Supporting Information

Quantitative Evaluation of the Activity of Low-Spin Tetravalent Nickel Ion Sites for the Oxygen Evolution Reaction

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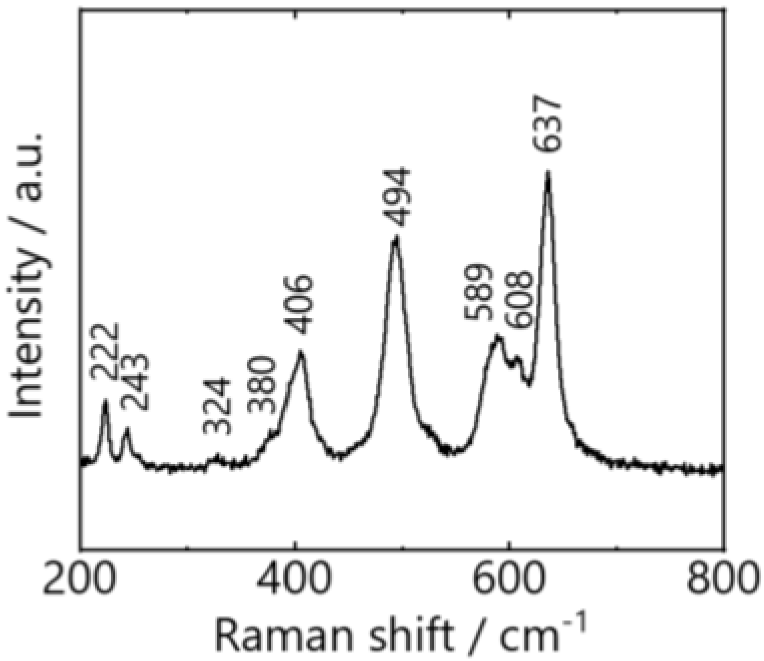

Figure S1. Raman spectrum for the pristine $Li_{0.96}Ni_{0.49}Mn_{1.51}O_4$.

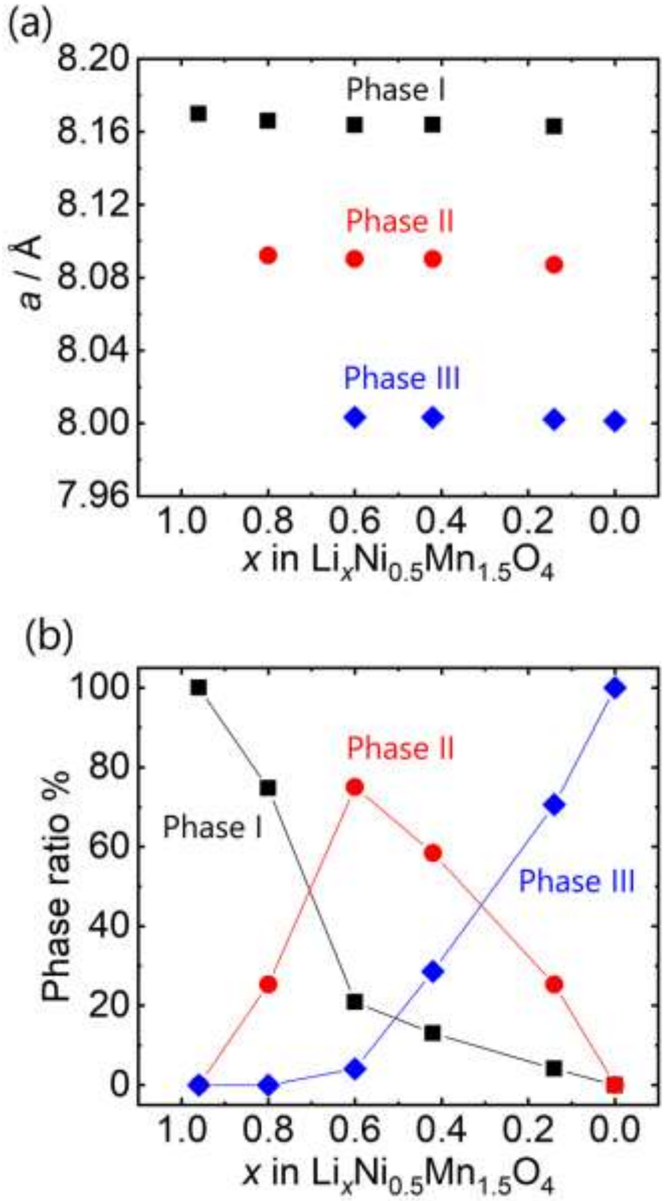

Figure S2. (a)Lattice parameters and (b) ratio of Phase I, II, III in $Li_xNi_{0.5}Mn_{1.5}O_4$.

