LiNiO$_2$ has high energy density but easily reacts with moisture in the atmosphere and deteriorates. We performed qualitative and quantitative evaluations of the degraded phase of LiNiO$_2$ and the influence of the structural change on the electrochemical properties of the phase. Li$_{1-x}$H$_x$NiO$_2$ phase with cation exchange between Li$^+$ and H$^+$ was confirmed by thermogravimetric analysis and Karl Fischer titration measurement. As the H concentration in LiNiO$_2$ increased, the rate capability deteriorated, especially in the low-temperature range and under low state of charge. Experimental and density functional theory (DFT) calculation results suggested that this outcome was due to increased activation energy of Li$^+$ diffusion owing to cation exchange. Rietveld analysis of X-ray diffraction and DFT calculation confirmed that the c lattice parameter and Li-O layer reduced because of the Li$^+$/H$^+$ cation exchange. These results indicate that LiNiO$_2$ modified in the atmosphere has a narrowed Li-O layer, which is the Li diffusion path, and the rate characteristics are degraded.
Electrochemical Properties and Crystal Structure of Li$^+$/H$^+$ Cation-exchanged LiNiO$_2$

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Abstract

LiNiO$_2$ has high energy density but easily reacts with moisture in the atmosphere and deteriorates. We performed qualitative and quantitative evaluations of the degraded phase of LiNiO$_2$ and the influence of the structural change on the electrochem-
ical properties of the phase. $\text{Li}_{1-x}\text{H}_x\text{NiO}_2$ phase with cation exchange between $\text{Li}^+$ and $\text{H}^+$ was confirmed by thermogravimetric analysis and Karl Fischer titration measurement. As the H concentration in LiNiO$_2$ increased, the rate capability deteriorated, especially in the low-temperature range and under low state of charge. Experimental and density functional theory (DFT) calculation results suggested that this outcome was due to increased activation energy of $\text{Li}^+$ diffusion owing to cation exchange. Rietveld analysis of X-ray diffraction and DFT calculation confirmed that the $c$ lattice parameter and Li-O layer reduced because of the $\text{Li}^+$/H$^+$ cation exchange. These results indicate that LiNiO$_2$ modified in the atmosphere has a narrowed Li-O layer, which is the Li diffusion path, and the rate characteristics are degraded.

Introduction

Increasing environmental awareness has raised the demand for vehicles with low CO$_2$ emissions. In recent years, global environmental concerns have accelerated the development and spread of hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles, pure electric vehicles, and fuel-cell-based electric vehicles equipped with lithium-ion batteries (LIBs). LIBs installed in electric vehicles are required to have high energy density, rate capability, safety, and lifetime.\textsuperscript{1} Ni-rich cathode active materials such as LiNiO$_2$\textsuperscript{2-5} and LiNi$_x$Co$_y$Al$_z$O$_2$\textsuperscript{6-11} are used in automotive lithium ion secondary battery applications owing to their high energy density. However, Ni-rich cathode active materials have the problem that they easily react with moisture in the atmosphere, causing structural change of the material and generation of residual Li impurities such as LiOH, Li$_2$CO$_3$, and LiHCO$_3$. As a result, the $\text{Li}^+$ insertion and desorption reactions with the active material are inhibited, and the electrochemical characteristics are deteriorated.\textsuperscript{11-15} Regarding the structural change caused by the reaction between LiNiO$_2$ and H$_2$O, a structure in which Li and H are cation-exchanged as shown in eq (1) has been proposed.\textsuperscript{4,14} However, a result that confirms the existence of $\text{Li}_{1-x}\text{H}_x\text{NiO}_2$
experimentally has not been obtained.

\[ \text{H}_2\text{O} + \text{LiNiO}_2 \rightarrow (1 - x)\text{H}_2\text{O} + x\text{LiOH} + \text{Li}_{1-x}\text{H}_x\text{NiO}_2 \]  

(1)

One of the reasons why it is difficult to identify substances experimentally is the extremely low content of the target. Usually, X-ray powder diffraction is effective in identifying the generated heterogeneous phase, but if the amount of phase is very small, such as a phase that has been altered by exposure to the atmosphere, it may be impossible to evaluate it directly because it is below the detection limit of the measuring device.

