Ultrasound-assisted extraction of metals from Lithium-ion batteries using natural organic acids

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| Acid         | Battery type                | pre-treatment          | Optimum treatment condition | Leached percentage | ref  |
|--------------|----------------------------|------------------------|----------------------------|--------------------|------|
|              |                            |                        |                            |                    |      |
|              |                            |                        | Reductant | Acid conc. | Temp. | time | S/L | assistant |                  |      |
| Citric acid  | LiCo$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ | none                   | D-glucose  | 1.5 M     | 353 K | 2 h  | 20 g/L | none        | 99% Li, 91% Ni, 92% Co, 94% Mn | 51   |
| Acetic acid  | LiCo$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ | none                   | 4.0 vol% H$_2$O$_2$ | 3.5 M     | 353 K | c.a. 1 h | 40 g/L | none        | 99.97% Li, 92.67% Ni, 93.62% Co, 96.32% Mn | 52   |
| Acetic acid  | LiCo$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ | 2 M NaOH solution, 1 h | 4.0 vol% H$_2$O$_2$ | 6.0 M     | 353 K | 10 min | 33 g/L | none        | ca. 99% | 53   |
| lactic acid  | LiCo$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ | NaOH treatment, 883 K, 5 h, air | 0.5 vol% H$_2$O$_2$ | 1.5 M     | 353 K | 20 min | 20 g/L | none        | 97.7% Li, 98.2% Ni, 98.9% Co, 98.4% Mn | 54   |
| L-Tartaric Acid | LiCo$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ | Ultrasonic cleaning | 4 vol% H$_2$O$_2$ | 2 M       | 353 K | 0.5 h  | 17 g/L | none        | 99.3% Ni, 98.6% Co, 98.3% Mn, 99.1% Li | 55   |
| TCA          | LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ | none                   | 4 vol% H$_2$O$_2$ | 3 M       | 353 K | 0.5 h  | 50 g/L | none        | ca. 93.0% Ni, 91.8% Co, 89.8% Mn, 99.7% Li | 56   |
| Formic acid  | LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ | none                   | 6 vol% H$_2$O$_2$ | 2 M       | 353 K | -      | 50 g/L | none        | ca. 85% Ni, ca. 85% Co, ca. 85% Mn, 99.93% Li | 57   |
| DL-malic acid | LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ | NMP immersion, thermal treatment (973 K, 2 h, air) | 1.25 vol% H$_2$O$_2$ | 1.2 M     | 353 K | 0.5 h  | 40 g/L | none        | 98.9% Li, 94.3% Co, 95.1% Ni, 96.4% Mn | 58   |
Table S2. pKₐ values and prices for various organic acids with related purity

| Acid                     | pKₐ values | Price   | All the data is from sigma Aldrich website, date of access: 2021-07-22 |
|--------------------------|------------|---------|---------------------------------------------------------------------|
| Citric acid (99%)        | pKₐ₁ = 3.13, pKₐ₂ = 4.76, pKₐ₃ = 6.40 | 33.4 €/kg | https://www.sigmaaldrich.com/SE/en/product/sial/c0759?context=product |
| Acetic acid (≥ 99%)      | 4.76       | 44.8 €/L | https://www.sigmaaldrich.com/SE/en/product/sigald/a6283?context=product |
| Formic acid (97.5-98.5%) | 3.75       | 113.6 €/L | https://www.sigmaaldrich.com/SE/en/product/supelco/00940?context=product |
| Lactic acid (≥ 85%)      | 3.86       | 94.0 €/kg | https://www.sigmaaldrich.com/SE/en/product/sial/252476?context=product |
| Glycolic acid (99%)      | 3.83       | 159.8 €/kg | https://www.sigmaaldrich.com/SE/en/product/sial/124737?context=product |
| DL-malic acid(≥ 99%)     | pKₐ₁ = 3.40, pKₐ₂ = 5.20 | 359.6 €/kg | https://www.sigmaaldrich.com/SE/en/product/aldrich/240176?context=product |
| Tartaric acid (≥99.5%)   | pKₐ₁ = 3.22, pKₐ₂ = 4.85 | 132.0 €/kg | https://www.sigmaaldrich.com/SE/en/product/aldrich/251380?context=product |
| Oxalic acid dihydrate (≥99%) | pKₐ₁ = 1.2, pKₐ₂ = 4.2 | 70.4 €/kg | https://www.sigmaaldrich.com/SE/en/product/sial/247537?context=product |
| Ascorbic acid (99%)      | pKₐ₁ = 4.17, pKₐ₂ = 11.6 | 151.5 €/kg | https://www.sigmaaldrich.com/SE/en/product/sial/a92902 |

Fig S1. Effect of citric acid concentration (left) and S/L ratio (right) on metal extraction from the fine ground LIBs powder. Conditions: H₂O₂, 0 vol%; ultrasonic bath temperature, 323 K.
Fig. S2 photograph of (a) the fine ground and (b) the coarse ground LiBs powder.

