Supplementary materials for:

Recovery of high-purity MnO_2 from the acid leaching solution of spent Li-ion batteries

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3.1 Initial purification of the leaching solution

1) Cu recovery by iron powder reduction

In order to optimize the copper removal, different process parameters were investigated at this stage. Fig.S1 displays the copper recovery as a function of pH and iron powder consumption. It is clear from the results that copper recovery increases linearly with the increasing amount of iron in the stoichiometric range of 0.6 to 1.3~1.4. Maximum Cu recovery achieved was nearly 100% - with less than 20 ppm Cu left in the solution - with 1.4 times the stoichiometric amount of iron at pH 1.5 or 1.3 times the stoichiometric amount of iron at pH = 2.0 and 2.5. The results indicate that copper recovery is more efficient at higher pH, most likely as a result of lower Fe acidic dissolution. Iron has lower reduction potential compared to H_2 evolution, which makes hydrogen evolution, i.e. H^+ reduction by Fe, thermodynamically more likely in acidic solutions. This may also explain the efficiency of Cu recovery (only between 70 to 85%) when a stoichiometric amount of iron is added. The Cu products obtained were filtered and then dried in oven at 80 °C for 8 hours.

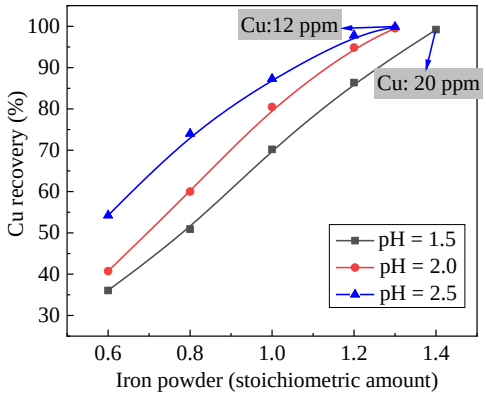

Fig.S-1. Influence of iron powder dosage and pH on the recovery of copper.

Fig.S-2 displays the level of different impurities detected in the final copper product (Fig.S-2a) with a typical associated XRD pattern and SEM image included as an inset (Fig.S-2b). There is a clear increase in the amount of impurities found within the Cu product as pH increases from 1.5 to 2.5. At pH 2.5, the content of impurities in the Cu product are in order of 3.6% Fe, 0.1% Co, 0.1% Mn and 0.08% Ni. In contrast, the impurity contents in the Cu product produced at pH 1.5 and pH 2.0 are all lower than 0.2%. This observed difference especially in Fe content is due to iron precipitation or

hydrolysis that is known to initiate at pH > 2, which results in an increase within the product material [1].

The typical XRD and SEM results presented in Fig.S-2b show that the copper particles produced are aggregated together in the form of spherical powders that have a particle size of < 1 µm. In addition, both elemental copper and cuprous oxide (Cu_2O) peaks could be clearly identified. It is most likely that the cuprous oxide formed during the copper precipitate drying process, as this was conducted in air rather than a vacuum oven. Given the fact that lower pH favors the side reactions other than cementation and higher pH values (e.g. 2.5) co-precipitation of impurities, specifically Fe, the optimized conditions for Cu recovery were defined as pH 2.0 with 1.3 times the stoichiometric amount of iron.

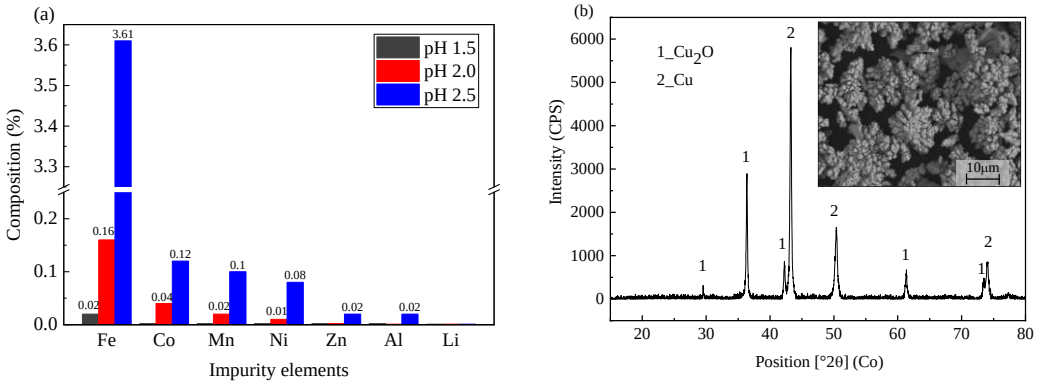

Fig.S-2 (a). Change in composition of the impurity elements at different pH and (b) an example XRD pattern and SEM image measured for the copper product.

