Supporting Information

Realizing the Ultimate Thermal Stability of a Lithium-Ion Battery Using Two Zero-Strain Insertion Materials

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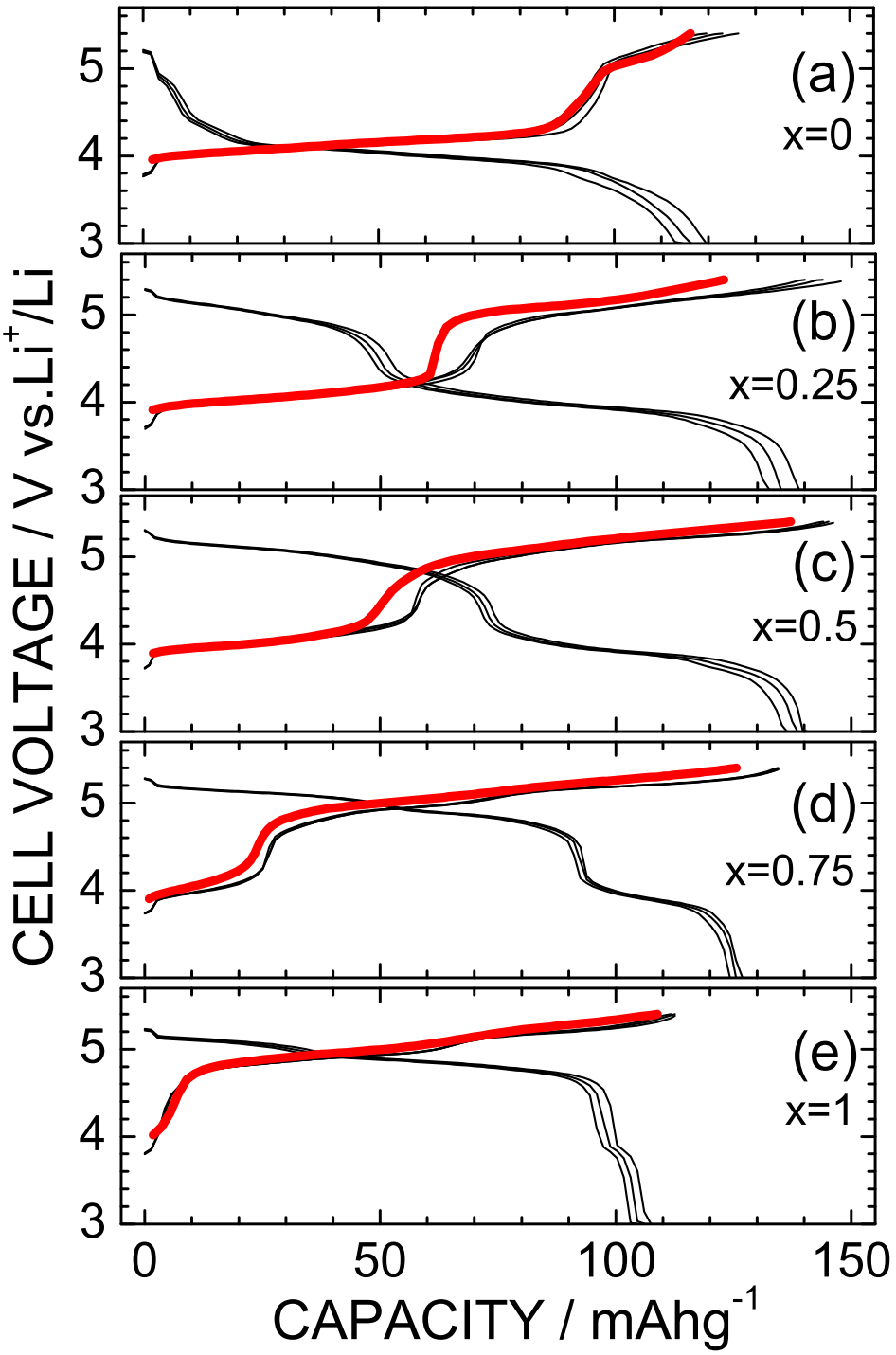

Figure S1 | Charge and discharge curves of the $LiCo_xMn_{2-x}O_4$/Li cells with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.5$, (d) $x = 0.75$, and (e) $x = 1$. The cells were operated at a current of 0.3 mA ($\simeq 0.15$ mA·cm^{-2}) at 25 °C. The red and lines indicate the charge curves for preparing the DSC samples.

