A Comparative Mechanistic Study on the Intercalation Reactions of Mg^{2+} and Li^{+} Ions into $(Mg_{0.5}Ni_{0.5})_3(PO_4)_2$

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Supplementary Information

Table S1. Crystal and refinement parameters for MNP at room temperature.

Nominal composition	$Mg_{1.5}Ni_{1.5}O_8P_2$
Primary phase	$(Mg_{0.5}Ni_{0.5})_3(PO_4)_2$
Weight fraction primary phase	0.99214(4)
Formula weight primary phase	314.48 g mol^{-1}
Crystal system primary phase	Monoclinic
Space group primary phase	$P2_1/c$
Unit cell dimensions primary phase	a = 5.8860(1) Å b = 4.70841(9) Å c = 10.1717(2) Å β = 90.777(1)°
Volume primary phase	281.87(1) $Å^3$
Z primary phase	2
Density (calculated) primary phase	3.705 g cm^{-3}
Secondary phase	NiO
Weight fraction secondary phase	0.0078(5)
Formula weight secondary phase	74.71 g mol^{-1}
Crystal system secondary phase	Trigonal
Space group secondary phase	$R\bar{3}m$
Lattice parameter secondary phase	a = 2.961(1) Å, c = 7.231(7) Å
Volume secondary phase	54.91(3) $Å^3$
Z secondary phase	3
Density (calculated) secondary phase	6.777 g cm^{-3}
R-factors	R_{wp} = 0.0188 R_p = 0.0111 R_{ex} =0.0061 R_F^2 = 0.0716 χ^2 = 9.44
No. of observations/restraints/parameters	3290/0/46
Total no. of reflections used	888

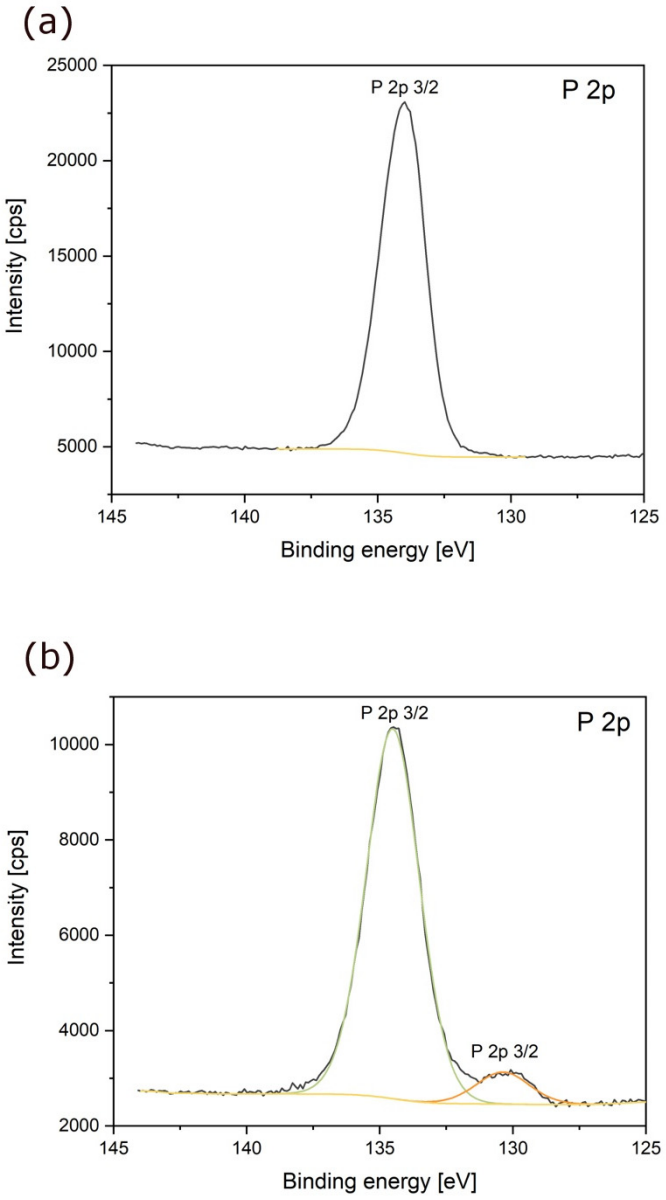

Figure S1. P 2*p* X-ray photoelectron spectra for MNP powder (a) before and (b) after Ar-ion etching.

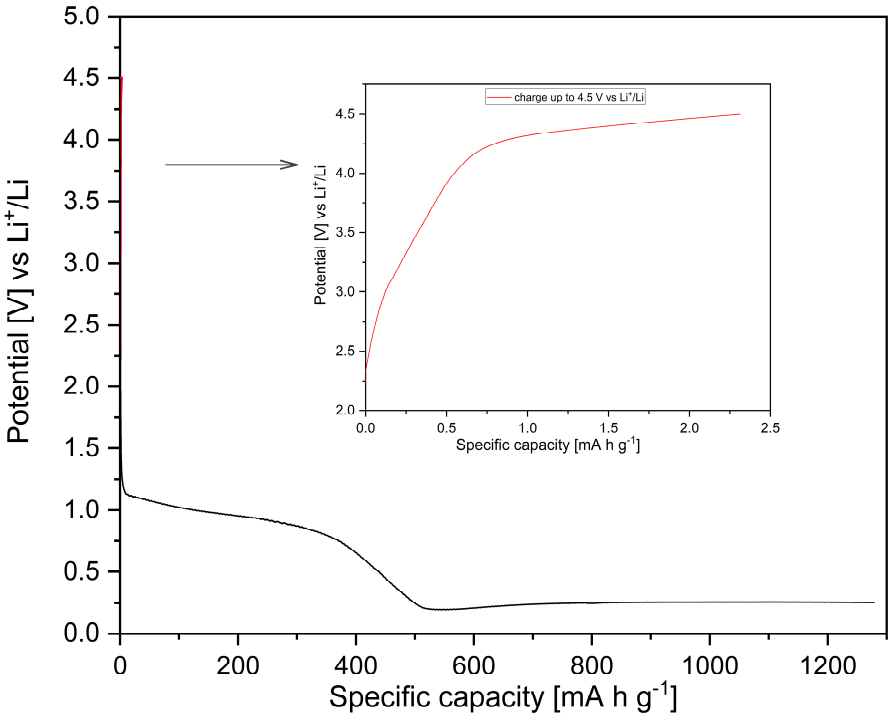

Figure S2. Charge (red line) and discharge (black line) curves for MNP active material, coated on Al and cycled in a Li-half cell with Li-electrolyte between 4.5 V and 0.25 V vs. Li^+/Li. The inset shows the poor charging behaviour of MNP (red line) up to 4.5 V vs. Li^+/Li.

