Supporting Information for
Unexpectedly Large Contribution of Oxygen on Charge Compensation
Triggered by Structural Disordering: Detailed Experimental and Theoretical Study on Li$_3$NbO$_4$-NiO Binary System

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Supporting Results and Discussion

S1. Structural changes of stoichiometric $Li_{1-y}Ni_{2/3}Nb_{1/3}O_2$ and Li-excess $Li_{4/3-y}Ni_{2/9}Nb_{4/9}O_2$

*Ex-situ* XRD patterns of the stoichiometric $LiNi_{2/3}Nb_{1/3}O_2$ and Li-excess $Li_{4/3}Ni_{2/9}Nb_{4/9}O_2$ samples during the first cycle were collected ([Supporting Figure S8](#)). Highly reversible changes in the crystal structure are noted in $Li_{y}Ni_{2/3}Nb_{1/3}O_2$. Diffraction lines shift toward higher diffraction angles upon charge to 4.8 V. The unit cell volume is reduced from 880.7 to 866.0 Å³ from the as-prepared to fully charged sample. After discharge to 1.5 V, identical diffraction lines compared to the as-prepared sample are noted with no increase in peak width. From this observation, it is concluded that Li extraction/re-insertion proceeds through a reversible topotactic reaction without oxygen loss. For the Li-excess system, a clearly different trend is found. The original highly crystalline phase is lost on charge and significant peak broadening is evidenced during charge. After full discharge to 1.5 V, the peak width narrows relative to the charged state but it is still relatively broad compared to the as-prepared sample. This finding suggests that irreversible structural changes occur in the Li-excess system, probably associated with oxygen loss on charge.

[Supporting Figure 9a](#) shows the background subtracted and normalized *in operando* XRD contour map of the $LiNi_{2/3}Nb_{1/3}O_2$ ($x = 0.33$) sample. As seen in the figure, no additional crystalline phases appear during cycling. In addition, little-to-no structural changes, *i.e.* changes in peak positions and relative reflection intensities, are observed as seen in the enhancements of selected $2\theta$-regions in
Sequential Rietveld refinements of the data were carried out based on the structure of LiNi$_{2/3}$Nb$_{1/3}$O$_2$ adopting orthorhombic symmetry with the space group *Fddd*. Reliable refinement of atomic structures in the *operando* data was not deemed feasible and the atomic structure was consequently fixed to the structure obtained from the neutron diffraction data (Table S1) during the sequential refinements. The lattice parameters, scale-factor, zero-shift, and background (Chebychev polynomial) were refined. The contribution from the aluminum foil was accounted for by implementing an aluminum phase (space group *Fm*-3*m*) with a high degree of preferred orientation in the modelling. No additional crystalline phases were observed in the data. The quantitative structural analysis was limited to the relative changes in lattice parameters (which do not rely on peak intensities) and relative variations in the scale factor (see Supporting Figure 9b). The scale factor encompasses 2θ-independent contributions, such as incident beam flux, instrumental geometry, detector efficiency, sample volume, *etc.* Assuming the instrumental contributions to be constant in time, observed variations in the refined scale factor of a given phase will be proportional to changes in the amount of coherently scattering material of the given phase. For the LiNi$_{2/3}$Nb$_{1/3}$O$_2$ sample, a small continuous increase (~10%) in the scale factor over the entire two electrochemical cycles is observed (Supporting Figure S9 b-1). No significant changes are observed in the unit cell parameters, suggesting highly reversible structural changes on electrochemical cycles, which is consistent with the *ex-situ* XRD data. It should be noted that the *ex-situ* and *operando* experiments...
were run at different current rates.

