

Supplementary information

**Non-aqueous direct leaching using a reusable nickel-selective amic-acid extractant for efficient lithium-ion battery recycling**

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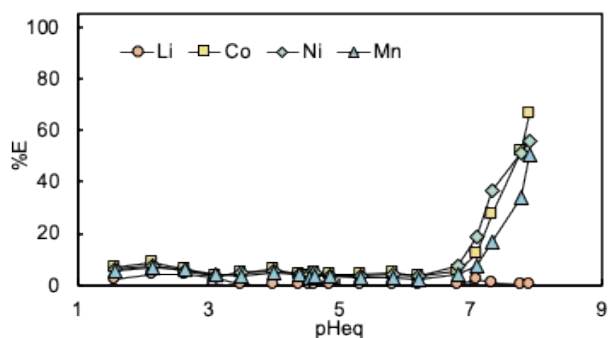


Figure S1 Liquid-liquid extraction efficiencies of Li, Co, Ni and Mn with Versatic10. Organic phase: 0.1M Versatic10 diluted in n-dodecane. Aqueous phase: 0.001M metals and 0.1M  $\text{NH}_4(\text{SO}_4)_2$ . Adjust pH with sulfuric acid and ammonia solution. Experimental conditions: O/A = 1, at 298 K at 1500 rpm for 1 h.

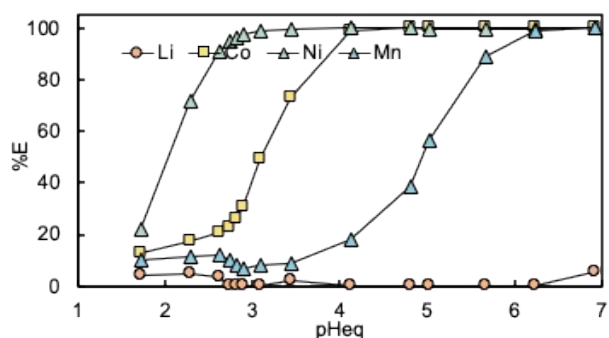


Figure S2 Liquid-liquid extraction efficiencies of Li, Co, Ni and Mn with D2EHAG. Organic phase: 0.1M D2EHAG diluted in n-dodecane. Aqueous phase: 0.001M metals and 0.1M  $\text{NH}_4(\text{SO}_4)_2$ . Adjust pH with sulfuric acid and ammonia solution. Experimental conditions: O/A = 1, at 298 K at 1500 rpm for 1 h.

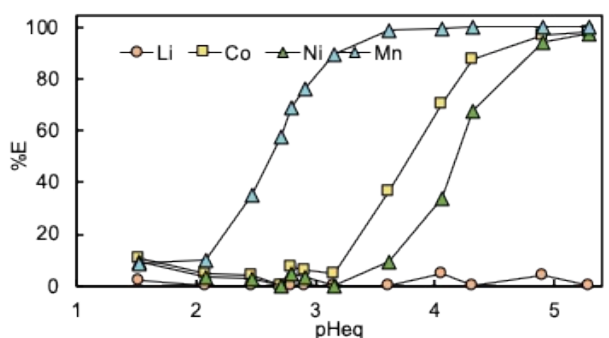


Figure S3 Liquid-liquid extraction efficiencies of Li, Co, Ni and Mn with D2EHPA. Organic phase: 0.1M D2EHPA diluted in n-dodecane. Aqueous phase: 0.001M metals and 0.1M  $\text{NH}_4(\text{SO}_4)_2$ . Adjust pH with sulfuric acid and ammonia solution. Experimental conditions: O/A = 1, at 298 K at 1500 rpm

for 1 h.

Table S1 Component of the black mass recovered from a hybrid electric vehicle.

Metal	Li	Cu	Ni	Mn	Co	Al	Fe
[g kg <sup>-1</sup> ]	37.6	15.0	30.7	38.5	149.5	28.7	5.3

### Data reproducibility

Table S2 Leaching efficiencies of the metals from NMC by different concentrations of Versatic10, D2EHPA, and D2EHAG diluted in *n*-dodecane with 0.1 mol/L ascorbic acid and a saturated amount of water. Experimental conditions: S/L = 10 g/L, heating at 333 K at 400 rpm for 24 h. SE represent standard error (n=3).

