectroscopy (XAS) is used to capture the electronic behavior and localized structures of the material. High intensity synchrotron radiation available at SPring-8 was used as the X-ray source, enabling the collection of information from the targeted interface among other

cell components. The focus of the research was placed on LiCoO_2 , a common material used in the positive electrode of lithium ion batteries, and a thin, flat film was prepared for the experiment for easier observation of the interface (Fig. 1). Comparison of XAS data taken before and after the immersion of the LiCoO_2 electrode in an electrolyte solution showed that the cobalt species were reduced at the wetted outermost surface of the electrode, while no change was observed in the bulk of the electrode (Fig. 2). When the system undergoes charging and discharging, reversible reactions were observed in the bulk of the electrode. In contrast, irreversible behaviors were apparent at the outermost surface, indicating that the reduction of cobalt species, induced through contact with the electrolyte, can hinder the electrode reactions from proceeding smoothly. To theoretically verify this unexpected reduction of cobalt species at the outermost surface, density function theory calculations were carried out to evaluate energy relationships. The results of these theoretical calculations clearly indicate that the oxidation of organic solvents and reduction of cobalt species can take place simultaneously at the outermost LiCoO_2 electrode surface when the LiCoO_2 electrode is in contact with the electrolyte solution (Fig. 3).

Reference: "First in situ Observation of LiCoO_2 Electrode/Electrolyte Interface by Total-reflection X-ray Absorption Spectroscopy"

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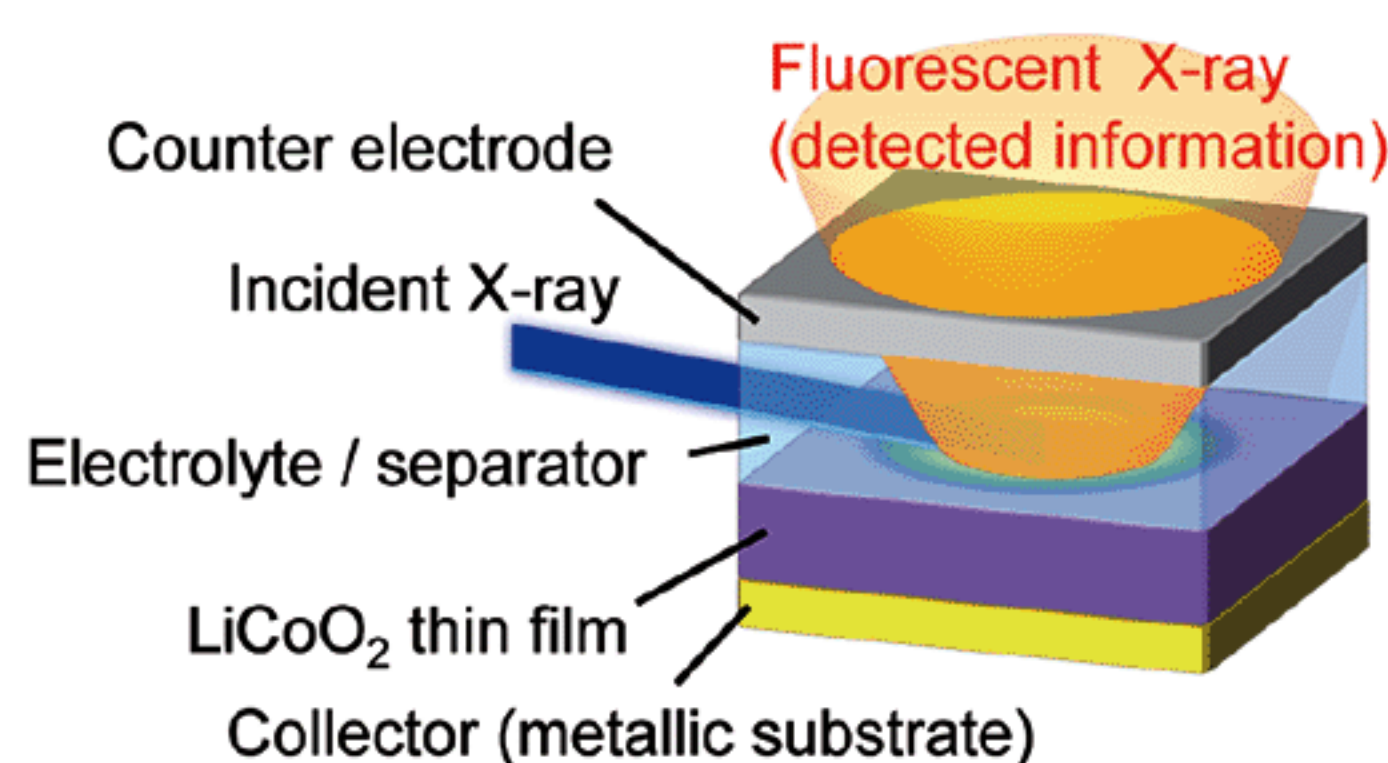