Fig. S3 SEM image of a) residue after aqua regia treatment, and EDS maps for b) C, c) O, d) F, e) P, f) Ni, g) Co, h) Mn, i) Al, and j) Cu was taken from a).
Fig. S4 Effect of leaching method (ultrasound vs. oil bath) on metal extraction from the fine ground LiBs powder. Conditions: citric acid, 1.5 mol L\textsuperscript{-1}; S/L, 25 g L\textsuperscript{-1}; H\textsubscript{2}O\textsubscript{2}, 0 vol\%; ultrasonic bath temperature, 323 K; temperature for oil bath, 343 K; stirring speed for oil bath, 500 rpm.
**Fig. S5** XRD patterns of residues with respect to different leaching time (a) with/ (b) without ultrasound at 323 K.

**Scheme S1** Schematic diagram of shrinking core model. Shrinking core (non-degraded NMC 111) and a shell (released metal ions and their related complex with citrate) on the core surface.
**Fig. S6** Kinetics analysis during the leaching of the fine ground LIBs powder with/without ultrasound by (left) $X$ vs. $t$, (right) $1-(1-X)^{1/3}$ vs. $t$.

Conditions: citric acid, 1.5 mol L$^{-1}$; S/L, 25 g L$^{-1}$, $\text{H}_2\text{O}_2$, 0 vol%; temperature, 323 K; stirring speed for oil bath, 500 rpm.
Fig. S7 Scanning electron micrographs of the pristine LIBs powder before (a), and after (b-g) citric acid leaching treatment. The bottom row shows the ultrasound assisted leaching while the top row shows the oil bath leaching for different leaching times, where (b, c) is 1.5 h, (d, e) 3 h, and (f, g) 6 h.

Fig. S8 (a) \( X \), (b) \( 1 - (1 - X)^{1/3} \), and (c) \( 1 - 3(1 - X)^{2/3} + 2(1 - X) \) vs. \( t \) at various oil bath temperatures. Conditions: fine ground LIBs powder; citric acid, 1.5 mol L\(^{-1}\); S/L, 25 g L\(^{-1}\); \( H_2O \), 0 vol%; stirring speed for oil bath, 500 rpm.

Based on the curves shown in Fig. 8 and shrinking core model, \( X \), \( 1 - (1 - X)^{1/3} \), and \( 1 - 3(1 - X)^{2/3} + 2(1 - X) \) vs. \( t \) was plotted for all temperatures, shown in Fig. S8. The fitting of the data showed that the leaching of Ni, Co, Mn, and Al was always in agreement with the residue layer diffusion (see section 3.3 in main text), demonstrating a linear relationship with higher \( R^2 \) (≥ 0.9939) with the exception of Al (\( R^2 \) ≥ 0.9404). At the same time, all of the \( k_3 \) values of metals ions were increased with the increasing temperature. The lithium leaching was separated into two stages as mentioned in section 3.3. The \( k_3 \) values of Li leaching at the first stage were ca. 2-4 times higher than those of its second stage as well as the \( k_3 \) values for Co, Ni, and Mn, regardless of the temperature. This was further discussed in correlation to Fig. 5 and Table 4.

Moreover, Fig. S9 shows the \( k_1 \) values of metal ions vs. temperature based on Fig. S8 and Table S3. The increasing rate of \( k_3 \) of Li (1st stage) is ca. 3 times higher than the rate of Co, Ni, Mn, and Li (2nd stage), which indicated that the 1st stage Li leaching was more sensitive with the temperature compared to Co, Ni, Mn, and Li (2nd stage).

For the leaching of Cu, all the fitting lines based on different temperatures fitted well by the reaction contribution with the highest \( R^2 \) (≥ 0.9810), which was in agreement with the discussion in the last section, i.e., the Cu leaching in the oil bath were controlled by the reaction control model. The kinetic constants (\( k_2 \) or \( k_3 \)) obtained at various temperatures through the slope analysis were used to draw the Arrhenius plots (Eq. 9) of the respective metals.
Fig. S9 The effect of temperature on $k_3$ values obtained from fitting slopes of residue layer diffusion control model.
Table S3 Kinetic parameters during the leaching process of valuable metals from the fine ground spent battery powder at different oil bath temperature by residue layer diffusion control model except Cu which fitted better by reaction control model. (Conditions: citric acid, 1.5 mol L\(^{-1}\); S/L, 25 g L\(^{-1}\); \(\text{H}_2\text{O}_2\), 0 vol%; stirring speed for oil bath, 500 rpm)