Supporting Figure S10a shows the background subtracted and normalized in operando XRD contour map of the Li$_{4/3}$Ni$_{2/9}$Nb$_{4/9}$O$_2$ ($x = 0.67$) sample. As seen in the figure, no major additional crystalline phases are formed during cycling. However, closer inspection of the reflections shows a gradual decrease in the main peak intensities, which is associated with the appearance of a shoulder on the left side (lower 2θ) of the peaks (see Figure 3a). The shoulder is observed for all reflections, indicating the formation of an isostructural compound with a larger unit cell, which is expected to be a delithiated (or partially delithiated) disordered rocksalt phase formed upon charge. Notably, the in operando XRD study reveals that the degradation of the main phase is seemingly irreversible as it does not reform upon discharge. Supporting Figure S10b shows an enhancement of the (200) and (220) reflections at selected times throughout the two electrochemical cycles. Closer inspection of the data also reveals that a more complex series of structural transitions takes place, in particular during the initial charge, where the peaks initially shift to higher 2θ values (unit cell decrease) and subsequently back again along with the appearance of a broad shoulder at lower 2θ. A decrease in the overall combined intensity of the reflections (~25%) is also observed during the first charge (see Supporting Figure S10b top left). Sequential Rietveld refinements of the data were carried out based on the disordered rock salt structure of Li$_{4/3-y}$Ni$_{2/9}$Nb$_{4/9}$O$_2$ (space group Fm-3m). Again, reliable refinement of atomic structure in the operando data was not deemed feasible and the
atomic structure was fixed to the structure obtained from the neutron diffraction data (Table S2) during the sequential refinements. Based on the observation of peak shoulders above, an additional delithiated phase (space group Fm-3m) was implemented in the modelling. Lattice parameters, scale-factor, zero-shift, background (Chebychev polynomial) and one Lorentzian profile parameter associated with isotropic microstrain per phase were refined. The contribution from the aluminum foil was accounted for by implementing an aluminum phase (space group Fm-3m) with a high degree of preferred orientation in the modelling. Representative Rietveld fits at different levels of charge are shown in Supporting Figure S10c. Here, the data has been modelled by the two endmember phases, i.e. the original disordered rock salt structure of Li_{4/3}Ni_{2/9}Nb_{4/9}O_2 and a delithiated disordered rock salt structure. However, the asymmetrical peak shapes likely arise from a non-trivial distribution of lattice parameters caused by gradual extraction of various amounts of Li from the structure and thus non-uniform Li distributions in certain parts of the sample. The implementation of a third highly strained (partially delithiated) rock salt phase in the refinement did not give substantially better fit and furthermore destabilized the refinement due to parameter correlations (see Supporting Figure S10d). The fits to the peak profiles were not entirely robust, and care must be taken not to draw false conclusions based on the Rietveld refined parameters. The refined scale factors suggest a continuous decrease in the amount of the main Li_{4/3}Ni_{2/9}Nb_{4/9}O_2 phase along with a concurrent increase in the secondary range of delithiated phases, which confirms the gradual
transformation of the main phase (also see Figure 3a). The original phase does not reform but rather continues to diminish during discharge indicating an irreversible degradation. This also supports the observations from ex-situ data.

S2. Determination of cation arrangements for LiNb1/3Ni2/3O2 and Li arrangements for delithiated Li1-xNb1/3Ni2/3O2 by genetic algorithm (GA) approach

For the determination of cation arrangements by GA approach, firstly, arbitrary cationic arrangements in fully lithiated compounds (x = 0.00) are regarded as ternary strings, consisting of three labels: 0 (Li), 1 (Nb), and 2 (Ni). Likewise, binary strings of 0 (Li) and 1 (vacancy) are considered for delithiated samples (x > 0). In each combinatorial optimization, we prepare first 20 configurations (ternary/binary strings), where all labels are arranged randomly in the first generation, and evaluate total energies. Twelve low energy configurations among 20 candidates (60%) are selected as survivors and their structural features are succeeded to the next generation by the following four processes: (1) three best structures are succeeded as they are, (2) eight new structures are generated by a two-point crossover technique, (3) another eight are generated by uniform crossover technique with a 50% probability, and (4) the others (i.e. four structures) are generated by a mutation technique with 2% probability. To preserve the composition, we used a permutation encoding technique for the above binary or ternary string representations. The generated structure is selected
not to be consistent with the previously calculated configuration (a random arrangement is chosen, in the case above genetic operation cannot produce a new structure). By repeating this procedure, the lowest energy configuration is determined heuristically.

