Preparation and electrode properties of novel redoxable nanosheets of Mn–Ni oxide with and without vacancy defects

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As potential cathode materials for thin-film energy storage devices, Mn–Ni oxide nanosheets with the chemical composition $\text{H}_{0.46}\text{Mn}_{0.81}\text{Ni}_{0.19}\text{O}_2$ (M81N19) were prepared. Upon restacking in HNO_3 aqueous solution and re-exfoliation, the Mn–Ni oxide nanosheets produced the novel $\text{H}_{0.58}\text{Mn}_{0.81}\text{Ni}_{0.13}\text{O}_2$ (M81N13) nanosheets with vacancy defects. The chemical composition of the nanosheets was characterized using X-ray absorption spectroscopy, inductively coupled plasma atomic emission spectroscopy, and thermogravimetry. The sizes of the M81N19 and M81N13 nanosheets were compared, and no structural change was observed after Ni dissolution from the nanosheets. The optical properties, the local structure and the electrochemical properties when used as cathodes in Li-ion batteries of the M81N19 and M81N13 nanosheets, were compared.

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1. Introduction

In recent years, nanostructured materials have attracted great interest due to their unusual electrical, optical, and mechanical properties. Among these new materials are nanosheets, which are synthesized by the exfoliation of a layered compound to form nanoscale sheets composed of a single or several layers.^{1)–3)} Various nanosheets with a wide variety of applications have been synthesized, and semiconducting,^{1),4)} dielectric,⁵⁾ electron-conducting,^{6),7)} ion-conducting,^{8),9)} ferromagnetic,^{10),11)} photocatalytic,^{12),13)} and redoxable nanosheets^{4),6),7)} have been realized even just limited to oxide nanosheets.

One major application of nanosheets is nanoscale coating via simple, green wet processes; since they are electrically charged colloidal particles with homogeneous dispersion.¹⁴⁾ Thin-film devices can be fabricated by combining several varieties of nanosheets.^{11),15),16)} Because MnO_2 nanosheets are redoxable, they are expected to be suitable for energy storage devices or solar cells, and their electrode properties for use lithium-ion batteries have been examined.¹⁷⁾

Lithium-ion rechargeable batteries have the advantage of higher energy density than other types of commercial batteries, therefore they are used as energy-storage instruments in various mobile electric devices. Large-scale lithium-ion batteries are widely adopted in many systems such as electric vehicles and energy backup in power grids. These large-scale batteries create increasing demands for low-cost electrode materials. The Li–Ni–Co–Mn oxide system is a promising alternative to commercial LiCoO_2 or $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ cathode materials, owing to its large capacity and low cost.¹⁸⁾ Therefore the effect of Li–Ni–Co–Mn oxide composition on its electrode properties has been extensively investigated.^{19),20)} The Ni–Co–Mn oxide nanosheets are potential electrode materials for thin-film energy storage devices. However, very few studies have been conducted on their pre-

paration, other than the reported $(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ and $\text{Co}_x\text{Mn}_{1-x}\text{O}_2$ nanosheet compositions.^{2),21),22)}

In this study, we prepared novel redoxable nanosheets of Mn–Ni oxide as the stage prior to the Ni–Co–Mn oxide nanosheets. Dahn and co-workers have reported the preparation of layered $\text{Na}_{2/3}(\text{Mn}_{2/3}\text{Ni}_{1/3})\text{O}_2$, where Mn and Ni are in tetravalent and divalent state respectively.²³⁾ In this compound, the negatively charged oxide layer $(\text{Mn}_{2/3}\text{Ni}_{1/3})\text{O}_2$ was neutralized by the interlayer guest cations. In our preliminary study, exfoliation into nanosheets could not be achieved using $\text{Na}_{2/3}(\text{Mn}_{2/3}\text{Ni}_{1/3})\text{O}_2$ as starting material. A smaller amount of interlayer Na is preferable as a lower charge density of the oxide layers facilitates their exfoliation into nanosheets. However, this also leads to the formation of $\text{Na}_4\text{Mn}_9\text{O}_{18}$ -type tunnel structure. Consequently, in this study we prepared a layer-structured $\text{Na}_{0.50}(\text{Mn}_{1-x}\text{Ni}_x)\text{O}_2$ ($x = 0.10, 0.15, 0.20$), and exfoliated it to obtain the novel redoxable nanosheets of Mn–Ni oxide. Then, we prepared the restacked Mn–Ni oxide nanosheets and investigated their electrode properties for use in lithium-ion batteries.