Extractant	mol/L	n	Leaching efficiency (%L)			
			Li	Co	Ni	Mn
Versatic10	0.15	1	1.51267578	0	0	0.26702785
		2	1.41738398	0	0	0.26467302
		3	1.36423444	0	0	0.26375447
		Average	1.4314314	0	0	0.26515178
		SE	0	0	0	0.00097479
Versatic10	0.3	1	1.51132029	0	0	0.26297221
		2	1.44979045	0	0	0.26166196
		3	1.3869538	0	0	0.26283709
		Average	1.44935485	0	0	0.26249042
		SE	0.03590218	0	0	0.00041606
Versatic10	0.45	1	1.64346819	0	0	0.26323245
		2	1.54949818	0	0	0.26101364
		3	1.57719222	0	0	0.26480477
		Average	1.59005286	0	0	0.26301695
		SE	0.02787853	0	0	0.0010997
Versatic10	0.6	1	1.6459114	0	0	0.26623391
		2	1.59770479	0	0	0.27145418
		3	1.53420435	0	0	0.26857786
		Average	1.59260685	0	0	0.26875532
		SE	0.03234763	0	0	0.00150957
D2EHPA	0.15	1	25.6734633	31.196325	0.32741045	40.9269382
		2	24.185945	25.4291417	0.06841412	41.6838778

		3	28.418061	32.7538049	0.2335079	41.7494304
		Average	1.23954145	2.22781456	0.07570144	0.26391793
		SE	1.23954145	2.22781456	0.07570144	0.26391793
D2EHPA	0.3	1	28.2938575	23.8351436	0.07627336	35.8509784
		2	31.0640967	26.2921407	0.06838024	38.7413272
		3	34.3271682	27.4810211	0.00975894	43.4203223
		Average	31.2283742	25.8694351	0.05147085	39.3375426
		SE	1.7436026	1.07348586	0.02098005	2.20532284
D2EHPA	0.45	1	46.3862982	35.9040574	0.19321706	51.9409887
		2	47.7176574	36.9391743	0.29076003	53.8471132
		3	38.5374467	33.0959842	0.23315921	42.7358186
		Average	44.2138008	35.313072	0.23904543	49.5079735
		SE	2.86408078	1.1481108	0.02831162	3.43049507
D2EHPA	0.6	1	40.8111155	30.1890582	0.142705	43.8412258
		2	45.4851326	37.1160222	0.29363992	48.2287138
		3	43.1977706	27.8697888	0.16834169	46.1308346
		Average	43.1646729	31.7249564	0.2015622	46.0669247
		SE	1.34937399	2.77743561	0.04662989	1.26696172
D2EHAG	0.15	1	24.8239338	39.5571196	40.1092374	33.9595918
		2	26.7032172	43.7855728	45.2389614	30.7867401
		3	31.2070772	44.2053097	44.6540508	37.9689986
		Average	27.5780761	42.5160007	43.3340832	34.2384435
		SE	1.89386407	1.48439414	1.62123953	2.07802215
D2EHAG	0.3	1	48.4063233	72.7833137	74.8890329	48.6529419
		2	51.8831677	77.7454647	79.816527	52.5424962
		3	44.42153	70.5215245	72.7714002	48.3246436
		Average	48.237007	73.6834343	75.8256533	49.8400272
		SE	2.15565226	2.13338472	2.0869752	1.35455391
D2EHAG	0.45	1	68.1399363	93.9645119	94.738731	68.1905157
		2	67.9360914	92.8322911	93.8012357	67.3621082
		3	62.6381506	91.3126267	92.7178662	65.66354
		Average	66.2380594	92.7031432	93.752611	67.0720546
		SE	1.80091606	0.76825193	0.58387979	0.74375173
D2EHAG	0.6	1	72.5946232	96.2111082	96.5800361	79.820383
		2	70.694544	93.2847565	93.4947641	75.8034688

	3	70.2850793	94.678574	94.6961235	78.2059728
	Average	71.1914155	94.7248129	94.9236412	77.9432749
	SE	0.71149119	0.84508128	0.89787697	1.16699865

Table S3 Saturated water contents in *n*-dodecane containing the extractants D2EHAG and D2EHPA. SE represent standard error (n=5).