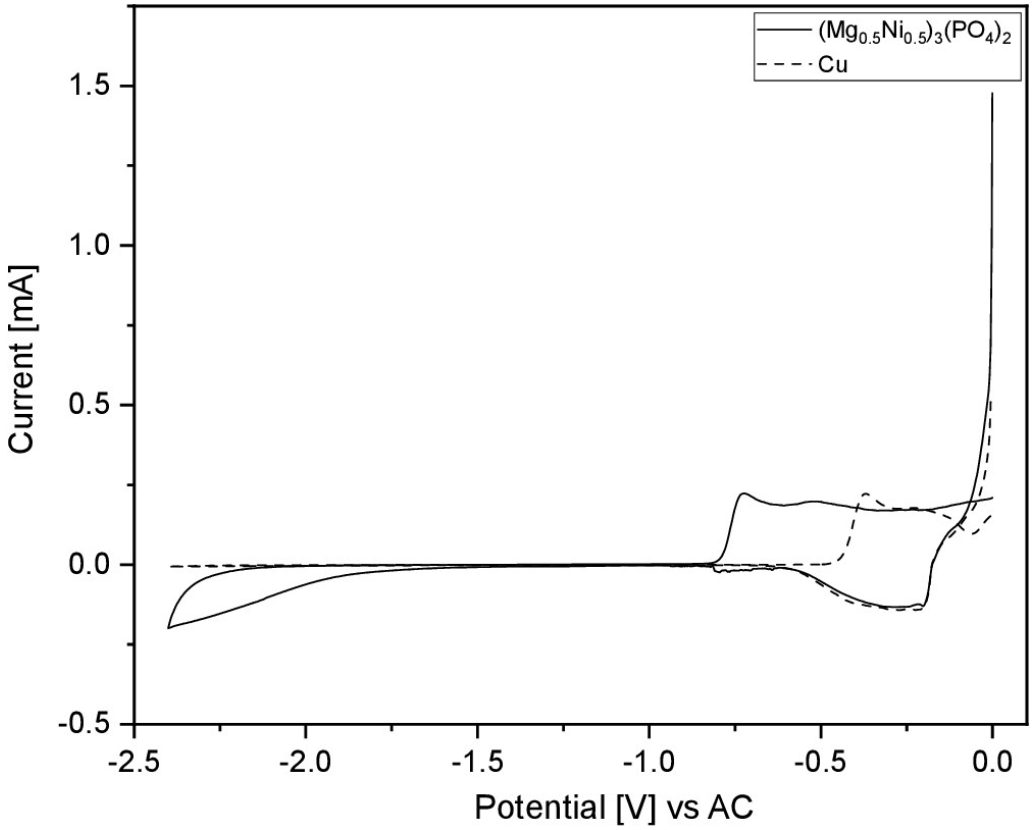

Figure S3. Cyclic voltammograms of MNP (solid-line) and Cu (dashed) working electrodes recorded at a scan rate of 0.07 mV s^{-1} using AC as the counter electrode and Mg-electrolyte. Irregular effects, associated with an interaction between the Cu current collector and the electrolyte, were observed at *ca*. -0.75 V vs. AC and -0.3 V vs. AC for the MNP and Cu working electrodes, respectively. Therefore, further galvanostatic discharge-charge cycling of the MNP working electrode was performed in the voltage window between -2.4 V and -0.8 V vs. AC.

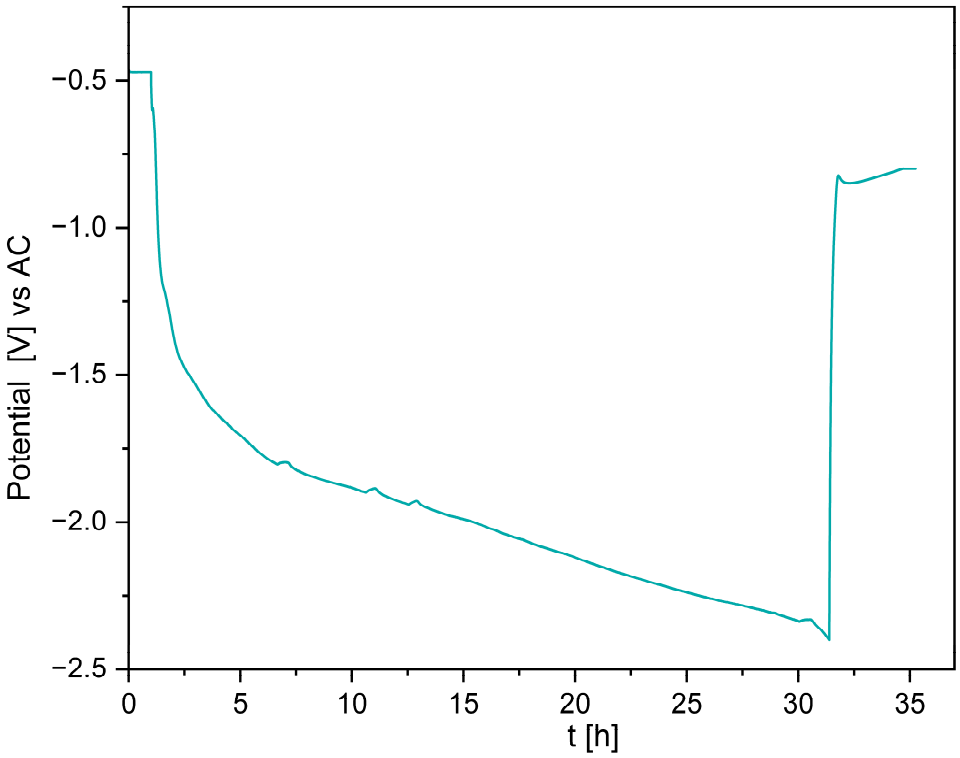

Figure S4. Charge and discharge curves with constant voltage step for MNP vs AC-Mg electrolyte cell.

Table S2. Crystal and refinement parameters for the MNP pristine electrode.

Nominal composition	$Mg_{1.5}Ni_{1.5}O_8P_2$
Primary phase	$(Mg_{0.5}Ni_{0.5})_3(PO_4)_2$
Weight fraction primary phase	0.42(7)
Formula weight primary phase	314.48 g mol^{-1}
Crystal system primary phase	Monoclinic
Space group primary phase	$P2_1/c$
Unit cell dimensions primary phase	a = 5.8808(3) Å b = 4.7060(3) Å c = 10.1656(5) Å β = 90.80(0)°
Volume primary phase	281.30(9) Å^3
Z primary phase	2
Density (calculated) primary phase	3.172 g cm^{-3}
Secondary phase	Cu
Weight fraction secondary phase	0.536(2)
Formula weight secondary phase	63.55 g mol^{-1}
Crystal system secondary phase	Cubic
Space group secondary phase	$Fm\bar{3}m$
Lattice parameter secondary phase	a = 3.61438(8) Å
Volume secondary phase	42.21(7) Å^3
Z secondary phase	4
Density (calculated) secondary phase	8.939 g cm^{-3}
Tertiary phase	$Mg_2P_2O_7$
Weight fraction tertiary phase	0.036(8)
Formula weight tertiary phase	222.55 g mol^{-1}
Crystal system tertiary phase	Monoclinic
Space group tertiary phase	$P2_1/c$
Lattice parameter tertiary phase	a = 6.720(4) Å b = 8.347(4) Å c = 9.032(5) Å β = 113.40(4)°
Volume tertiary phase	464.9(2) Å^3
Z tertiary phase	4
Density (calculated) tertiary phase	3.179 g cm^{-3}
R-factors	R_{wp} = 0.0226 R_p = 0.0143 R_{ex} = 0.0052 R_F^2 = 0.2324 χ^2 = 19.41
No. of observations/restraints/parameters	2223/0/51
Total no. of reflections used	1531

Table S3. Crystal and refinement parameters for the MNP active material electrode after discharging up to −2.4 V vs. AC and after charging up to −0.8 V vs. AC using Mg-electrolyte.