| T (K) | Li (1\(^{\text{st}}\) stage) | Li (2\(^{\text{nd}}\) stage) | Mn | Co | Ni | Al | Cu |
|-------|-----------------|-----------------|----|----|----|----|----|
|       | \(k_3\times10^4\) (min\(^{-1}\)) | \(R^2\) | \(k_3\times10^4\) (min\(^{-1}\)) | \(R^2\) | \(k_3\times10^4\) (min\(^{-1}\)) | \(R^2\) | \(k_3\times10^4\) (min\(^{-1}\)) | \(R^2\) | \(k_3\times10^4\) (min\(^{-1}\)) | \(R^2\) |
| 303   | 2.51            | 0.9961          | -  | -  | 1.01  | 0.9968 | 0.89 | 0.978 | 0.98 | 0.9939 | 0.29 | 0.9404 | 1.02 | 0.9960 |
| 313   | 5.86            | 0.9979          | 2.33 | 0.9690 | 2.08  | 0.9943 | 1.71 | 0.9934 | 1.99 | 0.9942 | 0.38 | 0.9617 | 1.60 | 0.9817 |
| 323   | 15.3            | 0.9888          | 3.52 | 0.9750 | 4.41  | 0.9980 | 3.81 | 0.9981 | 4.36 | 0.9981 | 0.79 | 0.9866 | 3.03 | 0.9859 |
| 333   | 26.4            | 0.9841          | 5.82 | 0.9716 | 7.14  | 0.9988 | 5.92 | 0.9990 | 6.95 | 0.9976 | 1.08 | 0.9917 | 3.59 | 0.9877 |
| 343   | 40.3            | 0.9618          | 10.3 | 0.9752 | 13.7  | 0.9932 | 12.6 | 0.9995 | 14.4 | 0.9946 | 2.11 | 0.9974 | 4.46 | 0.9810 |
Fig. S10 Arrhenius plots for Al and Cu leaching using the k values obtained from fitting slopes of residue layer diffusion control model and reaction control model, respectively. Conditions: citric acid, 1.5 mol L\(^{-1}\); S/L, 25 g L\(^{-1}\); H\(_2\)O\(_2\), 0 vol%; stirring speed for oil bath, 500 rpm.

Table S4 Fitting results of Arrhenius plots in Fig. S5 and Fig. S9. Conditions: citric acid, 1.5 mol L\(^{-1}\); S/L, 25 g L\(^{-1}\); H\(_2\)O\(_2\), 0 vol%; stirring speed for oil bath, 500 rpm

| Metal  | Slope     | \(R^2\) | \(E_a\) (KJ mol\(^{-1}\)) | comment               |
|--------|-----------|---------|---------------------------|-----------------------|
| Li (1\(^{st}\) stage) | -8167.128 | 0.9804  | 67.9                      |                       |
| Li (2\(^{nd}\) stage) | -4766.326 | 0.9968  | 39.6                      |                       |
| Mn     | -6703.941 | 0.9966  | 55.7                      |                       |
| Co     | -6809.893 | 0.9928  | 56.6                      |                       |
| Ni     | -6880.301 | 0.9949  | 57.2                      |                       |
| Al     | -5187.134 | 0.9630  | 43.1                      | Except the point at 343 K |
| Cu     | -4469.372 | 0.9481  | 37.2                      |                       |
Fig. S11 Effect of leaching method (ultrasound vs. oil bath) on metal extraction from the fine ground LiBs powder. Conditions: acetic acid, 4.5 mol L\(^{-1}\); S/L, 25 g L\(^{-1}\); H\(_2\)O\(_2\), 0 vol%; temperature for oil bath, 323 K; stirring speed for oil bath, 500 rpm.
Fig. S12 Effect of organic acid species on extraction of metal ions from the fine ground LiBs powder with ultrasound. Conditions: citric acid, 1.5 mol L$^{-1}$; acetic acid, 4.5 mol L$^{-1}$; 0 vol% H$_2$O$_2$; S/L, 25 g L$^{-1}$; ultrasonic bath temperature, 323 K.
Fig. S13 Effect of oil bath temperature on leaching behaviour of metals from the fine ground LiBs powder depending on leaching time. Conditions: acetic acid, 4.5 mol L$^{-1}$; S/L, 25 g L$^{-1}$; H$_2$O$_2$, 0 vol%; stirring speed for oil bath, 500 rpm.