Fig. 1 Acquisition of information regarding the outermost electrode surface using XAS

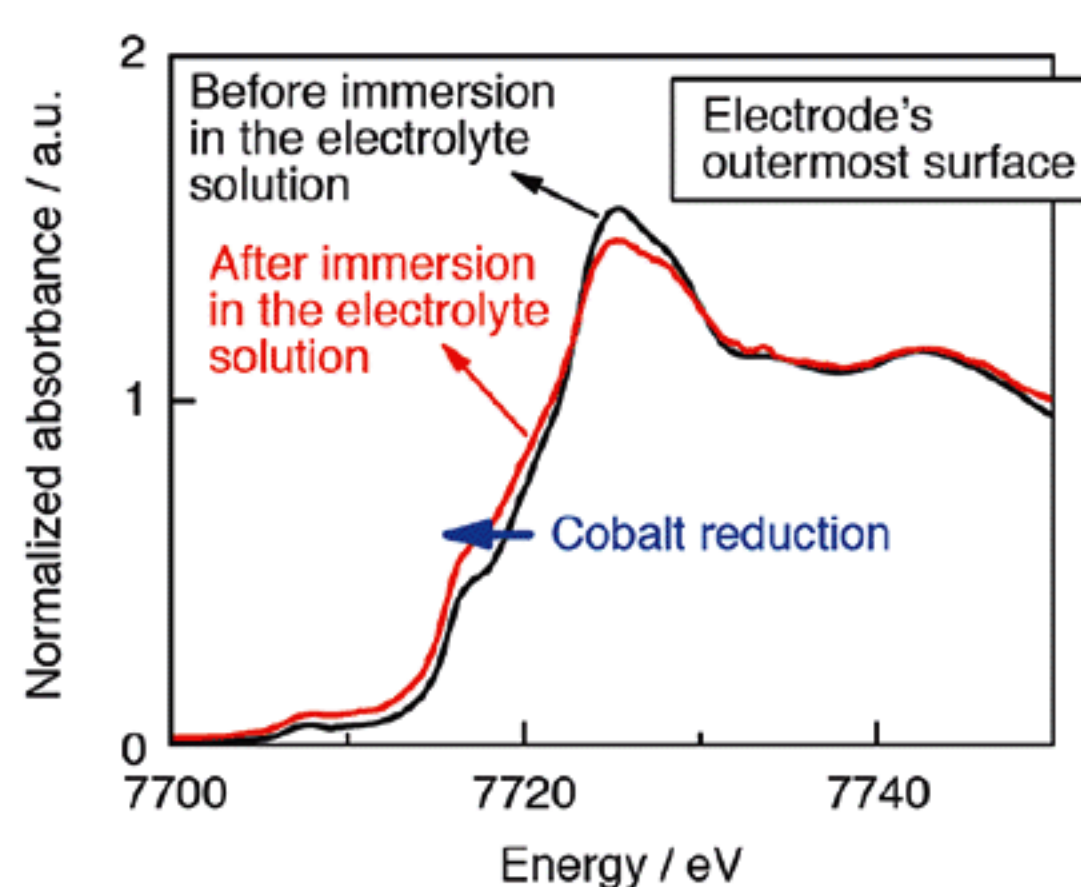


Fig. 2 Variations of the XAS spectrum of cobalt species at the outermost electrode induced by immersion in an electrolyte solution

