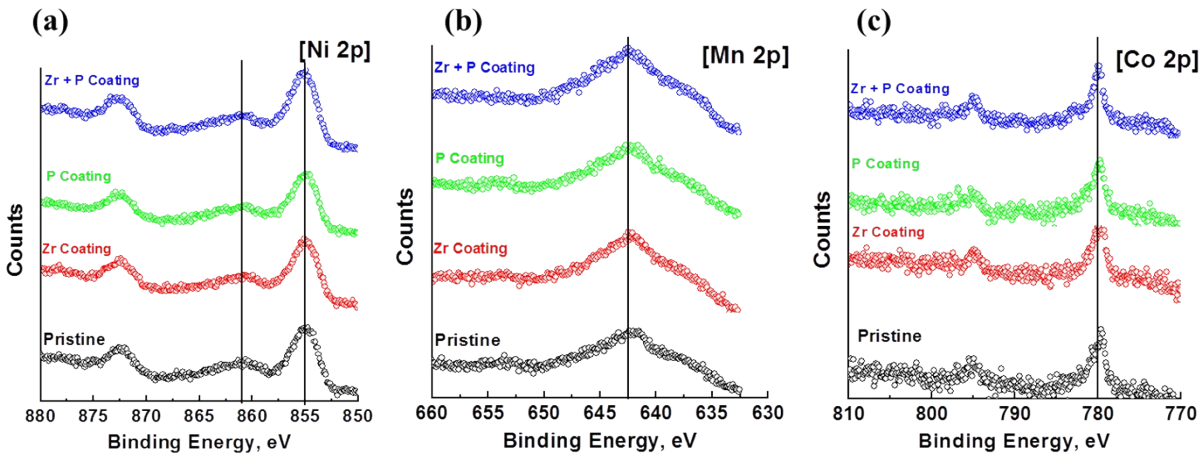
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

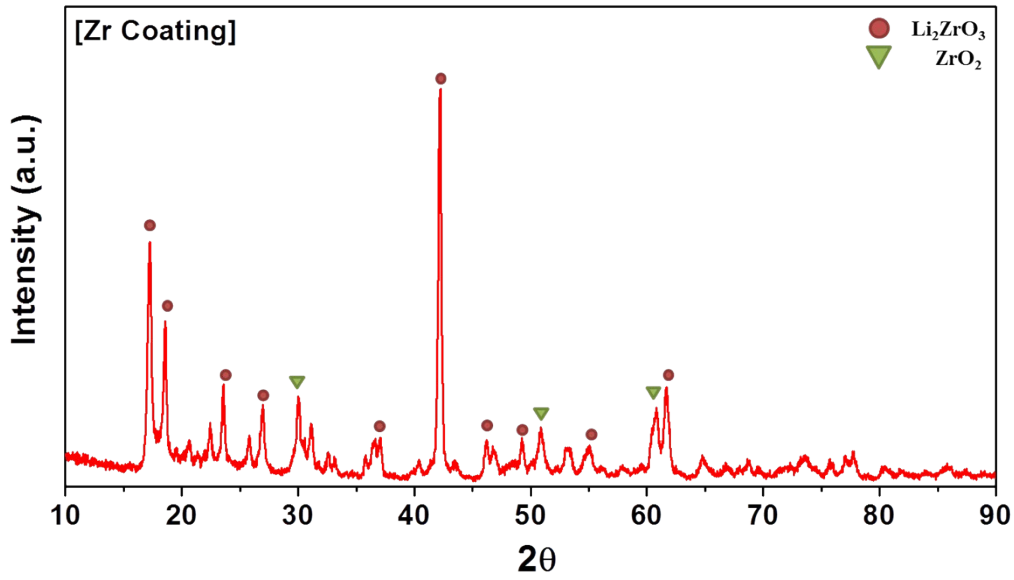
SI 1. Lattice parameters calculated for the coated NCM samples

Samples	Space Group	**a** (Å) (±0.0003)	**c** (Å) (±0.0003)
Pristine	*R-3m*	2.86736	14.1880
Zr coated NCM		2.86768	14.1933
P coated NCM		2.86801	14.1948
Zr + P coated NCM		2.86883	14.1959