	−2.4 V	−0.8 V
Nominal composition	$Mg_{1.5}Ni_{1.5}O_8P_2$	$Mg_{1.5}Ni_{1.5}O_8P_2$
Primary phase	$(Mg_{0.5}Ni_{0.5})_3(PO_4)_2$	$(Mg_{0.5}Ni_{0.5})_3(PO_4)_2$
Weight fraction primary phase	0.565(6)	0.569(4)
Formula weight primary phase	314.48 g mol^{-1}	314.48 g mol^{-1}
Crystal system primary phase	Monoclinic	Monoclinic
Space group primary phase	$P2_1/c$	$P2_1/c$
Unit cell dimensions primary phase	a = 5.8699(6) Å b = 4.6994(5) Å c = 10.150(1) Å β = 90.76(5)°	a = 5.8852(5) Å b = 4.7120(4) Å c = 10.1709(9) Å β = 90.77(2)°
Volume primary phase	279.9(7) Å^3	282.3(6) Å^3
Z primary phase	2	2
Density (calculated) primary phase	3.730 g cm^{-3}	3.703 g cm^{-3}
Secondary phase	Cu	Cu–Ni
Weight fraction secondary phase	0.253(7)	0.379(4)
Formula weight secondary phase	63.55 g mol^{-1}	63.55 g mol^{-1}
Crystal system secondary phase	Cubic	Cubic
Space group secondary phase	$Fm\bar{3}m$	$Fm\bar{3}m$
Lattice parameter secondary phase	a = 3.6118(2) Å	a = 3.61334(3) Å
Volume secondary phase	47.11(6) Å^3	47.17(7) Å^3
Z secondary phase	4	4
Density (calculated) secondary phase	8.958 g cm^{-3}	8.947 g cm^{-3}
Tertiary phase	Cu–Ni	$Mg_2P_2O_7$
Weight fraction tertiary phase	0.090(8)	0.051(2)
Formula weight tertiary phase	63.55 g mol^{-1}	222.55 g mol^{-1}
Crystal system tertiary phase	Cubic	Monoclinic
Space group tertiary phase	$Fm\bar{3}m$	$P2_1/c$
Lattice parameter tertiary phase	a = 3.6047(3) Å	a = 6.735(6) Å b = 8.387(7) Å c = 9.003(8) Å β = 113.18(4)°
Volume tertiary phase	46.84(1) Å^3	467.5(3) Å^3
Z tertiary phase	4	4
Density (calculated) tertiary phase	2.324 g cm^{-3}	3.163 g cm^{-3}

Table S3 continued. Crystal and refinement parameters for the MNP active material electrode after discharging up to −2.4 V vs. AC and after charging up to−0.8 V vs. AC using Mg-electrolyte.

	−2.4 V	−0.8 V
Fourth phase	$Mg_3(PO_4)_2$	
Weight fraction fourth phase	0.044(6)	
Formula weight fourth phase	314.48 g mol^{-1}	
Crystal system fourth phase	Monoclinic	
Space group fourth phase	$P2_1/c$	
Lattice parameter fourth phase	a = 5.844(6) Å b = 4.770(6) Å c = 10.54(1) Å β = 91.79(9)°	
Volume fourth phase	293.7(4) $Å^3$	
Z fourth phase	2	
Density (calculated) fourth phase	2.984 g cm^{-3}	
Fifth phase	$Mg_2P_2O_7$	
Weight fraction fourth phase	0.045(3)	
Formula weight fourth phase	222.55 g mol^{-1}	
Crystal system fourth phase	Monoclinic	
Space group fourth phase	$P2_1/c$	
Lattice parameter fourth phase	a = 6.734(8) Å b = 8.333(9) Å c = 9.01(1) Å β = 113.20(6)°	
Volume fourth phase	464.6(4) $Å^3$	
Z fourth phase	4	
Density (calculated) fourth phase	3.184 g cm^{-3}	
R-factors	R_{wp} = 0.0346 R_p = 0.0239 R_{ex} = 0.0070 R_F^2 = 0.1472 χ^2 = 25.08	R_{wp} = 0.0308 R_p = 0.0197 R_{ex} = 0.0047 R_F^2 = 0.1773 χ^2 = 44.34
No. of observations/restraints/parameters	2662/0/64	2692/0/49
Total no. of reflections used	2186	1596

