Supplementary materials

Table S1 XRF analysis results of LIBs black powder %

O	F	P	Mn	Fe	Co	Ni	Cu	Al
25.758	7.058	9.213	18.076	15.018	8.343	13.653	0.959	0.557

Na	Si	S	Cl	Ca	Ti	Tb	Zn	Zr	Nb
0.235	0.099	0.317	0.275	0.1	0.197	0.081	0.011	0.029	0.021

Table S2 Equations of possible chemical reactions in solution and their Gibbs free energy versus temperature change

Reaction formula	ΔG/(kJ·mol^{-1})	No.
$2C_6H_8O_7+3Li_2CO_3=2Li_3(C_6H_5O_7)+3H_2O+3CO_2\uparrow$	$\Delta G=-49.502-0.225T$	1-1
$C_6H_8O_7+9MnO_2+18H^+=9Mn^{2+}+4H_2O+6CO_2\uparrow$	$\Delta G=-1123.111-1.447T$	1-2
$2C_6H_8O_7+3MnO=Mn_3(C_6H_5O_7)_2+3H_2O$	$\Delta G=-85.917+0.029T$	1-3
$C_6H_8O_7+9Co_2O_3+36H^+=18Co^{2+}+4H_2O+6CO_2\uparrow$	$\Delta G=-1539.898-2.663T$	1-4
$2C_6H_8O_7+3CoO=Co_3(C_6H_5O_7)_2+3H_2O$	$\Delta G=-51.469+0.255T$	1-5
$C_6H_8O_7+9Ni_2O_3+36H^+=18Ni^{2+}+4H_2O+6CO_2\uparrow$	$\Delta G=-2510.595-2.460T$	1-6
$2C_6H_8O_7+3NiO=Ni_3(C_6H_5O_7)_2+3H_2O$	$\Delta G=-40.883+0.267T$	1-7
$2C_6H_8O_7+3CuO=Cu_3(C_6H_5O_7)_2+3H_2O$	$\Delta G=3.541+0.220T$	1-8
$2C_6H_8O_7+3Cu=Cu_3(C_6H_5O_7)_2+3H_2\uparrow$	$\Delta G=167.444+0.118T$	1-9
$2C_6H_8O_7+Al_2O_3=2Al(C_6H_5O_7)+3H_2O$	$\Delta G=14.530+0.730T$	1-10
$2C_6H_8O_7+2Al=2Al(C_6H_5O_7)+3H_2\uparrow$	$\Delta G=-426.020+0.281T$	1-11

Table S3 Levels and codes of factors for Box-Behnken design

Factor	Symbol	Unit	Level	
			Low	High
Citrate concentration	*A*	mol/L	0.4	0.5
Temperature	*B*	℃	80	90
Liquid-solid ratio	*C*	mL/g	12	16

Table S4 The results of the designed experiments

No.	*A*	*B*	*D*	Li leaching efficiency/%	Co leaching efficiency/%	Ni leaching efficiency/%
1	0.5	80	14	91.33	90.78	88.36
2	0.45	85	14	97.59	97.11	97.01
3	0.50	85	16	96.02	95.62	95.78
4	0.45	85	14	96.89	97.10	95.89
5	0.45	80	16	92.15	93.94	89.95
6	0.45	85	14	97.42	96.89	96.32
7	0.45	85	14	97.62	97.42	96.82
8	0.45	80	12	90.54	90.35	87.42
9	0.50	90	14	95.62	96.78	95.94
10	0.45	90	12	92.43	95.75	92.46
11	0.40	85	12	89.74	88.27	86.03
12	0.40	85	16	92.21	90.06	91.04
13	0.40	90	14	91.52	90.01	88.32
14	0.50	85	12	91.67	92.43	93.54
15	0.45	85	14	97.21	97.39	96.68
16	0.4	80	14	89.82	87.65	83.52
17	0.45	90	16	97.32	97.48	96.79

Table S5 Analysis of variance and significance for Li leaching regression model

Source	Sum of squares	df	Mean square	*F*-value	*P*-value
Model	148.89	9	16.54	220.77	< 0.0001
A- citrate concentration	16.1	1	16.1	214.89	< 0.0001
B- temperature	21.29	1	21.29	284.08	< 0.0001
C- liquid-solid ratio	22.18	1	22.18	295.96	< 0.0001
AB	1.68	1	1.68	22.38	0.0021
AC	0.8836	1	0.8836	11.79	0.0109
BC	2.69	1	2.69	35.89	0.0005
A^2	37.56	1	37.56	501.24	< 0.0001
B^2	22.02	1	22.02	293.83	< 0.0001
C^2	16	1	16	213.49	< 0.0001
Residual	0.5245	7	0.0749		
Lack of fit	0.158	3	0.0527	0.5749	0.6613
Pure error	0.3665	4	0.0916		
Correct total	149.42	16			

