Lithium intercalation properties of the restacked MnO_2-based nanosheets with vacancy defects

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[Introduction]

The Li–Ni–Co–Mn oxide system is a promising alternative to $LiCoO_2$ or $LiNi_xCo_{1-x}O_2$ cathode materials, owing to the large capacity and low cost, and dependence of the electrode properties of Li–Ni–Co–Mn oxide on chemical composition have been extensively investigated. Ni–Co–Mn oxide nanosheets are the potential electrode materials for thin-film energy storage devices. We tried to prepare novel redoxable nanosheets of Ni–Co–Mn oxide nanosheets. In the process, we obtained the novel nanosheets with vacancy defects. In this study, the restacked Ni–Co–Mn oxide nanosheets with vacancy defects were prepared and its electrode properties for lithium-ion batteries were examined.

[Experimental]

A layered $Na_{0.55}Mn_{0.75}Ni_{0.25}O_2$(**1**) was prepared by solid state reaction. Nanosheets of Mn–Ni oxide with a chemical composition of $H_xMn_{0.75}Ni_{0.19}O_2$ (M75N19 nanosheets, **3**) were obtained by exfoliation of the proton-exchanged form of $Na_{0.55}Mn_{0.75}Ni_{0.25}O_2$(**2**) by the reaction with tetrabutylammonium hydroxide (TBAOH). The reaction of M75N19 nanosheets with HNO_3 resulted in the formation of a restacked material with a chemical composition of $H_xMn_{0.75}Ni_{0.12}O_2$(**4**). Then, $H_xMn_{0.75}Ni_{0.12}O_2$ (M75N12) nanosheets(**5**) were obtained by exfoliation of $H_xMn_{0.75}Ni_{0.12}O_2$. Restacked M75N12 nanosheets were prepared by the reaction with LiOH solution, and the electrode properties were examined for the prepared restacked materials.

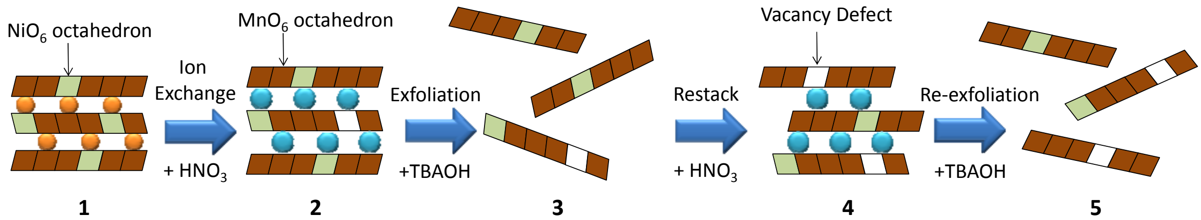

Figure 1. Schematic image of the preparation of MnO_2-based nanosheets with vacancy defects.

[Results and Discussion]

Lateral dimensions were 50–500 nm for M75N19 nanosheets, which were composed of 1–2 oxide layers. M75N12 was obtained by re-exfoliation of restacked $H_xMn_{0.75}Ni_{0.12}O_2$ nanosheets. **Figure 2** shows atomic force micrograph of M75N12 nanosheets (upper) and cross section of the region indicated by the line in the upper image (lower). The structure of M75N19 and M75N12 nanosheets was the same, and this indicates that dissolution of Ni occurs without any structural change, resulting in nanosheets with vacancy defects. The vacancy defects generated by Ni dissolution may serve as ionic conducting paths for small cations such as H^+ or Li^+ penetrating through oxide layer. Lithium intercalation properties of the restacked nanosheets and lithium-ion diffusion behavior through nanosheets via the vacancy defects will be discussed.

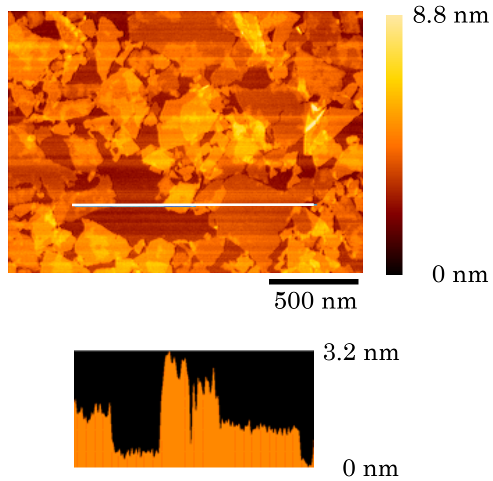

Figure 2. Atomic force micrograph of M75N12 nanosheets (upper), and cross sectional analysis by the line (lower).

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