Herein, we performed experimental and computational approaches, to find out the qualitative and quantitative identification of the structural phase of \( \text{Li}_{1-x}\text{H}_x\text{NiO}_2 \) and the investigation of its influence on the electrochemical properties. The qualitative and quantitative identifications of structural change phases were attempted by combining thermogravimetric analysis and Karl Fischer titration measurements. Although it may not be possible to clearly deduce the structural change phase itself in experiments, its influence on the electrochemical properties and lattice parameter can be clearly observed even with a small amount. Therefore, we simulated the crystal structure and electrochemical properties of \( \text{Li}_{1-x}\text{H}_x\text{NiO}_2 \) which was estimated structural change phase, using first-principles calculations and confirmed the agreement between the experimental and simulation results. This study is a new initiative that shows the effects of atmospheric exposure of cathode active materials on the crystal structure and electrochemical properties accurately and quantitatively, and proposes factor to be considered especially for Ni-rich cathode active materials.

**Experimental methods**

**Substitution of Li\(^+\)/H\(^+\) in LiNiO\(_2\)**

\( \text{LiNiO}_2 \) samples were obtained by solid phase synthesis of \( \text{Ni(OH)}_2 \) and \( \text{LiOH} \). \( \text{Ni(OH)}_2 \)
precursors were synthesized by co-precipitation. A 2.0 M aqueous solution of NiSO$_4$ was pumped into a continuously stirred tank reactor in nitrogen atmosphere. The pH of the solution inside the reactor was controlled at approximately 11 by adding NaOH solution. NH$_4$OH solution, which acts as a chelating agent to control the Ni ion neutralization reaction time, was separately pumped into the reactor. The Ni(OH)$_2$ powder sample was washed, filtered, and dried in an oven at 120 °C for several hours. The prepared precursors were thoroughly mixed with LiOH powder at the ratio of Li/Ni = 1.01. The mixture was synthesized for 12 h at 710 °C in O$_2$ flow. The synthesized LiNiO$_2$ was placed in a chamber (LHL-113, ESPEC) maintained at 30 °C and 60% relative humidity under air circulation for 0, 9, 25, and 49 h. The four prepared LiNiO$_2$ samples are denoted as LNO_0 h, LNO_9 h, LNO_25 h, and LNO_49 h depending upon the exposure time.

LiNiO$_2$ contains LiOH and Li$_2$CO$_3$ produced by exposure to the atmosphere; therefore, the effects of the structural change phase and the residual Li compounds cannot be distinguished. In order to isolate the influence of the structural change phase, we attempted to remove the residual Li compound by washing the active material. The solvent used for removing the residual Li compound should be selected by considering its reactivity with LiNiO$_2$. For example, excessive extraction of Li (eq. (1)) from the bulk can occur by using water as the solvent. Excessive delithiation causes significant degradation of the electrochemical properties, making it difficult to evaluate the effects of atmospheric exposure properly. Therefore, we used ethanol, which has poor reactivity with Li, as the washing solvent. To obtain LiNiO$_2$ without residual Li compound, 10 g LiNiO$_2$ powder was added to 200 mL of distilled ethanol under constant stirring with a magnetic stirrer for 5 min.

**Material characterization**

The surface morphologies of the samples were observed by field emission scanning electron microscopy (FE-SEM, JSM-7001, JEOL). The phase transformation of the surface layer was observed by spherical-aberration-corrected scanning transmission electron microscopy.
(CS-STEM, JEM-ARM200F, JEOL). The samples were sliced to a thickness of 100 nm or less using a focused ion beam (FIB, NIB-5000, Hitachi), and the samples were observed under the acceleration voltage of 200 kV. The crystalline phases of the prepared samples were identified using X-ray powder diffractometer (XRD, X'Pert Pro MPD, PANalytical) with Cu-Kα radiation. The XRD data pattern was recorded at the scan rate of 5° min−1 in the 2θ range of 15° to 100°. Rietan-FP software was used for Rietveld analysis. The thermal behavior of the LiNiO₂ samples were investigated by thermogravimetric analysis (TGA) (DSCX3100SA, NETSZCH). Karl Fischer (KF) titration (CA-200, MITSUBISHI CHEMICAL ANALYTICAL) was used to evaluate to H₂O concentration.