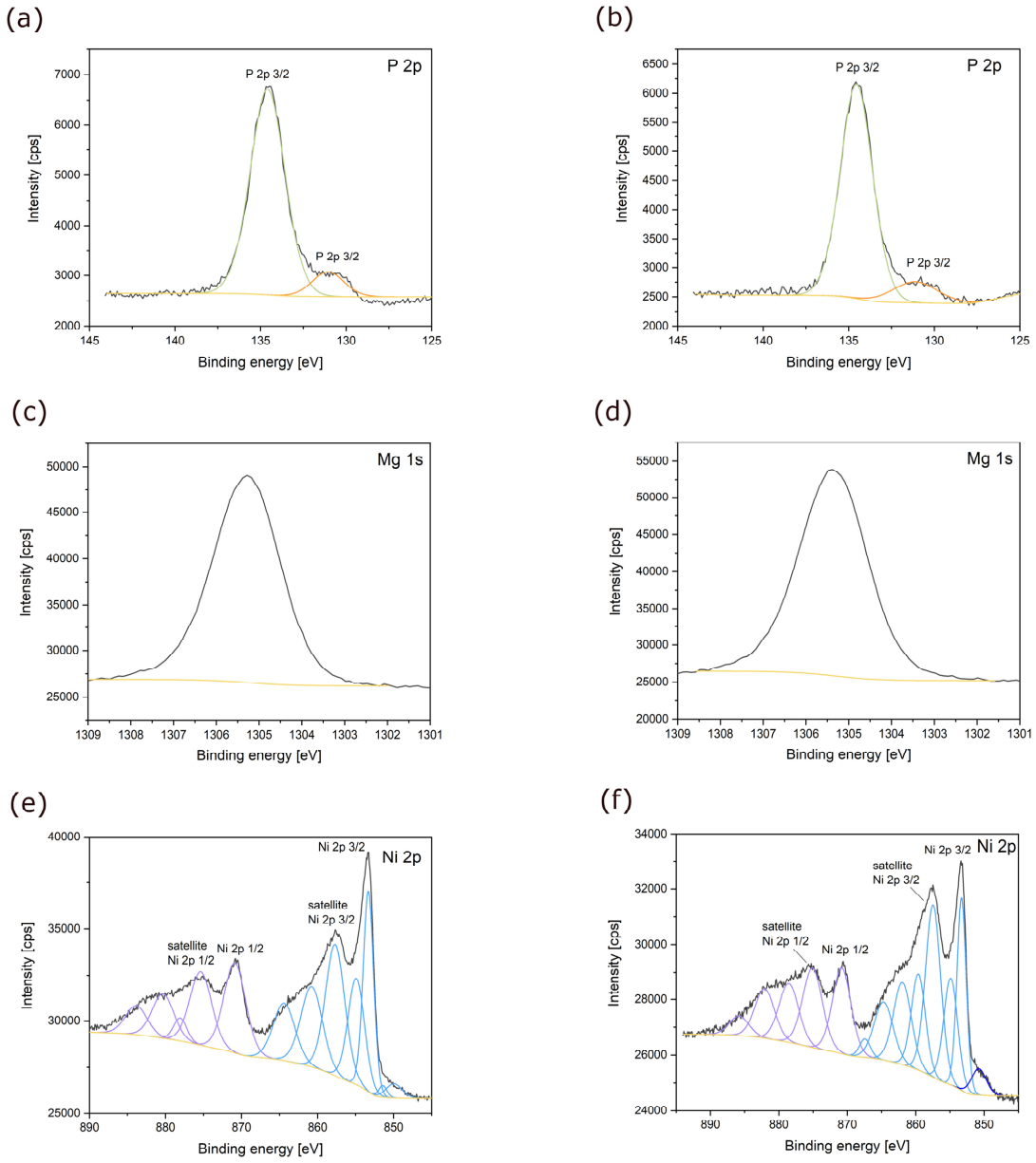

Figure S5. P 2*p*, Mg 1*s* and Ni 2*p* X-ray photoelectron spectra of MNP active material in (a, c and e, respectively) pristine and (b, d and f, respectively) discharged up to –2.4 V vs. AC electrodes using Mg-electrolyte.

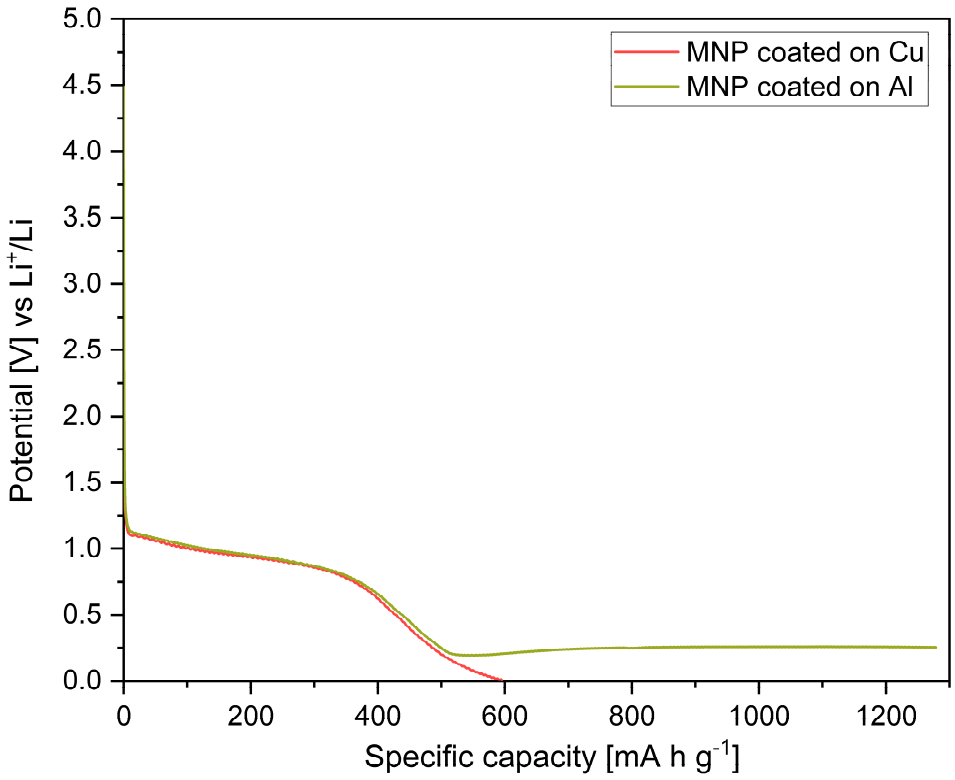

Figure S6. Discharge curves for MNP active material coated on Cu (red line) and Al (green line) current collectors cycled in a Li-half cell with Li-electrolyte.