2. Experimental procedures

Layer-structured Na–Mn–Ni oxides were synthesized by a conventional solid-state reaction. Reagent-grade Na_2CO_3 , Mn_2O_3 , MnO_2 , and NiO were mixed, and ball-milled in acetone. The dried mixture was pressed to form pellets, which were then heated at 1100°C for 20 h. A 5% excess of Na_2CO_3 was used to compensate for the loss due to volatilization upon heating. The pellets were grounded and used as the starting material. X-ray powder diffraction measurements were conducted using a Bruker AXS D8 Advance diffractometer equipped with a VANTEC-1 position-sensitive detector and a Cu target X-ray tube. Scanning electron microscopy (SEM) observations were performed using a Hitachi SU9000.

The proton-exchanged form of the Na–Mn–Ni oxide was prepared by reacting the powder form of Na–Mn–Ni oxide with 1 M HNO_3 for 5 days under room temperature for ion exchange, with the HNO_3 solution replaced daily. Nanosheets of Mn–Ni oxide were then prepared by exfoliating the proton-exchanged

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Na–Mn–Ni oxide via reaction with a tetrabutylammonium hydroxide (TBAOH) aqueous solution for 3 days at room temperature. The molar ratio of TBAOH to Na–Mn–Ni oxide was 1:2. After 3 days, the unreacted particles were separated by centrifugation at 5,000 rpm, and the colloidal dispersion of nanosheets was obtained as the supernatant. The size and shape of nanosheets were observed by atomic force microscopy (AFM) using a Hitachi High-Technologies nanocute/NanoNavII.

The restacked nanosheets were prepared via the reaction of Mn–Ni oxide nanosheets with 1 M LiOH aqueous solution, followed by washing with purified water and drying at 150°C. A chemical composition of the restacked nanosheets was determined by thermogravimetric (TG) analysis using a Hitachi High-Tech Science TG/DTA6300, inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis using a Hitachi High-Tech Science SPS3100, and X-ray absorption spectroscopy (XAS) measurements. XAS measurements were conducted at both K- and L_{2,3}-edges. The measurements at the K-edge were performed using a transmission method at the BL-12C beamline of KEK Photon Factory (KEK-PF) in Tsukuba, Japan, and those at the L_{2,3}-edge were conducted using the total electron yield mode of the BL-11 beamline at the SR Center of Ritsumeikan University. Fourier transforms (FTs) were performed over the k range 3.1–14.6 Å^{−1} with k^3 weighting on the Mn K-edge XAS spectra. The structural parameters were determined by curve-fitting procedures with the software Athena/Artemis.

Properties of the restacked Mn–Ni oxide nanosheets as electrode materials in lithium-ion batteries were examined. Test electrodes were prepared by pressing a mixture of restacked Mn–Ni oxide nanosheets, acetylene black (conducting additive), and polytetrafluoroethylene (binder) on to a piece of Al mesh. The nanosheets/carbon/binder weight ratio was 75:20:5. Beaker-type cells with three electrodes were fabricated under an Ar atmosphere, with the prepared electrodes as working electrode and lithium strips pressed onto Cu mesh as reference and counter electrodes. The electrolyte solution was 1 M Li[(CF₃SO₂)₂N] in ethylene carbonate/dimethyl carbonate (50:50 v/v). Galvanostatic charge/discharge tests were carried out in the voltage range of 2.0–4.2 V (vs. Li/Li⁺) using a Hokuto Denko HAG-5001 potentiostat/galvanostat.

3. Results and discussion

Figure 1 is a SEM image of the prepared powder with a charging composition of Na_{0.50}Mn_{0.80}Ni_{0.20}O₂, showing hexagonal plate-like particles of size 2–5 μm. The powders of Na_{0.50}Mn_{0.90}Ni_{0.10}O₂ and Na_{0.50}Mn_{0.85}Ni_{0.15}O₂ had similar shape and size to that shown in Fig. 1. The actual chemical compositions were determined for each powders as Na_{0.51±0.01}Mn_{1− x} Ni _{x} O₂ using ICP-AES.