**Electrochemical techniques**

Electrochemical measurements were carried out with a laminated-type full cell and CR2032 coin-type symmetric cell with positive electrodes facing each other. These cells were used for rate capability test and electrochemical impedance spectroscopy (EIS) measurement, respectively. Each LiNiO₂ sample was mixed with a conducting agent (carbon black) and polyvinylidene fluoride (PVDF) at 85:10:5 weight ratio in N-methyl-2-pyrroldone (NMP) to prepared a slurry. Then, each slurry was applied to an aluminum current collector and dried in a vacuum oven for 8 h at 120 °C. The dried coating foil was then compressed to a layer of 20 µm thickness using a roll press. Cu foil coated with graphite was used as the negative electrode in the laminate type cell. The electrolyte was 1.0 M LiPF₆ in ethylene carbonate (EC) - dimethyl carbonate (DMC) solution (3:7 by volume). For the rate capability test of the laminate-type cells, discharge rates at different current densities varying from 0.1 to 10C were applied using constant current (CC) with fixed charge rate of 0.1C and constant current - constant voltage (CC-CV) within the voltage range from 2.5 to 4.2 V at 25 °C. EIS measurements of the symmetric cells were carried out by applying an AC - amplitude of 10 mV at 100 kHz to 1 mHz frequency between -20 °C and 45 °C. The resulting Nyquist plots were analyzed using ZView software (Scribner Associates, Inc.).
Computational methodology

All first-principles calculations using DFT were performed with the Vienna Ab initio Simulation Package (VASP)\textsuperscript{19,20} with projector augmented wave (PAW) potentials. A plane-wave basis set cutoff energy of 650 eV and a Monkhorst-Pack $3 \times 3 \times 1$ k-points mesh was used for all calculations. The calculation was performed using a supercell constructed from the primitive cell by tripling the system along the directions of the $a$ and $b$ axes. Energy optimizations were based on the tetrahedron method with Blöchl corrections for Brillouin-zone integrations; their convergence criteria for the self-consistent field (SCF) and maximum force were set to 0.1 meV/atm and 1.0 meV/Å, respectively. We adopted the optB86b-vdW functional\textsuperscript{21–23} as the exchange-correlation (XC) functional because it is known to accurately reproduce experimental results such as voltage and volume in the Li detachment state. Considering the Coulomb interaction of the Ni 3$d$ orbit, a correction of $U = 6.7$ eV was added to Ni 3$d$.\textsuperscript{24} In this study, the structural configuration was drawn using VESTA software.\textsuperscript{25} In the structure relaxation calculation of the Li desorption structure, all symmetry structures that are Li defect sites were calculated, and the lowest energy configuration was defined as the Li desorption structure. The climbing image nudged elastic band (CI-NEB) method was used to determine the Li-ion diffusion barriers and paths.\textsuperscript{26,27} The initial and final configurations were determined by separately optimizing the structure with a vacancy at each of the two adjacent sites. A group of images generated by linear interpolation between the two endpoint configurations was optimized to converge to points on the minimum energy path. The five intermediate images between the two endpoints were generated by linear interpolation between the two endpoint configurations. The convergence criterion used in the CI-NEB calculations was that the forces acting on each atom was lesser than 0.02 meV/Å.
Results and Discussion

Characterization

SEM and STEM observations were performed to evaluate the changes in the primary and secondary particles and surface structure changes before and after exposure to the atmosphere and washing. Each sample was confirmed to be free of primary and secondary particle size changes, particle collapse, and deformation (Figure 1(a)-(j)). On the other hand, the particle surface changed smoothly as the exposure time to the atmosphere increased, suggesting structural changes due to exposure. In the HAADF-STEM images of the particle surface (Figure 1(k)-(l)), layered stripes representing the R3m structure of LiNiO₂ were observed both inside and on the surface of pristine (k) and LNO_0 h(l). The results also confirmed that the washing process in this study removed the residual Li compound without changing the structure of the active material. In contrast, the LNO_9 h(m), LNO_25 h(n), and LNO_49 h(o) samples had altered layers with thickness of approximately 1 nm on the outermost surface. This alteration phase on the outermost surface was suggested to be NiO with Fm̅3m structure caused by the change in the arrangement of Ni atoms.²⁸⁻³² Because the NiO thickness was almost constant regardless of the samples exposed to the atmosphere, the influence of NiO is considered not to appear as a difference between the samples in the results of the electrochemical evaluation described later.

TGA analysis was performed to identify the structural change phases owing to phenomena such as thermal decomposition and oxidation. Figure 2 shows the TGA results of LiNiO₂ after atmospheric exposure.