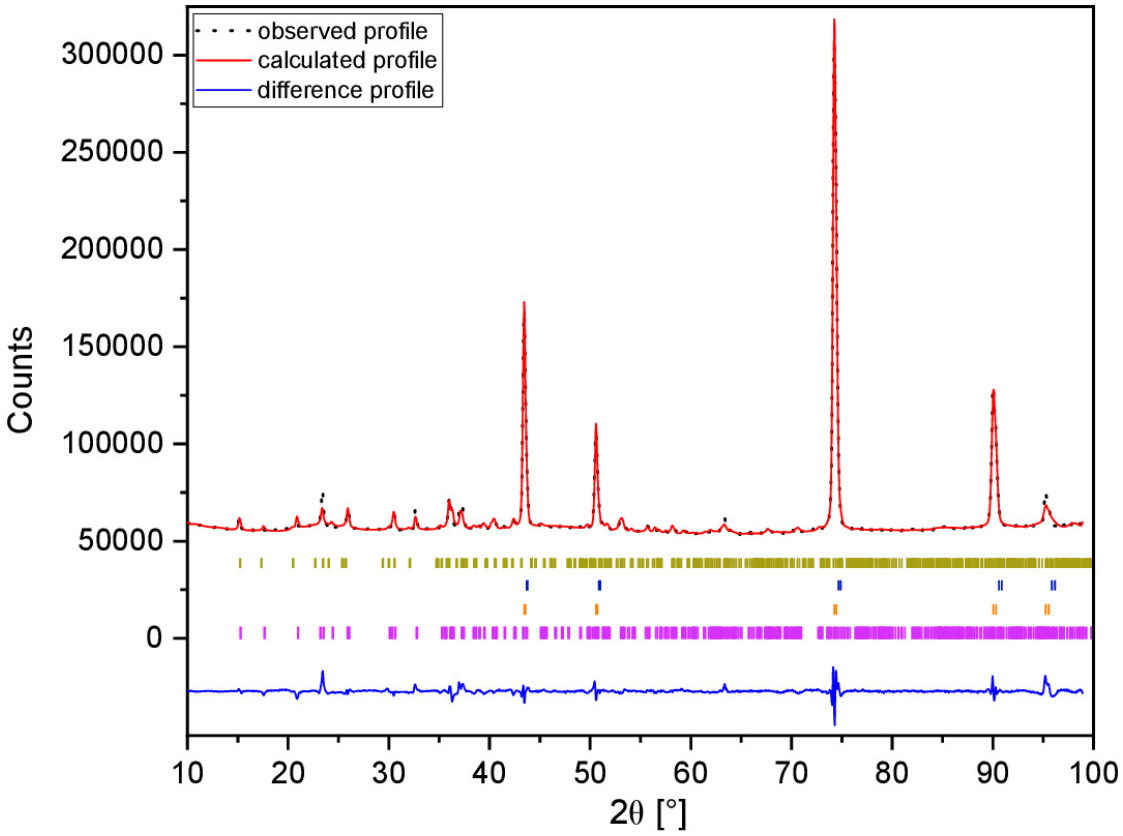

Figure S7. Fitted ex-situ XRD pattern of MNP active material discharged up to 1.0 vs. Li^+/Li in Li-electrolyte. Observed (black dots), calculated (red line) and difference (blue line) profiles are shown. Reflection positions for MNP (pink bars), Cu (orange bars), Cu–Ni alloy (blue bars) and sarcopside-$Mg_3(PO_4)_2$ (dark yellow bars) are indicated.

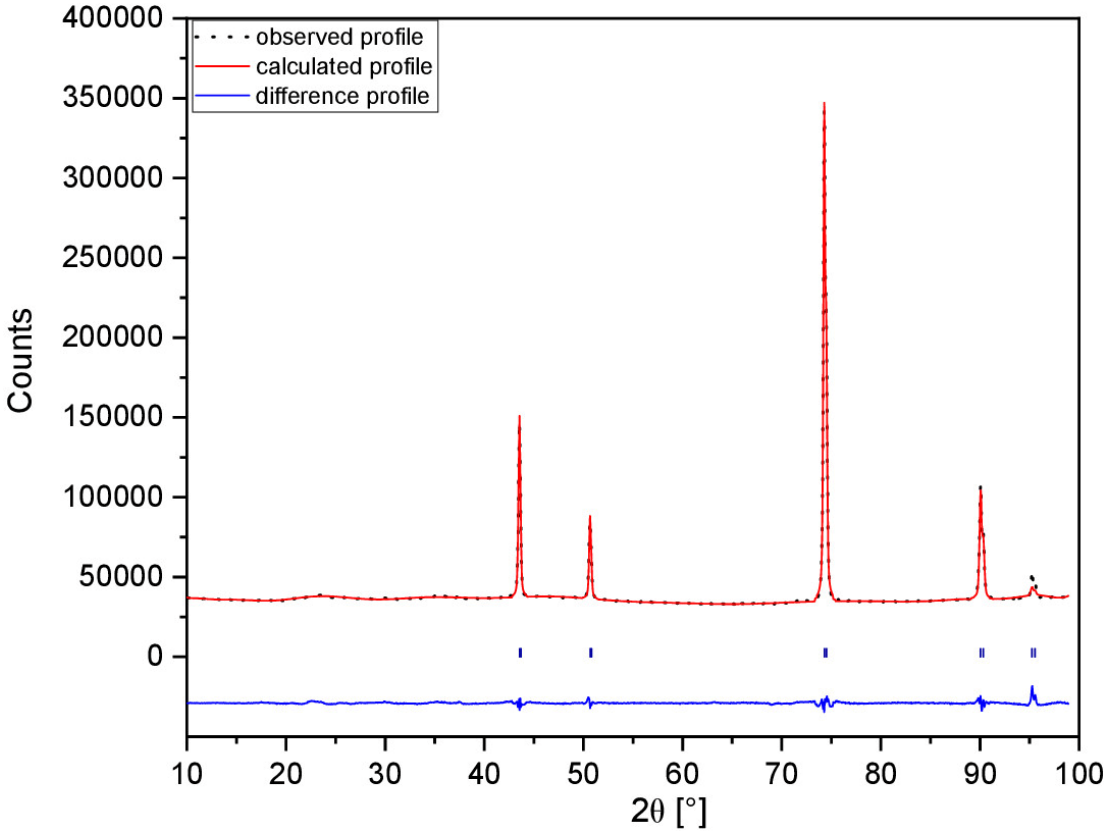

Figure S8. Fitted ex-situ XRD pattern of MNP active material discharged up to 0.8 vs. Li^+/Li in Li-electrolyte. Observed (black dots), calculated (red line) and difference (blue line) profiles are shown. Reflection positions for Cu–Ni alloy (blue bars) are indicated.

