Enhanced electrochemical properties of Li$_x$Ti$_2$O$_5$ epitaxial thin film electrode with surface modification

Kyungsu Kim,1 Kota Suzuki,1 Sou Taminato,1 Kazuhiisa Tamura,2 Jun’ichiro Mizuki,2 Jin-young Son,1 Masaaki Hirayama1, Ryoji Kanno1

1Department of Electronic Chemistry, Tokyo Institute of Technology, Japan
2Japan Atomic Energy Agency, Synchrotron Radiation Research Center, Japan
3Japan Synchrotron Radiation Research Institute, Japan

Corresponding e-mail: kanno@echem.titech.ac.jp

Introduction
Lithium titanium oxide, Li$_x$Ti$_2$O$_5$ is one of the most promising negative electrode materials for lithium batteries because of its high rate capability, good cyclability and excellent structural stability. It has been known that Li$_x$Ti$_2$O$_5$ shows good structural stability during charge discharge reactions.[1] However, nano size Li$_x$Ti$_2$O$_5$ electrode exhibits poor cyclability because electrode surface shows a different reaction behavior compare to the bulk region of the electrodes.[2] In addition, the bulk structural changes during electrochemical reaction have been widely investigated for the crystalline Li$_x$Ti$_2$O$_5$ materials, but little is known for the surface structural changes.[3] To overcome the poor cycle life problems of nano size electrode, it is necessary to analyze the surface structural changes during electrochemical reaction. In this study, surface modified Li$_x$Ti$_2$O$_5$ epitaxial thin films were examined to investigate the possibility of enhancing cyclability of nano electrode by surface treatment. Surface structural changes were investigated by in situ surface X-ray diffraction (XRD) and hard X-ray photoelectron spectroscopy (HXPES) measurements to find out the reaction mechanisms related with the effect of surface coating on electrochemical properties and structural stability.

Experimental
Li$_x$Ti$_2$O$_5$ electrode and Li$_x$PO$_4$ solid electrolyte were deposited on the (111) plane of the SrTiO$_3$ substrate by pulsed laser deposition (PLD) method. Orientation and crystallinity of the films were characterized by out-of-plane and in-plane XRDs recorded by a thin-film X-ray diffractometer, ATX-G (Rigaku) with Cu K$_\alpha$ radiation. The thickness, roughness, and density of the films were analyzed by X-ray reflectometry. Electrochemical characteristics were examined using 2032 type coin cell with lithium metal and 1M LiPF$_6$ in ethylene carbonate / diethyl carbonate (3:7) as counter/reference electrode and electrolyte, respectively. The bulk and surface structure changes of the electrode were analyzed by in situ surface XRD at Spring-8 BL14XU during the electrochemical reactions. HXPES measurements were carried out to at Spring-8 BL46XU to find out the variation of the oxidation state, chemical state of elements and band structure. Li$_x$Ti$_2$O$_5$ and Li$_x$PO$_4$/Li$_x$Ti$_2$O$_5$ electrodes were analyzed as a pristine condition, 1.0 V with the Li inserted state, and after 10 cycle cyclic voltammetry measurement conditions. After the electrochemical reactions, all the cells were disassembled in an argon-filled glove box and rinsed using salt-free dimethyl carbonate electrolyte to avoid contamination.

Results and Discussion
The XRD measurements confirmed the epitaxial growth of (111) oriented Li$_x$Ti$_2$O$_5$ thin films on the SrTiO$_3$ (111) substrate. Li$_x$PO$_4$ solid electrolyte was also successfully deposited on the surface of Li$_x$Ti$_2$O$_5$ thin film as an amorphous phase. From the fitting of X-ray reflectivity measurement, thicknesses of the Li$_x$Ti$_2$O$_5$ and Li$_x$PO$_4$ films were about 25 nm and 20 nm, respectively. Fig. 1 shows galvanostatic charge-discharge curves of Li$_x$Ti$_2$O$_5$ and Li$_x$PO$_4$/Li$_x$Ti$_2$O$_5$ thin film electrodes with cut-off voltages of 1.0 and 3.0 V (versus Li/Li$^+$) and a constant current density of 0.5 mA/cm$^2$. Both electrodes showed large capacity of 400 mAh g$^{-1}$, which exceed its theoretical value of 175 mAh g$^{-1}$ (Li$_x$Ti$_2$O$_5$ ↔ Li$_x$Ti$_2$O$_3$). While the capacity faded rapidly for the Li$_x$Ti$_2$O$_5$ films, the surface modified electrode showed enhanced cyclability. In addition, the Li$_x$PO$_4$/Li$_x$Ti$_2$O$_5$ electrode showed higher rate capability than that of the Li$_x$Ti$_2$O$_5$ electrode. The Li$_x$PO$_4$ layer played a role in forming a stable surface phase and improved the electrochemical properties.

To clarify the role of Li$_x$PO$_4$ layer, we observed the surface structural changes during electrochemical reaction using in situ surface XRD. Valence changes at the surface region were analyzed by HXPES measurements. The reaction mechanism at the electrode surface will be discussed.

![Fig. 1 Constant current charge–discharge curves of (a) Li$_x$Ti$_2$O$_5$ and (b) Li$_x$PO$_4$/Li$_x$Ti$_2$O$_5$ electrode. Cycling performances are also indicated in the figure.](image-url)