Weight loss from approximately 100-120 °C indicates water adsorption–desorption reactions. In the higher temperature region, large weight loss peaks were observed at 200–220 °C and 300–320 °C. These weight change peaks have been reported to be due to H₂O and O₂ elimination from NiOOH, as shown in eq. (2).³³,³⁴ Ni(OH)₂ and NiOOH may also be generated by the mixing of Li⁺/H⁺. However, the Ni(OH)₂ decomposition temperature is
Figure 1: Low-magnification surface SEM images (a)-(e) and high-magnification SEM images (f)-(j) of the samples. Cross-sectional HAADF-STEM images ((k)-(o)). (a),(f),(k) Pristine samples (no exposure to air, no washing); (b),(g),(l) LNO_0 h; (c),(h),(m) LNO_9 h; (d),(i),(n) LNO_25 h; and (e),(j),(o) LNO_49 h panels.

Figure 2: Normalized thermogravimetric rate of change of LiNiO₂ exposed to air for 0 h, 9 h, and 49 h. The upper panel shows the results of heating from 25 °C to 400 °C in Ar atmosphere. The lower panel shows the result of differentiating the weight change rate with temperature (dRM/ dT).
approximately 300°C, and the existence of one weight loss peak has been reported. Therefore, the phase generated by atmospheric exposure is considered to be NiOOH.

\[
\text{NiOOH} \rightarrow \text{NiO} + \frac{1}{4}\text{O}_2 + \frac{1}{2}\text{H}_2\text{O} \tag{2}
\]

Because LiNO\_0h had little weight reduction reaction in the temperature ranges of 200–220 °C and 300–320 °C, the amount of NiOOH in the active material is considered to be small. On the other hand, in LNO\_9h and LNO\_49h, two peak changes at 200 °C or higher increased with increasing exposure time. From these results, it was suggested that the cation exchange of Li\(^+\)/H\(^+\) proceeded at atmospheric exposure, and the production of NiOOH increased.

TGA can estimate the relationship between temperature and weight change reaction, but it is difficult to identify and quantitatively analyze the reacted substance. Therefore, quantitative analysis of the amount of NiOOH, that is, the amount of H\(^+\) exchange, was attempted by quantifying the amount of H\(_2\)O produced by the reaction in eq.(2). In order to separate the amount of H\(_2\)O derived from the adsorbed water and the amount of H\(_2\)O derived from the decomposition reaction of NiOOH, KF titration analysis was performed under two conditions of 120 °C and 300 °C. Titration at 120 °C detects the adsorbed water, and that at 300 °C detects the total amount of H\(_2\)O generated by decomposition of adsorbed water and NiOOH. Therefore, the amount of H\(_2\)O derived from the decomposition of NiOOH can be determined by taking the difference between the titration results of 300 °C (KF 300°C) and 120 °C(KF 120°C). Figure 3 shows the results of KF titration. The value of KF300°C-KF120°C increased in proportion to the square root of the exposure time, that is, the amount of NiOOH produced increased with the exposure time. We assumed that the H desorption reaction was due to heating during KF titration, as expressed in eq.(3). In this case, the amount of H contained in LiNiO\(_2\) can be calculated as shown in eq.(4) by using the amount of H\(_2\)O derived from NiOOH, \(\alpha_{\text{H}_2\text{O}}\) (Δ KF 300°C - KF 120°C). The H concentrations of
Figure 3: Relationship between atmospheric exposure time and moisture content of LiNiO$_2$. The black square and the white square are the titration results at 300 °C and 120 °C, respectively. The blue square shows the difference between the results at 300 °C and 120 °C.

LNO_0 h, LNO_9 h, LNO_25 h, and LNO_49 h were determined to be 0.08, 0.28, 0.40, and 0.51 at%, respectively.

Li$_{1-\delta}$H$_{\delta}$NiO$_2$ + $\frac{\delta}{4}$ O$_2$ → Li$_{1-\delta}$NiO$_2$ + $\frac{\delta}{2}$ H$_2$O  \hspace{1cm} (3)

$\frac{\delta}{2} = \frac{\alpha_{H_2O} \cdot M_{LiNiO_2}}{M_{H_2O}}$  \hspace{1cm} (4)