Extractant	n	Water content (vol%)				
		0 mol/L	0.15 mol/L	0.3 mol/L	0.45 mol/L	0.6 mol/L
D2EHAG	1	0.004409448	0.835144567	1.6513731	2.492672468	3.399062056
	2	0.010631398	0.844592742	1.72815292	2.550757924	3.240164876
	3	0.010271958	0.804080449	1.71559882	2.525633539	3.25773812
	4	0.005495412	0.822850824	1.71922556	2.598452571	3.307490541
	5	0.01714745	0.861421609	1.73256382	2.73564005	3.409355395
	Average	0.009591133	0.833618038	1.709382844	2.58063131	3.322762198
	SE	0.002261287	0.009706222	0.014816074	0.042425958	0.035074009
D2EHPA	1	0.004409448	0.017367882	0.066214032	0.110932771	0.169010372
	2	0.010631398	0.009647313	0.052894225	0.095871157	0.17084401
	3	0.010271958	0.01003688	0.066081925	0.09901963	0.145503374
	4	0.005495412	0.02660409	0.061576929	0.101707684	0.160052863
	5	0.01714745	0.029793915	0.055256686	0.11295527	0.153895203
	Average	0.009591133	0.018690016	0.060404759	0.104097302	0.159861164
	SE	0.002261287	0.004149243	0.002741009	0.003349252	0.004722851

Table S4 Effects of the ascorbic acid concentration with the saturated amount of water on the leaching of the metals from NMC by 0.6 mol/L D2EHAG diluted in *n*-dodecane. Experimental conditions: S/L = 10 g/L, heating at 333 K at 400 rpm for 24 h. SE represent standard error (n=5).

Ascorbic acid	n	Leaching efficiency (%L)			
		Li	Co	Ni	Mn
0 mol/L	1	21.0473749	12.3308513	11.9669511	12.224691
	2	30.201688	19.7750153	19.2074861	21.0302529
	3	24.6332828	14.2313765	13.5733946	15.1430345
	Average	25.2941152	15.4457477	14.9159439	16.1326595
	SE	2.66319899	2.23307839	2.19531059	2.58965881
0.05 mol/L	1	69.0385305	76.6904399	72.2126858	74.4518817
	2	68.4602731	76.0927523	70.9307871	77.2339351

	3	65.7850656	75.679922	70.6037422	74.50342
	Average	67.7612897	76.1543714	71.2490717	75.3964123
	SE	1.00211308	0.29333388	0.49096968	0.91888186
0.1 mol/L	1	85.675712	93.7726475	90.8493791	91.9741778
	2	74.1973266	84.6507156	83.3254513	72.2343919
	3	80.6248976	86.9777304	79.8455889	78.6297946
	Average	80.1659787	88.4670312	84.6734731	80.9461214
	SE	3.32145989	2.73653814	3.24724097	5.81488933
0.2 mol/L	1	82.6361992	80.7269212	72.9046777	74.7331177
	2	91.0677156	83.5437307	75.2529753	78.5399327
	3	74.3390749	96.9233866	96.3672947	76.986974
	Average	82.6809965	87.0646795	81.5083159	76.7533415
	SE	4.82919456	4.99597115	7.46035216	1.10512417
0.3 mol/L	1	77.8602979	97.8742916	97.255887	81.1463022
	2	81.2178529	96.05394	97.7274339	74.983403
	3	72.5853816	94.3189984	94.5092265	73.7363524
	Average	77.2211775	96.08241	96.4975158	76.6220192
	SE	2.51238573	1.02642346	1.00342081	2.29060666
0.4 mol/L	1	65.9895617	94.7625411	93.9708104	79.8355271
	2	75.5660146	92.9207315	95.2749419	71.5753065
	3	68.8690334	99.2062143	98.979131	75.9410286
	Average	70.1415365	95.6298289	96.0749611	75.7839541
	SE	2.83675642	1.86556199	1.50009353	2.38581329

Table S5 Effects of the amount of water with 0.1 mol/L ascorbic acid on the leaching of the metals from NMC by 0.6 mol/L D2EHAG diluted in *n*-dodecane. Experimental conditions: S/L = 10 g/L, heating at 333 K at 400 rpm for 24 h. SE represent standard error (n=3).

