Separation of nickel from cobalt and manganese in lithium ion batteries using deep eutectic solvents

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Supplementary Information:

a) **b)**

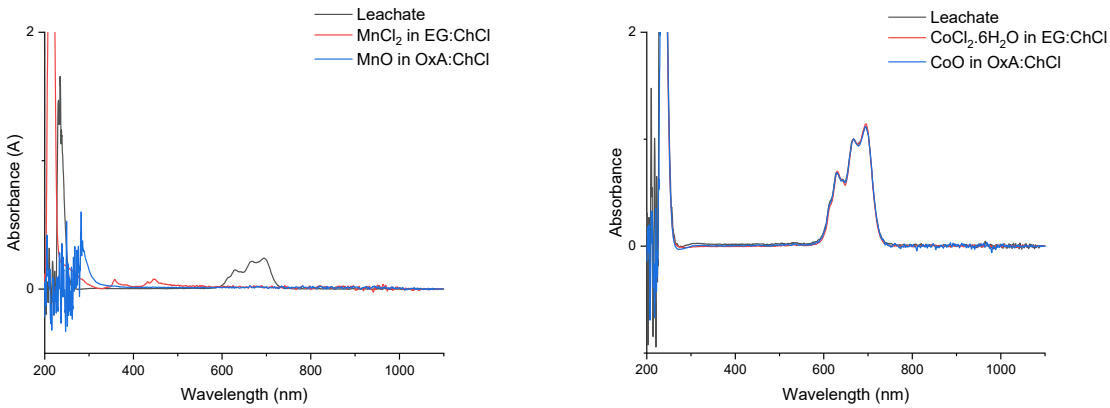
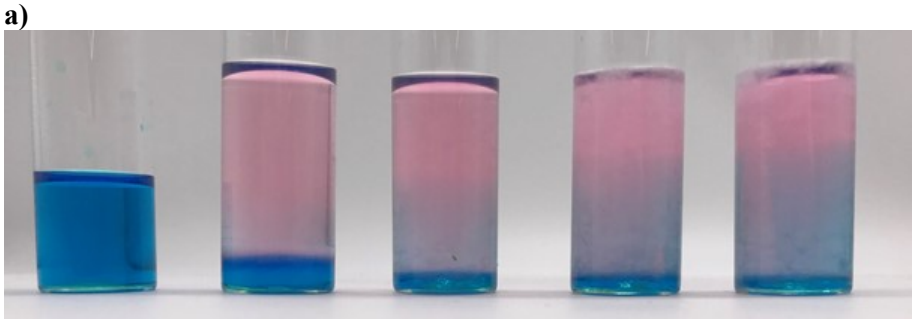


Figure S1: UV-Vis spectra of MnO_2 and Co_3O_4 in OxA:ChCl (l = 0.1 mm) overlaid with a) MnO in OxA: ChCl (Mn^{2+} = 0.108 mol/dm^3, l = 0.5 mm) and $MnCl_2$ in EG: ChCl (Mn^{2+} = 0.108 mol/dm^3, l = 10 mm) b) CoO in OxA: ChCl and $CoCl_2$ in EG: ChCl normalised to 666.8 nm.

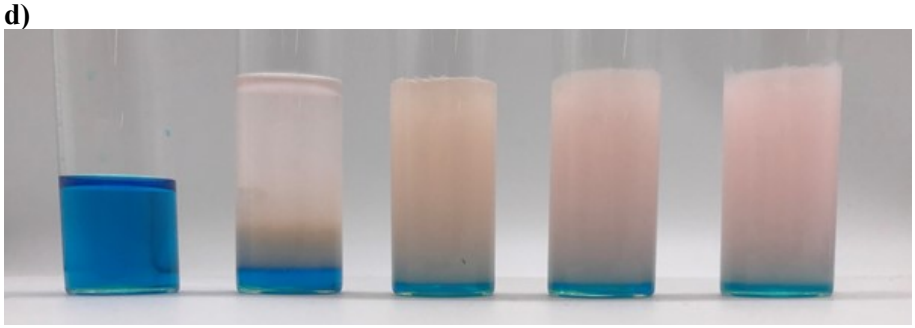
a)



b)

c)

d)



e)