XRD evaluation was performed to investigate the crystal structure change due to cation exchange of Li$^+$/H$^+$. Figure 4(a),(b) shows the XRD profile of each sample. From the results of Fig. 4(a), it was confirmed that no significant heterogeneous formation was observed in any sample, and LiNiO$_2$ was the main phase. The (003) diffraction peak near 18.8°, i.e., the 3a site (Li site) in the R$\bar{3}$m structure, showed a shift of the diffraction angle toward the higher angle side with increasing atmospheric exposure time (Figure 4(b)). In order to verify whether this peak shift was caused by Li$^+$/H$^+$ cation exchange, the XRD peak of Li$_{1-x}$H$_x$NiO$_2$ was simulated using first principles calculations. Figure 4(c), (d) shows the XRD profiles calculated for the crystal structure of LiNiO$_2$ obtained by structural relaxation calculation with Li replaced by 0 at%, 3.7 at%, and 100 at% of H. Similar to the experimental results, the relationship between the H content and the shift of the (003) peak position was
Figure 4: Panel (a) shows the entire XRD profile of each sample, and panel (b) shows an enlarged view near the (003) diffraction angle. Panel (c) shows the result of simulating the XRD profile of LiNiO$_2$ with 0, 3.7, and 100 at% substitution of Li with H by DFT calculation, and panel (d) is an enlarged graph of (003) diffraction angle of profile (c).

also confirmed by calculation. From these results, it was found that the (003) peak position shifts to the higher angle side due to the exchange of Li$^+$/H$^+$, i.e., the c-axis lattice constant shrinks. In addition, the lattice constants obtained by Rietveld analysis and first-principles calculation are summarized in Table 1.

Table 1: Lattice constant of Li$^+$/H$^+$ cation exchange structure obtained by Rietveld analysis and first-principles calculation

| Samples          | H (at%) | a (Å)  | c (Å)  |
|------------------|---------|--------|--------|
| LNO$_{0h}$       | 0.08    | 2.8776 | 14.2057|
| LNO$_{9h}$       | 0.28    | 2.8766 | 14.2005|
| LNO$_{25h}$      | 0.40    | 2.8761 | 14.1988|
| LNO$_{49h}$      | 0.51    | 2.8755 | 14.1962|
| LiNiO$_2$(calc)  | 0       | 2.8500 | 14.1966|
| Li$_{0.96}$H$_{0.04}$NiO$_2$(calc) | 3.70 | 2.8446 | 14.1052|
| HNiO$_2$(calc)   | 100     | 2.7554 | 12.9179|
Electrochemical properties

Rate capability test results measured at different current densities (0.1–10C) are shown in Figure 5. At low discharge rate (0.1–1C), all samples showed almost the same discharge capacity. On the other hand, at high discharge rate (3–10C), a significant decrease in the discharge capacity was confirmed in the LNO_25 h and LNO_49 h samples. This result implies that a material with a large amount of Li$^{+}$/H$^{+}$ is slow to exhibit the Li$^{+}$ transfer reaction at high discharge rate.

![Figure 5: Rate characteristics measured at different rates of 0.1–10C. The samples are denoted as black square (LNO_0 h), blue circle (LNO_9 h), red triangle (LNO_25 h), and gray rhombus (LNO_49 h).](image)

EIS measurements were carried out to investigate the electrochemical resistance. In this study, the positive electrode resistance was measured using a symmetric coin cell with the positive electrodes facing each other. The resistance components of the cathode and anode are intermixed in the impedance spectrum of a normal full cell, and distinguishing the resistance of the positive electrode alone is difficult. Furthermore, in order to evaluate the relationship between the amount of Li contained in LiNiO$_2$ and the resistance, measurements were performed under the conditions of Li$_{0.50}$NiO$_2$ and Li$_{0.75}$NiO$_2$. In addition, EIS measurements were performed under four conditions of 253, 273, 298, and 318 K to obtain the
temperature dependence of Li\textsuperscript{+} diffusion coefficient and the activation energy of the diffusion. Figure 6 and Figure 7 show the Nyquist plots of Li\textsubscript{0.50}NiO\textsubscript{2} and Li\textsubscript{0.75}NiO\textsubscript{2}, respectively. In Li\textsubscript{0.50}NiO\textsubscript{2}, the charge transfer resistance (R\textscript{ct}) increased with increase in the amount of Li\textsuperscript{+}/H\textsuperscript{+} cation exchange in the temperature range of 253–318 K. On the other hand, in Li\textsubscript{0.75}NiO\textsubscript{2}, R\textscript{ct} markedly increased in the LNO\textsubscript{25 h} and LNO\textsubscript{49 h} samples in the low-temperature region of 253 K, but no significant difference in R\textscript{ct} was observed in any sample in the region of 273–318 K. To summarize these results, the higher the Li concentration in LiNiO\textsubscript{2} or the lower the operating temperature, the greater the effect on Li insertion reaction due to Li\textsuperscript{+}/H\textsuperscript{+} cation exchange. Some studies have shown that the increase in resistance in the low-temperature range is caused by a decrease in the diffusion rate of Li\textsuperscript{+}\textsuperscript{37–39} and the relationship between the Li concentration in the bulk and the diffusion coefficient of Li\textsuperscript{+}\textsuperscript{40,41}. Therefore, we believe that the Li\textsubscript{1-x}H\textsubscript{x}NiO\textsubscript{2} phase that underwent structural change due to atmospheric exposure affected the Li\textsuperscript{+} diffusion.