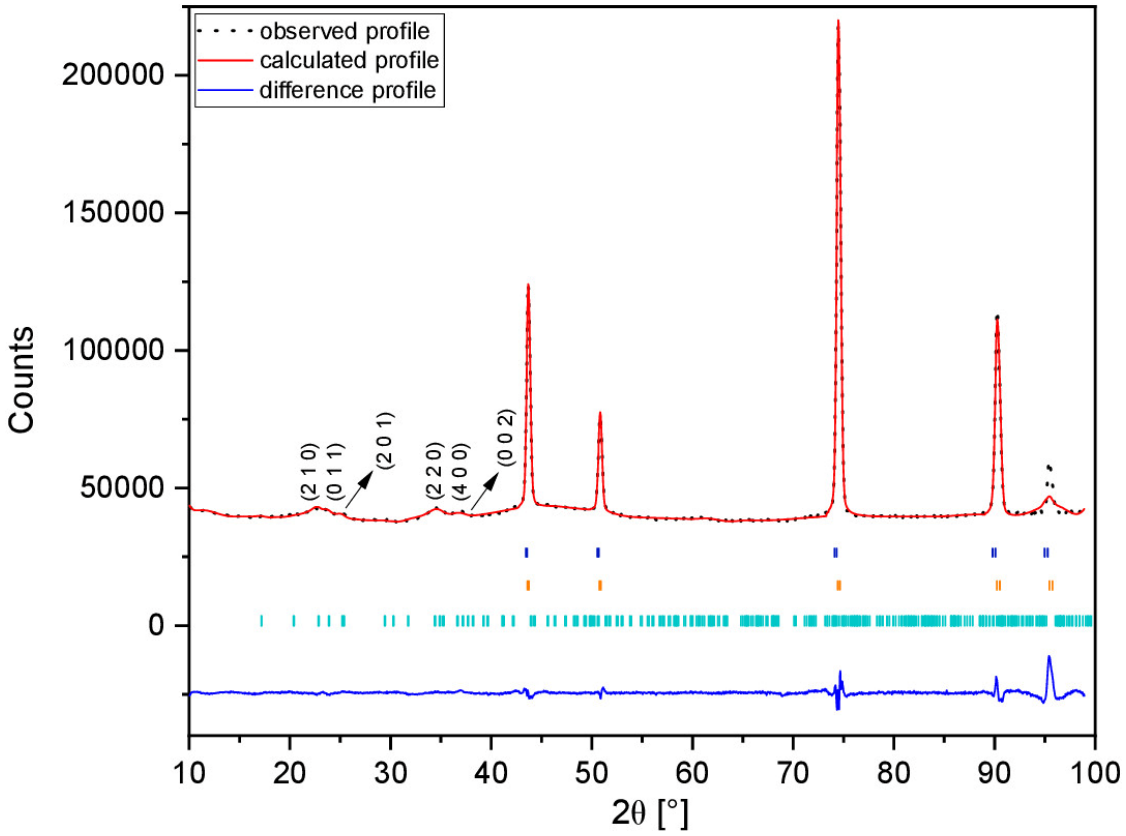

Figure S9. Fitted ex-situ XRD pattern of MNP active material discharged up to 0.01 vs. Li^+/Li in Li-electrolyte. Observed (black dots), calculated (red line) and difference (blue line) profiles are shown. Refection positions for Li_3PO_4 (cyan bars), Cu (orange bars) and Cu–Ni alloy (blue bars) are indicated. The strongest reflections for the Li_3PO_4 phase are reported in brackets.

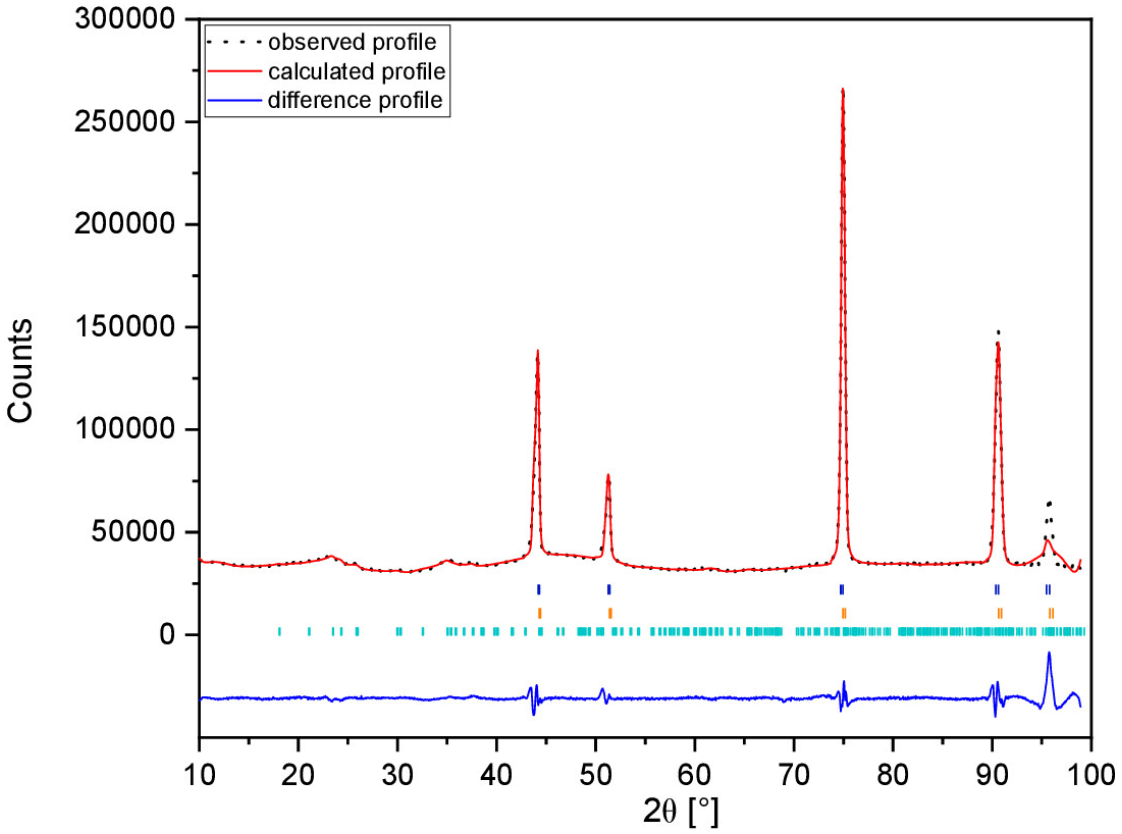

Figure S10. Fitted ex-situ XRD pattern of MNP active material charged up to 2.9 vs. Li^+/Li in Li-electrolyte. Observed (black dots), calculated (red line) and difference (blue line) profiles are shown. Reflection positions for Li_3PO_4 (cyan bars), Cu (orange bars) and Cu–Ni alloy (blue bars) are indicated.

Table S4. Crystal and refinement parameters for the MNP active material discharged up to 1.0 vs. Li^+/Li, discharged up to 0.8 vs. Li^+/Li and fully discharged at 0.01 V vs. Li^+/Li in Li-electrolyte.

	1.0 V	0.8 V	0.01 V
Nominal composition	$Mg_{1.5}Ni_{1.5}O_8P_2$	$Mg_{1.5}Ni_{1.5}O_8P_2$	$Mg_{1.5}Ni_{1.5}O_8P_2$
Primary phase	$(Mg_{0.5}Ni_{0.5})_3(PO_4)_2$	Cu	Li_3PO_4
Weight fraction primary phase	0.43(3)	1	0.14(9)
Formula weight primary phase	314.48 g mol^{-1}	63.55 g mol^{-1}	115.79 g mol^{-1}
Crystal system primary phase	Monoclinic	Cubic	Orthorhombic
Space group primary phase	$P2_1/c$	$Fm\bar{3}m$	$Pnma$
Unit cell dimensions primary phase	a = 5.878(2) Å b = 4.707(2) Å c = 10.157(3) Å β = 90.75(2)°	a = 3.62216(8) Å	a = 10.52(4) Å b = 5.97(2) Å c = 4.88(1) Å
Volume primary phase	281.0(2) $Å^3$	47.523(3) $Å^3$	306.(1) $Å^3$
Z primary phase	2	4	4
Density (calculated) primary phase	3.718 g cm^{-3}	8.882 g cm^{-3}	2.513 g cm^{-3}
Secondary phase	Cu		Cu
Weight fraction secondary phase	0.480(0)		0.84(4)
Formula weight secondary phase	63.55 g mol^{-1}		63.55 g mol^{-1}
Crystal system secondary phase	Cubic		Cubic
Space group secondary phase	$Fm\bar{3}m$		$Fm\bar{3}m$
Lattice parameter secondary phase	a = 3.61800(2) Å		a = 3.6156(4) Å
Volume secondary phase	47.36(1) $Å^3$		47.27(1) $Å^3$
Z secondary phase	4		4
Density (calculated) secondary phase	8.913 g cm^{-3}		8.930 g cm^{-3}
Tertiary phase	Cu–Ni		Cu–Ni
Weight fraction tertiary phase	0.016(3)		0.00(7)
Formula weight tertiary phase	63.55 g mol^{-1}		63.55 g mol^{-1}
Crystal system tertiary phase	Cubic		Cubic
Space group tertiary phase	$Fm\bar{3}m$		$Fm\bar{3}m$
Lattice parameter tertiary phase	a = 3.6003(2) Å		a = 3.6293(7) Å
Volume tertiary phase	46.67(2) $Å^3$		47.80(3) $Å^3$
Z tertiary phase	4		4
Density (calculated) tertiary phase	8.354 g cm^{-3}		8.830 g cm^{-3}

Table S4 continued. Crystal and refinement parameters for the MNP active material discharged up to 1.0 vs. Li^+/Li, discharged up to 0.8 vs. Li^+/Li and fully discharged at 0.01 V vs. Li^+/Li in Li-electrolyte.