Table S6 Analysis of variance and significance for Ni leaching regression model

Source	Sum of squares	df	Mean square	*F*-value	*P*-value
Model	315.32	9	35.04	290.07	< 0.0001
A-citrate concentration	76.32	1	76.32	631.89	< 0.0001
B-temperature	73.57	1	73.57	609.09	< 0.0001
C-liquid-solid ratio	24.89	1	24.89	206.04	< 0.0001
AB	1.93	1	1.93	16	0.0052
AC	1.92	1	1.92	15.88	0.0053
BC	0.81	1	0.81	6.71	0.036
A^2	60.27	1	60.27	498.95	< 0.0001
B^2	58.45	1	58.45	483.89	< 0.0001
C^2	5.7	1	5.7	47.17	0.0002
Residual	0.8455	7	0.1208		
Lack of fit	0.0558	3	0.0186	0.0942	0.9593
Pure error	0.7897	4	0.1974		
Correct total	316.17	16			

Table S7 Analysis of variance and significance for Co leaching regression model

Source	Sum of squares	df	Mean square	*F*-value	*P*-value
Model	206.33	9	22.93	622.91	< 0.0001
A-citrate concentration	48.12	1	48.12	1307.4	< 0.0001
B-temperature	37.41	1	37.41	1016.49	< 0.0001
C-liquid-solid ratio	13.26	1	13.26	360.32	< 0.0001
AB	3.31	1	3.31	90	< 0.0001
AC	0.49	1	0.49	13.31	0.0082
BC	0.8649	1	0.8649	23.5	0.0019
A^2	78.98	1	78.98	2145.92	< 0.0001
B^2	10.06	1	10.06	273.44	< 0.0001
C^2	6.64	1	6.64	180.48	< 0.0001
Residual	0.2576	7	0.0368		
Lack of fit	0.0606	3	0.0202	0.4096	0.7533
Pure error	0.1971	4	0.0493		
Correct total	206.59	16			

The full-component pyrolysis process of $LiFePO_4$:

$LiFePO_4$ has a typical olivine structure, which endows it with good chemical stability and thermal stability. In order to systematically study the structural evolution law of $LiFePO_4$ during the pyrolysis process, this study carried out a full-component pyrolysis experiment on spent $LiFePO_4$ batteries. The specific process is as follows: Firstly, the spent $LiFePO_4$ batteries were immersed in brine for discharging for 24 h to fully release the remaining power. Subsequently, the batteries were manually disassembled, and components such as the positive electrode, negative electrode, and separator were collected. Then, a shearing crusher was used to crush each component to make them evenly mixed. Finally, 30 g of the crushed sample was taken and pyrolyzed at a high temperature of 550 °C for 2 h, and the pyrolysis products were obtained for XRD analysis.