S3. Voltage estimation on hypothetical layered-type LiNb\(_{1/3}\)Ni\(_{2/3}\)O\(_2\) and Li arrangements for delithiated Li\(_{1-x}\)Nb\(_{1/3}\)Ni\(_{2/3}\)O\(_2\)

For the purpose of comparison, variations of electronic structures during the delithiation process in the hypothetical layered-type Li\(_{1-x}\)Nb\(_{1/3}\)Ni\(_{2/3}\)O\(_2\) are examined by first-principles calculations using the HSE06 hybrid functional. Supporting Figure S23a displays cation arrangements of hypothetical layered-type LiNb\(_{1/3}\)Ni\(_{2/3}\)O\(_2\) in which Li and transition metals ions (Ni and Nb) stack alternately along c-axis, and Ni and Nb ions are assumed to form a honeycomb arrangement in the a-b plane as seen in Li\(_2\)MnO\(_3\). Therefore, the formation of the linear Ni-O-Ni environment is eliminated in this model. Total electronic energies of symmetrically distinct Li/vacancy arrangements for delithiated phases, Li\(_{1-y}\)Nb\(_{1/3}\)Ni\(_{2/3}\)O\(_2\), are computed and corresponding voltage profiles are obtained using lowest energies for each composition as shown in Supporting Figure S23b. Note that no oxygen dimers are visible over the entire range of the composition y (0 \(\leq y \leq 1\) in Li\(_{1-y}\)Nb\(_{1/3}\)Ni\(_{2/3}\)O\(_2\)), as the minimum bond distance between two oxygen atoms is 2.49 Å (see Supporting Figure S20). The calculated voltages are almost constant ranging from ~4.3 to 4.5 V at \(y < 2/3\), and at \(y > 2/3\) abruptly increase in the voltage.
reaching to \( > 5V \).
Supporting Tables and Figures

**Table S1.** Refined structural parameters of LiNi\(_{2/3}\)Nb\(_{1/3}\)O\(_2\) (\(x = 0.33\)) synthesized at 1000 °C for 48 h by the Rietveld method. For stoichiometric LiNi\(_{2/3}\)Nb\(_{1/3}\)O\(_2\), refined results reveal perfect ordering for Nb ions at 8\(a\) site. However, partial cation mixing between Li and Ni ions at 16\(g\) and 8\(b\) sites is also noted, and Li ions preferentially occupy the 8\(b\) site. Ordering of Nb ions in the structure results in the appearance of additional diffraction lines and leads to distortion of the orthorhombic lattice.

| Atom | Site | Occupancy | \(x\) | \(y\) | \(z\) | \(\beta\) (Å\(^2\)) |
|------|------|-----------|------|------|------|-----------------|
| Li   | 16g  | 0.576     | 0.125| 0.125| 0.292(3) | 0.4             |
| Ni   | 16g  | 0.424     | 0.125| 0.125| 0.292(3) | 0.4             |
| Li   | 16g  | 0.599     | 0.125| 0.625| 0.287(4) | 0.4             |
| Ni   | 16g  | 0.401     | 0.125| 0.625| 0.287(4) | 0.4             |
| Li   | 8b   | 0.649     | 0.125| 0.625| 0.125   | 0.6             |
| Ni   | 8b   | 0.351     | 0.125| 0.625| 0.125   | 0.6             |
| Nb   | 8a   | 1.0       | 0.125| 0.125| 0.125   | 0.3             |
| O    | 16f  | 1.0       | 0.125| 0.370(2)| 0.125(2)| 1.2             |
| O    | 32h  | 1.0       | 0.122(2)| 0.374(2)| 0.291(4)| 0.8             |

Space group; \(Fd\dd\), \(a = 5.9365\) (1) Å, \(b = 8.4105\) (1) Å, \(c = 17.8136\) (2) Å

