

Microstructure of Cathodic LiMn_2O_4 Thin Films for Lithium Ion Secondary Batteries

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Rechargeable lithium-ion batteries has been widely used in portable electronic devices such as personal computers and mobile phones. They have been further developed for use in high power applications such as fully electric vehicles and hybrid electric vehicles because of their high energy density, high power density and lightweight design compared to other battery technologies. Lithium manganese oxide (LiMn_2O_4) is a promising cathode material for such batteries because of its low cost, abundance of Mn, higher safety and environmental compatibility than the conventional layered cathode. The crystal structure of LiMn_2O_4 is of the spinel type (space group $\text{Fd}\bar{3}\text{m}$), and lithium ions can be reversibly intercalated into the structure in all three crystallographic directions. For the application of all-solid-state batteries, it is important to control the microstructure, including grain size, interface structures, and crystal orientations, to optimize the cathode's properties. In particular, the crystal orientation and quality are influenced by the processing method and the nature of the substrate.

In this study, LiMn_2O_4 thin film was deposited on the substrates by a chemical solution deposition (CSD) method, and the microstructures in LiMn_2O_4 thin film and the interfaces between the film and substrate were observed by HRTEM and Cs-corrected scanning transmission electron microscopy (STEM).

LiMn_2O_4 thin films were fabricated using [Li-Mn-O] metalorganic precursor solution. Ligand exchange reactions of the $\text{LiOCH}(\text{CH}_3)_2$ and $\text{Mn}(\text{OCH}(\text{CH}_3)_2)_2$ with 2-ethoxyethanol were proceeded and the modified precursors were further mixing and reacted to prepare [Li-Mn-O] metalorganic precursor solution. LiMn_2O_4 precursor films were fabricated by spin coating onto the kinds of single crystal substrates and synthesized at elevating temperature in oxygen. X-ray diffraction (XRD) measurements on heat-treated film were performed with $\text{Cu K}\alpha$ radiation using a diffractometer equipped with monochromator, operating at 40 kV and 50 mA. The microstructure of prepared samples were analyzed using a Cs-corrected STEM (JEM-2100F) operated at 200 kV with a high-angle annular dark-field (HAADF) detector.

To clarify the oriented structure of the thin film, pole-figure measurements were performed, as this is a powerful method for obtaining the three-dimensional information about crystal structure. The crystallographic oriented structure of the LiMn_2O_4 thin film prepared by CSD method on Al_2O_3 (0001) and Au/ Al_2O_3 (0001) was characterized using the (110) LiMn_2O_4 reflection. The pole figures of the LiMn_2O_4 on the substrates showed the three fold symmetry when the (110) plane of LiMn_2O_4 were set normal to

the x-ray direction, which indicated that oriented LiMn_2O_4 thin film was fabricated on the substrate.

The interface structure of LiMn_2O_4 film and substrate and crystallinity of the LiMn_2O_4 film were analysed. According to the selected area diffraction pattern and the HAADF image, $(111)_{\text{LiMn}_2\text{O}_4}$ is grown epitaxially parallel to the $(0001)_{\text{Al}_2\text{O}_3}$ and $(111)_{\text{Au}}$ surface. Figure 1 shows the cross-sectional HAADF-STEM image of the interface between LiMn_2O_4 and Au/ Al_2O_3 suggesting that Au atoms are directly bonded to O atoms at the interface. Since the misfit parameter between LiMn_2O_4 thin film and Au is as small as 1%, the epitaxial thin film is grown, but there existed interfacial strain along the interface, which was confirmed by LAADF (Low Angle Annular Dark Field) STEM images.

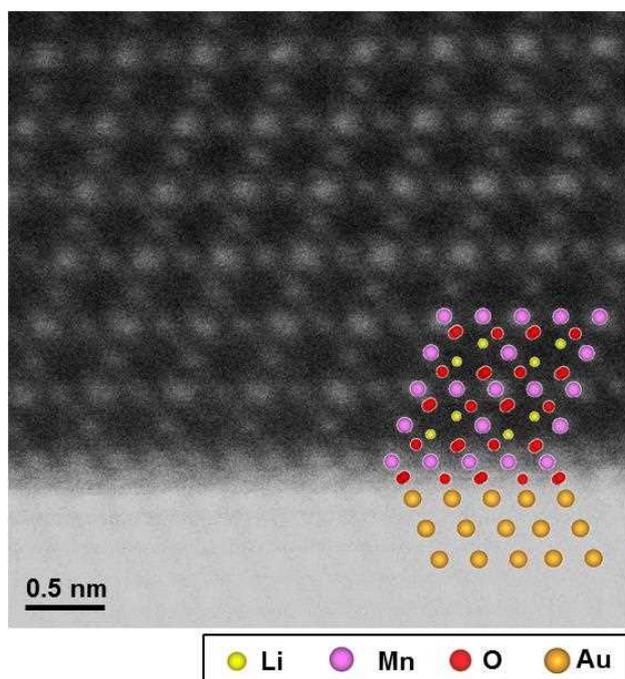


Figure 1 Cross-sectional HAADF-STEM image of the interface structure of LiMn_2O_4 and Au/ Al_2O_3 .

References

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