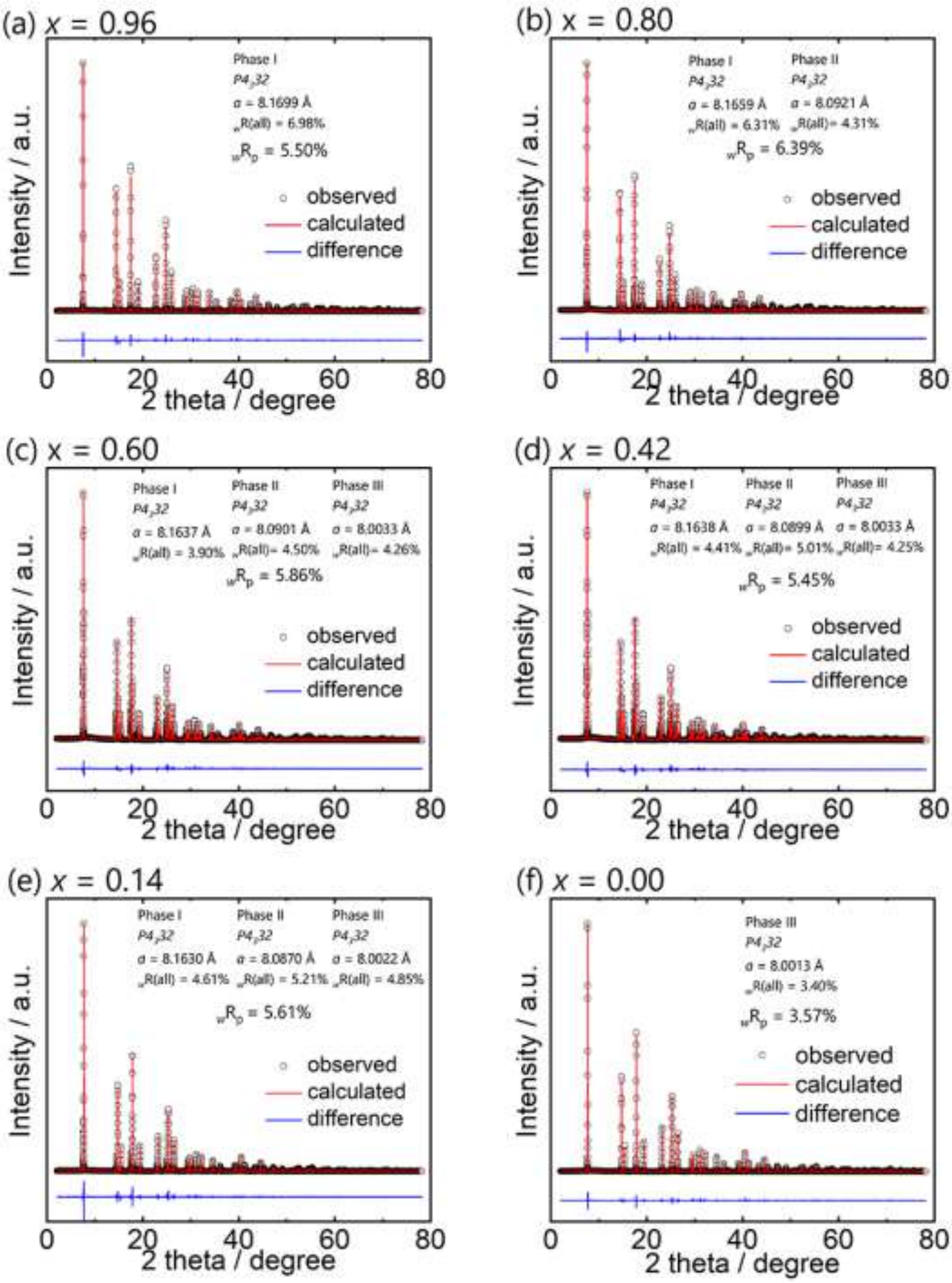

Figure S3. Rietveld refinement results for $Li_xNi_{0.5}Mn_{1.5}O_4$.