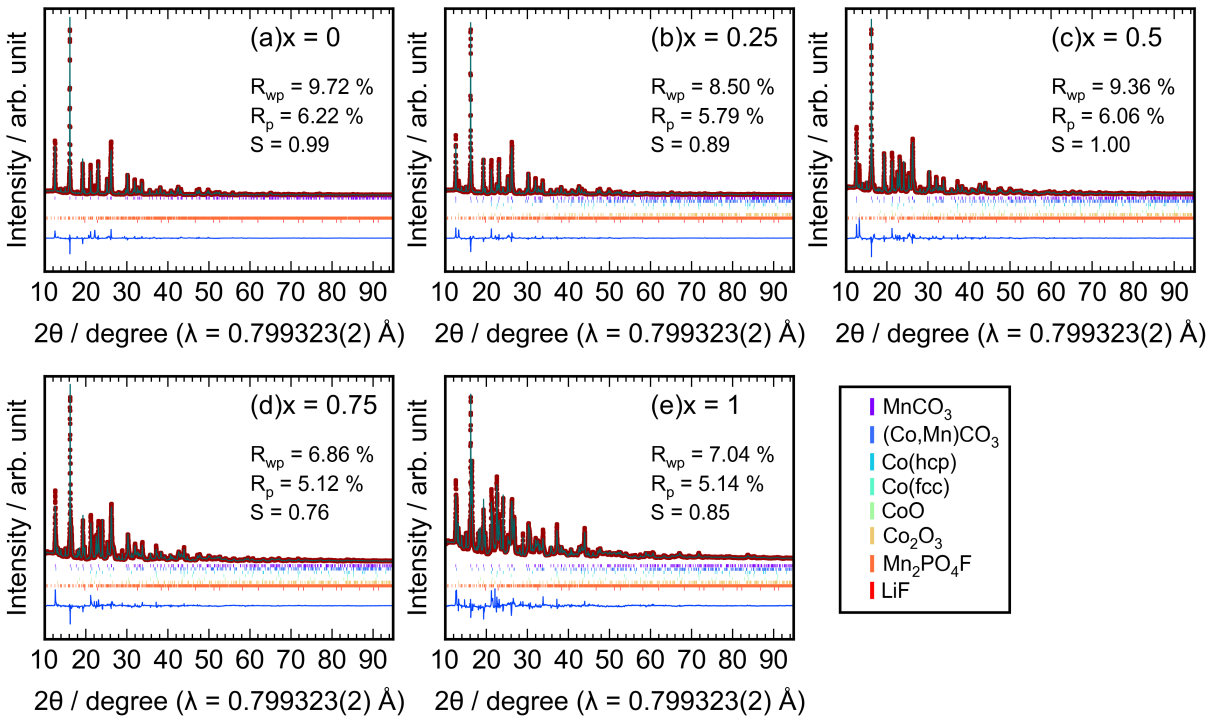

Figure S2 | Results of the Rietveld analyses. The $LiCo_xMn_{2-x}O_4$ samples with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.5$, (d) $x = 0.75$, and (e) $x = 1$.

Table S1 | Structural parameters of the $LiCo_xMn_{2-x}O_4$ samples after the DSC analyses

