Development of Spectroelectrochemical Cells for \textit{in situ} Neutron Reflectometry

M Yonemura\textsuperscript{1}, M Hirayama\textsuperscript{2}, K Suzuki\textsuperscript{2}, R Kanno\textsuperscript{2}, N Torikai\textsuperscript{3} and N L Yamada\textsuperscript{1}

\textsuperscript{1} Neutron Science Division, Institute of Materials Structure Science, High Energy Accelerator Research Organization, 203-1 Shirakata, Tokai, Ibaraki 319-1107, Japan
\textsuperscript{2} Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuda, Midori-ku, Yokohama 226-8502, Japan
\textsuperscript{3} Department of Chemistory for Materials, Graduate school of Engineering, Mie University, 1577 Kurimamachiya-cho, Tsu 514-8507, Japan

masao.yonemura@kek.jp

Abstract. A new spectroelectrochemical cell for \textit{in situ} neutron reflectometry was developed. Electrochemical reactions were determined using this \textit{in situ} cell with a LiMn\textsubscript{2}O\textsubscript{4}/SrRuO\textsubscript{3} multi layer thin film. Changes in interfacial structures on the surface of the thin film are also observed by \textit{in situ} neutron reflectivity measurements. The performances of this \textit{in situ} cell were expected the determination of changes on the interface between the electrodes and electrolytes.

1. Introduction
Rechargeable lithium-ion batteries have been studied to improve their performance even after they were commercialized in 1990s. Applications of the batteries such as hybrid electric vehicles (HEV) and pure electric vehicles (EV) require fast charge and discharge performance. In order to achieve high current and power, various studies have examined electrochemical reactions in bulk structures. [1-6] Studies of crystal structural changes have resulted in a better understanding of the reaction mechanism in the bulk electrodes. However, electrochemical reactions occur not only in the bulk electrode but also at the electrode/electrolyte interface of lithium batteries. A comprehensive understanding of interface reactions provides a new viewpoint for the designing of electrode materials that can operate at high powers and have long-life properties. The surface layers of electrodes have been widely examined using \textit{ex situ} methods such as transmission electron microscopy, spectroscopic and electrochemical measurements. [7-13] However, the surface structural changes during the battery reactions are still unclear. High-resolution data of the interface is absolutely essential for gaining an atomistic understanding to control the kinetics in lithium battery reactions.

In order to investigate the surface structure, an ideal electrode with very flat and highly orientated model electrodes is required because polycrystal electrodes have surface morphology, grain boundaries and surface detecting which affect surface reactions. Epitaxial thin film is a possible one of the candidates for the ideal electrode that can be analyzed. Epitaxial thin film electrodes have advantages for mechanistic studies on lithium (de)intercalation and surface structural changes because the two dimensional interface restricts their reaction fields, which could enables the lattice plane dependence of the reaction to be examined directly. The surface structural changes have already been observed using \textit{in situ} x-ray scattering techniques. [14-20] It is well known that neutrons are powerful probes for determining structural information about light elements such as hydrogen and lithium, especially in comparison with X-ray. Furthermore, the neutron scattering technique will allow us to

\textsuperscript{1} To whom any correspondence should be addressed.
elucidate the behavior of lithium ions on the surfaces between electrodes and electrolytes. In the present study, we developed a new spectroelectrochemical *in situ* cell to carry out *in situ* neutron reflectivity measurements.

2. **In situ** cell design

An original *in situ* spectroelectrochemical cell was designed for neutron reflectivity measurements. It is necessary to irradiate a wide area of the thin film because the neutron beam intensity is much weaker than synchrotron X-rays. Therefore, the fabricated thin films should be wider than those used in X-ray reflectivity measurements. In this study, an epitaxial thin film with a very flat surface was successfully synthesized on a 20 × 20 mm\(^2\) square SrTiO\(_3\) (STO) single crystal substrate with a height of 5 mm. To measure reflectivity over a wide \(q\) range, the incoherent scattering of hydrogen, \(^1\)H in the electrolyte should be considered. In general, to reduce the background noise from the incoherent scattering of \(^1\)H, the cells should be designed to favor neutron beams incident on the substrate side of the film and reflected at the interface between the electrolyte and thin film electrode. (Figure 1(a))

