

Electrochemical and X-ray Absorption Spectroscopy Studies of d Metal Oxide Nanosheets

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It is important to investigate the reaction mechanism at the electrode/electrolyte interface, not only for the fundamental electrochemistry but also for the development of electrochemical applications, such as lithium ion battery, fuel cell etc. Most of the interface reaction studies have been performed by single crystal of novel metal (such as Pt, Au) materials. However, the structure at the interface at 3d transition metal oxide is still uncertain. Here we focus on the 3d and 4d metal oxide nanosheets to investigate the interface reaction behavior. By measuring of the nanosheets by X-ray absorption spectroscopy (XAS) technique, the information of the interface can be obtained. Especially manganese oxides have been investigated for electrochemical applications, because of their attractive electrochemical properties.

The manganese oxide nanosheets were obtained by ion-exchange process and exfoliation of layered manganese oxide $K_{0.45}MnO_2$ [1] (Schematic figures are shown in Figure 1). Cyclic voltammogram was carried out using a three-electrode cell; Scan rate 20 mV s^{-1} ; potential range $1.5 \text{ V} - 4.2 \text{ V}$ vs. Li^+/Li . Multilayered manganese oxide nanosheet electrode (Si wafer/PEI/ MnO_2 /(PDDA/ MnO_2)₉) was used as a working electrode, lithium foil was used as the counter and reference electrodes, and $1 \text{ mol dm}^{-3} LiClO_4$ in EC/DEC (1:1 volume ratio) was used as the electrolyte.

In the cyclic voltammogram of multilayered manganese oxide nanosheets electrode, the reduction peak appeared at 3.4 V vs. Li^+/Li on the negative going sweep, whereas the oxidation peak was observed at 3.8 V vs. Li^+/Li . These redox peaks may be attributable to the electrochemical conversion between Mn^{4+} and Mn^{3+} in the manganese oxide nanosheets.

The Mn L_{III} -edge XANES spectra were obtained using synchrotron radiation at the beam line 11A at photon factory in Tsukuba, Japan. The absorption was determined by total-electron-yield method. Electrochemical and ex-situ X-ray absorption spectroscopy studies were performed by manganese oxide nanosheets fixed on a Si wafer as an electrode. The energy of the absorption peaks in the Mn L_{III} -edge XANES spectra of manganese oxide nanosheets at various potential shift correlated with the manganese oxidation states.

The Mn L_{III} -edge XANES spectra for a monolayer manganese oxide nanosheet (Si wafer/PEI/ MnO_2) at various potentials are shown in Figure 2. The Mn L_{III} -edge XANES spectra gradually shifted to lower energy, correlated with the potential shift to lower potential. This result supports the redox reaction between Mn^{4+} and Mn^{3+} in the manganese oxide nanosheet during the electrochemical reaction. In addition, considering a monolayer nanosheet, the redox reaction is attributable to the absorption reaction because of the

nonexistence of intercalate site in the monolayer.

The local structure change around Mn ion during the electrochemical reaction was determined by Mn K-edge EXAFS.

References

[1] L. Wang *et al.*, *Chem. Mater.*, **15** 2878 (2003).

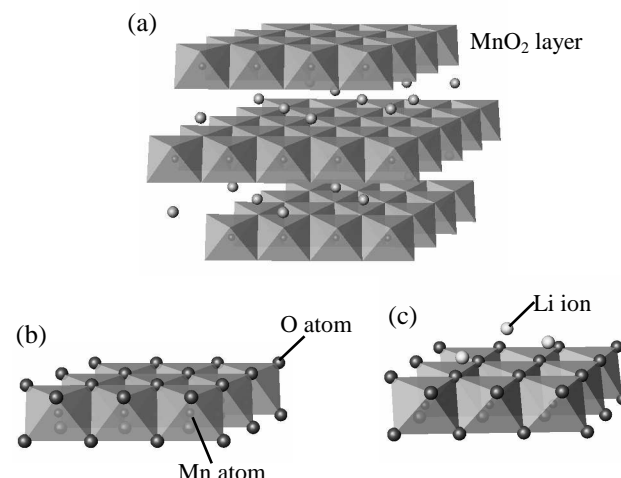


Fig. 1 Schematic figures of (a) layered manganese oxide $K_{0.45}MnO_2$, (b) manganese oxide nanosheet MnO_2 , (c) Li^+ absorption on the manganese oxide nanosheet.

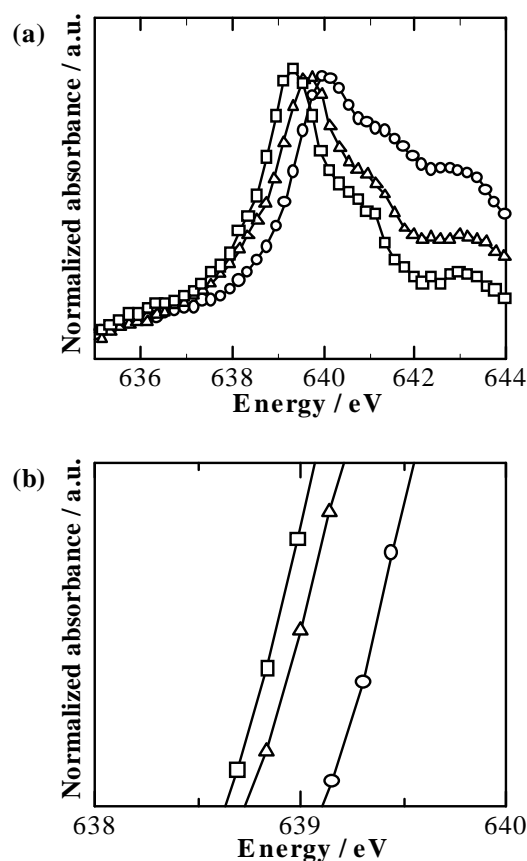


Fig. 2 (a) The Mn L_{III} -edge XANES spectra for a monolayer manganese oxide nanosheet (Si wafer/PEI/ MnO_2) at various potentials. \circ : at 4.0 V vs. Li^+/Li , Δ : at 3.5 V vs. Li^+/Li , \square : at 3.0 V vs. Li^+/Li . entire view, (b) enlarged view from 638 eV to 640 eV .