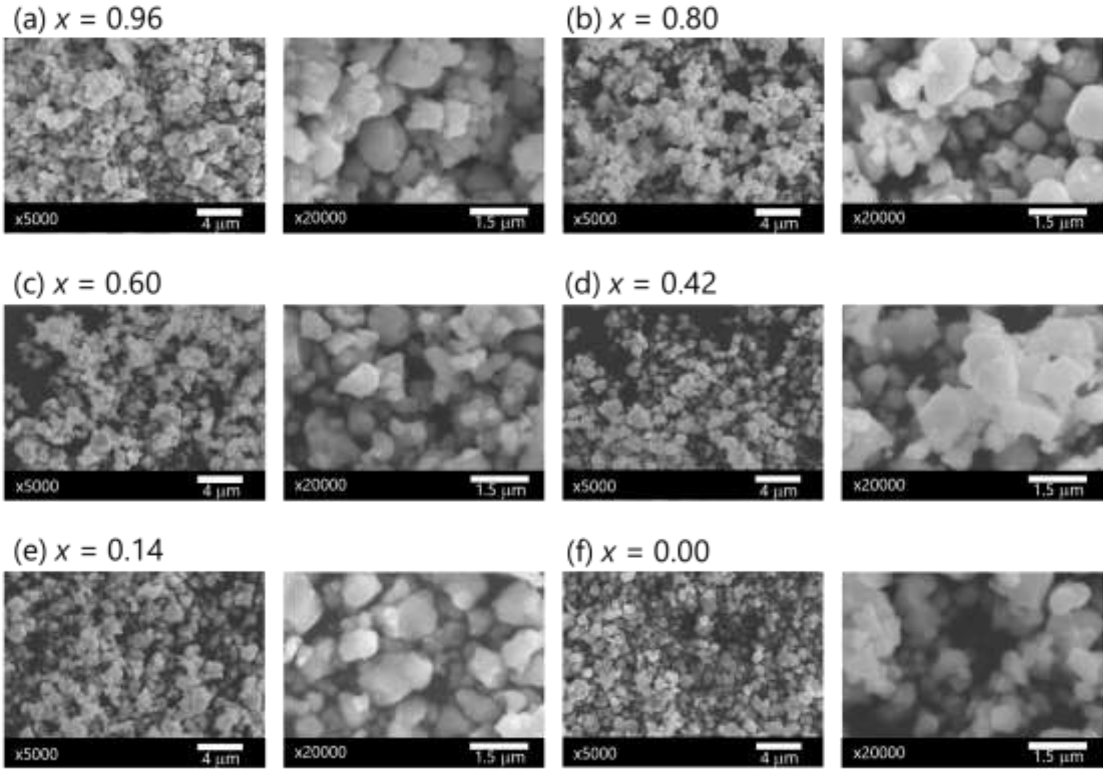

Figure S4. SEM images for $Li_xNi_{0.5}Mn_{1.5}O_4$.

