Supporting information of

Defect chemical studies on oxygen release of Li-rich cathode material $Li_{1.2}Ni_{0.2}Mn_{0.6}O_{2-\delta}$

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Experimental

Battery test of the pristine $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$

The cathode slurry was made by mixing $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$: AB : PVDF = 80 : 10 : 10 and adding a small amount of 1 methyl-2 pirolydone. The slurry was printed on an Al foil current collector by using a film applicator (Automatic film applicator 542-AB4, YASUDA SEIKI SEISAKUSHO, LTD.). The cathode slurry was dried in an oven at 353 K for more than 24 h. The thickness of the composite cathode layer was about 50 μm. The composite electrode was cut into 13 mm in diameter. An electrochemical cell was fabricated in a glovebox with an Li metal foil (Honjo Metal Co., Ltd.) as an anode, EC-DMC with 1 mol L^{-1} of $LiPF_6$ (EC:DMC = 3:7 in volume, Kishida Chemical Co., Ltd.) as an electrolyte, a polymer separator (Cell-Gard #2500, Polypore International, Inc.), and the composite cathode. After the fabrication, the cell was kept for more than 3 h for ensuring the sufficient infiltration of the liquid electrolyte into the electrode. Thereafter, the charge-discharge test was carried out in a voltage range 2.0-4.8 V with 10 mA g^{-1}.

Statistical thermodynamic model for $Li_{1.2}Ni_{0.2}Mn_{0.6}O_{2-\delta}$

Statistical thermodynamic is established by considering the defect equilibrium. As is the defect chemical model, defect species are treated as pseudo-chemical species. Then, Gibbs free energy of the system, G, is expressed by

$$G = \sum_i \chi_i \mu_i^\circ + \sum_i \chi_i RT ln\gamma_i \chi_i \tag{S1}$$

where χ_i, μ_i°, R, T, and γ_i are the molar fraction of *i*, the standard chemical potential of *i*, the gas constant, the temperature, and the activity coefficient of *i*, respectively. Oxygen chemical potential, μ_O, is the derivation of *G* with oxygen content

$$\mu_O = \frac{\partial G}{\partial(2-\delta)} = -\frac{\partial}{\partial\delta}\left(\sum_i \chi_i \mu_i^\circ + \frac{\partial}{\partial\delta}\right) \tag{S2}$$

$$\mu_O = -\sum_i \frac{\partial \chi_i}{\partial\delta}\mu_i^\circ - RT\sum_i \frac{\partial \chi_i}{\partial\delta} ln\gamma_i - RT\frac{\partial}{\partial\delta}\sum_i \chi_i ln\chi_i \tag{S3}$$

Here, configurational entropy in $Li_{1.2}Ni_{0.2}Mn_{0.6}O_{2-\delta}$ is calculated assuming the imaginary transition metal M as introduced into the defect equilibrium model.

$$S_O(conf) = k\left[ln\left(\frac{N_A!}{\left(\chi_{M_{TM}^{\times}} N_A\right)!\left(\chi_{Mn_{TM}^{'}} N_A\right)!}\right) + ln\left(\frac{(2N_A)!}{\left(\chi_{O_O^{\times}} N_A\right)!\left(\chi_{V_O^{\cdot\cdot}} N_A\right)!}\right)\right] \quad \text{(S4)}$$

where k and N_A are the Boltzmann constant and the Avogadro number. Partial molar entropy of the configuration, $s_O(conf)$, is obtained by the derivation of $S_O(conf)$ with the oxygen content. Considering the relations $R = kN_A$ and the Stirling's formula, $s_O(conf)$ can be expressed by

$$s_O(conf) = \frac{\partial S_O(conf)}{\partial(2-\delta)} = R\frac{\partial}{\partial\delta}\sum_i \chi_i ln\chi_i \quad \text{(S5)}$$

Eq. S5 times T is exactly the same to the 3rd term in the Eq. S3. Then, μ_O can be expressed by

$$\mu_O = -\sum_i \frac{\partial\chi_i}{\partial\delta}\mu_i^{\circ} - RT\sum_i \frac{\partial\chi_i}{\partial\delta} ln\gamma_i - Ts_O(conf) \quad \text{(S6)}$$

The parameters in the defect chemical analysis are introduced into the statistical thermodynamic model.