Figure 2(a) shows X-ray diffraction (XRD) patterns for the prepared Na_{0.50}(Mn_{1− x} Ni _{x})O₂ (x = 0.10, 0.15, 0.20). All peaks

Fig. 1. SEM image of the prepared powder with a charging composition of Na_{0.50}Mn_{0.80}Ni_{0.20}O₂.

are indexed to the hexagonal P2-type layered structure (space group, P_{63}/mmc) shown in Fig. 2(b), except a few and weak peaks from impurity. The lattice parameters were refined by Rietveld analyses using the RIETAN-FP code²⁴) with the powder XRD patterns, and the results are shown in Fig. 2(c). The lattice parameter a decreased almost linearly with an increase in Ni content x . A substitution by Ni causes the raise in an average valence number of Mn. This decrease is reasonable because Mn⁴⁺ (ionic radius is 53 pm when coordination number is 6²⁵) is rather smaller than Ni²⁺ (69 pm²⁵) or Mn³⁺ (64.5 pm, High Spin²⁵). Consequently, this result clearly shows that the Ni substitution was successfully conducted. The lattice parameter c didn't change linearly with the increase in Ni content. The lattice parameter c is strongly influenced by the interlayer Na content, and this may be the cause of the complicated dependence.

The prepared powders were reacted with nitric acid to form the proton-exchanged Na–Mn–Ni oxides. A reddish-brown dispersion of Mn–Ni oxide nanosheets was obtained with nanosheets yielding of more than 60% by exfoliation of the proton-exchanged Na–Mn–Ni oxide for each chemical compositions of Na_{0.50}-(Mn_{1− x} Ni _{x})O₂ (x = 0.10, 0.15, 0.20). The following examinations were conducted on the Mn–Ni oxide nanosheets prepared from Na_{0.50}Mn_{0.80}Ni_{0.20}O₂ with larger Ni content. The chemical composition of the Mn–Ni oxide nanosheets was determined

Fig. 2. (a) XRD patterns for the prepared Na_{0.50}(Mn_{1− x} Ni _{x})O₂ (x = 0.10, 0.15, 0.20), (b) schematic image of the crystal structure of Na_{0.50}-(Mn_{1− x} Ni _{x})O₂, (c) the lattice parameters Na_{0.50}(Mn_{1− x} Ni _{x})O₂ refined by Rietveld analyses as a function of Ni content x . Na_{0.50}(Mn_{1− x} Ni _{x})O₂ has 2 kinds of Na sites in the interlayer, but the minor one is omitted for clear view.

Fig. 3. AFM images of (a) M81N19 nanosheets deposited onto a mica substrate and (b) the cross section of the region indicated by the white line in (a).

using ICP-AES and XAS [see Fig. 9(a)] as $\text{H}_{0.46}\text{Mn}_{0.81}\text{Ni}_{0.19}\text{O}_2 \cdot n\text{H}_2\text{O}$. The chemical composition ratio of Mn/Ni was changed during exfoliation. XRD analysis have shown that the $\text{Na}_{0.50-}$ ($\text{Mn}_{1-x}\text{Ni}_x$) O_2 samples contain small amount of impurity, and the impurity is removed from nanosheets by centrifugal separation. Thus the Mn/Ni ratio in Mn–Ni oxide nanosheets is the actual one. This obtained dispersion of nanosheets is referred to as M81N19 hereafter.

Figure 3(a) shows an AFM image of M81N19 nanosheets deposited onto a mica substrate. Small flakelets were observed, and the lateral dimension of these particles was 50–500 nm. The thickness of these particles was less than 10 nm, so the structure of the nanosheets is clearly visible. Figure 3(b) shows the cross section at the region indicated by the white line in 3(a). Nanosheets were observed with thicknesses of 0.7 (oxide layer)²⁾ or 1.8 nm (two oxide layers and one water molecule in between). Although perfect exfoliation to obtain monolayer M81N19 nanosheets could not be achieved, nanosheets of Mn–Ni oxide were clearly obtained.