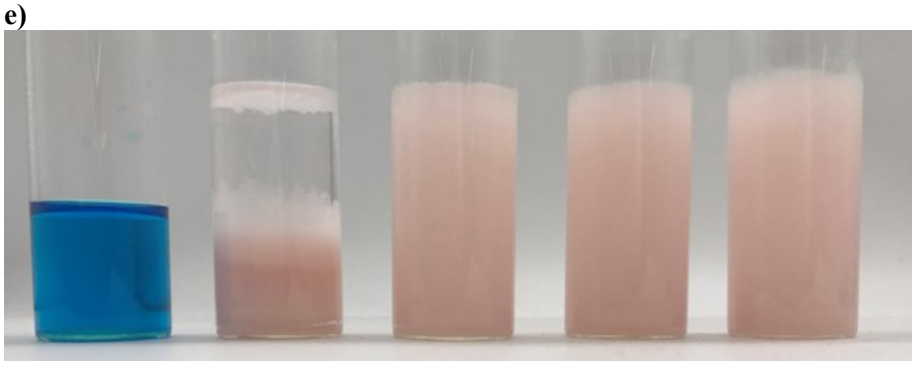


Figure S2: From left to right: PLS, and PLS after the addition of water, 0.5 mol/dm^3, 1 mol/dm^3 or 1.8 mol/dm^3 oxalic acid, after a) 0 min, b) 1 min, c) 5 min, d) 20 min and e) 1 day.

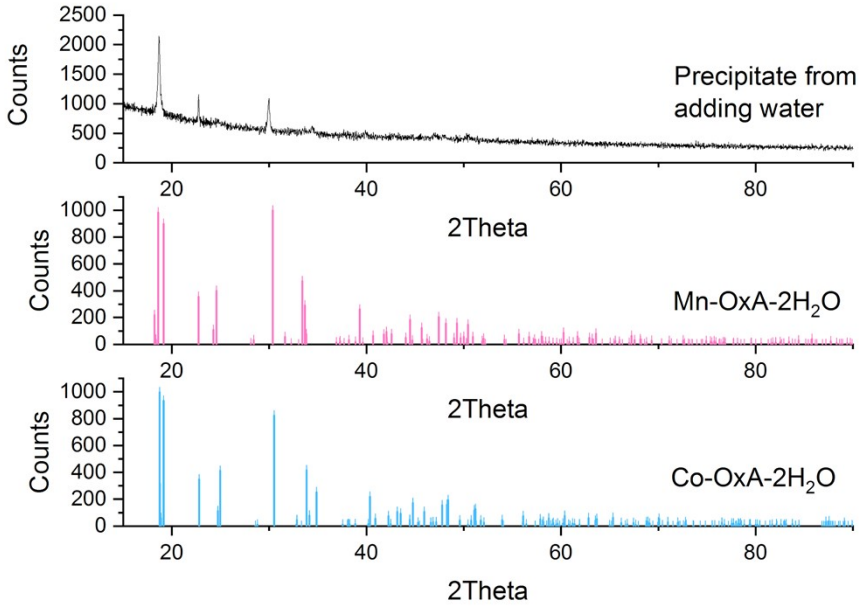


Figure S3: XRD pattern of the precipitate recovered using water as the anti-solvent, and literature data for Mn and Co oxalate dihydrate.