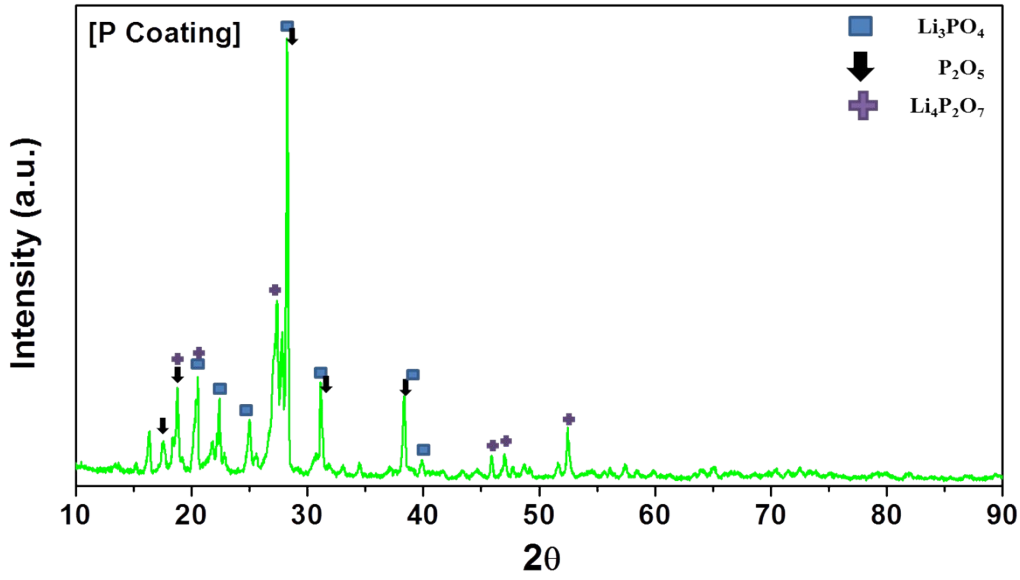


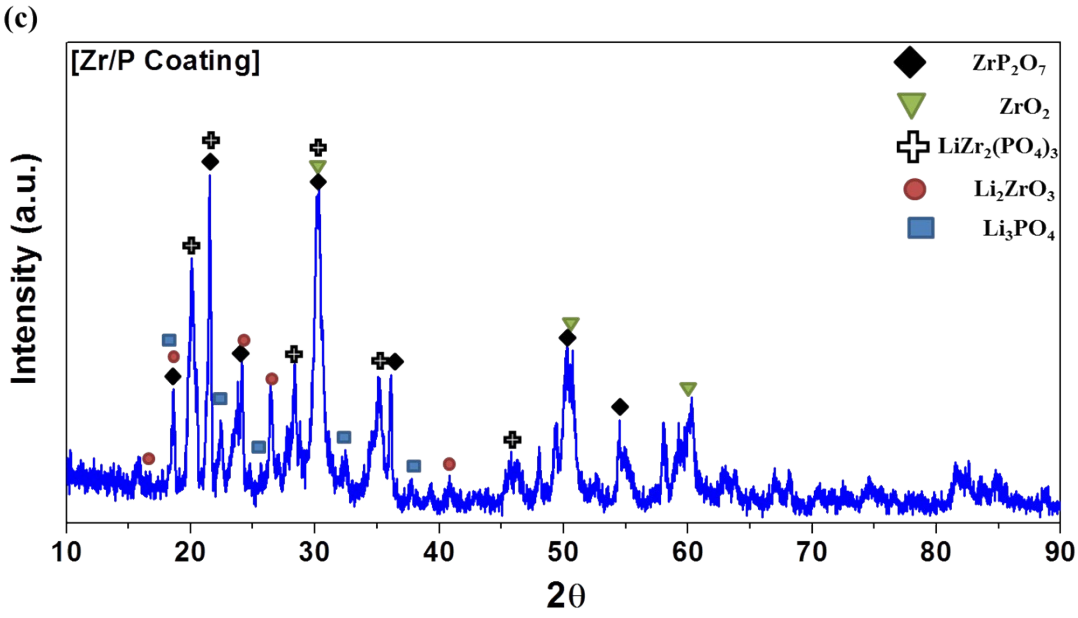
SI 2. XPS spectra of the pristine and surface modified NCM samples at the (a) Ni 2*p,* (b) Mn 2*p,* and (c) Co 2*p* levels

(a)


[Zr Coating]
Li2ZrO3
ZrO2
Intensity (a.u.)
10
20
30
40
50
60
70
80
90
2θ

(b)


[P Coating]
Li3PO4
P2O5
Li4P2O7
Intensity (a.u.)
10
20
30
40
50
60
70
80
90
2θ



SI 3. XRD pattern of the coating material after heat treatment (a) Zr-only, (b) P-only, and (c) Zr/P coating