2) Initial removal of Fe and Al by neutralization precipitation.

During the recovery of Cu, Fe ions were introduced into the solution, resulting an increase of Fe concentration from 0.5 g/L to 3.5 g/L (Table I, PLS2). In order to remove such detrimental impurities like Fe and Al before Mn recovery, neutralization-precipitation of the copper-free solution was explored. The neutralization process was carried out over an 8 hour period at room temperature using 25 mL of PLS at different pH values (1.5 - 6.5). pH values of the solutions were adjusted with sodium hydroxide pellets (Sigma-Aldrich, purity ≥ 97%) and measured by a pH meter (Mettler-Toledo, SevenExcellence™). Behaviors of the different elements during this neutralization-precipitation are outlined in Fig.S-3.

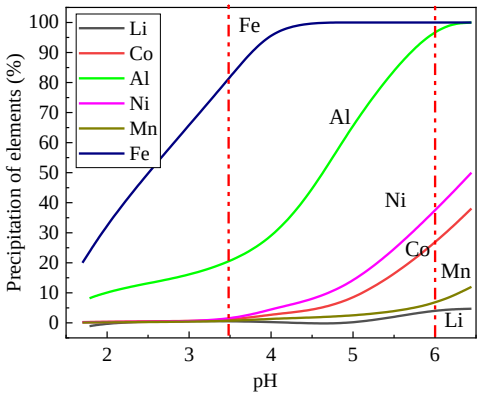

Fig.S-3. Precipitation of different elements as a function of pH for PLS (RTP, 8 hours).

As can be observed, the precipitation of the different elements increases as the pH is changed towards more neutral values. Nevertheless, it is impossible to totally remove the impurity Fe and Al by neutralization without the significant loss of valuable metals. At pH above 6, high levels of both Fe and Al can be removed, although nearly 40% Ni, 30% Co, 7% Mn and 4% Li are also lost within the same precipitate as a result of co-precipitation or mechanical entrainment especially with colloidal Al in the form of $Al(OH)_3$ [2]. From the results, the optimum pH for the removal of Fe and Al by neutralization is ca. 3.5, as around 90% Fe and 20% Al are removed with only minor associated losses of the target metals (< 0.5%).

3.2 Mn separation from other elements by solvent extraction

Table S-I displays the separation factors of Mn compared to other elements using D2EHPA at 25 °C. It can be seen that separation factors of Mn relative to Li, Ni and Co were much higher than those for Fe and Al. Generally, if the separation factor between two elements is above 100, it suggests a good separation efficiency between the two, for example, clear separation of Mn from Co, Ni, and Li can be achieved easily. Conversely, the separation factors between Mn and Al are all close to 1, which means that the clear separation of these two elements is difficult to obtain under the conditions investigated.

Table S-I. Separation factors of Mn compared to other elements under different conditions (25 °C).

Parameters		Separation factors				
		Mn/Co	Mn/Al	Mn/Fe	Mn/Ni	Mn/Li
pH values	2.20	3415.0	0.28	0.07	-	-
	2.54	2850.3	0.18	0.01	-	-
	2.84	249.8	0.15	0.01	-	-
	3.17	142.9	0.16	0.01	1270	-
	3.65	113.7	0.08	0.02	1169	-
	4.45	47.5	0.03	0.04	1442	-
D2EHPA (mol/L)	0.30	377.3	0.28	0.03	686	-
	0.40	149.2	0.33	0.04	1322	-
	0.60	91.0	0.26	0.00	1553	-
	0.80	83.9	0.34	0.00	2273	-
	1.00	77.3	0.33	0.01	2261	-
A/O ratios	1:10	123.3	0.43	0.04	2442	21842
	1:5	132.9	0.58	0.02	1615	14157
	1:2	138.1	0.43	0.01	480	4157
	1:1	189.3	0.25	0.00	5728	8593
	2:1	155.1	0.28	0.00	3350	3350