\(R_{wp} = 5.72\%\) and \(R_B = 5.79\%\).
Table S2. Refined structural parameters of Li$_{4/3}$Ni$_{2/9}$Nb$_{4/9}$O$_2$ ($x = 0.67$) synthesized at 1000 °C for 48 h by the Rietveld method. For Li-excess Li$_{4/3}$Ni$_{2/9}$Nb$_{4/9}$O$_2$, all cations, Li, Ni and Nb ions, are located at the same 4$a$ site, forming a completely disordered rocksalt structure, and Li$_{4/3}$Ni$_{2/9}$Nb$_{4/9}$O$_2$ is isostructural with NiO.

| Atom | Site | Occupancy | x   | y   | z   | B (Å$^2$) |
|------|------|-----------|-----|-----|-----|-----------|
| Li   | 4$a$ | 0.670     | 0   | 0   | 0   | 0.4       |
| Ni   | 4$a$ | 0.111     | 0   | 0   | 0   | 0.4       |
| Nb   | 4$a$ | 0.219     | 0   | 0   | 0   | 0.4       |
| O    | 4$b$ | 1.0       | 0.5 | 0.5 | 0.5 | 1.0       |

Space group; $Fm\overline{3}m$, $a = 4.2009$ (3) Å
$R_{wp} = 4.91\%$ and $R_B = 1.34\%$

Table S3. Refined structural parameters of SrFeO$_3$ by the Rietveld method.

| atom | site | g       | x   | y   | z   | B (Å$^2$) |
|------|------|---------|-----|-----|-----|-----------|
| Sr   | 1$b$ | 0.978(1)| 0.5 | 0.5 | 0.5 | 0.445     |
| Fe   | 1$a$ | 0.980(3)| 0   | 0   | 0   | 0.170     |
| O    | 3$d$ | 0.988(6)| 0   | 0   | 0.5 | 0.563     |

Space group; $Pm\overline{3}m$, $a = 3.5809(9)$ Å
$R_{wp} = 8.81\%$ and $R_B = 7.63\%$
Table S4. Refined structural parameters of LaFeO₃ by the Rietveld method.

| atom | site | $g$    | $x$    | $y$    | $z$    | $B$ (Å²) |
|------|------|--------|--------|--------|--------|----------|
| La   | 4c   | 0.9631 | 0.0289(5) | 0.25 | -0.00769 | 0.55     |
| Fe   | 4b   | 1      | 0      | 0      | 0.5    | 0.56     |
| O1   | 4c   | 0.9659 | 0.4859(6) | 0.25 | 0.0762(9) | 2.52(5) |
| O2   | 8d   | 0.9827 | 0.2839(2) | 0.0316(8) | 0.7175(2) | 0.879   |

Space group; Pnma, $a = 5.5437(9)$ Å, $b = 7.8253$ Å, and $c = 5.5348(6)$ Å

$R_{wp} = 7.63\%$ and $R_\beta = 6.49\%$

Table S5. The GA optimized ionic arrangement of the computational supercell model for Li₁₈Ni₁₂Nb₆O₃₆ (LiNi₂/₃Nb₁/₃O₂). Lattice parameters for the supercell are $(a, b, c, \alpha, \beta, \gamma) = (8.90954$ Å, 7.85748 Å, 9.84987 Å, 83.4563°, 81.3293°, 79.1066°). This structure model is input for structural relaxation in first-principles calculations.