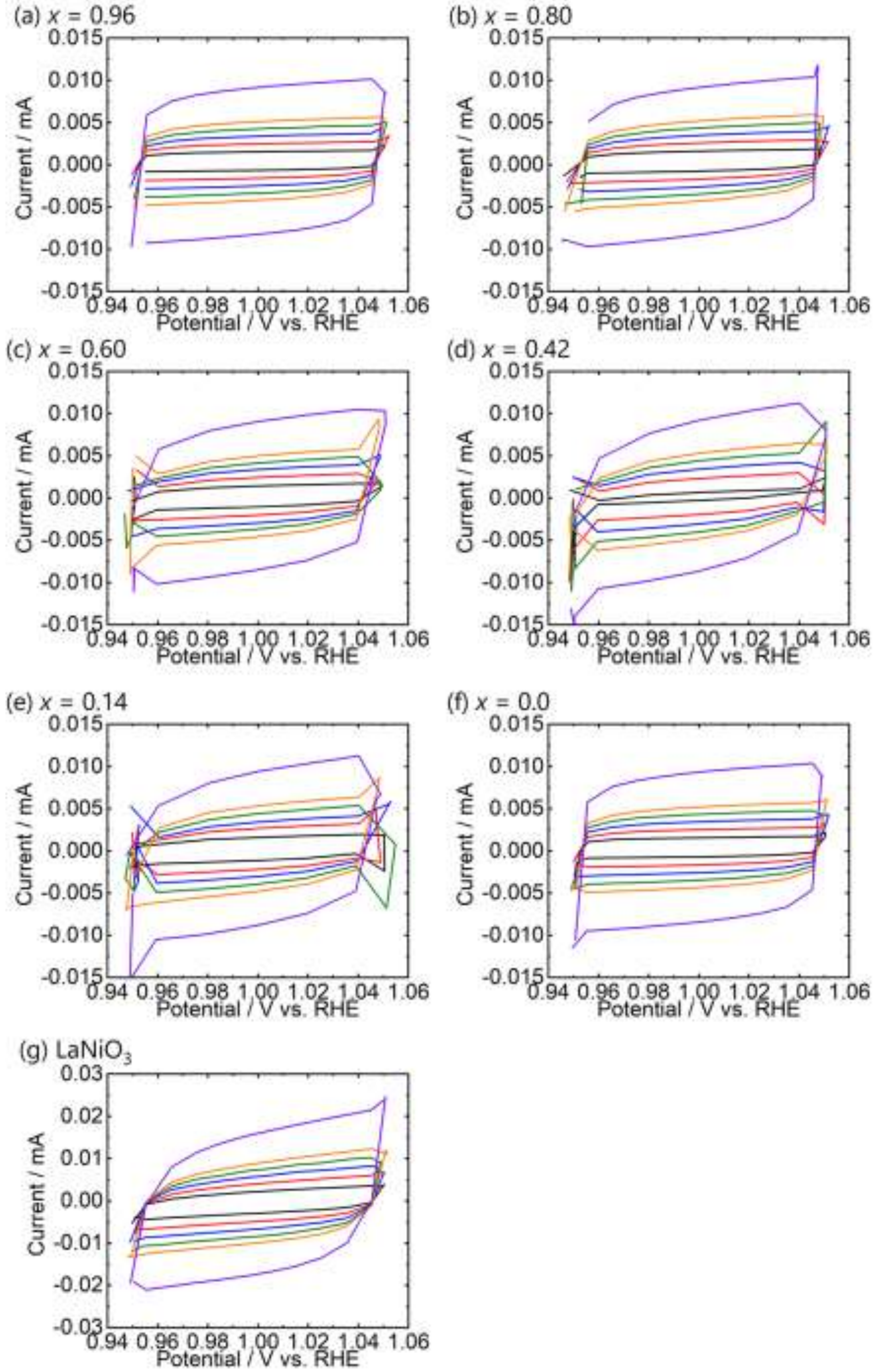

Figure S5. Double layer capacity measurement results for $Li_xNi_{0.5}Mn_{1.5}O_4$.

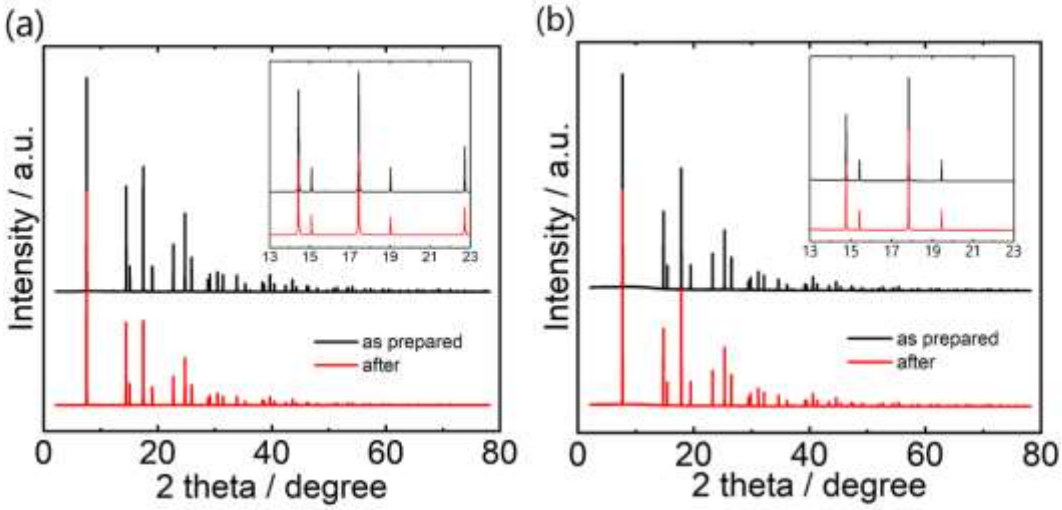

Figure S6. XRD of as prepared and after electrolysis samples for (a) x = 0.96 and (b) x = 0.0.