x	phase	space group	molar fraction[a]	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
0	$MnCO_3$	$R\bar{3}c$	0.773(4)	4.7778(1)	4.7778(1)	15.681(1)	90	90	120
	$(Co,Mn)CO_3$	$R\bar{3}c$	0	–	–	–	–	–	–
	Co(hcp)	$P6_3/mmc$	0	–	–	–	–	–	–
	Co(ccp)	$Fm\bar{3}m$	0	–	–	–	–	–	–
	CoO	$Fm\bar{3}m$	0	–	–	–	–	–	–
	Co_2O_3	$R\bar{3}c$	0	–	–	–	–	–	–
	Mn_2PO_4F	$C2/c$	0.033(2)	13.424(4)	6.517(1)	10.101(3)	90	120.0(1)	90
	LiF	$Fm\bar{3}m$	0.194(20)	4.032(1)	4.032(1)	4.032(1)	90	90	90
0.25	$MnCO_3$	$R\bar{3}c$	0.627(4)	4.7734(1)	4.7734(1)	15.655(1)	90	90	120
	$(Co,Mn)CO_3$	$R\bar{3}c$	0.057(4)	4.799(2)	14.799(2)	15.413(7)	90	90	120
	Co(hcp)	$P6_3/mmc$	0.025(9)	2.5081(5)	2.5081(5)	4.0750(1)	90	90	120
	Co(ccp)	$Fm\bar{3}m$	0.039(9)	3.5432(3)	3.5432(3)	3.5432(3)	90	90	90
	CoO	$Fm\bar{3}m$	0	–	–	–	–	–	–
	Co_2O_3	$R\bar{3}c$	0.004(3)	4.765(2)	4.765(2)	12.981(4)	90	90	120
	Mn_2PO_4F	$C2/c$	0.055(2)	13.418(4)	6.513(8)	10.091(3)	90	119.9(2)	90
	LiF	$Fm\bar{3}m$	0.192(20)	4.033(1)	4.033(1)	4.033(1)	90	90	90
0.5	$MnCO_3$	$R\bar{3}c$	0.579(4)	4.7689(2)	4.7689(2)	15.622(1)	90	90	120
	$(Co,Mn)CO_3$	$R\bar{3}c$	0.075(4)	4.775(2)	4.775(2)	15.264(5)	90	90	120
	Co(hcp)	$P6_3/mmc$	0.070(9)	2.5078(1)	2.5078(1)	4.0719(3)	90	90	120
	Co(ccp)	$Fm\bar{3}m$	0.063(9)	3.5433(2)	3.5433(2)	3.5433(2)	90	90	90
	CoO	$Fm\bar{3}m$	0.005(7)	4.338(2)	4.338(2)	4.338(2)	90	90	90
	Co_2O_3	$R\bar{3}c$	0.008(3)	4.7650(1)	4.760(1)	12.993(3)	90	90	120
	Mn_2PO_4F	$C2/c$	0.063(2)	13.417(4)	6.512(8)	10.080(3)	90	119.9(2)	90
	LiF	$Fm\bar{3}m$	0.136(20)	4.032(3)	4.032(3)	4.032(3)	90	90	90
0.75	$MnCO_3$	$R\bar{3}c$	0.447(4)	4.7640(1)	4.7640(1)	15.606(4)	90	90	120
	$(Co,Mn)CO_3$	$R\bar{3}c$	0.127(4)	4.721(9)	4.721(9)	15.200(3)	90	90	120
	Co(hcp)	$P6_3/mmc$	0.061(8)	2.5076(1)	2.5076(1)	4.0708(2)	90	90	120
	Co(ccp)	$Fm\bar{3}m$	0.047(8)	3.5427(2)	3.5427(2)	3.5427(2)	90	90	90
	CoO	$Fm\bar{3}m$	0.064(1)	4.313(2)	4.313(2)	4.313(2)	90	90	90
	Co_2O_3	$R\bar{3}c$	0.009(6)	4.761(1)	4.761(1)	12.991(1)	90	90	120
	Mn_2PO_4F	$C2/c$	0.041(3)	13.410(4)	6.512(8)	10.076(3)	90	119.9(2)	90
	LiF	$Fm\bar{3}m$	0.204(20)	4.030(1)	4.030(1)	4.030(1)	90	90	90
1	$MnCO_3$	$R\bar{3}c$	0.247(4)	4.7694(2)	4.7694(2)	15.622(8)	90	90	120
	$(Co,Mn)CO_3$	$R\bar{3}c$	0.312(4)	4.732(4)	4.732(4)	15.205(1)	90	90	120
	Co(hcp)	$P6_3/mmc$	0.039(7)	2.5072(1)	2.5072(1)	4.0708(3)	90	90	120
	Co(ccp)	$Fm\bar{3}m$	0.066(7)	3.5433(1)	3.5433(1)	3.5433(1)	90	90	90
	CoO	$Fm\bar{3}m$	0.093(6)	4.309(3)	4.309(3)	4.309(3)	90	90	90
	Co_2O_3	$R\bar{3}c$	0.026(3)	4.760(3)	4.760(3)	12.993(1)	90	90	120
	Mn_2PO_4F	$C2/c$	0.135(2)	13.388(4)	6.506(9)	10.065(3)	90	119.9(2)	90
	LiF	$Fm\bar{3}m$	0.082(20)	4.031(1)	4.031(1)	4.031(1)	90	90	90

[a]Deviations of molar fractions were determined by the estimation that the limit of detection in the Rietveld analyses is 0.5 wt% for each phase.