![EIS spectra](image)

Figure 6: EIS spectrum of Li\textsubscript{0.50}NiO\textsubscript{2} at (a) 253 K, (b) 273 K, (c) 298 K, (d) 318 K

The diffusion region of the EIS spectrum was analyzed to obtain the Li diffusion coefficient of each sample. The linear behavior in the low-frequency region of the EIS spectrum shows the Li\textsuperscript{+} diffusion behavior, and the Li\textsuperscript{+} diffusion coefficient $D_{Li^+}$ is calculated using the
Figure 7: EIS spectrum of Li$_{0.75}$NiO$_2$. Each panel shows the results of (a) 253 K, (b) 273 K, (c) 298 K, (d) 318 K.

expression eq.(5).$^{39,42–45}$

\[ D_{\text{Li}^+} = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2}, \]  

(5)

where \( R \) denotes the gas constant, \( T \) is the absolute temperature, \( A \) is the area of the cathode/electrolyte interface (\( A = 1.33\text{cm}^2 \)), \( n \) is the charge number of the electroactive species (\( n=1 \)), \( F \) is Faraday’s constant, \( C \) is the concentration of lithium ion, and \( \sigma \) is the Warburg factor. The Warburg factor was obtained from the slope of the plots of \( Z' \) vs \( \omega^{-1/2} \) (\( \omega \) is the angular frequency) in the Warburg region.$^{43}$ \( D_{\text{Li}^+} \) obtained by the formula (5) is shown in Figure 8. \( D_{\text{Li}^+} \) increased with rising temperature, and the calculated value of \( D_{\text{Li}^+} \) was in good agreement with the previously reported LiNiO$_2$ measurement result.$^{46,47}$

Furthermore, we derived the activation energy of diffusion using the following Arrhenius equation.$^{39,46,48,49}$

\[ D_{\text{Li}^+} = D_0 \exp \left( \frac{E_a}{RT} \right) \]  

(6)

The determined activation energy (\( E_a \)) is shown in Table2. Increase in \( E_a \) was confirmed by increasing Li concentration in LiNiO$_2$ and decreasing temperature, and this result corresponded to the EIS spectrum variation. Therefore, the influence of Li$^+$/H$^+$ cation exchange
Figure 8: Li$^+$ diffusion coefficient determined from EIS measurement. The temperature dependences of $D_{Li^+}$ in Li$_{0.75}$NiO$_2$ and Li$_{0.50}$NiO$_2$ are shown in (a) and (b), respectively. Panels (c) and (d) show the Arrhenius plots of $D_{Li^+}$ for Li$_{0.75}$NiO$_2$ and Li$_{0.50}$NiO$_2$, respectively.

on the electrochemical properties (increased resistance and degradation of rate capability) is attributed to the increase in the activation energy of Li$^+$ diffusion.

Table 2: Relationship between activation energy and exposure time (Li$^+$/H$^+$ exchange amount) in Li$_{1-x}$NiO$_2$ ($x = 0.25, 0.50$)

| Sample       | LNO$_{0h}$ | LNO$_{9h}$ | LNO$_{25h}$ | LNO$_{49h}$ |
|--------------|------------|------------|-------------|-------------|
| Li$_{0.75}$NiO$_2$ | 0.488      | 0.498      | 0.518       | 0.534       |
| Li$_{0.50}$NiO$_2$ | 0.351      | 0.351      | 0.364       | 0.396       |