	1.0 V	0.8 V	0.01 V
Fourth phase	$Mg_3(PO_4)_2$		
Weight fraction fourth phase	0.070(7)		
Formula weight fourth phase	314.48 g mol^{-1}		
Crystal system fourth phase	Monoclinic		
Space group fourth phase	$P2_1/c$		
Lattice parameter fourth phase	a = 5.869(7) Å b = 4.841(6) Å c = 10.34(1) Å β = 92.2(1)°		
Volume fourth phase	293.4(4) $Å^3$		
Z fourth phase	2		
Density (calculated) fourth phase	2.966 g cm^{-3}		
R-factors	R_{wp} = 0.0268 R_p = 0.0168 R_{ex} = 0.0054 R_F^2 = 0.1830 χ^2 = 25.74	R_{wp} = 0.0170 R_p = 0.0102 R_{ex} = 0.0051 R_F^2 = 0.0245 χ^2 = 11.16	R_{wp} = 0.0313 R_p = 0.0161 R_{ex} = 0.0060 R_F^2 = 0.1376 χ^2 = 27.56
No. of observations/restraints/parameters	2224/0/72	2224/0/36	2224/0/49
Total no. of reflections used	1225	2223	420

Table S5. Crystal and refinement parameters for the MNP active material charged up to 2.9 vs. Li^+/Li in Li-electrolyte.

Nominal composition	$Mg_{1.5}Ni_{1.5}O_8P_2$
Primary phase	Li_3PO_4
Weight fraction primary phase	0.03(2)
Formula weight primary phase	115.79 g mol^{-1}
Crystal system primary phase	Orthorhombic
Space group primary phase	*Pnma*
Unit cell dimensions primary phase	a = 10.49(3) Å b = 6.13(2) Å c = 4.93(1) Å
Volume primary phase	318.(1) $Å^3$
Z primary phase	4
Density (calculated) primary phase	2.422 g cm^{-3}
Secondary phase	Cu
Weight fraction secondary phase	0.94(1)
Formula weight secondary phase	63.55 g mol^{-1}
Crystal system secondary phase	Cubic
Space group secondary phase	*Fm*−3*m*
Lattice parameter secondary phase	a = 3.6303(5) Å
Volume secondary phase	47.85(2) $Å^3$
Z secondary phase	4
Density (calculated) secondary phase	8.822 g cm^{-3}
Tertiary phase	Cu–Ni
Weight fraction tertiary phase	0.02 (7)
Formula weight tertiary phase	63.55 g mol^{-1}
Crystal system tertiary phase	Cubic
Space group tertiary phase	*Fm*−3*m*
Lattice parameter tertiary phase	a = 3.6399(5) Å
Volume tertiary phase	48.22(2) $Å^3$
Z tertiary phase	4
Density (calculated) tertiary phase	8.753 g cm^{-3}
R-factors	R_{wp} = 0.0399 R_p = 0.0203 R_{ex} = 0.0051 R_F^2 = 0.2010 χ^2 = 61.49
No. of observations/restraints/parameters	2224/0/48
Total no. of reflections used	406

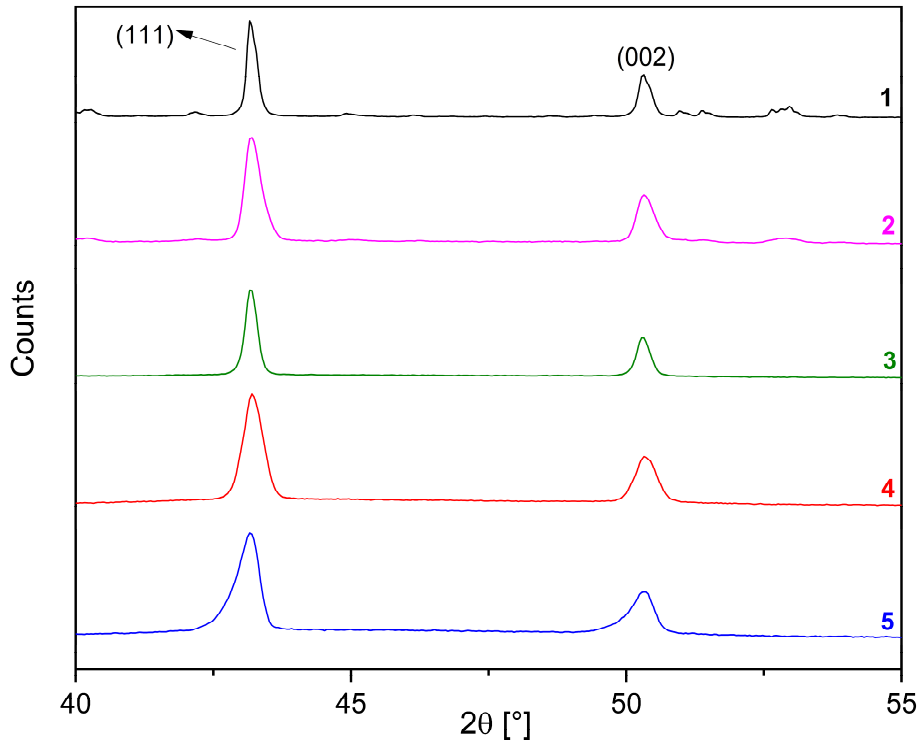

Figure S11. *Ex-situ* XRD patterns comparing the (1 1 1) and (0 0 2) reflections of the Cu current collector for the MNP electrode at the open circuit voltage (3.0 V vs. Li^+/Li, black curve, 1), discharged up to 1.0 vs. Li^+/Li (pink curve, 2), discharged up to 0.8 vs. Li^+/Li (green curve, 3), fully discharged (0.01 V vs. Li^+/Li, 4) and fully charged (2.9 V vs. Li^+/Li, 5) states using Li-electrolyte.