A basic layout of the new *in situ* cell is shown in Figure 1(b). The top and bottom flange of the cell was made from aluminum metal. The substrate put on the cell body made from poly-chloro-trifluoro-ethylene (PCTFE). The substrates and cell body structure was put between the top and bottom flanges and tightened by the screw pillars. The window hole in the top flange was used to make an electric contact to connect between the substrate and a potentiostat/galvanostat for carrying out electrochemical measurements. The in/outlets on the both sides of the cell body supply the electrolyte to the surface of the thin film electrode. The big tapered screw in Figure 1(d) is an anodic electrode. This screw has trench shape so that it can be wrapped with Li metal.

![Figure 1](image-url)  

*Figure 1.* Design illustrations of a new *in situ* spectroelectrochemical cell for neutron reflectivity measurements. (a) Neutron beam passes through the substrate before reflection at the interface between the electrode and electrolyte. (b) Photo of the assembled *in situ* cell. (c) Design schematic from above. Foot print size is 16 ×16 mm\(^2\). The depth of the electrolyte reservoir on the surface of the thin film is 0.5 mm. (d) Design schematic side-on view. The anode is located under the thin films and connected through the duct filled with electrolyte.
3. Performance and recent data

Electrochemical and reflectivity measurements have been demonstrated using the developed in situ spectrotelectrochemical cell. A LiMn$_2$O$_4$/SrRuO$_3$ multi-layer thin film was fabricated on an Nb-doped STO (111) substrate (0.5% Nb) using a KrF excimer laser with a wavelength of 248 nm and PLD apparatuses (PLAD131, AOV inc. and PLD 3000, PVD Products, Inc.) to serve as a test model electrode. [21] The in situ cell was assembled in an argon-substituted glove box with lithium metal as the counter electrode and the LiMn$_2$O$_4$/SrRuO$_3$ thin film as the working electrode. Deuterated-propylene carbonate (d-PC) was employed as a solvent and a supporting electrolyte of 1M-LiPF$_6$ was used. Cyclic voltammetry (CV) was carried out using a potentiostat/galvanostat (Ivium Tech., CompactStat). Neutron reflectivity measurements were performed using the BL16, Soft Interface Analyzer (SOFIA) at the Materials and Life Science Experimental Facility (MLF) in the Japan Proton Accelerator Research Complex (J-PARC), which is a time-of-flight (TOF) reflectometer. [22]

Figure 2. shows the 2nd - 5th CV cycles of the model electrode, which were recorded with a scan rate of 5 mV/s in the potential range of 3.7 to 4.5 V. Two pairs of well-separated oxidation and reduction peaks were observed. These redox peaks occurred in bulk electrode and are attributed to the lithium insertion and extraction. [23,24]

The in situ neutron reflectivity spectra and fitting curves of the model electrode are shown in Figure 3(a). They were obtained during the in situ charge-discharge process; specifically, after setting in the thin film/d-PC/Li cell (OCV), during charging (4.1 V, 4.5 V) and during discharging (4.0 V, 3.7 V) in first cycle. Figure 3(b) shows the voltage dependence of the scattering length density profiles, which provides information on the density changes in the depth direction. The scattering length density of LiMn$_2$O$_4$ increased and decreased in accordance with the delithiation and lithiation processes, respectively. An interfacial layer (approx. 40 nm) was observed between the LiMn$_2$O$_4$ electrodes and the electrolytes. This interfacial layer could be related to the concentration gradients that results from diffusing ions in the electrolyte when an electric double layer forms. These results indicate that this in situ cell functions successfully in electrochemical and neutron reflectivity measurements.

4. Conclusion

A new spectrotelectrochemical in situ cell has been developed for neutron reflectivity measurements. Initial in situ experiments have been conducted. The redox reactions of a multi layer thin film electrode during CV cycles were determined. They were consistent with those for bulk electrodes. Changes in the interfacial reaction between the electrode and the electrolyte were adequately observed by neutron reflectivity measurements. This cell was confirmed to provide good performance for in situ neutron reflectivity measurements and electrochemical measurements.

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