| Atom | Label | $x$ | $y$ | $z$ |
|------|-------|-----|-----|-----|
| Li   | Li1   | 0   | 0.25| 0.75|
| Li   | Li2   | 0   | 0.75| 0.25|
| Li   | Li3   | 0.11111| 0.08333| 0.25|
| Li   | Li4   | 0.11111| 0.33333| 0 |
| Li   | Li5   | 0.22222| 0.16667| 0.5 |
| Li   | Li6   | 0.22222| 0.41667| 0.25|
| Li   | Li7   | 0.22222| 0.91667| 0.75|
| Li   | Li8   | 0.33333| 0.75 | 0.25|
| Li   | Li9   | 0.44444| 0.08333| 0.25|
| Element | Symbol | Li10       | Li11       | Li12       | Li13       | Li14       | Li15       | Li16       | Li17       | Li18       | Nb1        | Nb2        | Nb3        | Nb4        | Nb5        | Nb6        | Ni1        | Ni2        | Ni3        | Ni4        | Ni5        | Ni6        | Ni7        | Ni8        | Ni9        | Ni10       | Ni11       | Ni12       | O1         | O2         | O3         | O4         | O5         | O6         | O7         | O8         | O9         | O10        |
|---------|--------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| Li      | Li     | 0.55556    | 0.55556    | 0.66667    | 0.66667    | 0.25       | 0.25       | 0.25       | 0.25       | 0.25       | 0.75       | 0.75       | 0.75       | 0.75       | 0.75       | 0.75       | 0.75       | 0.75       | 0.75       | 0.75       | 0.75       | 0.75       | 0.75       | 0.75       | 0.75       | 0.75       | 0.75       | 0.75       | 0.75       | 0.75       |
| Nb      | Nb     | 0          | 0.11111    | 0.33333    | 0.33333    | 0          | 0          | 0          | 0          | 0          | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        |
| Ni      | Ni     | 0          | 0.11111    | 0.22222    | 0.33333    | 0.33333    | 0.33333    | 0.44444    | 0.44444    | 0.44444    | 0.44444    | 0.44444    | 0.44444    | 0.44444    | 0.44444    | 0.44444    | 0.44444    | 0.44444    | 0.44444    | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        |
| O       | O      | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    | 0.05556    |

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| O   | O11   | 0.27778 | 0.70833 | 0.625 |
|-----|-------|---------|---------|-------|
| O   | O12   | 0.27778 | 0.95833 | 0.375 |
| O   | O13   | 0.38889 | 0.04167 | 0.625 |
| O   | O14   | 0.38889 | 0.29167 | 0.375 |
| O   | O15   | 0.38889 | 0.54167 | 0.125 |
| O   | O16   | 0.38889 | 0.79167 | 0.875 |
| O   | O17   | 0.5     | 0.125   | 0.875 |
| O   | O18   | 0.5     | 0.375   | 0.625 |
| O   | O19   | 0.5     | 0.625   | 0.375 |
| O   | O20   | 0.5     | 0.875   | 0.125 |
| O   | O21   | 0.61111 | 0.20833 | 0.125 |
| O   | O22   | 0.61111 | 0.45833 | 0.875 |
| O   | O23   | 0.61111 | 0.70833 | 0.625 |
| O   | O24   | 0.61111 | 0.95833 | 0.375 |
| O   | O25   | 0.72222 | 0.04167 | 0.625 |
| O   | O26   | 0.72222 | 0.29167 | 0.375 |
| O   | O27   | 0.72222 | 0.54167 | 0.125 |
| O   | O28   | 0.72222 | 0.79167 | 0.875 |
| O   | O29   | 0.83333 | 0.125   | 0.875 |
| O   | O30   | 0.83333 | 0.375   | 0.625 |
| O   | O31   | 0.83333 | 0.625   | 0.375 |
| O   | O32   | 0.83333 | 0.875   | 0.125 |
| O   | O33   | 0.94444 | 0.20833 | 0.125 |
| O   | O34   | 0.94444 | 0.45833 | 0.875 |
| O   | O35   | 0.94444 | 0.70833 | 0.625 |
| O   | O36   | 0.94444 | 0.95833 | 0.375 |
Figure S1. Rietveld-refined fits of LiNi$_{2/3}$Nb$_{1/3}$O$_2$ ($x = 0.33$) and Li$_{4/3}$Ni$_{2/3}$Nb$_{4/9}$O$_2$ ($x = 0.67$) samples synthesized at 1000 °C for 48 h.