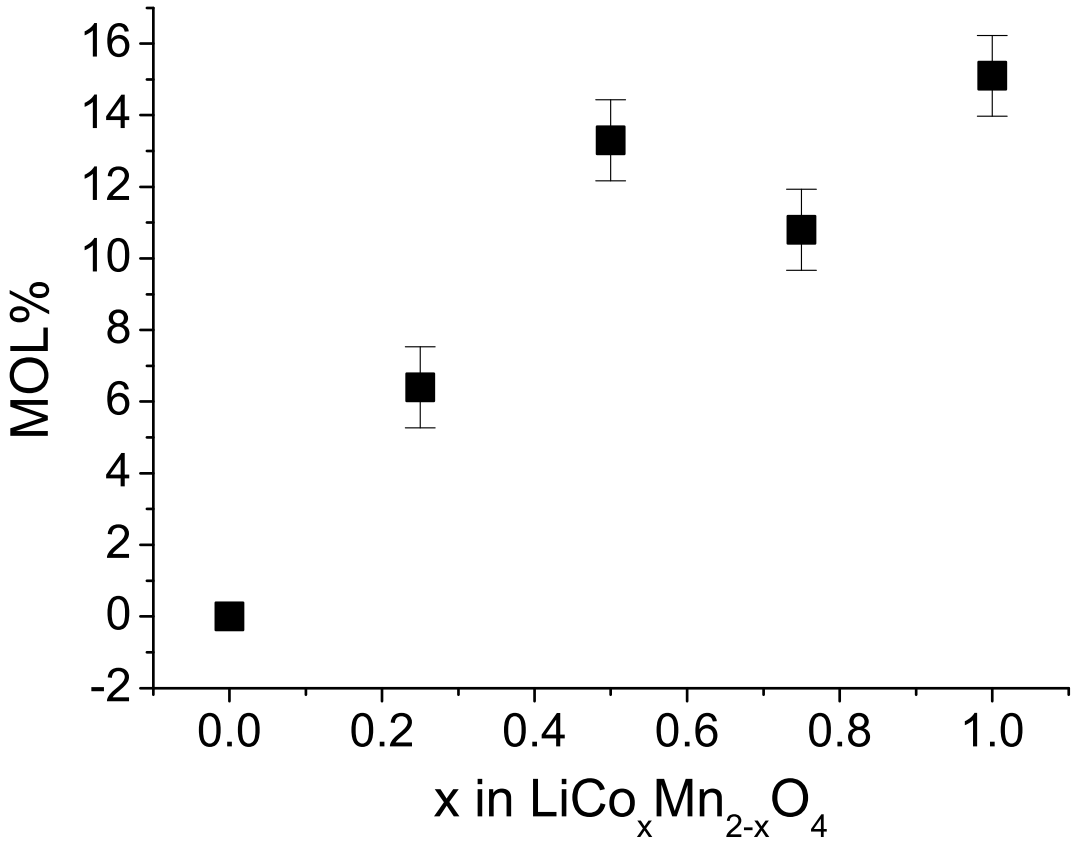

Figure S3 | Molar fraction of the Co metals in $LiCo_xMn_{2-x}O_4$ after the DSC analyses. The Co metals consist of the Co(hcp) and Co(ccp) phases.