SI 4. **Phase data**

Materials	Formation Energy (eV/atom)	Space group
Zr	0.0000	$P6_3/mmc$
O	0.0000	n/a
P	0.0000	$Pm\bar{3}m$
N	0.0000	n/a
H	0.0000	n/a
Li	0.0000	$Im\bar{3}m$
H_2O	-1.1718	n/a
Li_2O	-2.0044	$Fm\bar{3}m$
LiH	-0.4531	$Fm\bar{3}m$
LiOH	-1.7115	P4/nmm
CO_2	-1.4626	n/a
Li_2CO_3	-2.1171	C2/c
Li_2O_2	-1.5839	$P6_3/mmc$
Li_3P	-0.8273	$P6_3/mmc$
Li_2ZrO_3	-3.0087	C2/c
Li_3PO_4	-2.7098	$P2_1nm$
$LiOH{\cdot}H_2O$	-1.4470	C2/m
LiP	-0.6871	$P2_1/c$
$LiPO_3$	-2.5917	$P2_1/c$
$LiZr_2(PO_4)_3$	-3.0952	$P2_1/c$
P_2O_5	-2.3448	F2dd
H_3PO_4	-1.7869	$P2_1/c$
$Zr_2P_2O_9$	-3.2231	C2/m
Zr_3O	-1.5591	$P6_322$
Zr_3P	-0.9350	$P4_2/n$
Zr_7P_4	-1.3098	C2/m
ZrH_2	-0.6465	I4/mmm
ZrO_2	-3.7676	$P2_1/c$
ZrP	-1.5499	$P6_3/mmc$
ZrC	-1.7466	$Fm\bar{3}m$
ZrP_2	-1.0841	Pmnb
ZrP_2O_7	-3.0298	Pa3
ZrN	-1.8985	$Fm\bar{3}m$
LiP_7	-0.1792	$I4_1/acd$
NO_2	-0.2407	n/a
$Li_4P_2O_7$	-2.6563	$P\bar{1}$
P_2O_3	-1.7887	$P2_1/m$
N_2O_5	-0.1913	$P6_3/mmc$
$Li_6Zr_2O_7$	-2.8295	C2/c
H_3NO_4	-0.8263	$P2_1cn$
$PH_9N_2O_4$	-1.1585	$P2_1/c$
$LiNO_3$	-1.1164	$R\bar{3}c$

SI 5. Reactions shown in the ZrO_2-LiOH-P_2O_5 phase diagram

S.5.1. ZrO_2-P_2O_5

Reactant						Product			dH (eV)
1	ZrO_2	+	1	P_2O_5	→	1	ZrP_2O_7	=	-3.046
2	ZrO_2	+	1	P_2O_5	→		$Zr_2P_2O_9$	=	-3.345

S.5.2. ZrO_2-LiOH

Reactant						Product				dH (eV)
1	ZrO_2	+	3	LiOH	→	1	Li_2ZrO_3	+	1 $LiOH·H_2O$	= -0.027

S.5.3. P_2O_5-LiOH

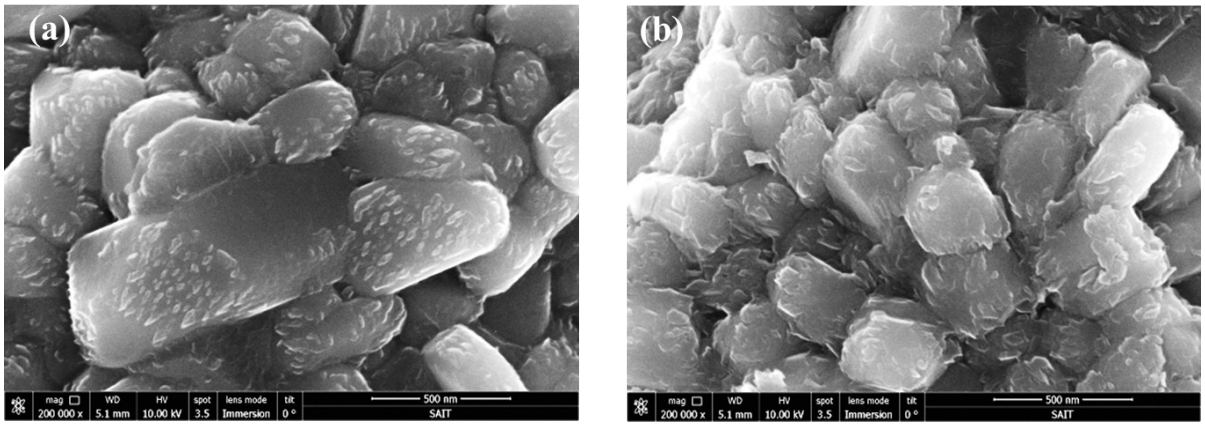
Reactant						Product					dH (eV)
1	P_2O_5	+	6	LiOH	→	2	Li_3PO_4	+	3 H_2O	=	-6.681
1	P_2O_5	+	3	LiOH	→	1	Li_3PO_4	+	1 H_3PO4	=	-4.156
2	P_2O_5	+	3	LiOH	→	3	$LiPO_3$	+	1 H_3PO4	=	-5.636
1	P_2O_5	+	9	LiOH	→	2	Li_3PO_4	+	3 $LiOH·H_2O$	=	-6.778