Water content	n	Leaching efficiency (%L)			
		Li	Co	Ni	Mn
No loading water	1	9.90690142	6.95000709	6.59141761	8.54849612
	2	5.44557649	2.82525636	2.52051885	3.03567815
	3	5.6321635	2.89607091	2.60388231	3.09330103
	Average	6.99488047	4.22377812	3.90527292	4.89249177
	SE	1.45700643	1.36326776	1.34328792	1.82807786
1 vol%	1	45.1540568	69.6424473	69.0690816	76.874162

	2	48.2496304	79.1957082	78.3660374	84.2655957
	3	38.1450584	44.9855959	44.4106083	54.1371313
	Average	43.8495818	64.6079171	63.9485758	71.758963
	SE	2.98897056	10.1913823	10.1309341	9.06559499
2 vol%	1	62.2404418	94.7676902	95.1306912	86.3462977
	2	63.4506814	91.9311432	92.6982073	81.2938294
	3	61.0654609	88.56138	88.1180215	89.6476403
	Average	62.2521947	91.7534045	91.9823067	85.7625891
	SE	0.68857891	1.79381018	2.0557861	2.42913398
3 vol%	1	66.3773282	93.1232201	95.0026467	77.1323517
	2	78.3414718	92.4453572	94.6221999	77.6795105
	3	71.7703003	97.1608779	94.2923416	77.1201706
	Average	72.1630335	94.2431517	94.6390627	77.3106776
	SE	3.45932857	1.47192831	0.2052207	0.18444998
Saturated water	1	77.8602979	97.8742916	97.255887	81.1463022
	2	81.2178529	96.05394	97.7274339	74.983403
	3	72.5853816	94.3189984	94.5092265	73.7363524
	Average	77.2211775	96.08241	96.4975158	76.6220192
	SE	2.51238573	1.02642346	1.00342081	2.29060666

Table S6 Summary of the effects of D2EHAG and the additives on the leaching efficiency. Experimental conditions: S/L = 10 g/L, heating at 333 K at 400 rpm for 24 h. SE represent standard error (n=3).

	n	Leaching efficiency (%L)			
		Li	Co	Ni	Mn
0.6 mol/L D2EHAG	1	3.68703269	0.44486478	0.46877273	0.68429746
	2	3.4517925	0.4016669	0.42544226	0.63049439
	3	3.26953921	0.34830591	0.35958179	0.57618825
	Average	3.4694548	0.3982792	0.41793226	0.6303267
	SE	0.12084311	0.02792556	0.03174358	0.03120855
0.6 mol/L D2EHAG 0.1 mol/L Ascorbic acid	1	9.90690142	6.95000709	6.59141761	8.54849612
	2	5.44557649	2.82525636	2.52051885	3.03567815
	3	5.6321635	2.89607091	2.60388231	3.09330103
	Average	6.99488047	4.22377812	3.90527292	4.89249177
	SE	1.45700643	1.36326776	1.34328792	1.82807786

0.6 mol/L D2EHAG Saturated water	1	21.0473749	12.3308513	11.9669511	12.224691
	2	30.201688	19.7750153	19.2074861	21.0302529
	3	24.6332828	14.2313765	13.5733946	15.1430345
	Average	25.2941152	15.4457477	14.9159439	16.1326595
	SE	2.66319899	2.23307839	2.19531059	2.58965881
0.6 mol/L D2EHAG 0.3 mol/L Ascorbic acid Saturated water	1	77.8602979	97.8742916	97.255887	81.1463022
	2	81.2178529	96.05394	97.7274339	74.983403
	3	72.5853816	94.3189984	94.5092265	73.7363524
	Average	77.2211775	96.08241	96.4975158	76.6220192
	SE	2.51238573	1.02642346	1.00342081	2.29060666