Figure S2. SEM images of Li$_{12/11}$Ni$_{6/11}$Nb$_{4/11}$O$_2$ ($x = 0.40$) and Li$_{6/5}$Ni$_{2/5}$Nb$_{2/5}$O$_2$ ($x = 0.50$) samples synthesized at 1000 °C for 2 h.
Figure S3. TEM images of (a, b) as-prepared stoichiometric LiNi$_{2/3}$Nb$_{1/3}$O$_2$ ($x = 0.33$) and (c, d) Li-excess Li$_{4/3}$Ni$_{2/3}$Nb$_{4/9}$O$_2$ ($x = 0.67$).
$x = 0.33$

![100] Simulated Pattern

$x = 0.67$

![110] Simulated Pattern

**Figure S4.** Comparison of observed and simulated ED patterns for the samples of $x = 0.33$ and $0.67$.

Lattice points indexed with red color correspond to superlattice reflections on the basis of the cation-disordered rock salt phase.
$x = 0.33$

**Figure S5.** Simulated electron diffraction patterns of the samples of $x = 0.33$ and 0.67. For the stoichiometric sample ($x = 0.33$), the superlattice reflections are only observed along [100], and not observed for [001] because the unit cell length is three times larger than the parent rock salt phase in
the c-axis direction.

Figure S6. Comparison of XRD patterns, SEM images, and electrode performance of LiNi$_{2/3}$Nb$_{1/3}$O$_2$ synthesized at 1000 °C for 48 and 2 h. Synthesis with longer time results in higher degree of cation ordering, but similar cation ordering is also noted for the sample synthesized for 2 h. Moreover, much better electrode performance is observed for the sample synthesized for 2 h, likely associated with particle size differences between the samples.
Figure S7. (a) Capacity retention of LiNi$_{2/3}$Nb$_{1/3}$O$_2$ and Li$_{4/3}$Ni$_{2/9}$Nb$_{4/9}$O$_2$ at a rate of 20 mA g$^{-1}$ at 50 °C, and (b) initial charge/discharge profiles of Li$_{4/3}$Ni$_{2/9}$Nb$_{4/9}$O$_2$ at a rate of 5 mA g$^{-1}$ with different charge capacities.
Figure S8. *Ex-situ* XRD patterns of LiNi$_{2/3}$Nb$_{1/3}$O$_2$ ($x = 0.33$) and Li$_{4/3}$Ni$_{2/9}$Nb$_{4/9}$O$_2$ ($x = 0.67$) samples during the first electrochemical cycle.
**Figure S9.**  (a) *In operando* synchrotron XRD contour map (background subtracted and normalized) of the first two complete electrochemical cycles at 50 °C for LiNi_{2/3}Nb_{1/3}O_2 (x = 0.33). The corresponding electrochemical load curves (rate and voltage) are shown on the left side of the figure. The asterisks denote the reflections from the aluminium foil in the electrode.  (b) b-1) Normalized scale factor as function of time. b-2) Unit cell volume as function of time. b-3) Potential as function of time.
Figure S10. (a) In operando synchrotron XRD contour map (background subtracted and normalized) of the first two complete electrochemical cycles at 50 °C for Li$_{43}$Ni$_{29}$Nb$_{49}$O$_2$ ($x = 0.67$). The corresponding electrochemical load curves (rate and voltage) are shown on the left side of the figure. The asterisks denote the reflections from the aluminium foil in the electrode. (b) Evolution
of the (200) and (220) reflections during the two initial electrochemical cycles. The integrated intensities as function of time are plotted in the top left and the electrochemical load curves are plotted in the bottom left. The dashed lines indicate the times at which the patterns shown on the right were obtained. 

(c) Rietveld-refined fits with structural models to XRD data collected after c-1) prior to electrochemical cycling (OCV, 0 hrs), c-2) in the charged state (4.8 V, 6.5 hrs) and c-3) discharged state (1.5 V, 9.8 hrs). The patterns are plotted with the same absolute y-scale to illustrate the degradation of the main phase. An enhancement of the main (200) peak is shown on the right. The formation of the delithiated low crystallinity phase is observed from the appearance of a shoulder on the left side (larger cell) of the reflections as indicated by the arrow in c-3). 

