Microstructure of cathode material LiMn$_2$O$_4$ thin film for lithium ion secondary batteries

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Rechargeable lithium-ion secondary batteries are receiving considerable attention for use in electronic devices due to their high energy density, lightweight design compared to other battery technologies[1,2]. LiMn$_2$O$_4$ spinel is expected as cathodic materials in lithium secondary batteries, and contains a three-dimensional interstitial network through which lithium ions can diffuse and allows reverse insertion between MnO$_6$ octahedra. It is thus important to control the microstructure of grains, interface structure, crystal orientation of LiMn$_2$O$_4$ to provide better performance of Li ion transport when used in the lithium-ion batteries.

In this study, LiMn$_2$O$_4$ thin film was deposited on the Al$_2$O$_3$ substrates by a chemical solution deposition method, and the microstructures of LiMn$_2$O$_4$ thin film and the interfaces between the film and substrate were observed by HRTEM and Cs-corrected scanning transmission electron microscopy(STEM).

LiMn$_2$O$_4$ thin films were fabricated using [Li-Mn-O] metalorganic precursor solution[3]. Ligand exchange reactions of the LiOCH(CH$_3$)$_2$ and Mn(OCH(CH$_3$)$_2$)$_2$ with 2-ethoxyethanol were proceeded and the modified precursors were further mixed and reacted to prepare [Li-Mn-O] metalorganic precursor solution. LiMn$_2$O$_4$ precursor films were fabricated from the brown-colored precursor solution by spin coating onto the Al$_2$O$_3$ (0001) substrates. LiMn$_2$O$_4$ thin film was synthesized by heating the film at elevating temperatures.

X-ray diffraction (XRD) measurements on heat-treated film were performed with Cu K$_\alpha$ radiation using a diffractometer equipped with monochromator, operating at 40 kV and 40 mA. Pole-figure measurements were conducted with a pole-figure attachment using the Schulz method to evaluate the film orientation. The microstructure of prepared samples were characterized using a Cs-corrected STEM (JEM-2100F) operated at 200 kV with a high-angle annular dark-field (HAADF) detector.

Pole-figure measurements showed that six fold symmetry appeared when the (111) plane of LiMn$_2$O$_4$ were set normal to the x-ray direction, which indicated that oriented LiMn$_2$O$_4$ thin film is formed on the present substrate.

Figure 1 shows the cross-sectional HAADF-STEM image and the corresponding selected area diffraction patterns of the interface between LiMn$_2$O$_4$ spinel (space group, Fd3m) and Al$_2$O$_3$ (space group, R3c) with the incident electron beam parallel to [11$ar{2}$]LiMn$_2$O$_4$ // [11$ar{2}$ 0]Al$_2$O$_3$ direction.

The interface orientation relationship was found to be (111)LiMn$_2$O$_4$//(0001)Al$_2$O$_3$, (3 1 1)LiMn$_2$O$_4$//(1 1 0 2)Al$_2$O$_3$, [1 1 2 ]LiMn$_2$O$_4$/ [1 1$ar{2}$ 0]Al$_2$O$_3$, which resulted in the (111) LiMn$_2$O$_4$ planes grew parallel to the surface plane of Al$_2$O$_3$. Since the image contrast is roughly proportional to the square of the
atomic number, image contrast of the heavier Mn (sky blue spots) atoms are brighter than that of Al (dark blue spots) atoms. The model structures of LiMn$_2$O$_4$ and Al$_2$O$_3$ were overlaid respectively in the figure and they matched well the HAADF-STEM image.

The image revealed the lattice connectivity of the respective atomic layers across the interface, where aluminum layer for Al$_2$O$_3$ and oxygen layer for LiMn$_2$O$_4$ are directly bonded as terminate layers as shown in the figure.

Figure 1 Cross-sectional HAADF-STEM image and the selected area diffraction patterns of the interface structure of LiMn$_2$O$_4$ and Al$_2$O$_3$.

References