To further verify whether the change in activation energy was due to the effect of Li$^+$/H$^+$ cation exchange, the barrier energy for Li$^+$ diffusion in Li$_{1-x}$H$_x$NiO$_2$ was calculated by the CI-NEB method. The calculation was performed using a structure in which one of the 27 Li atoms contained in the supercell was replaced with an H atom ($x = 0.037$). In addition, the barrier energies of Li$_{0.481}$H$_{0.037}$NiO$_2$ and Li$_{0.741}$H$_{0.037}$NiO$_2$, which are close to the amount of Li desorption in the experiment, were calculated. Figure 9(a)(b) shows the Li$^+$ diffusion paths of Li$_{0.481}$NiO$_2$ as an example of the calculated structure. The energy profiles of Li$_{0.741}$NiO$_2$, Li$_{0.741}$H$_{0.037}$NiO$_2$, Li$_{0.481}$NiO$_2$, and Li$_{0.481}$H$_{0.037}$NiO$_2$ are shown in Figure 9(c); the barrier
energies were determined to be 0.567, 0.760, 0.193, and 0.286 eV, respectively. At the Li concentrations of \((1-x) = 0.48\) and 0.75, the barrier energy increased with increase in the \(\text{H}^+\) concentration in \(\text{LiNiO}_2\), and the same tendency as observed in the experimental results was obtained. In literature,\(^{50}\) the barrier energy of \(\text{Li}_{0.50}\text{NiO}_2\) is reported as approximately 0.20–0.30 eV, and the calculation result of \(\text{Li}_{0.481}\text{NiO}_2\) shows a close value (0.193 eV).

After structural relaxation calculation, Figure 10 shows that O atoms are attracted to H atom in the Li-O layer of \(\text{Li}_{0.963}\text{H}_{0.037}\text{NiO}_2\). In NiOOH, it has been reported\(^{51-54}\) that the \(\text{NiO}_2\) and \(\text{Ni(OH)}_2\) slabs are alternately stacked by bonding through hydrogen bonds. From the reported phenomenon, it is presumed that the H atoms in the Li-O layer cause an attractive action in the form of hydrogen bonds between the upper and lower \(\text{NiO}_2\) slabs, resulting in the shrinkage of the Li-O layer thickness. In addition, the inverse relationship between the Li-O layer thickness and the activation energy is known,\(^{50}\) which is presumed to be the cause of increase in the activation energy due to \(\text{Li}^+/\text{H}^+\) cation exchange.

Furthermore, we investigated changes in the c lattice constant, Li-O layer thickness,
LiNiO$_2$ and Li$_{0.963}H_{0.037}$NiO$_2$ after structural relaxation.

Figure 10: Crystal structure of LiNiO$_2$ and Li$_{0.963}H_{0.037}$NiO$_2$ after structural relaxation.

and Ni-O layer thickness with respect to the amount of Li desorption in Li$_x$NiO$_2$ and Li$_x$H$_{0.037}$NiO$_2$. The structures in which Li was sequentially desorbed one after the other were determined by DFT calculation, and the parameters for each structure were obtained. Li$_x$NiO$_2$ has larger $c$ lattice parameter than Li$_x$H$_{0.037}$NiO$_2$ in the region of $x = 0.4$–1.0 (Figure 11(a)). Based on the trend of the change in the layer thicknesses of the Li-O layer and Ni-O layer, it was confirmed that the change in the c-axis lattice constant due to Li$^+/H^+$ cation exchange was dominated by the change in thickness of the Li layer (Figure 11(b),(c)). This result agrees with the change in the activation energy determined by the experiment and CI-NEB method.

**SUMMARY**

The structural changes and their effects on the electrochemical properties of LiNiO$_2$ exposed to the atmosphere were investigated. Thermal and chemical analyses revealed that LiNiO$_2$ exposed to the atmosphere assumes the structure of Li$_{1-x}$H$_x$NiO$_2$ with Li$^+/H^+$ cation exchange. We synthesized LiNiO$_2$ with different amounts of H$^+$ exchange, and investigated the influence of Li$_{1-x}$H$_x$NiO$_2$ on the electrochemical properties. As a result, it was found that the activation energy of Li$^+$ diffusion increased by the exchange of H$^+$, resulting in higher resistance and lower rate capability. Our first principles analysis calculation revealed that the increase in the activation energy was caused by decrease in the Li layer thickness, that
Figure 11: (a): Relationship between Li concentration and c-axis lattice constant of Li$_x$H$_y$NiO$_2$. Panels (b) and (c) show the relationship between the amount of Li desorption and the change in thickness of the Li-O and Ni-O layers, respectively.
is, constriction of the diffusion path of Li$^+$. 

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Graphical TOC Entry