(d) Enhancement of the (111), (200) and (220) reflections fitted by a single-, two-, and three rock salt phases.

Figure S11  Change in the Ni K-edge XAS spectra of (a) Li$_{1-y}$Ni$_{2/3}$Nb$_{1/3}$O$_2$ ($x = 0.33$) and (b) Li$_{4/3-y}$Ni$_2$Nb$_{2/9}$O$_2$ ($x = 0.67$).
Figure S12. Changes in XAS spectra at Ni L-edge and O K-edge for layered Li$_{1-y}$Ni$_{0.5}$Mn$_{0.5}$O$_2$. A clear change in a Ni L-edge spectrum is observed for the half charged state (ca. 110 mA h g$^{-1}$) when compared with Li$_{1-y}$Ni$_{2/3}$Nb$_{1/3}$O$_2$. On further oxidation to 4.8 V, the formation of Ni$^{4+}$ is noted, which is not evidenced for Li$_{1-y}$Ni$_{2/3}$Nb$_{1/3}$O$_2$. Peak shift of O K-edge to a lower energy region is also noted, and this observation is also clearly different from Li$_{1-y}$Ni$_{2/3}$Nb$_{1/3}$O$_2$. 

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\[ Li_{1-y}Ni_{0.5}Mn_{0.5}O_2 \]
Figure S13. Comparison of normalized Ni L-edge XAS spectra for Li$_{1-y}$Ni$_{2/3}$Nb$_{1/3}$O$_2$ and Li$_{1-y}$Ni$_{1/2}$Mn$_{1/2}$O$_2$. From differences in the integrated peak area, the average oxidation state of Ni ions in fully charged Li$_{1-y}$Ni$_{2/3}$Nb$_{1/3}$O$_2$ (charged to 4.8 V) is expected to be lower than that of Ni ions in half charged Li$_{1-y}$Ni$_{1/2}$Mn$_{1/2}$O$_2$ because the change in integrated area before and after charge is relatively small for Li$_{1-y}$Ni$_{2/3}$Nb$_{1/3}$O$_2$. The estimated nominal oxidation state of Ni ions in half charged Li$_{1-y}$Ni$_{1/2}$Mn$_{1/2}$O$_2$ is calculated to be +2.78 on the basis of charge capacity (110 mA h g$^{-1}$).
Figure S14. Extended X-ray absorption fine structure (EXAFS) spectra of stoichiometric 
LiNi$_{2/3}$Nb$_{1/3}$O$_2$ and Li-excess Li$_{4/3}$Ni$_{2/9}$Nb$_{4/9}$O$_2$ on charge/discharge processes. First and second 
coordination shells correspond to Ni-O and Ni-Ni pairs, respectively. Because the structures of both 
phases are classified as the disordered rocksalt structure for Ni ions, peak heights of second 
coordination shells are much lower compared with layered LiNiO$_2$. For the stoichiometric sample, 
distances of the Ni-O coordination are almost unchanged on charge, and this fact also supports the 
small contribution of Ni ions for charge compensation. Although the height of peaks is slightly
reduced on charge, this observation originates from the presence of the small amount of Ni$^{3+}$, which is known as a Jahn-Teller active ion. For the Li-excess system, after full discharge, the peak height of the first coordination shell is drastically reduced, and the interatomic distance for the second coordination clearly is shortened. This observation also supports the formation of nanosized and/or metallic nickel. An interatomic distance of Ni-Ni in metallic Ni is calculated to be 2.5 Å, which is shorter than Ni-Ni distances of ca. 2.9 Å for oxides.