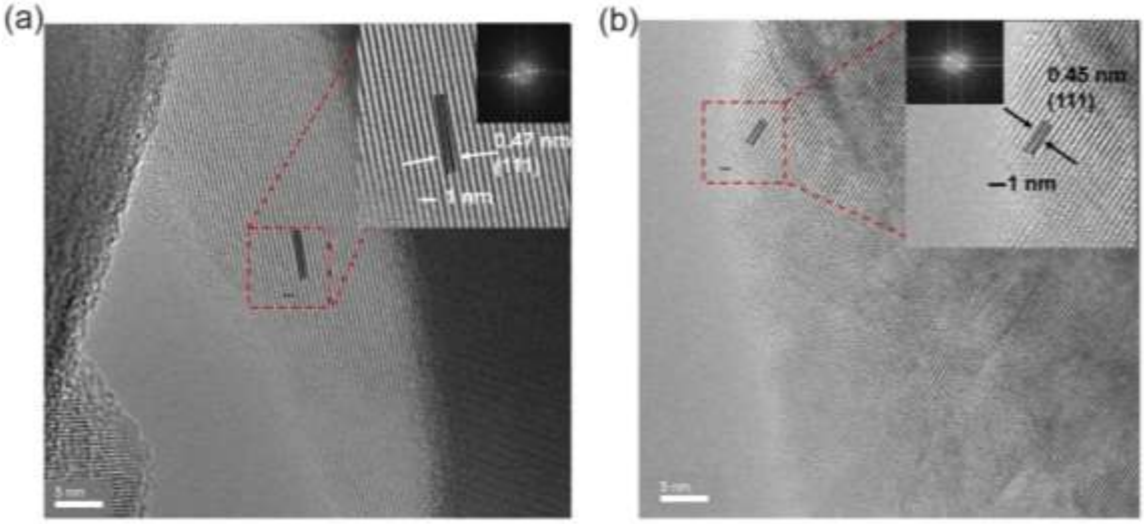

Figure S7. TEM after electrolysis for (a) $x = 0.96$ and (b) $x = 0.0$.

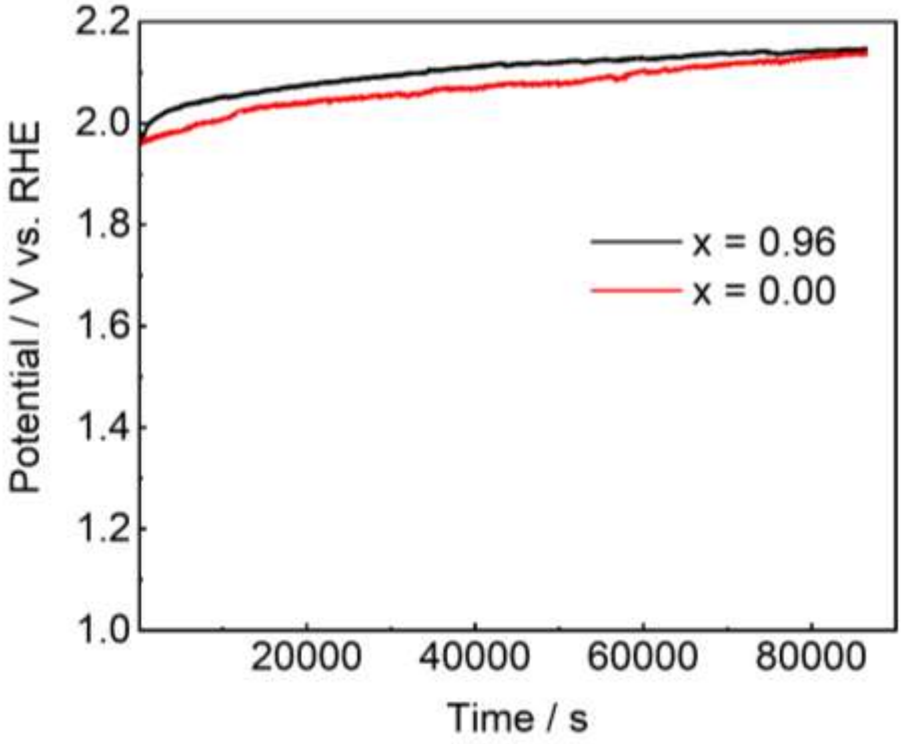

Figure S8. Long-term stability tests for $Li_{0.96}Ni_{0.49}Mn_{1.51}O_4$ and $Li_{0.00}Ni_{0.49}Mn_{1.51}O_4$. For $Li_{0.00}Ni_{0.49}Mn_{1.51}O_4$ sample, the current density was kept at 10 mA/cm^2. For $Li_{0.96}Ni_{0.49}Mn_{1.51}O_4$ sample, the current was kept at 6 mA/cm^2, making the initial potential the same for both samples before the long-term stability test.