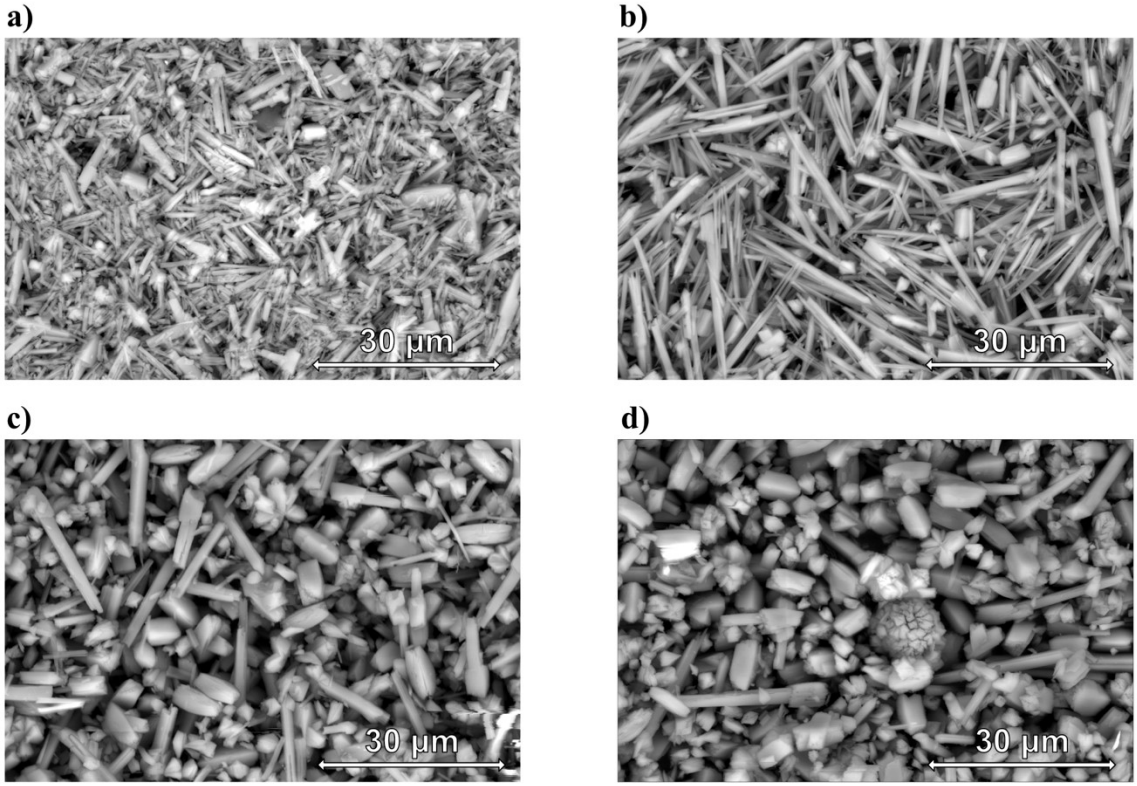


Figure S4: Backscattered SEM images at 20 kV of precipitate after the addition of a) water, b) 0.5 mol/dm^3 OxA, c) 1 mol/dm^3 OxA and d) 1.8 mol/dm^3 OxA.

a) **b)**

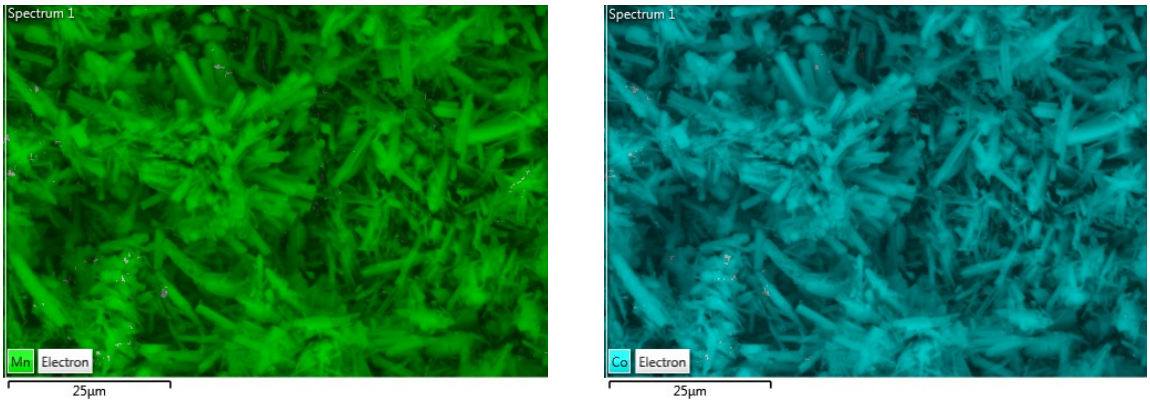


Figure S5: EDX overlaid map images from precipitate after the addition of water.