Table S7 Leaching efficiencies of the metals from the LiB black mass by 0.6 mol/L D2EHAG in *n*-dodecane with 0.3 mol/L ascorbic acid and a saturated amount of water. Experimental conditions: S/L = 10 g/L, heating at 333 K at 400 rpm for 24 h. SE represent standard error (n=3).

n	Leaching efficiency (%L)					
	Li	Co	Ni	Mn	Cu	Al
1	68.5583988	101.133978	104.817603	96.7547682	34.0751848	77.7774225
2	69.9488481	99.8632273	103.557236	95.0120597	28.4317758	81.8706596
3	70.7350628	97.2642906	100.862919	90.713034	26.9491956	85.0437286
Average	69.7474366	99.4204987	103.079253	94.159954	29.8187187	81.5639369
SE	0.63636769	1.13880449	1.16636647	1.79538307	2.17083997	2.10320075

Table S8 Stripping efficiencies of the metals from loaded D2EHAG in *n*-dodecane at different concentrations of sulfuric acid. Experimental conditions: A/O = 1/1, shaking at room temperature at 1500 rpm for 1 h. SE represent standard error (n=3).

H <sub>2</sub> SO <sub>4</sub> in water phase	n	Stripping efficiency (%S)			
		Li	Co	Ni	Mn
0.001 mol/L	1	95.5926251	2.64067127	-0.7730673	59.8978289
	2	96.0598291	3.75383044	0.15120968	61.3684211
	3	96.4041746	1.96078431	-2.4301965	60.4247788
	Average	96.0188762	2.78509534	-1.0173514	60.5636762
	SE	0.2351673	0.52262075	0.75513144	0.43016653
0.005 mol/L	1	95.5838455	3.06021718	-1.2219451	63.1545338
	2	96.1965812	1.07252298	0.75604839	66.245614



	3	96.3946869	4.8245614	-0.0258532	63.9646018
	Average	96.0583712	2.98576719	-0.1639166	64.4549165
	SE	0.24405768	1.08375969	0.57515527	0.92538292
0.01 mol/L	1	95.7418788	4.3928924	-1.4962594	67.4329502
	2	96.3076923	1.659857	-0.5040323	70.0140351
	3	96.6223909	5.93395253	-0.4136505	68.7079646
	Average	96.2239873	3.99556731	-0.8046474	68.7183166
	SE	0.25760451	1.24971644	0.34678888	0.74511301
0.015 mol/L	1	95.8735733	7.52714709	0.12468828	71.3346105
	2	96.4700855	6.2308478	1.28528226	73.8350877
	3	96.8026565	8.95252838	0.15511892	72.8035398
	Average	96.3821051	7.57017442	0.52169649	72.657746
	SE	0.27178688	0.785976	0.38189393	0.72549718
0.02 mol/L	1	95.8823529	6.63869694	-3.3665835	72.9885057
	2	96.4529915	10.7763023	2.09173387	76.7157895
	3	96.8975332	13.4932921	1.99069286	76.5061947
	Average	96.4109592	10.3027638	0.2386144	75.4034966
	SE	0.2938099	1.99286625	1.80283494	1.20901037
0.03 mol/L	1	96.2159789	14.0918065	-1.4214464	79.0038314
	2	96.6923077	16.8539326	1.89012097	80.9368421
	3	97.0208729	17.7244582	0.18097208	80.1699115
	Average	96.6430532	16.2233991	0.21654889	80.0368617
	SE	0.23365435	1.09502191	0.95613264	0.5619636
0.04 mol/L	1	96.3915716	23.9141165	-2.5187032	83.3333333
	2	96.8974359	31.6649642	1.83971774	85.5894737
	3	97.2011385	29.3085655	0.15511892	84.9132743
	Average	96.8300487	28.2958821	-0.1746222	84.6120271
	SE	0.23611822	2.29405435	1.26892412	0.66848205
0.05	1	96.0491659	31.6880553	0.42394015	84.9553001
	2	96.8803419	40.040858	3.15020161	86.8035088
	3	97.2296015	39.6026832	2.48190279	86.7469027
	Average	96.7197031	37.1105322	2.01868152	86.1685705
	SE	0.3501003	2.71418747	0.82037712	0.60685524
0.1 mol/L	1	96.8305531	75.9896347	4.21446384	91.9636015
	2	97.1196581	80.5388151	10.5090726	93.0070175