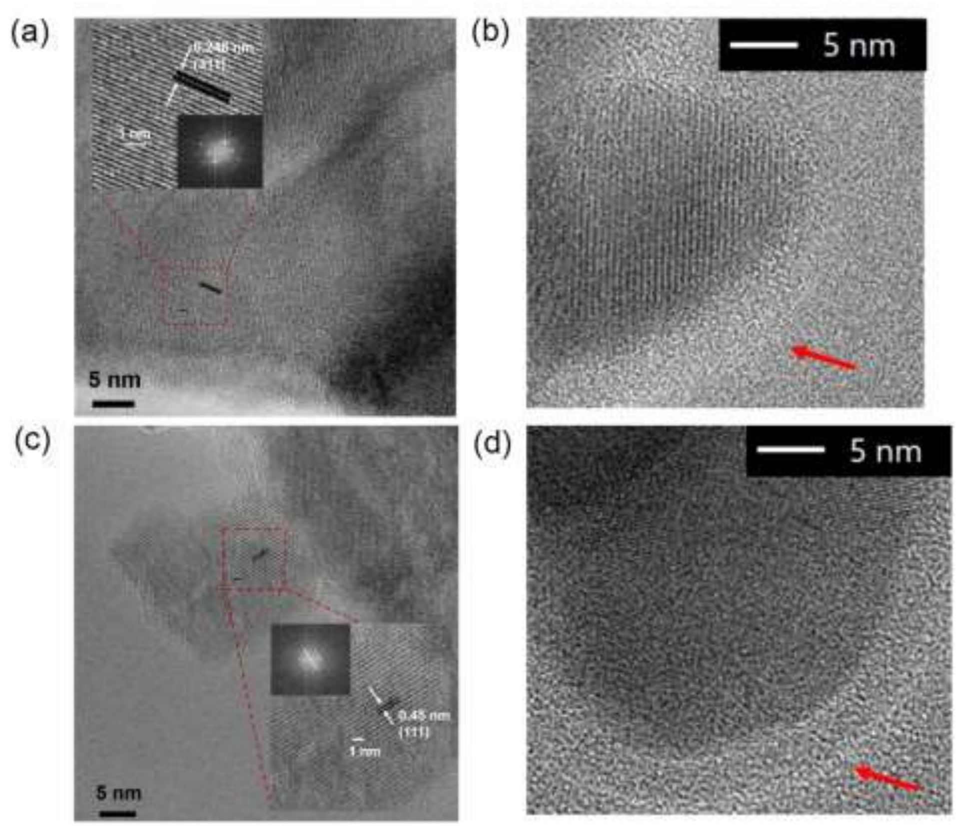

Figure S9. TEM images after long-term stability tests for (a) $Li_{0.96}Ni_{0.49}Mn_{1.51}O_4$ and (b) $Li_{0.00}Ni_{0.49}Mn_{1.51}O_4$.