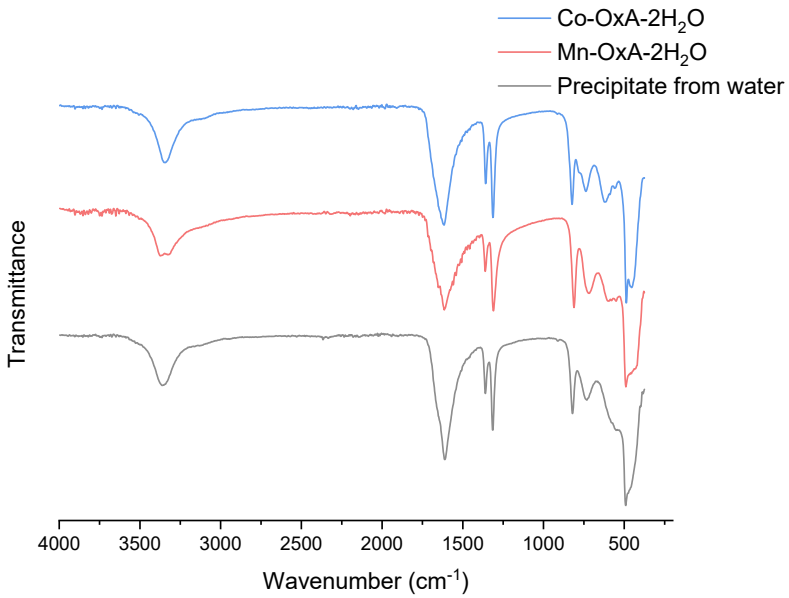


Figure S6: IR spectra of precipitate from adding water, and of pure Co and Mn oxalate dihydrates, stacked for clarity.