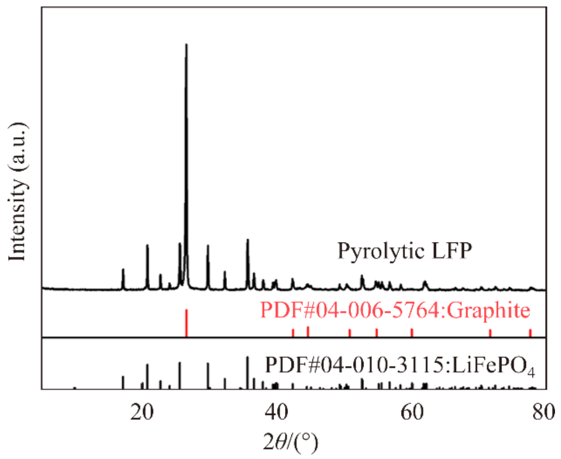

Figure S1 The XRD pattern of the full-component pyrolysis of $LiFePO_4$

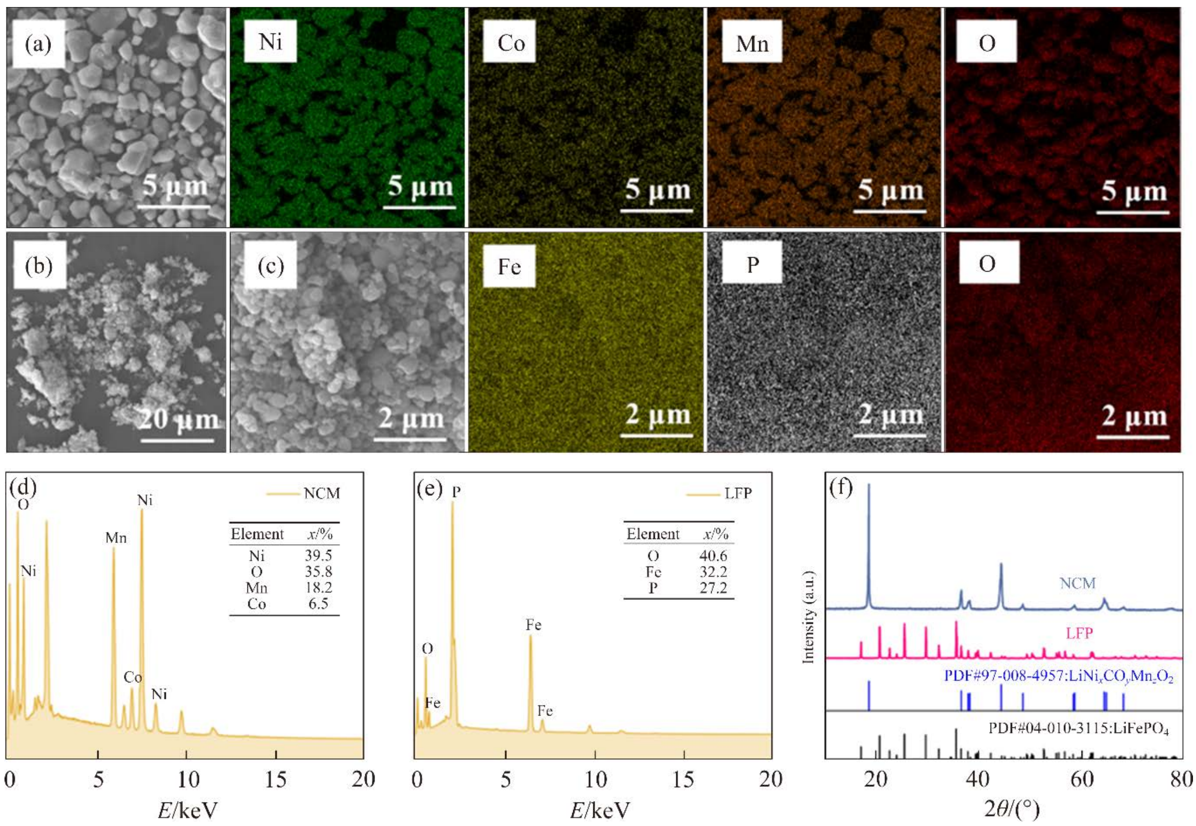

Figure S2 Analysis of laboratory-prepared NCM and LFP powder samples: (a, d) SEM-EDS analysis for NCM; (b, c, e) SEM-EDS analysis for LFP; (f) XRD analysis

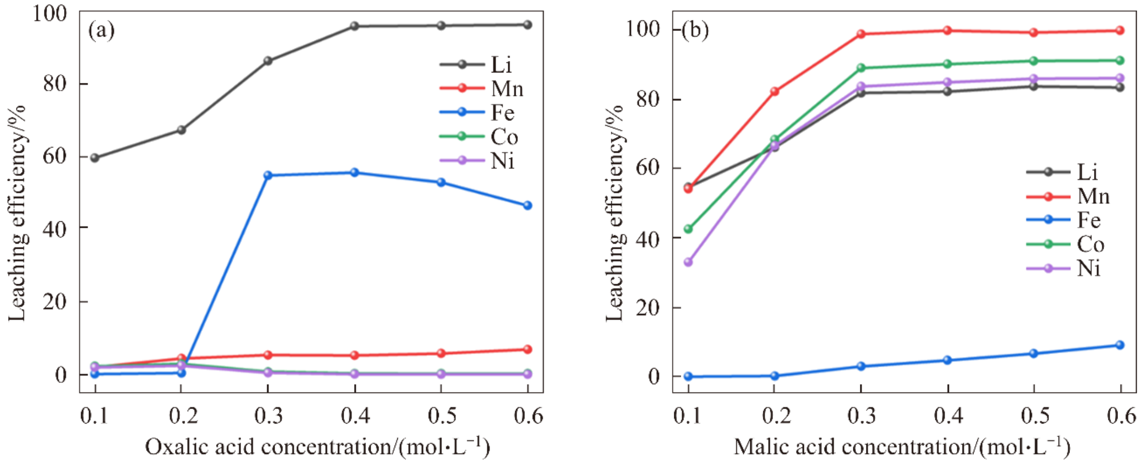

Figure S3 Effect of acid concentration on leaching efficiency: (a) Oxalic acid; (b) Malic acid