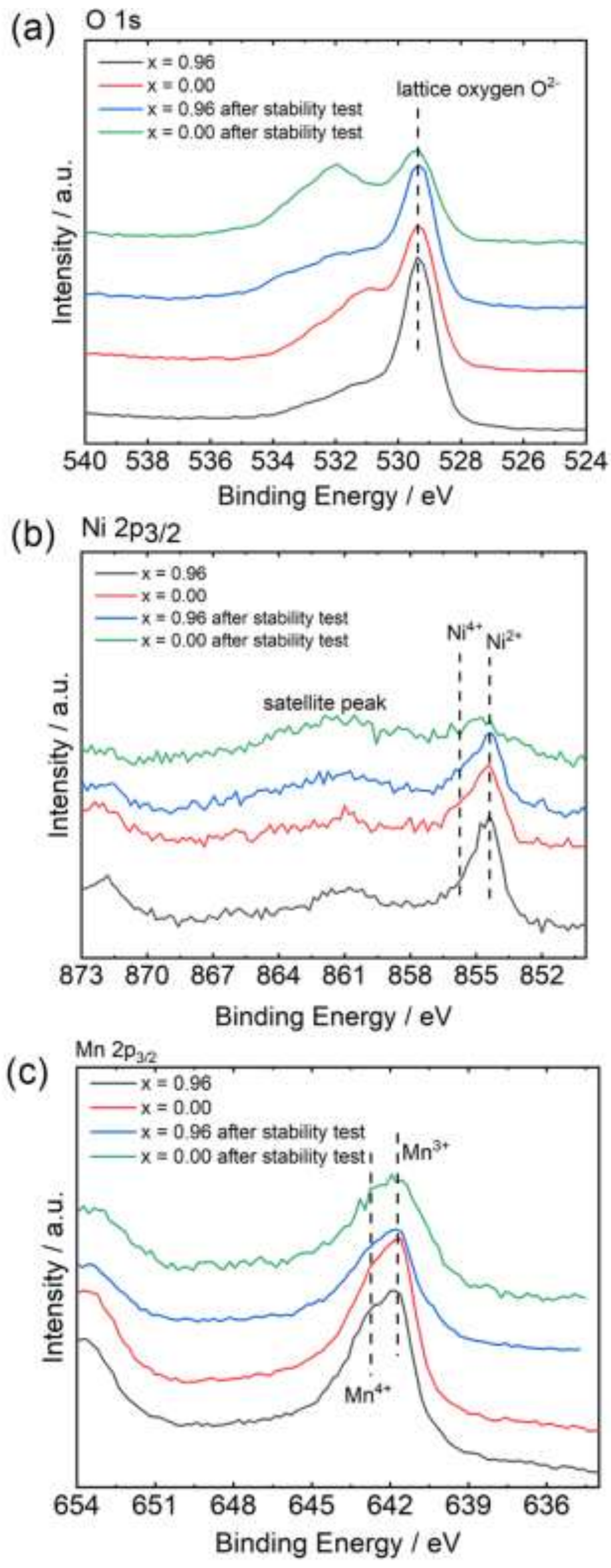

Figure S10. XPS spectra of (a) O 1s, (b) Ni 2p 3/2 and (c) Mn 2p 3/2 for x=0.00 and x = 0.96 before/after stability test.

Table S1. Rietveld refinement parameters for x = 0.96.

Phase	Spacegroup	Atom	Wyck	S.O.F	x / a	y / b	z / c	B / Å^2
I	$P4_332$ - Cubic	Li1	8*c*	1.000	0.004	0.004	0.004	=Mn1(*B*)
		Ni1	4*a*	1.000	0.625	0.625	0.625	=Mn1(*B*)
		Mn1	12*d*	1.000	0.125	0.379	-0.129	0.300
		O1	8*c*	1.000	0.384	0.384	0.384	=O2(*B*)
		O2	24*e*	1.000	0.149	-0.142	0.126	0.253

Table S2. Rietveld refinement parameters for x = 0.80.

Phase	Spacegroup	Atom	Wyck	S.O.F	x / a	y / b	z / c	B / Å^2	ratio
I	$P4_332$ - Cubic	Li1	8*c*	1.000	0.004	0.004	0.004	=Mn1(*B*)	74.70%
		Ni1	4*a*	1.000	0.625	0.625	0.625	=Mn1(*B*)	
		Mn1	12*d*	1.000	0.125	0.378	-0.128	0.325	
		O1	8*c*	1.000	0.389	0.389	0.389	=O2(*B*)	
		O2	24*e*	1.000	0.140	-0.144	0.121	0.273	
II	$P4_332$ - Cubic	Li1	8*c*	0.500	0.004	0.004	0.004	=Mn1(*B*)	25.30%
		Ni1	4*a*	1.000	0.625	0.625	0.625	=Mn1(*B*)	
		Mn1	12*d*	1.000	0.125	0.379	-0.129	0.324	
		O1	8*c*	1.000	0.384	0.384	0.384	=O2(*B*)	
		O2	24*e*	1.000	0.133	-0.142	0.126	0.271	

Table S3. Rietveld refinement parameters for *x* = 0.60.

Phase	Spacegroup	Atom	Wyck	S.O.F	*x* / a	*y* / b	*z* / c	*B* / Å^2	ratio
I	*P4$_3$32* - Cubic	Li1	8*c*	1.000	0.004	0.004	0.004	=Mn1(*B*)	20.90%
		Ni1	4*a*	1.000	0.625	0.625	0.625	=Mn1(*B*)	
		Mn1	12*d*	1.000	0.125	0.378	-0.128	0.326	
		O1	8*c*	1.000	0.389	0.389	0.389	=O2(*B*)	
		O2	24*e*	1.000	0.140	-0.144	0.121	0.274	
II	*P4$_3$32* - Cubic	Li1	8*c*	0.500	0.004	0.004	0.004	=Mn1(*B*)	75.01%
		Ni1	4*a*	1.000	0.625	0.625	0.625	=Mn1(*B*)	
		Mn1	12*d*	1.000	0.125	0.377	-0.127	0.324	
		O1	8*c*	1.000	0.386	0.386	0.386	=O2(*B*)	
		O2	24*e*	1.000	0.142	-0.143	0.126	0.251	
III	*P4$_3$32* - Cubic	Li1	8*c*	0.000	0.004	0.004	0.004	=Mn1(*B*)	4.09%
		Ni1	4*a*	1.000	0.625	0.625	0.625	=Mn1(*B*)	
		Mn1	12*d*	1.000	0.125	0.375	-0.125	0.328	
		O1	8*c*	1.000	0.388	0.388	0.388	=O2(*B*)	
		O2	24*e*	1.000	0.137	-0.142	0.132	0.291	

Table S4. Rietveld refinement parameters for *x* = 0.40.