The nanosheets were restacked by reacting with LiOH aqueous solution. The chemical composition ratio Li:Mn:Ni of the restacked compound was determined using ICP-AES, yielding 34:81:19. The ratio of interlayer guest cation was smaller than that of the original compound. The valence state of Mn and Ni determined by XAS measurements did not change during the exfoliation and restacking. Charge neutrality could be attained by either protons or partial deficiency of oxide ions. Since a high concentration of oxide defects is very unlikely to form in this soft process, we conclude that charge neutrality is conserved by protons which remain on the nanosheets through the restacking reaction with LiOH aqueous solution. Thus, M81N19 nanosheets have two kinds of protons, namely the exchangeable protons and hydroxy-protons. The composition of the nanosheets would be expressed as $\text{H}_{0.34}\text{Mn}_{0.81}\text{Ni}_{0.19}\text{O}_{1.88}(\text{OH})_{0.12} \cdot n\text{H}_2\text{O}$.

The amount of hydrated water in the restacked compound was determined by thermogravimetry analysis, and the full chemical composition was expressed as $\text{Li}_{0.34}\text{Mn}_{0.81}\text{Ni}_{0.19}\text{O}_{1.88}(\text{OH})_{0.12} \cdot 0.22\text{H}_2\text{O}$. The lamination period of the restacked compound was determined by X-ray diffraction analysis as 0.70 nm, a reasonable value considering that hydrated water existed between the oxide layers.¹⁷⁾ Therefore the protons would exist as hydronium ions in the restacked compound as $\text{Li}_{0.34}(\text{H}_3\text{O})_{0.12}\text{Mn}_{0.81}\text{Ni}_{0.19}\text{O}_2 \cdot 0.10\text{H}_2\text{O}$.

Fig. 4. Discharge and charge curves of restacked M81N19 nanosheets. The current density was 100 mA g⁻¹. The cycle numbers are labeled next to the curves.

Fig. 5. Cycling behavior of the restacked M81N19 nanosheets. The values inside the figure indicate the current densities (mA g⁻¹) for discharging/charging.

The charge/discharge curves of electrode with the restacked M81N19 nanosheets are shown in Fig. 4. At the initial discharge and subsequent charge, the restacked M81N19 nanosheets showed capacities of 140 and 160 mAh g⁻¹, respectively. The discharge capacity of 140 mAh g⁻¹ corresponds to 0.48 Li intercalation per formula unit. Nickel in the restacked M81N19 nanosheets was initially divalent, thus the reduction ($\text{Mn}^{4+} \rightarrow \text{Mn}^{3+}$) of 59% Mn is responsible for this capacity. The initial charge capacity exceeded the initial discharge capacity by 20 mAh g⁻¹. This is mainly because of the oxidation of Ni, which was initially divalent. The difference of 20 mAh g⁻¹ corresponds to the oxidation ($\text{Ni}^{2+} \rightarrow \text{Ni}^{3+}$) of 37% Ni. Two plateaus were observed in the initial charge curve. The oxidations of Mn and Ni are responsible for the plateaus at the lower and higher potential, respectively.²³⁾ The characteristic capacity of Ni above 3.7 V was observed at second discharge curve, but not in the fifth discharge curve. The electrode showed relatively large ohmic drop at the beginning of each discharge and charge cycle, and the ohmic drop increased with cycling. The loss of electrical conduction path due to re-exfoliation at the charged state is a reasonable cause of this increased ohmic drop. Substantial polarization due to the low electrical conductivity prevented the reaction of Ni after five cycles.

Figure 5 shows the cycling behavior of electrodes with restacked M81N19 nanosheets. The values inside the figure indicate the discharge/charge current densities (mA g⁻¹). The capacity decreased continuously during charge–discharge cycling. During the first few cycles, a relatively rapid decrease in the capacity was observed, for which the inactivation of Ni described above is responsible. The capacity fading slowed during high-rate discharge/charge (the middle of Fig. 5). The apparent good cycling durability would be caused by the narrow effective potential range due to the large ohmic drop.

The dispersion of M81N19 nanosheets was reacted with HNO_3 , another restacking agent. The chemical composition ratio

Fig. 6. AFM images of (a) M81N13 nanosheets obtained by re-exfoliating M81N19 with HNO_3 on a mica substrate, and (b) the cross section of the region indicated by the white line in (a).

Fig. 7. Schematic images of the crystal structures of (a) M81N19 and (b) M81N13 nanosheets.