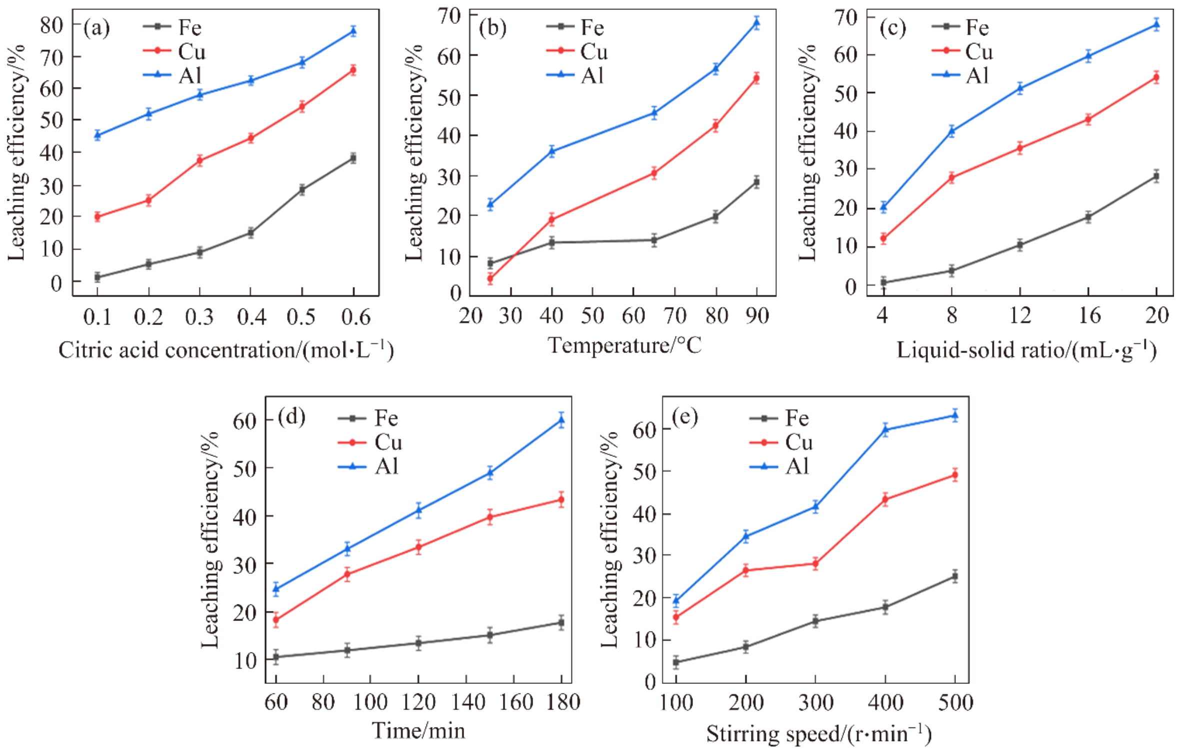

Figure S4 The effects of leaching conditions on the leaching of impurity metals: (a) Citric acid concentration; (b) Temperature; (c) Liquid-solid ratio; (d) Reaction time; (e) Stirring speed