$$\Delta G_{OX}^{\circ} = \mu_{V_O^{\cdot\cdot}}^{\circ} + 2\mu_{M_{TM}}^{\circ} - \mu_{O_O^{\times}}^{\circ} - 2\mu_{M_{TM}^{\times}}^{\circ} + \mu_O^{\circ} \quad \text{(S7)}$$

From Eqs. S7 and 16 in the main text, S6 can be converted as follows

$$\mu_O - \mu_O^{\circ} = -\Delta G_{OX}^{\circ} - \Delta H_{ex} - Ts_O(conf) \quad \text{(S8)}$$

Theoretical value of partial molar enthalpy and entropy, $h_O - h_O^{\circ}$ and $s_O - s_O^{\circ}$, can be calculated from the results of the defect chemical analysis.

$$h_O - h_O^{\circ} = -\Delta H_{OX}^{\circ} - \Delta H_{ex} \quad \text{(S9)}$$

$$s_O - s_O^{\circ} = -\Delta S_{OX}^{\circ} + s_O(conf) \quad \text{(S10)}$$

Supplemental figures and tables

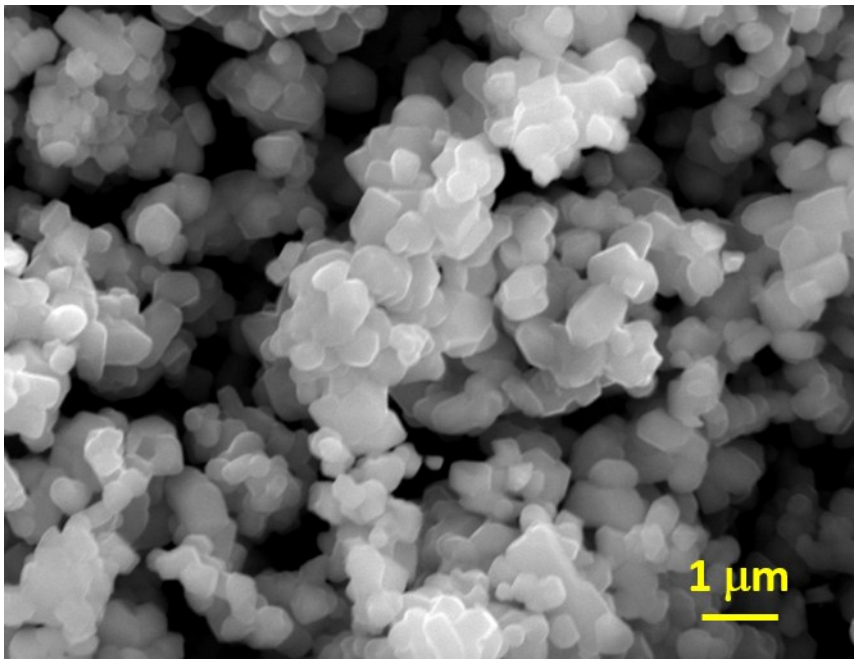

Figure S1. SEM image of the pristine $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ particles.

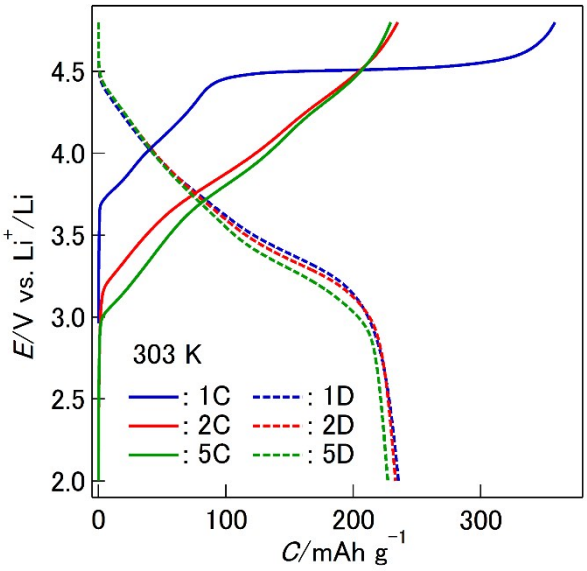

Figure S2. Charge-discharge curves of the pristine $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ composite cathode.