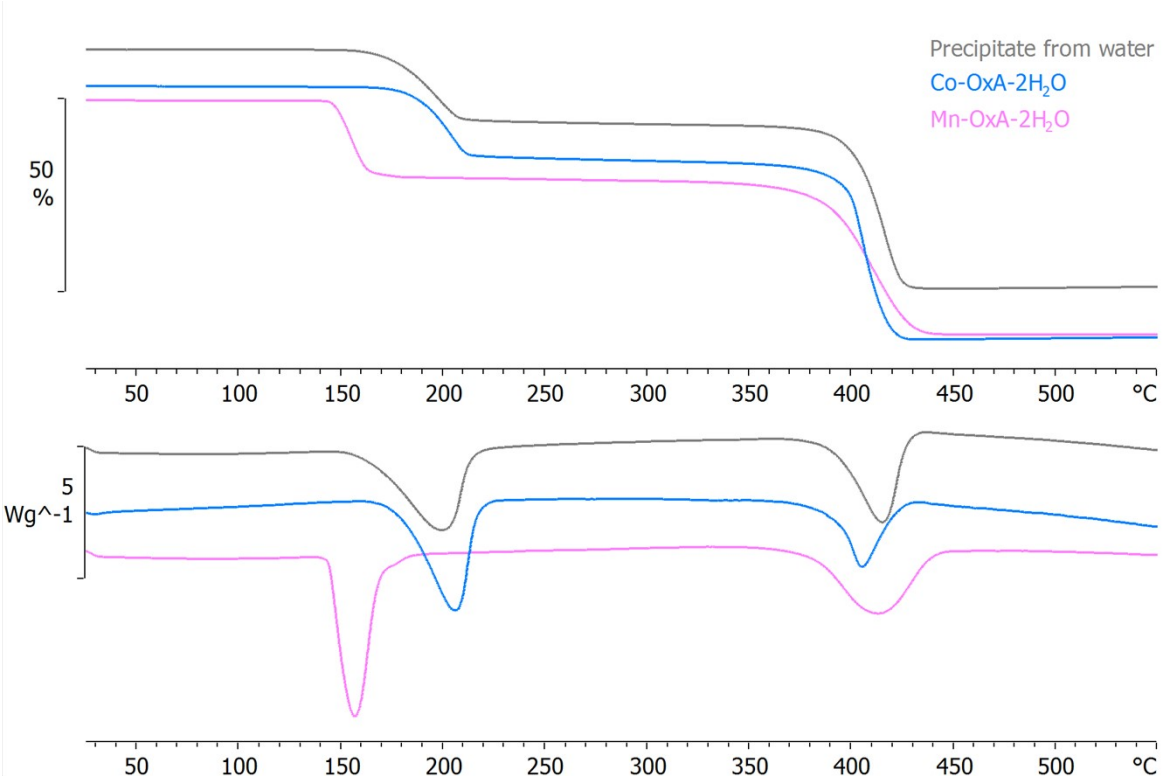


Figure S7: TGA mass loss and DSC curves of precipitate from adding water, and of pure Co and Mn oxalate dihydrate. N_2 flow 50 mL/min, heating rate 10 K/min, 70 µL alumina sample pan without cover, background subtracted.

Table S1: The metal content of the LiNMC powder was characterized via ICP-MS analysis, as described in the experimental section. It was determined to contain: $Ni_{0.3}Mn_{0.4}Co_{0.3}$.

Metal	**Wt.%**	**Mol.%**
Li	6.0(9)	0.86
Mn	19.8(8)	0.36
Co	17.5(8)	0.30
Ni	16.0(6)	0.27
Remainder	40.7	

Table S2: Assigned IR peaks of precipitate from adding water 0.5 mol/dm^3, 1 mol/dm^3 and 1.8 mol/dm^3 oxalic acid compared to α-Mn oxalate dihydrate, Co oxalate dihydrate, and literature values, all values quoted in wavenumber, cm^{-1}.

	Mn-O	**CoOH libration**	**O-C-O**	**C=O stretch, CO_2 wag**	**C-O**	**C-O / δ(OH_2) deformation**	**ν(OH_2) asymmetric stretch**
Literature	500*	746†	815* 827†	1316†	1362*	1625* 1622†	3380, 3150†
Water	494	732	820	1315	1360	1612	3362
0.5 mol/dm^3 OxA	491	733	820	1314	1360	1612	3353
1 mol/dm^3 OxA	490	731	818	1312	1359	1608	3340
1.8 mol/dm^3 OxA	489	732	817	1310	1358	1607	3339
Mn-OxA-2H_2O	487	723	812	1309	1359	1615	3354
Co-OxA-2H_2O	488	734	822	1315	1360	1620	3345

Vales taken from * ref 1, and † ref 2

Table S3: Thermogravimetric analysis showing mass loss and enthalpy values obtained for the different metal oxalate precipitates. Reference data for pure Co and Mn oxalate dihydrate are also included.				
Antisolvent	**Process**	***Temperature (°C)**	**Mass loss (%)**	**Enthalpy (J/g)**
Water	Dehydration	145.5(3)	18.61(5)	601(6)
	Decomposition	373.5(2)	42.1(1)	497(8)
0.5 mol/dm^3 OxA	Dehydration	145.2(3)	18.690(4)	577(13)
	Decomposition	373.6(1)	41.8(1)	473(10)
1 mol/dm^3 OxA	Dehydration	150.4(3)	18.69(2)	591(4)
	Decomposition	373.2(3)	41.7(2)	503(5)
1.8 mol/dm^3 OxA	Dehydration	150.1(6)	18.69(8)	606(11)
	Decomposition	373.5(3)	41.7(3)	512(4)
Reference sample	**Process**	***Temperature (°C)**	**Mass loss (%)**	**Enthalpy (J/g)**
Mn-OxA-2H_2O	Dehydration	125.3(2)	19.9(1)	601(1)
	Decomposition	363.2(5)	39.2(2)	555(9)
Co-OxA-2H_2O	Dehydration	161.8(1)	18.5(2)	584(11)
	Decomposition	375.0(1)	44.8(4)	290(3)
*Temperatures taken from the onset of the DSC peaks.				

References

1. H. L. Barazorda-Ccahuana, M. Nedyalkova, I. Kichev, S. Madurga, B. Donkova and V. Simeonov, *ACS Omega*, 2020, **5**, 9071–9077.
2. H. G. M. Edwards and P. H. Hardman, *J. Mol. Struct.*, 1992, **273**, 73–84.