**Figure S15.** Nb K-edge XNAES spectra of LiNi$_{2/3}$Nb$_{1/3}$O$_2$ ($x = 0.33$) and Li$_{4/3}$Ni$_{2/9}$Nb$_{4/9}$O$_2$ ($x = 0.44$) electrodes during the 1$^{st}$ cycle. Only minor changes are observed in the profiles of spectra, which are expected to originate from local structure changes around Nb ions associated with Li extraction (for instance, K. Kubobuchi *et al.*, *Journal of Applied Physics*, 120, 142125, 2016). Therefore, the result indicates that Nb ions are not directly involved in charge compensation.
Figure S16. HR-TEM observation of electrochemically cycled samples; (a) Li$_{1-y}$Ni$_{2/3}$Nb$_{1/3}$O$_2$ and (b) Li$_{4/3-y}$Ni$_{2/9}$Nb$_{4/9}$O$_2$. The low-magnification TEM image and ED pattern in (a) are also shown. [032] zone axis for the stoichiometric sample corresponds to [111] for the parent rock salt phase. HR-TEM images collected for the core-region and edge-region of Li$_{4/3-y}$Ni$_{2/9}$Nb$_{4/9}$O$_2$ particles are shown in (b).

Figure S17. Ni L-edge and O K-edge spectra of Li$_{4/3-y}$Ni$_{2/9}$Nb$_{4/9}$O$_2$; comparison of the pristine sample to the fully discharged state at 1.5 V after charge to 4.8 V. Reduction of Ni ions is clearly
noted in the Ni L-edge XAS spectrum, and new peaks at 533.5 and 539 eV observed for the O K-edge spectrum would originate from the formation of nanosized Li$_2$O on discharge. O K-edge XAS spectra of Li$_2$O is found in literature (for instance, Qiao et al., *PLOS ONE*, 7, e49182, 2012). Note that a crystalline Ni metal phase was not found by XRD (*Figure S8*), suggesting that metallic Ni with an amorphous phase or that is nanosized is formed.

*Figure S18.* Ni L-edge and O K-edge XAS spectra of LiNi$_{2/3}$Nb$_{1/3}$O$_2$ ($x = 0.33$) and Li$_{4/3}$Ni$_{2/9}$Nb$_{4/9}$O$_2$ ($x = 0.67$) electrodes obtained at PEY mode which is surface sensitive. Holes are stabilized in the bulk of particles as observed in PFY mode (*Figure 4c*).
Figure S19. Results of Rietveld refinements for SrFeO$_3$ and LaFeO$_3$ used as reference materials for the XAS study. Schematic illustrations of crystal structures are also shown. Refined structural parameters are found in Supporting Table S3 and S4.
Figure S20. The minimum oxygen-oxygen interatomic distance in the disordered/ordered RS-type Li$_{1-y}$Nb$_{1/3}$Ni$_{2/3}$O$_2$. The O-O bond length for oxygen molecule, O$_2$ (1.21 Å), and peroxide ion, O$_2^{2-}$ (~1.3 – 1.4 Å), is also shown for reference purposes.
Figure S21. (a) A schematic illustration of the crystal structure of hypothetical layered-type LiNb\textsubscript{1/3}Ni\textsubscript{2/3}O\textsubscript{2} for first-principles calculations using the HSE06 functional. (b) Calculated voltages for electrochemical delithiation as a function of composition $y$ in layered-type Li\textsubscript{1$-y$}Nb\textsubscript{1/3}Ni\textsubscript{2/3}O\textsubscript{2}.
Figure S22. Changes in Bader charges for Ni and O ions as a function of composition $y$ in the (a) disordered and (b) ordered RS-type Li$_{1-y}$Nb$_{1/3}$Ni$_{2/3}$O$_2$. Clear changes in Bader charge for O in the Ni-O-Ni configuration are noted for disordered Li$_{1-y}$Nb$_{1/3}$Ni$_{2/3}$O$_2$. For ordered Li$_{1-y}$Nb$_{1/3}$Ni$_{2/3}$O$_2$, the increase in Bader charge for O originates from the increase in covalency of Ni-O bonds by Ni oxidation on delithiation. Cross symbols represent Bader charges for individual ions, while red circles with a line correspond to averaged Bader charges.
Figure S23. Comparison of calculated net spin moments for LiNiO$_2$ and □NiO$_2$. From the net spin moments, no evidence of hole creation is noted. A residual spin moment (0.07) for oxygen originates from large spin of Ni ions associated with covalency in Ni-O bonds.