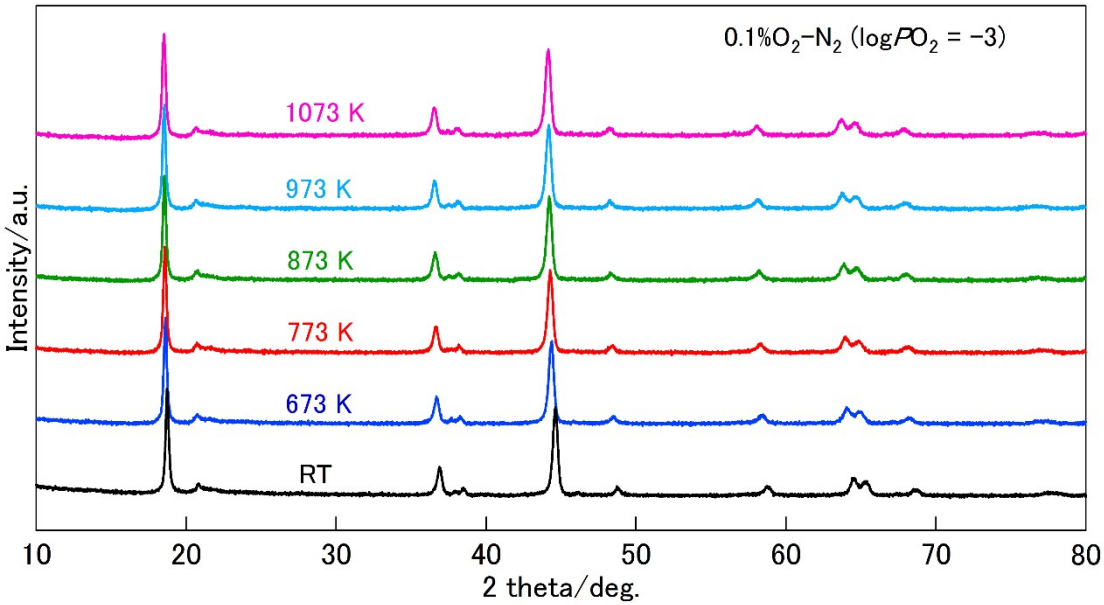

Figure S3. XRD patterns of the pristine $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ measured at different temperatures in 0.1%O_2-N_2.