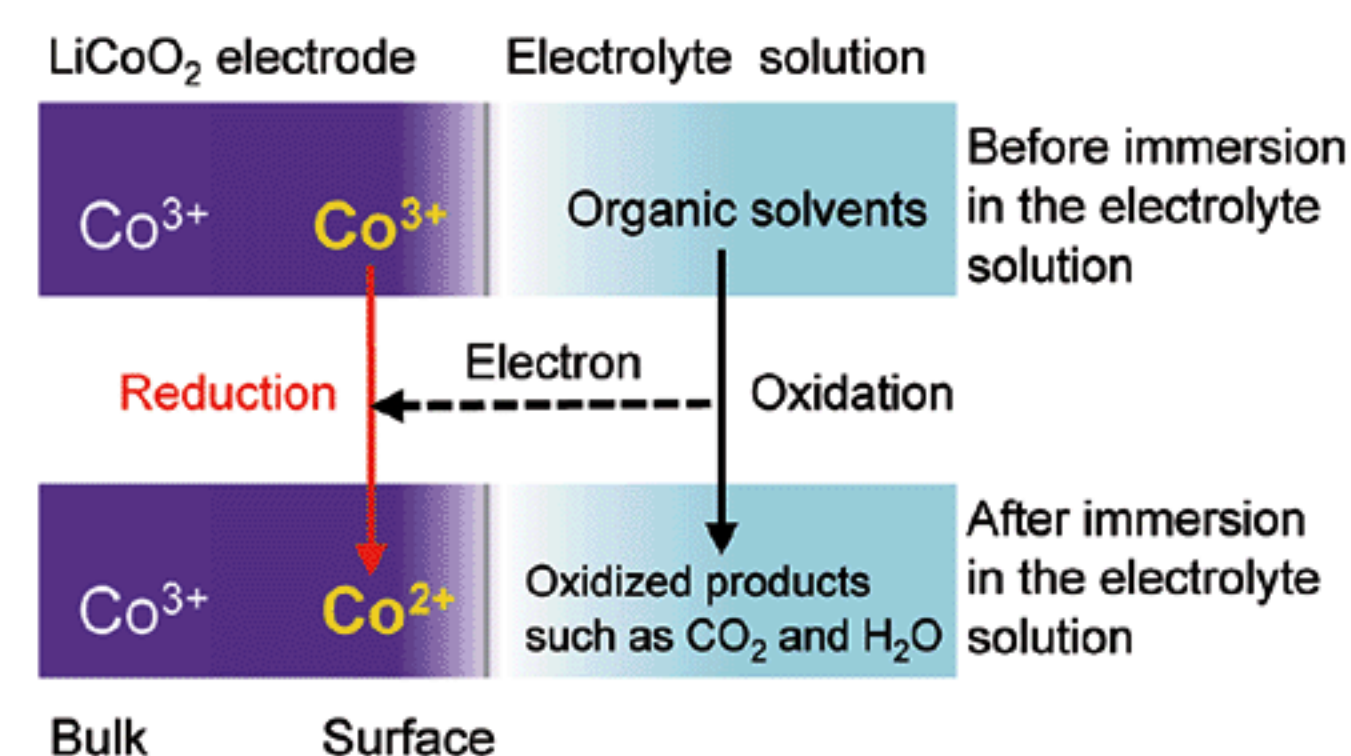


Fig. 3 Reduction behavior of cobalt species at the outermost surface of the electrode, induced by the contact with electrolyte solution