Mn:Ni = 81:13 of the resulting compound was determined using ICP-AES based on the assumption that the Mn content was unchanged. A reasonable amount of Ni^{2+} was observed in the resultant acid solution. Ni was dissolved from the nanosheets into the HNO_3 aqueous solution, and the Ni content of nanosheets decreased drastically. Therefore, the chemical composition of Mn–Ni oxide nanosheets can be changed by restacking reactions.

The HNO_3 -restacked compound was reacted with the TBAOH aqueous solution and exfoliated into nanosheets as a reddish-brown-colored dispersion. The re-exfoliated nanosheets were deposited onto a mica substrate, and the AFM image of the nanosheets is shown in Fig. 6(a). Figure 6(b) shows the cross section of the region indicated by the white line in 6(a). Partially overlapping nanosheets with lateral dimension of 50–500 nm and thickness of 0.7–1.0 or 1.8 nm are clearly observed. The re-exfoliated nanosheets are hereafter referred to as M81N13 nanosheets because of their chemical composition. The shapes of M81N19 and M81N13 nanosheets were the same, even though their Ni contents were different. The dissolution of Ni from nanosheets therefore occurred without shape change in the nanosheets.

Figure 7 schematically shows the crystal structures of M81N19 and M81N13 nanosheets. A similar type of nanosheets with Mn-site vacancy, called “nanomeshes”, had been prepared by exfoliating $\text{Na}_2\text{Mn}_3\text{O}_7$.²⁾ The Mn_3O_7 nanosheets can be expressed as $\text{Mn}_{6/7}\text{O}_2$ and 1/7 of the Mn-sites are unfilled. $\text{RuO}_{2.1}$ nanosheets (or $\text{Ru}_{0.95}\text{O}_2$ nanosheets) should also have the Ru-site vacancy of this type.^{6),16)} While in the other study the concentration of the vacancy defects is fixed, the process employed here has the potential to control the concentration of the vacancy defects by changing the composition of the starting material or the condition of acid-restacking.

Fig. 8. (a) Photographs of 20 mg/L colloidal suspensions of M81N19 (left) and M81N13 nanosheets (right), (b) UV–visible optical absorption spectra of M81N19 and M81N13 nanosheets at the concentration of 10 mg/L, and (c) typical Tauc plots for M81N19 and M81N13 nanosheets.

Photos of M81N19 and M81N13 nanosheets are shown in Fig. 8(a), and Fig. 8(b) shows their UV–visible absorption spectra. Both nanosheets exhibited optical absorption with a single broad peak at 363 and 383 nm for M81N19 and M81N13, respectively. The top of the absorption peak shifted after Ni dissolution. Figure 8(c) shows typical Tauc plots for M81N19 and M81N13. There was no apparent change in the estimated values of direct allowed bandgap between M81N19 and M81N13 (2.66 and 2.64 eV, respectively). Recently, Wang et al. used theoretical DFT calculations to show the shrinkage of band gap by introducing Mn defects into MnO_2 nanosheets.²⁶⁾ The details of the change in optical absorption are not clear yet, but the process used in this study has demonstrated the possibility to control the electronic structure of Mn oxide nanosheets.

The restacked M81N13 nanosheets were obtained with the same process as for M81N19 using LiOH aqueous solution. The chemical composition ratio Li:Mn:Ni of the restacked M81N13 nanosheets was determined using ICP-AES, yielding 24:81:13. The composition of M81N13 nanosheets was estimated using the same method as for M81N19, as $\text{H}_{0.58}\text{Mn}_{0.81}\text{Ni}_{0.13}\text{O}_2 \cdot n\text{H}_2\text{O}$ or $\text{H}_{0.24}\text{Mn}_{0.81}\text{Ni}_{0.13}\text{O}_{1.66}(\text{OH})_{0.34} \cdot n\text{H}_2\text{O}$. After determining the amount of hydrated water in the restacked M81N13 by thermogravimetry thermogravimetry analysis, the full chemical composition of the compound could be expressed as $\text{Li}_{0.24}\text{Mn}_{0.81}\text{Ni}_{0.13}\text{O}_{1.66}(\text{OH})_{0.34} \cdot 0.28\text{H}_2\text{O}$ or $\text{Li}_{0.24}(\text{H}_3\text{O})_{0.28}\text{Mn}_{0.81}\text{Ni}_{0.13}\text{O}_{1.94}(\text{OH})_{0.06}$. The latter form suggests the coexistence of hydronium-protons and hydroxy-protons in the restacked M81N13. The hydroxy-protons would exist on the oxide ions next to the

