

Observation of changes in crystal structure with charge/discharge in electrode of Li-ion battery

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Introduction

Generally, the crystalline structure and texture of the host material has a significant impact on the intercalation and deintercalation reaction of Li ion. In cases requiring the high-speed transfer of Li ions or electrons in rapid charges/discharges, its effect is especially large. Therefore, to ensure improvements in performance, it is important to specify the storage site of the Li ion, while the structure of synthesized TiN_xO_y is clarified. The storage site of it has measurable influence on the electron state of the Ti atom. Therefore, this study's aim was to examine the change of the electron state of the Ti atom in TiN_xO_y by preparation condition such as temperature and processing time under NH_3 gas atmosphere by conducting XAS measurements using synchrotron radiation.

Experimental

TiN_xO_y was synthesized by direct nitridation of the titanate by using NH_3 atmosphere as a negative-electrode active material for the Li ion battery or Li ion capacitor for which rapid discharge and charge were possible.

Result and Discussion

It was confirmed that the nitrogen concentration in the sample increased in conditions where the treatment temperature was high and processing time was long. That is, the nitrogen concentration in the sample depended on the treatment temperature and time. The compositions of the sample obtained consisted of TiN , TiN_xO_y , and TiO_2 through peak separation of the $\text{Ti}2p$, $\text{N}1s$, and $\text{O}1s$ spectrum in the XPS measurement, respectively. TiN_xO_y appeared to have a graded composition on the inside of the sample. It was experimentally deduced that the intercalation and deintercalation of the Li ion occurred at the active region having TiN_xO_y and TiO_2 phases. In this study, further structural information is obtained for synthesized TiN_xO_y , and its structure will be clarified. The final aim is to specify the occlusion site of the Li ion. The result of XAS

measurements using synchrotron radiation is shown in Fig. 1. $\text{TiO}_2(\text{P}25)$ is a sign to be the sample having anatase and rutile type structure in commercial and TNR-900-1h is a sign to be the sample heat-treated under the NH_3 atmosphere for 1 h at 900 °C. Other samples are also similarly shown in the Figure.

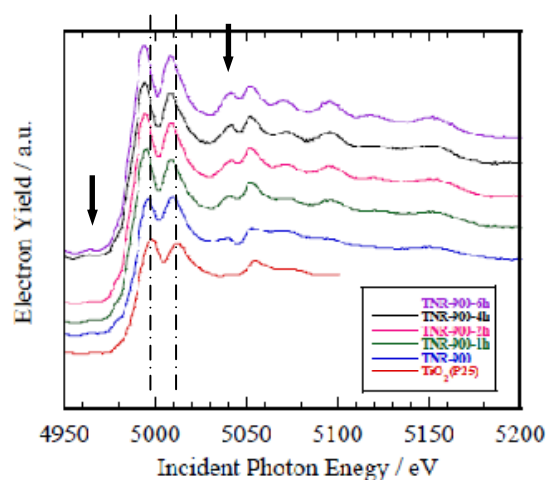


Fig. 1 XAS spectra of TiN_xO_y powders nitrided at 900°C for different keeping times and TiO_2 reference powders.

Adsorption of the energy of incident X-ray at 4967 eV and 5040 eV (shown by the arrows) strengthened with an increase in processing time. The absorption peaks of 4997 eV and 5013 eV that are shown by broken lines shifted to the low-energy side with an increase in processing time. It was confirmed that $\text{TiO}_2(\text{P}25)$ and TNR-900 in Fig. 1 were phases of TiO_2 resulting from the powder XRD pattern. Another sample was the TiN_xO_y phase. We considered that the distinction of TiO_2 and TiN_xO_y crystalline phases can be inferred to be shifted to the low-energy side of the absorption of 4997 eV and 5013 eV, and then the nitrogen content can also be inferred by the absorption intensity of the energy of incident X-ray on the 4967 eV and 5040 eV.

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