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Characterization of Restacked MoO_2 Nanosheets Material for High Capacity Lithium-Ion Storage

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1 Introduction

MoO_2 rutile has attracted much attention as a promising candidate for anode materials in lithium ion batteries (LIBs). For instance, it has a lithiation potential of ~1.5 V lower than that of recently-commercialized lithium titanate system, which could be a great advantage for practical LIB applications. However, its unstable nature of the crystal structure during the charge/discharge makes the battery performance worse. Besides, Wang et al and his co-workers have succeeded in making structurally-fragile MnO_2 electrode materials stable via a restacking reaction of the exfoliated MnO_2 nanosheets[1]. This pioneering work motivated us to fabricate a layered material in which MoO_2 nanosheets recently obtained from total exfoliation of $Na_{0.9}Mo_2O_4$[2] are stacked.

In this study, we report a characterization of turbostratic structure of the restacked materials being composed of the exfoliated MoO_2 nanosheets and highlight their electrochemical performance [3].

2 Experiment

Layered molybdates, $Na_{0.9}Mo_2O_4$, were soft-chemically delaminated into a mass of dispersed elemental host layers, i.e. MoO_2 nanosheet suspension [1]. Immersing Si substrate pre-coated with cationic polymers used as a binder into the obtained suspension yields sub-monolayer films in which the anionic nanosheets lay flat to the substrate. In-plane X-ray diffraction patterns (XRD) of these nanosheet films were measured by a four-axis diffractometer equipped with NaI scintillation counter at the BL-6C in Photon Factory. Composite electrodes were prepared by pasting a slurry including the restacked MoO_2 nanosheets onto a Cu current collector and incorporated into an Al pouch-type cell with a Li foil as the counter electrode and $LiPF_6$-related electrolyte. The cells were subjected to Galvanostatic discharge/charge analysis in a potential range between 3.0 and 0.1 V vs. Li^+/Li at a scan rate of 0.2 $mV{\cdot}sec^{-1}$.

3 Results and Discussion

Drying the suspension of the MoO_2 nanosheets yields dark-green sediment, called "restacked material" hereafter. Powder XRD patterns for the restacked material and the in-plane XRD pattern of the MoO_2 nanosheets directly extracted from the suspension on a Si substrate as a reference are displayed in Fig.1 a and b, respectively. The XRD pattern for the restacked materials shows several broad peaks at d^{-1} values below 2.5 nm^{-1} are attributable to basal diffractions of the layered structure. Comparing these XRD patterns indicated that the in-plane crystallinity of the MoO_2 host layer remains nearly unchanged after the restacking process. In addition, these diffractions of the restacked material entail a halo-like upsurge at larger d^{-1} values, implying disorder of the stacking in the neighboring MoO_2 nanosheets. This stacking fault is inevitable in the present procedure.

The cyclic voltammogram of the cells including the restacked-material-cathodes even after 2 charge/discharge cycles (Fig.1c) shows a specific capacity of ~400 $mAh{\cdot}g^{-1}$ with prominent cathodic and anodic peaks at 1.2 and 1.5 V, respectively, which stem from the Li^+ insertion/desertion reaction at specific sites. Surprisingly, the obtained capacity is almost twice the theoretical capacity of a single Li^+ injection into the MoO_2 rutile despite similar chemical composition system. This enhancement can be understood by the activation of both sides of the surface important to electrochemical lithium storage. In situ X-ray absorption near edge structure analysis for the cells (not shown) revealed the reversible reaction of about two Li^+ without a drastic structural rearrangement, indicating a great potential of the restacked MoO_2 nanosheets as a lithium storage material.

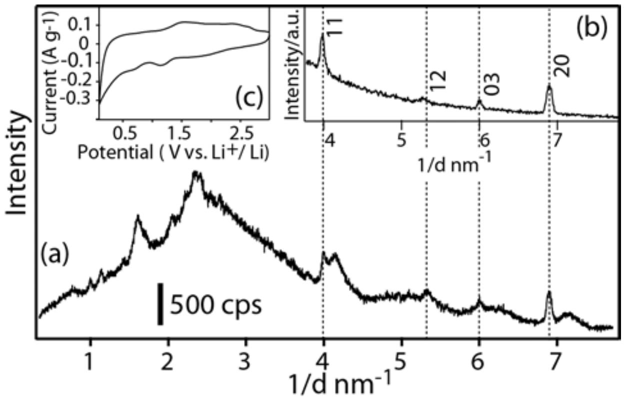

Fig. 1: XRD patterns for (a) the restacked MoO_2 nanosheets. Insets (b) and (c) are the in-plane XRD pattern for a MoO_2 nanosheet monolayer film and cyclic voltammograms for the restacked material of MoO_2 nanosheets, respectively. The in-plane diffraction peaks can be assignable to *kl* reflection of a 2D rectangular cell.

References

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