Table 1. Structural parameters for restacked M81N19 and M81N13 nanosheets determined by analyzing the Mn K-edge extended X-ray absorption fine structure spectra, where CN is coordination number (fixed value), R is bond length, and σ is Debye-Waller factor

	Mn–O (1)			Mn–O (2)			Mn–Mn (1)			Mn–Mn (2)		
	CN	R/nm	σ/nm	CN	R/nm	σ/nm	CN	R/nm	σ/nm	CN	R/nm	σ/nm
Mn81N19	4	0.1909	0.0064	2	0.2277	0.0070	4	0.2901	0.0069	2	0.2528	0.0103
Mn81N13	4	0.1901	0.0058	2	0.2265	0.0093	4	0.2893	0.0067	2	0.2506	0.0121
Mn81N13*	4	0.1901	0.0058	2	0.2264	0.0091	3.76	0.2894	0.0064	1.88	0.2501	0.0116

*fitted with 6% Mn(Ni)-site vacancy.

Fig. 9. (a) XANES spectra measured in the total electron yield mode of restacked M81N19 and M81N13 nanosheets at Mn $L_{2,3}$ -edge, and (b) the Fourier transforms (FTs) of the Mn K-edge extended X-ray absorption fine structure spectra of restacked M81N19, M81N13 and M76C24 nanosheets ($\text{Li}_{0.28}\text{Mn}_{0.76}\text{Co}_{0.24}\text{O}_2 \cdot n\text{H}_2\text{O}$).

vacancy defects generated by Ni dissolution.

The valence states of Mn and Ni were examined by XAS measurements at Mn or Ni $L_{2,3}$ -edges. Figure 9(a) shows a X-ray absorption near-edge structure (XANES) spectra measured in the total electron yield mode of restacked M81N19 nanosheets and restacked M81N13 nanosheets at Mn $L_{2,3}$ -edge. No change in the valence state of Mn between restacked M81N19 and M81N13, and the valence states of both samples were 3.9. The valence states of Ni in these samples were also determined by XAS measurements to be 2.0 (The results were omitted for the sake of simplicity.). The local structure around Mn of the restacked M81N19 and M81N13 nanosheets was studied using X-ray absorption fine structure (XAFS) analysis. Figure 9(b) shows the FTs of the Mn K-edge extended X-ray absorption fine structure spectra of restacked M81N19 and restacked M81N13. FTs is also shown in Fig. 9(b) for restacked $\text{H}_{0.28}\text{Mn}_{0.76}\text{Co}_{0.24}\text{O}_2 \cdot n\text{H}_2\text{O}$ (M76C24) nanosheets with a chemical composition of $\text{Li}_{0.28}\text{Mn}_{0.76}\text{Co}_{0.24}\text{O}_2 \cdot n\text{H}_2\text{O}$. The M76C24 nanosheets were obtained from $\text{Na}_{0.50}\text{Mn}_{0.76}\text{Co}_{0.24}\text{O}_2$ with the same crystal structure as $\text{Na}_{0.50}\text{Mn}_{0.80}\text{Ni}_{0.20}\text{O}_2$ using the same procedure as that for M81N19 nanosheets. The first peak around 0.15 nm in the FTs is due to the Mn–O contacts and that around 0.25 nm corresponds to Mn–Mn or Mn–Ni or Mn–Co interactions. The area and intensity of these two major peaks of restacked M81N19 and restacked M81N13 were smaller than those of M76C24. This result indicates that distortion of MnO_6 in M81N19 or M81N13 is larger than that in M76C24. A

Fig. 10. Discharge and charge curves of electrodes using the restacked M81N13 nanosheets. The current density was 100 mA g^{-1} . The cycle numbers are labeled next to the curves.