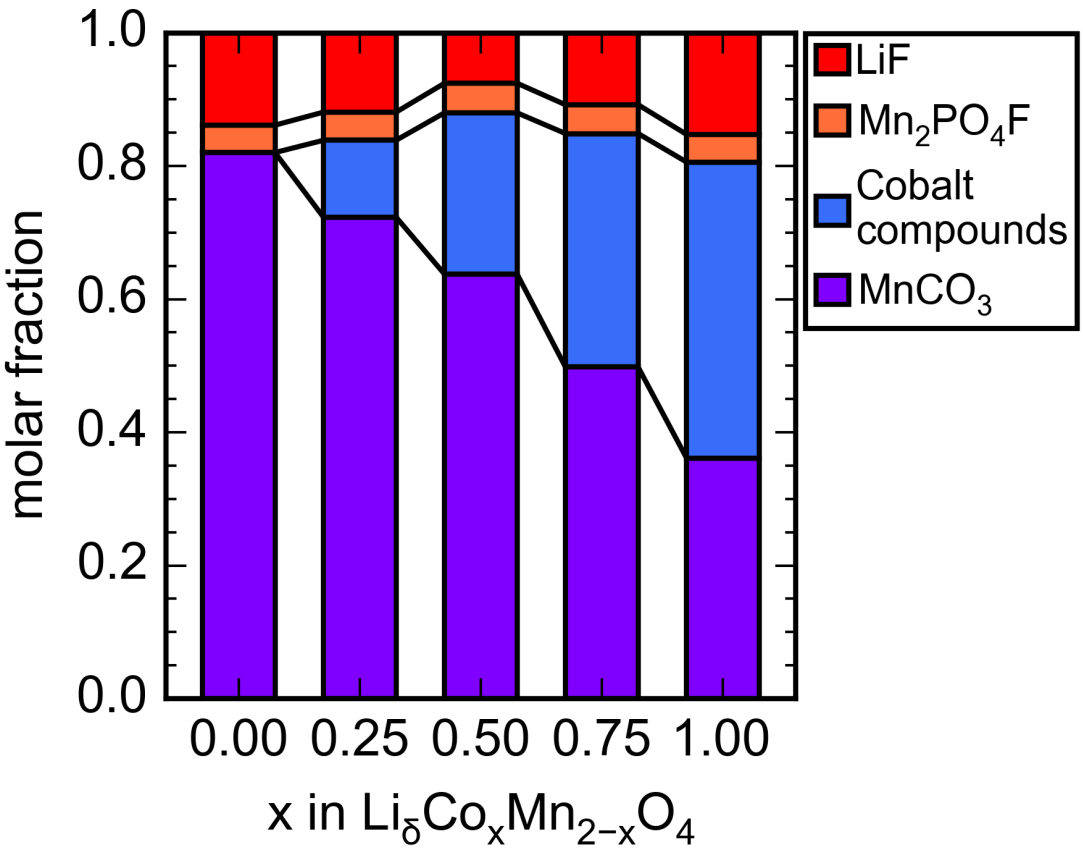

Figure S4 | Calculated molar fractions of LiF, Mn_2PO_4F, cobalt compounds, and $MnCO_3$ phases.

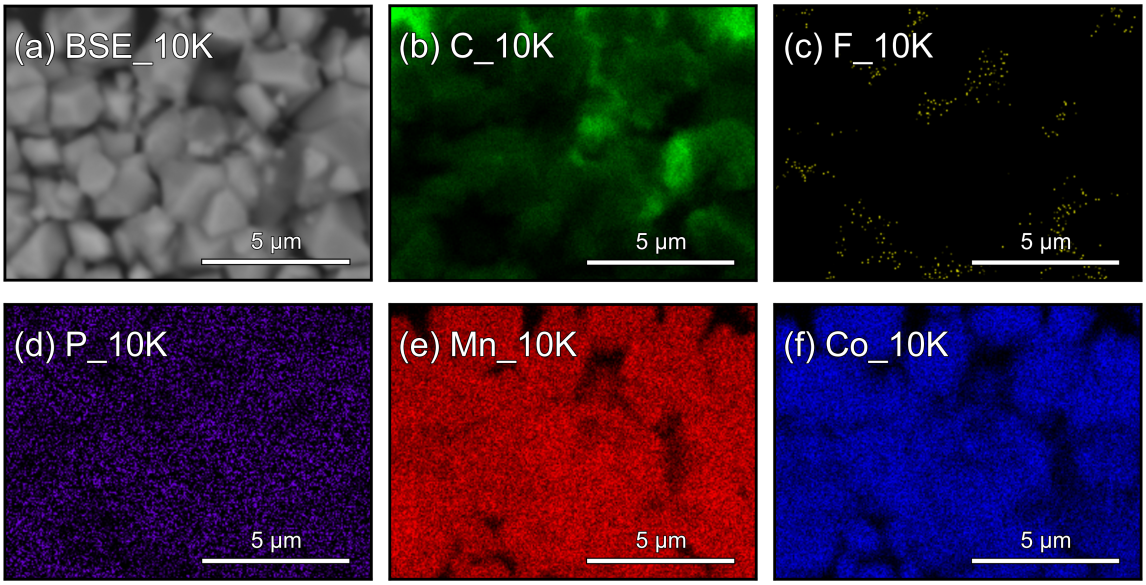

Figure S5 | SEM images and mappings of the elements Co, Mn, C, P, and F in the $x = 1$ sample. This data was obtained after the DSC analysis using the AIM method shown in Fig. 3(b). (a) Back scattered electron microscope image, and mappings of the elements of (b) C, (c) F, (d) P, (e) Mn, and (f) Co.