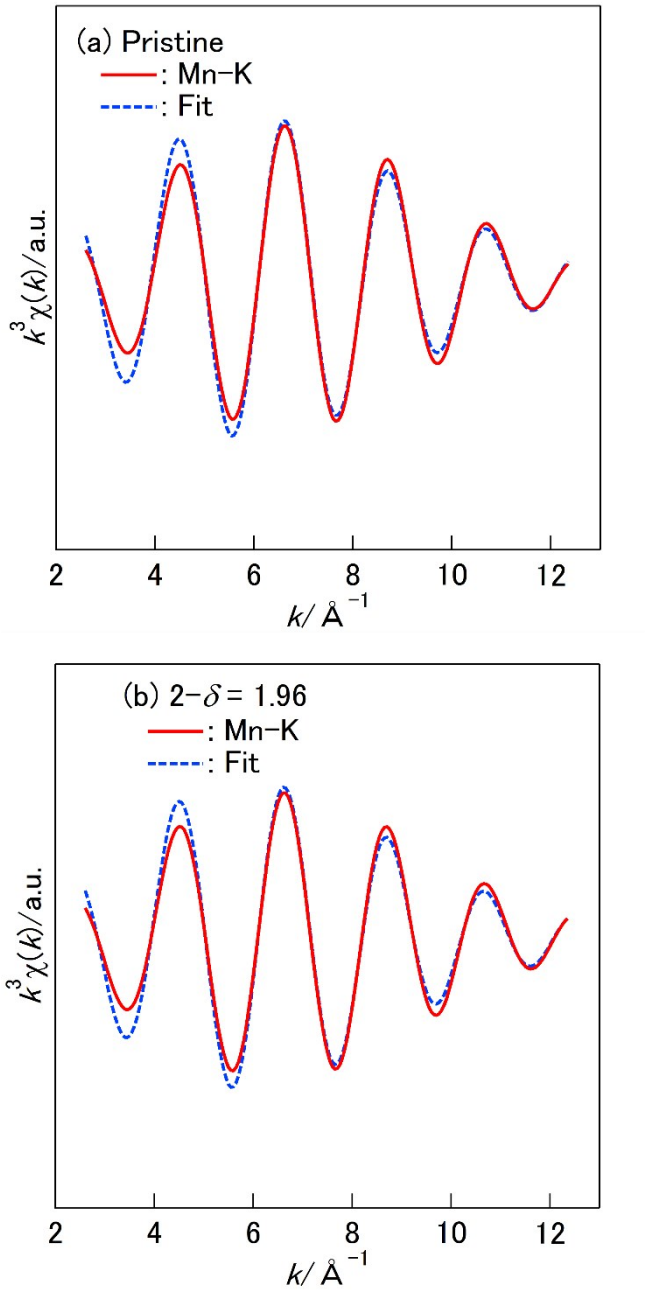

Figure S4. k^3 weighted signals from EXAFS of Mn-K edge spectra of (a) the pristine sample and (b) the oxygen extracted sample. The dashed lines are the fitting lines of the EXAFS analysis.

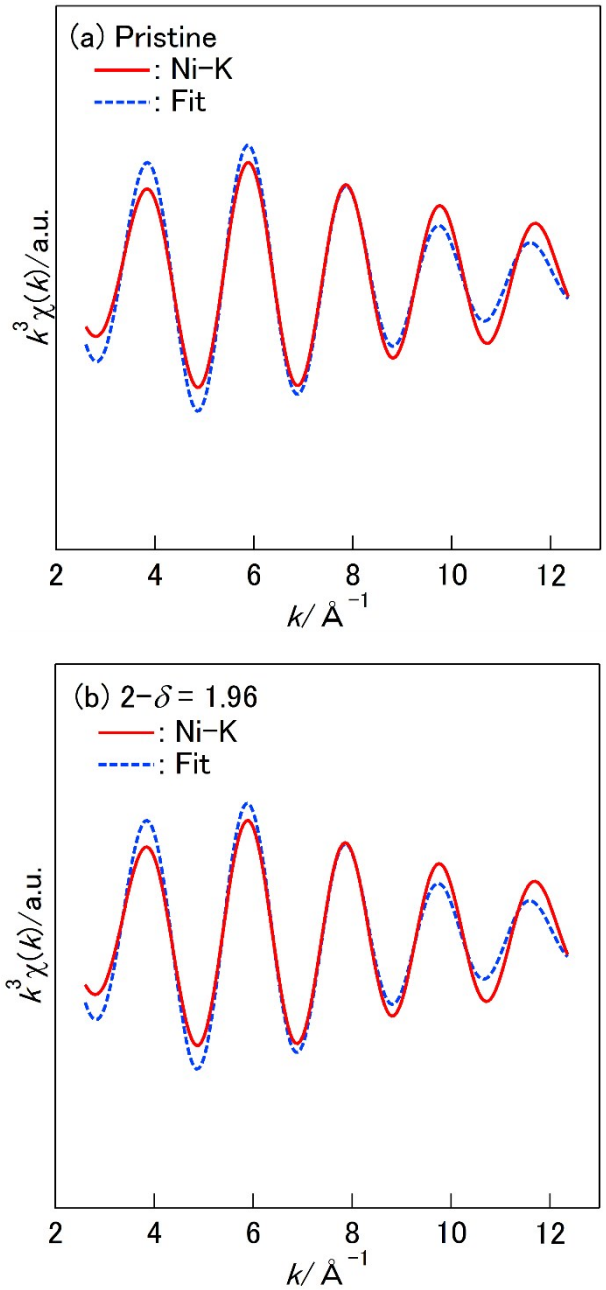

Figure S5. k^3 weighted signals from EXAFS of Ni-K edge spectra of (a) the pristine sample and (b) the oxygen extracted sample. The dashed lines are the fitting lines of the EXAFS analysis.

Table S1. Molar ratio of $Li_{1.2}Ni_{0.2}Mn_{0.6}O_{2-\delta}$ determined by ICP-OES.

	Li	Mn	Ni	Li/(Mn+Ni)
Pristine	1.26	0.60	0.20	1.58
Reduced ($2-\delta=1.96$)	1.22	0.60	0.19	1.54

Table S2. EXAFS parameters, the coordination number (N), the Debye-Waller factor (σ^2), and the energy shift (ΔE), respectively.

		N (fixed)	σ^2	ΔE	R value
Mn-O	pristine	6	0.079 ± 0.008	-7.2 ± 1.8	2.290
	reduced	5.88	0.081 ± 0.008	-6.0 ± 1.8	2.176
Ni-O	pristine	6	0.082 ± 0.008	-11.4 ± 1.8	3.073
	reduced	5.88	0.083 ± 0.008	-11.6 ± 1.8	5.436