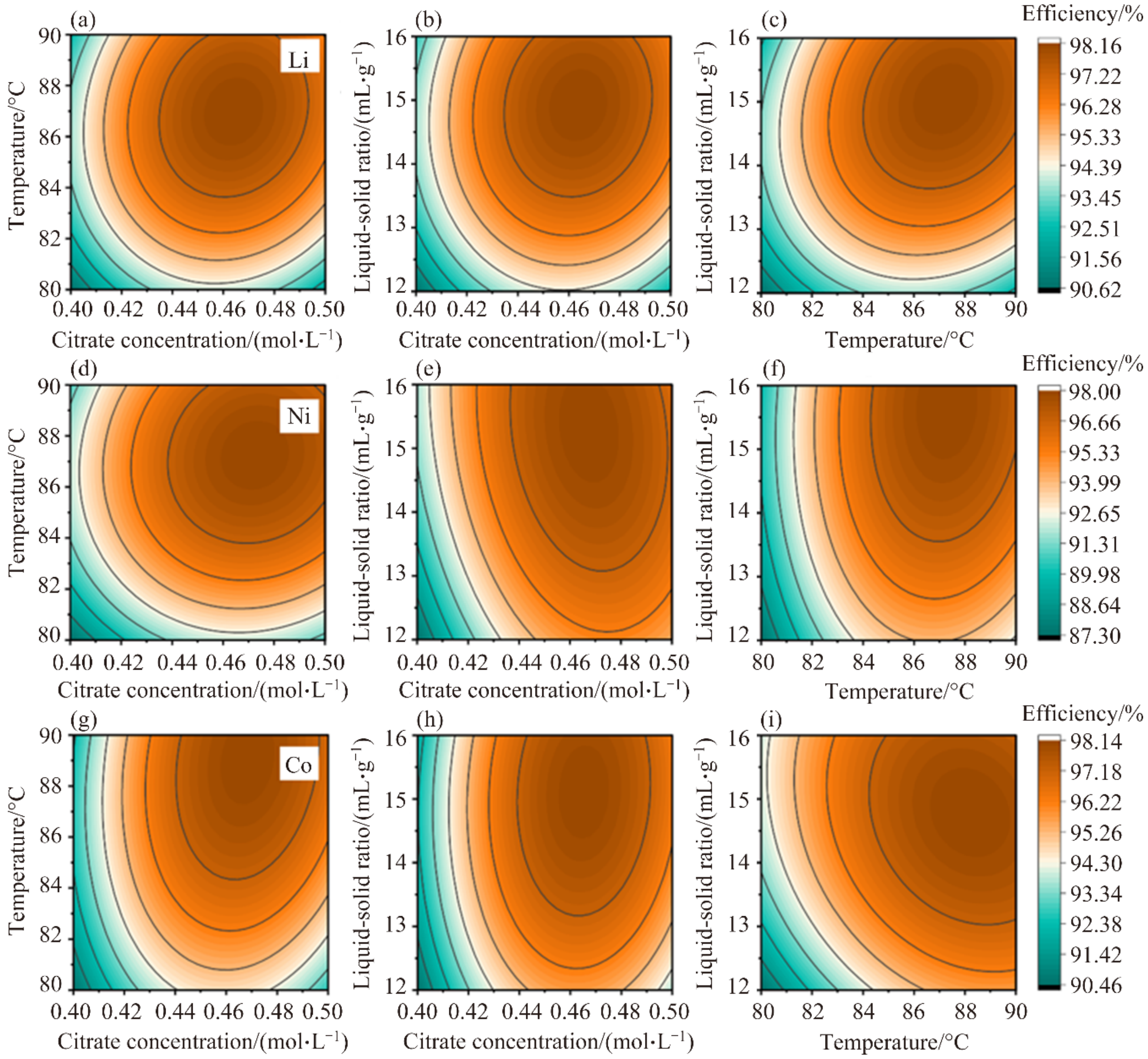

Figure S5 Contour plot of Li, Ni and Co leaching: (a, d, g) Effect of citric acid concentration and temperature on the leaching of Li, Ni and Co, respectively; (b, e, h) Effect of citric acid concentration and liquid-solid ratio on the leaching of Li, Ni and Co, respectively; (c, f, i) Effect of temperature and liquid-solid ratio on the leaching of Li, Ni and Co, respectively

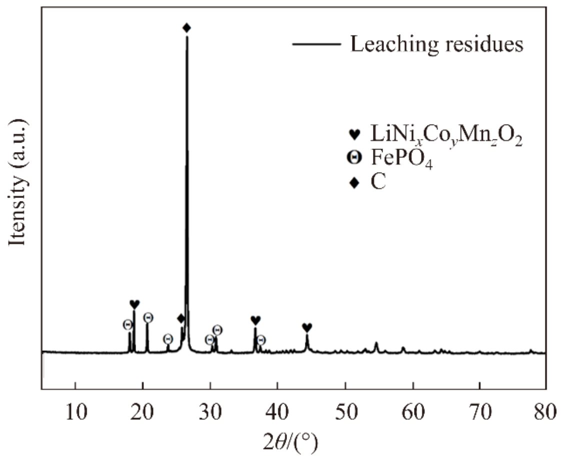

Figure S6 XRD Pattern of leaching residues from the reaction of $LiNi_xCo_yMn_zO_2$ with full-component pyrolytic $LiFePO_4$ in citric acid system