Phase	Spacegroup	Atom	Wyck	S.O.F	*x* / a	*y* / b	*z* / c	*B* / Å^2	ratio
I	$P4_332$ - Cubic	Li1	8*c*	1.000	0.005	0.005	0.005	=Mn1(*B*)	13.00%
		Ni1	4*a*	1.000	0.625	0.625	0.625	=Mn1(*B*)	
		Mn1	12*d*	1.000	0.125	0.378	-0.128	0.325	
		O1	8*c*	1.000	0.389	0.389	0.389	=O2(*B*)	
		O2	24*e*	1.000	0.140	-0.144	0.121	0.281	
II	$P4_332$ - Cubic	Li1	8*c*	0.500	0.004	0.004	0.004	=Mn1(*B*)	58.40%
		Ni1	4*a*	1.000	0.625	0.625	0.625	=Mn1(*B*)	
		Mn1	12*d*	1.000	0.125	0.377	-0.127	0.324	
		O1	8*c*	1.000	0.386	0.386	0.386	=O2(*B*)	
		O2	24*e*	1.000	0.142	-0.143	0.128	0.276	
III	$P4_332$ - Cubic	Li1	8*c*	0.000	0.004	0.004	0.004	=Mn1(*B*)	28.60%
		Ni1	4*a*	1.000	0.625	0.625	0.625	=Mn1(*B*)	
		Mn1	12*d*	1.000	0.125	0.375	-0.125	0.327	
		O1	8*c*	1.000	0.388	0.388	0.388	=O2(*B*)	
		O2	24*e*	1.000	0.137	-0.140	0.132	0.297	

Table S5. Rietveld refinement parameters for $x = 0.14$.

Phase	Spacegroup	Atom	Wyck	S.O.F	*x* / a	*y* / b	*z* / c	*B* / Å^2	ratio
I	$P4_332$ - Cubic	Li1	8*c*	1.000	-0.000	-0.000	-0.000	=Mn1(*B*)	4.08%
		Ni1	4*a*	1.000	0.625	0.625	0.625	=Mn1(*B*)	
		Mn1	12*d*	1.000	0.125	0.378	-0.128	0.315	
		O1	8*c*	1.000	0.389	0.389	0.389	=O2(*B*)	
		O2	24*e*	1.000	0.140	-0.144	0.121	0.276	
II	$P4_332$ - Cubic	Li1	8*c*	0.500	0.004	0.004	0.004	=Mn1(*B*)	25.31%
		Ni1	4*a*	1.000	0.625	0.625	0.625	=Mn1(*B*)	
		Mn1	12*d*	1.000	0.125	0.377	-0.127	0.322	
		O1	8*c*	1.000	0.386	0.386	0.386	=O2(*B*)	
		O2	24*e*	1.000	0.142	-0.143	0.128	0.288	
III	$P4_332$ - Cubic	Li1	8*c*	0.000	0.004	0.004	0.004	=Mn1(*B*)	70.61%
		Ni1	4*a*	1.000	0.625	0.625	0.625	=Mn1(*B*)	
		Mn1	12*d*	1.000	0.125	0.375	-0.125	0.325	
		O1	8*c*	1.000	0.388	0.388	0.388	=O2(*B*)	
		O2	24*e*	1.000	0.137	-0.140	0.132	0.256	

Table S6. Rietveld refinement parameters for $x = 0.0$.

Phase	Spacegroup	Atom	Wyck	S.O.F	*x* / a	*y* / b	*z* / c	*B* / Å^2
III	$P4_332$ - Cubic	Li1	8*c*	0.000	0.004	0.004	0.004	=Mn1(*B*)
		Ni1	4*a*	1.000	0.625	0.625	0.625	=Mn1(*B*)
		Mn1	12*d*	1.000	0.125	0.375	-0.125	0.312
		O1	8*c*	1.000	0.391	0.391	0.391	=O2(*B*)
		O2	24*e*	1.000	0.135	-0.138	0.137	0.156

Table S7. The electrochemical surface area parameters for $Li_xNi_{0.5}Mn_{1.5}O_4$.

	C_{DL} / mF	ECSA / cm^2
x = 0.96	0.043	1.1
x = 0.80	0.043	1.1
x = 0.60	0.042	1.1
x = 0.42	0.042	1.1
x = 0.14	0.043	1.1
x = 0.0	0.043	1.1
$LaNiO_3$	0.078	2.0

Table S8. Tafel slope value of $Li_xNi_{0.5}Mn_{1.5}O_4$ series and $LaNiO_3$.

	Tafel slope / mV dec^{-1}
x = 0.96	121.9
x = 0.80	98.2
x = 0.60	89.2
x = 0.42	92.4
x = 0.14	75.3
x = 0.0	66.0
$LaNiO_3$	73.3