S.5.4. ZrO_2-LiOH-P_2O_5

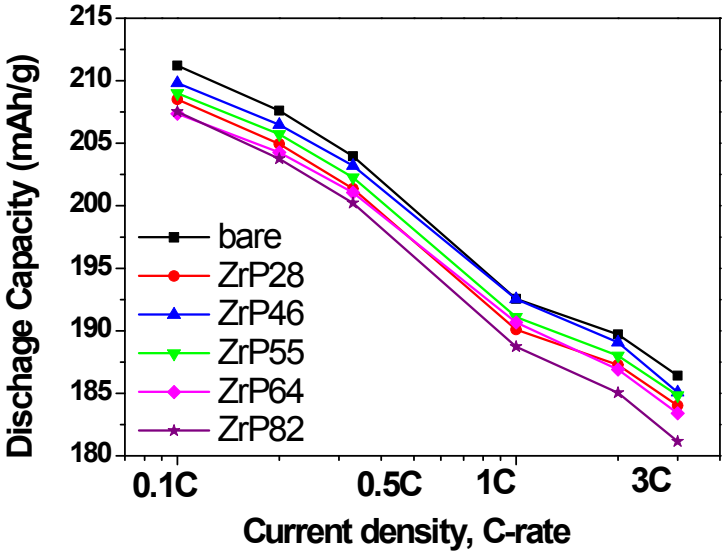
Reactant								Product							dH(eV)
4	ZrO_2	+	2	LiOH	+	3	P_2O_5	→	2	$LiZr_2(PO4)_3$	+	1	H_2O	=	-11.615

SI 6. ICP results

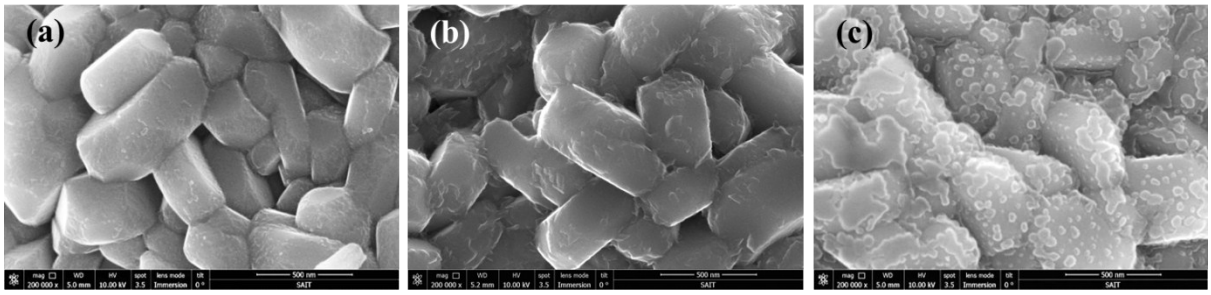
Samples	Mole ratio, %			
	Li	Ni	Co	Mn
Pristine	1.06	0.050	0.148	0.802
Zr coated NCM	1.06	0.050	0.148	0.802
P coated NCM	1.05	0.050	0.148	0.802
Zr + P coated NCM	1.08	0.050	0.148	0.802



SI 7. SEM images of NCM samples coated with (a) $LiCoPO_4$ and (b) $LiAlPO_4$



SI 8. Relative rate capabilities of the pristine sample and Zr/P coated NCM samples with various Zr/P ratios.



SI 9. . SEM images of the Zr/P coated NCM sample with coating weights of (a) 0.5 wt. %, (b) 1 wt. %, and (c) 2 wt. %.