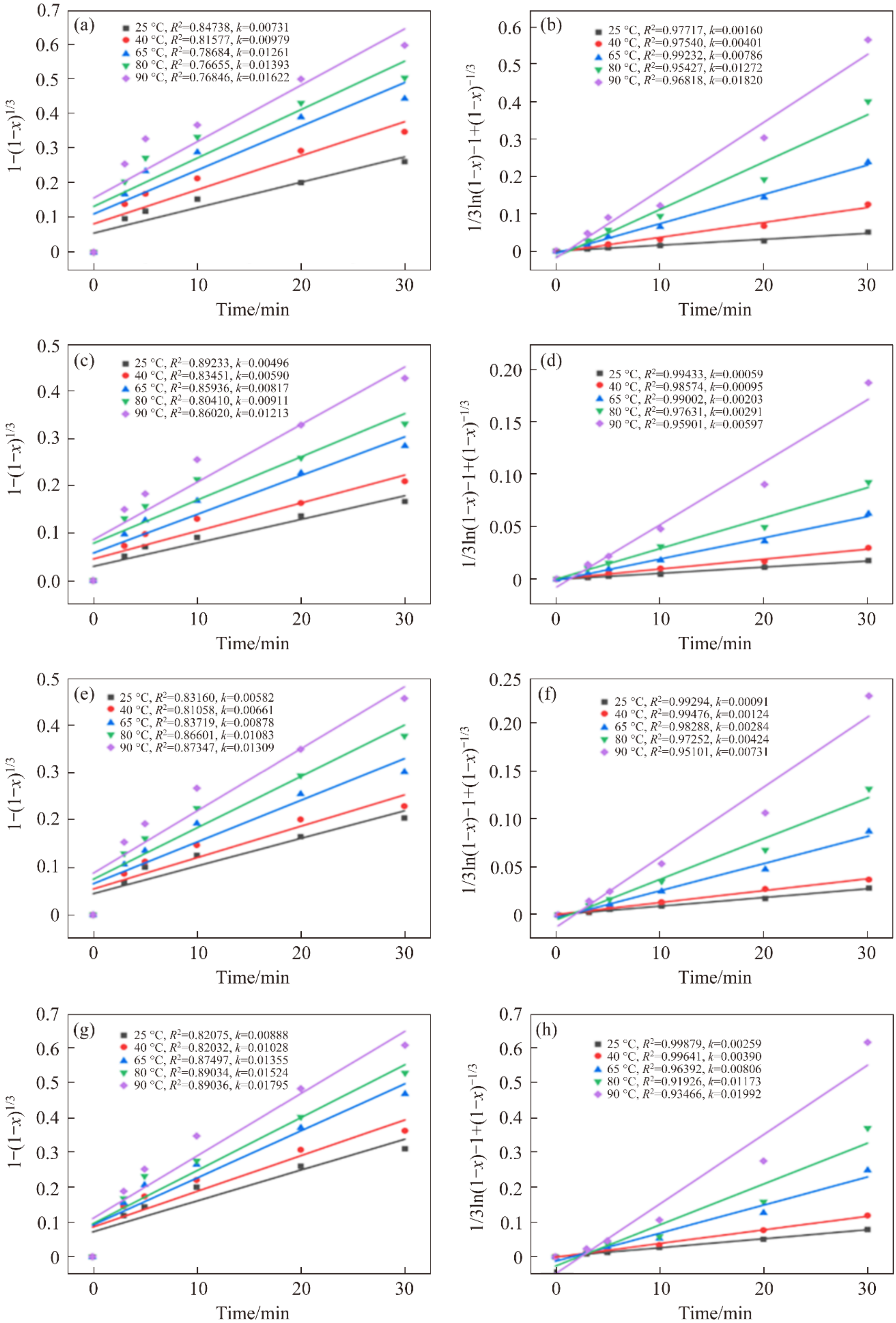

Figure S7 Linear relationship of $(1–(1–x)^{1/3})$ and reaction time t for (a) Li, (c) Ni, (e) Co and (g) Mn, and linear relationship of $(1/3\ln(1–x)–1+(1–x)^{–1/3})$ and reaction time t for (b) Li, (d) Ni, (f) Co and (h) Mn