	3	97.5996205	81.1377709	9.61737332	93.3061947
	Average	97.1832772	79.2220736	8.11363658	92.7589379
	SE	0.22427788	1.62544175	1.96650646	0.40693846
0.15 mol/L	1	98.4196664	93.1614018	36.7331671	96.2164751
	2	98.3760684	92.3008172	33.8205645	95.5263158
	3	98.5104364	92.4277606	33.3505688	95.5787611
	Average	98.4353904	92.6299932	34.6347668	95.7738506
	SE	0.03957747	0.26821943	1.05793617	0.22182946
0.2 mol/L	1	98.3933275	94.5261599	53.5660848	96.4623244
	2	98.4358974	95.3217569	59.2237903	96.8350877
	3	98.3586338	95.0954592	57.6525336	96.7787611
	Average	98.3959529	94.9811254	56.8141362	96.6920577
	SE	0.02234269	0.23667686	1.68617818	0.11601182
0.3 mol/L	1	98.4021071	97.55923	86.0349127	97.8863346
	2	98.4700855	97.5357508	86.3860887	97.7052632
	3	98.4914611	97.9798762	93.5935884	98.0106195
	Average	98.4830142	97.5213403	86.2439188	97.7600311
	SE	0.05085647	0.02701415	0.10674182	0.06333698
0.4 mol/L	1	98.3494293	98.0997038	93.925187	98.2535121
	2	98.4188034	97.9775281	93.6113911	97.9964912
	3	98.4914611	97.9798762	93.5935884	98.0106195
	Average	98.4198979	98.019036	93.7100555	98.0868743
	SE	0.04100469	0.0403396	0.10768845	0.08341869
0.5 mol/L	1	98.2528534	98.213228	95.957606	98.298212
	2	98.2136752	98.1562819	95.8694556	98.1017544
	3	98.4914611	98.0624355	95.6592554	98.0566372
	Average	98.3193299	98.1439818	95.8287724	98.1522012
	SE	0.08680552	0.04396236	0.08849597	0.07415807
1.0 mol/L	1	96.2949956	97.857848	97.1645885	97.4904215
	2	96.1794872	97.9341164	97.3210685	97.5789474
	3	96.7077799	97.876677	97.1535677	97.539823
	Average	96.3940876	97.8895471	97.2130749	97.5363973
	SE	0.16035139	0.02293796	0.05409045	0.02561257

Table S9 Reusability of the organic solvent using D2EHAG as the leaching agent. Before each

leaching, 0.3 mol/L ascorbic acid was added to the organic solvent. Leaching experiment conditions: S/L = 10 g/L, heating at 333 K at 400 rpm for 24 h. After leaching, the organic phase was stripped by 1.00 mol/L H<sub>2</sub>SO<sub>4</sub>. Stripping experiment conditions: A/O = 1:1, shaking at room temperature at 1500 rpm for 1 h. SE represent standard error (n=3).

		Leaching efficiency (%L)			
n		Li	Co	Ni	Mn
1 <sup>st</sup> times	1	92.4787995	102.693757	102.177647	91.3634139
	2	89.250684	96.8597117	96.6912141	89.1569912
	3	90.1426243	96.8801793	96.4392463	89.7397205
	Average	90.6240359	98.8112158	98.4360357	90.0867085
	SE	0.96246217	1.94127932	1.87221897	0.66014537
2 <sup>nd</sup> times	1	71.8681838	94.5288785	94.6459965	87.1072654
	2	89.3891722	96.252127	98.1711964	102.611598
	3	84.9910416	92.6302633	92.5195333	89.0295553
	Average	82.0827992	94.4704229	95.112242	92.9161396
	SE	5.26275162	1.04595045	1.6480658	4.87938644
3 <sup>rd</sup> times	1	72.7359973	98.9942461	100.969037	73.7939831
	2	86.467316	96.8627091	98.1951736	71.5199018
	3	85.9811544	97.4271485	98.9344095	71.2040244
	Average	81.7281559	97.7613679	99.3662067	72.1726364
	SE	4.49826912	0.63761	0.8293403	0.8157856