MnO_6 octahedron in the starting material $\text{Na}_{0.50}\text{Mn}_{0.80}\text{Ni}_{0.20}\text{O}_2$ is undistorted. Consequently, a structural transition was induced by exfoliation into nanosheets due to the cooperative Jahn–Teller effect of the slight Mn^{3+} . The exfoliation-induced structural transition is possible since exfoliation-induced distortion has been reported by Fukuda et al. for lepidocrocite-type TiO_2 nanosheets.²⁷⁾ The FTs of restacked M81N19 and M81N13 are similar to each other. Then, the vacancy defects did not cause the change in distortion of MnO_6 octahedra. The local structure around Mn in M81N19 and M81N13 was determined on the assumption that distortion of MnO_6 is the same type as that in the electrochemically-obtained $\text{Na}(\text{Mn}_{0.5}\text{Fe}_{0.5})\text{O}_2$ with the orthorhombic P2-type layered structure (space group, C_{mcm}).²⁸⁾ This assumption is reasonable because $\text{Na}_{0.50}\text{Mn}_{0.95}\text{Ni}_{0.05}\text{O}_2$ has this orthorhombic P2-type layered structure. (The result was omitted.) In this type of structure, two Mn–O bonds in MnO_6 octahedron are longer than the other four bonds, and two Mn–Mn lengths are relatively short among the lengths to six neighbor Mn atoms. The results of fitted structural parameters are summarized in Table 1. The values of 0.1909 and 0.2901 nm are approximately consistent with the previously reported values for MnO_2 nanosheets determined under the condition of Mn–O and Mn–Mn with six coordinates.²⁹⁾ No marked changes in interatomic distances were observed between the two samples with and without vacancy defects. It is possible that a 6% Mn(Ni)-site vacancy is too small to detect by XAFS analysis when measured at room temperature, and we will investigate further.

Figure 10 shows the discharge and charge curves of electrodes with the restacked M81N13 nanosheets. At the initial discharge and subsequent charge, the restacked M81N13 nanosheets showed capacities of 160 and 180 mAh g^{-1} , respectively. The discharge capacity of 160 mAh g^{-1} corresponds to 0.54 Li intercalation per formula unit, or the reduction ($\text{Mn}^{4+} \rightarrow \text{Mn}^{3+}$) of 67% Mn. The initial charge capacity exceeded that of initial discharge capacity by 20 mAh g^{-1} due to Ni oxidation, as explained above for M81N19. The reactivity of the restacked M81N13 nanosheets was comparable to that of restacked M81N19 nanosheets during the initial cycle, but the two characteristic plateaus observed in M81N19 were not clearly observed here. The capacity decreased

and the ohmic drop increased rapidly with increasing cycle number, and the fading rate of M81N13 was higher than that of M81N19. The loss of electrical conduction path due to the re-exfoliation at the charged state is again the reasonable cause of the increased ohmic drop, and this influence was more prominent in the restacked M81N13.

In summary, we have reported for the first time Ni dissolution into acid in the restacking reaction of Mn–Ni oxide nanosheets. As described above, the process used in this study has exhibited the possibility to control the electronic structure of Mn oxide nanosheets. Further, the vacancy defects generated by Ni dissolution may serve as ionic conducting paths for small cations such as H^+ and Li^+ , and we will investigate this possibility in the future. The ability to control the formation of vacancy defects in Mn oxide nanosheets will be powerful for adjusting the electrode properties.

4. Conclusions

Nanosheets of Mn–Ni oxide with the chemical composition of $H_{0.46}Mn_{0.81}Ni_{0.19}O_2$ (M81N19) were prepared using layered $Na_{0.51}Mn_{0.80}Ni_{0.20}O_2$ as the starting material. The lateral dimensions and thickness of M81N19 were 50–500 nm and 0.7–1.8 nm, respectively. Restacking these nanosheets with an aqueous solution of HNO_3 resulted in Ni dissolution without structural and local-structural change. Novel nanosheets with vacancy defects and the chemical composition of $H_{0.58}Mn_{0.81}Ni_{0.13}O_2 \cdot nH_2O$ (M81N13) were obtained by re-exfoliating of the restacked compound. The top of the optical absorption peak shifted from 363 nm (M81N19) to 383 nm (M81N13), and this suggests the possibility to control the electronic structure of Mn oxide nanosheets. Electrode properties of the restacked M81N19 and M81N13 nanosheets in lithium-ion batteries were examined. However, both electrodes exhibited unsatisfactory cycling durability, possibly due to the loss of electrical conduction path. Nevertheless, the ability to adjust the amount of vacancy defects in these nanosheets suggests potentials for improvement.

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