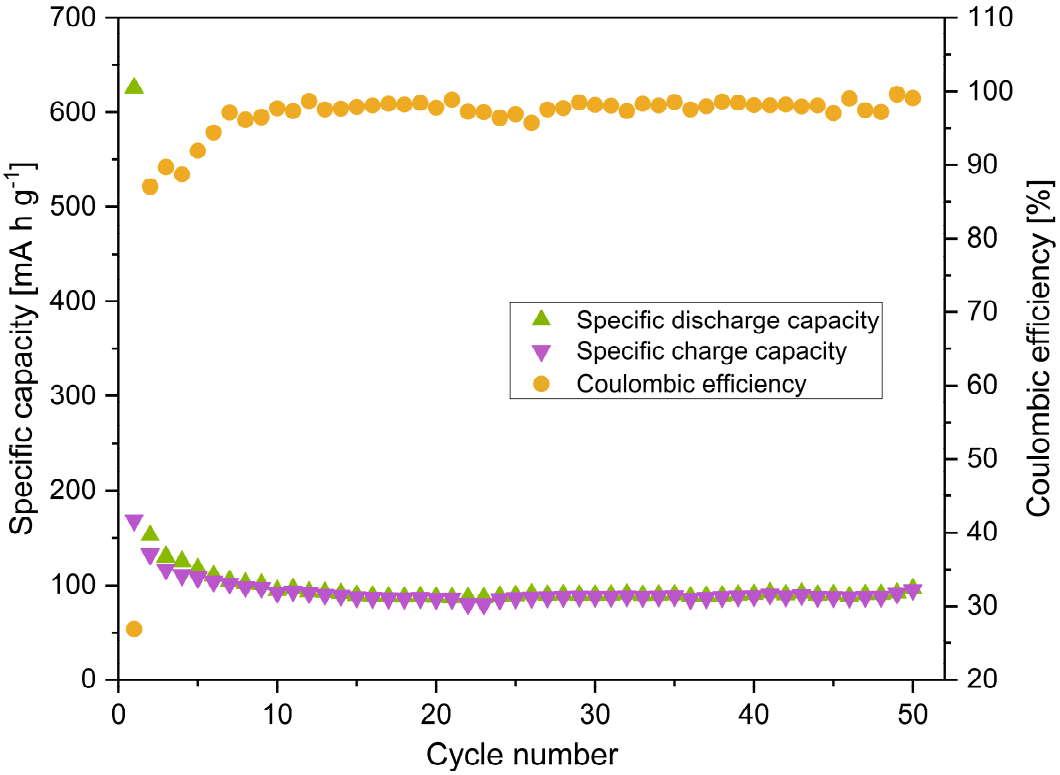

Figure S12. Specific discharge (green triangles) and charge (pink triangles) capacities over 50 cycles for discharge curves for MNP active material cycled in a Li-half cell with Li-electrolyte.

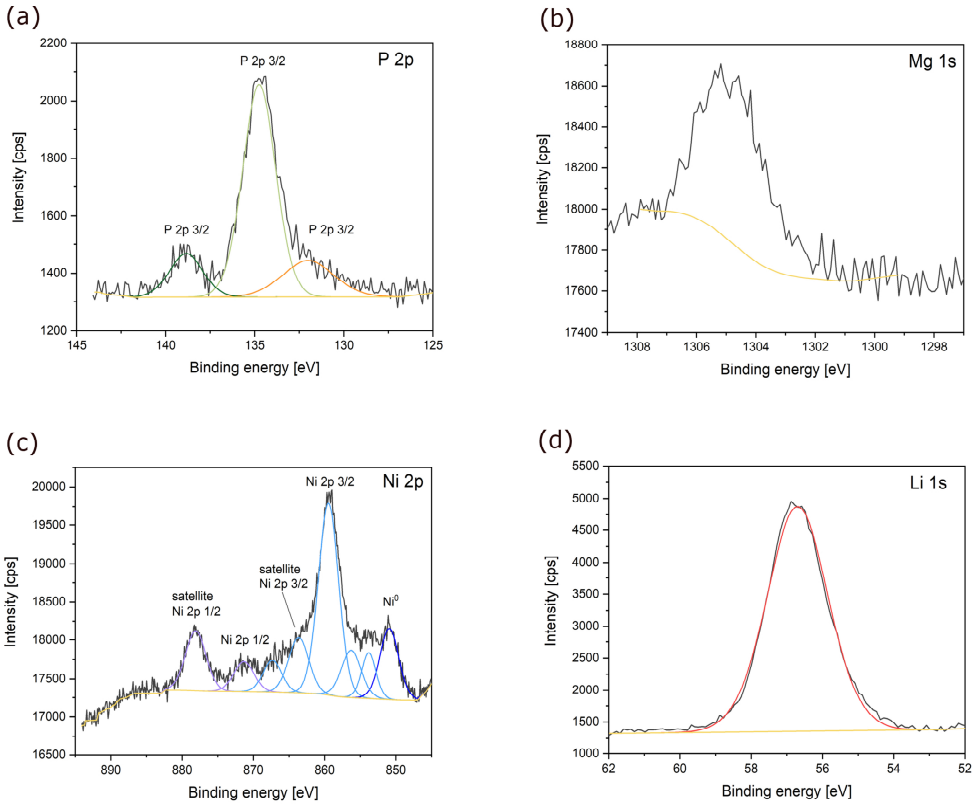

Figure S13. (a) P 2*p*, (b) Mg 1*s*, (c) Ni 2*p* and (d) Li 1*s* X-ray photoelectron spectra for MNP active material discharged up to 0.01 V vs. Li^+/Li in Li-electrolyte.

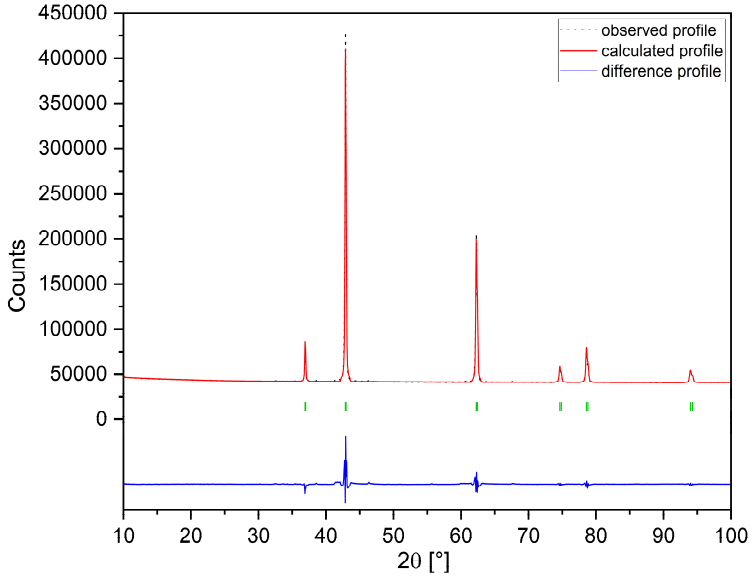

Figure S14. Fitted XRD pattern of MgO precursor. Observed (black dots), calculated (red line) and difference (blue line) profiles are shown. Reflection positions for MgO (green bars) are indicated.