Fig. S14 (a) $X$, (b) $1-(1-X)^{1/3}$, and (c) $1-3(1-X)^{1/2}+2(1-X)$ vs. $t$ at various oil bath temperatures. Conditions: fine ground powder; acetic acid, 4.5 mol L$^{-1}$; S/L, 25 g L$^{-1}$; H$_2$O$_2$, 0 vol%; stirring speed for oil bath, 500 rpm.
**Fig. S15** Arrhenius plots for Li, Ni, Co, Mn, Al and Cu leaching using the $k$ values obtained from fitting slopes of residue layer diffusion control model and reaction control model, respectively. Conditions: acetic acid, 4.5 mol L$^{-1}$; S/L, 25 g L$^{-1}$; H$_2$O$_2$, 0 vol%; stirring speed for oil bath, 500 rpm.
Table S5 Kinetic parameters during the leaching process of metals from the fine LiBs powder at different oil bath temperature by residue layer diffusion control model except Cu which fitted better by reaction control model. Conditions: acetic acid, 4.5 mol L\(^{-1}\); S/L, 25 g L\(^{-1}\), \(\text{H}_2\text{O}_2\), 0 vol%; stirring speed for oil bath, 500 rpm

| T (K) | Li (1\(^{st}\) stage) \(k_3 \times 10^4\) (min\(^{-1}\)) | Li (2\(^{nd}\) stage) \(k_3 \times 10^4\) (min\(^{-1}\)) | Mn \(k_3 \times 10^4\) (min\(^{-1}\)) | Co \(k_3 \times 10^4\) (min\(^{-1}\)) | Ni \(k_3 \times 10^4\) (min\(^{-1}\)) | Al \(k_3 \times 10^4\) (min\(^{-1}\)) | Cu \(k_3 \times 10^4\) (min\(^{-1}\)) | \(R^2\) |
|-------|---------------------------------|---------------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 303   | 2.45 0.9902 - - 1.25 0.9932 1.06 0.9936 1.21 0.9958 0.22 0.9207 2.18 0.9947 | 313 3.66 0.9933 1.40 0.9110 2.12 0.9935 1.78 0.9990 1.82 0.9925 0.23 0.9533 4.44 0.9902 | 318 9.11 0.9961 3.26 0.9877 3.01 0.9981 2.57 0.9978 2.88 0.9978 0.49 0.9856 6.03 0.9822 | 323 13.4 0.9985 3.59 0.9755 3.07 0.9938 2.92 0.9958 3.21 0.9944 0.60 0.9936 6.09 0.9938 | 333 14.8 0.9689 2.95 0.9153 6.31 0.9796 5.23 0.9745 5.63 0.9819 1.45 0.9880 9.51 0.9796 | 343 15.2 0.9551 2.56 0.9407 5.89 0.9739 4.61 0.9754 5.38 0.9752 1.66 0.9812 9.51 0.9796 |

Table S6 Fitting results of Arrhenius plots in Fig. S14. Conditions: acetic acid, 4.5 mol L\(^{-1}\); S/L, 25 g L\(^{-1}\), \(\text{H}_2\text{O}_2\), 0 vol%; stirring speed for oil bath, 500 rpm

| Metal (1\(^{st}\) stage) | Slope | \(R^2\) | \(E_a\) (KJ mol\(^{-1}\)) |
|-------------------------|-------|---------|-------------------------|
| Li                      | -8435.590 | 0.9848 | 70.1                    |
| Li (2\(^{nd}\) stage)    | -4992.210 | 0.9421 | 41.5                    |
| Mn                      | -5362.208 | 0.9709 | 44.4                    |
| Co                      | -5396.712 | 0.9894 | 45.1                    |
| Ni                      | -5237.012 | 0.9801 | 44.1                    |
| Al                      | -7216.710 | 0.9822 | 60.0                    |
| Cu                      | -5003.685 | 0.9735 | 41.4                    |
Fig. S16 Effect of H$_2$O$_2$ concentration on extraction of metal ions from the fine ground LiBs powder. Conditions: Ultrasound; citric acid, 1.5 mol L$^{-1}$; S/L, 25 g L$^{-1}$; oil bath temperature, 323 K; stirring speed, 500 rpm. The lines between measurement points serve as the guide to the eye.
Fig. S17 XRD patterns of residues depending on H$_2$O$_2$ concentration. Conditions: citric acid, 1.5 mol L$^{-1}$; S/L, 25 g L$^{-1}$; oil bath temperature, 323 K; stirring speed, 500 rpm; leaching time, 24 h.
Fig. S18 $1-3(1-X)^{(2/3)}=2(1-X)$ vs. $t$ with various $\text{H}_2\text{O}_2$ concentration. Conditions: citric acid, 1.5 mol L$^{-1}$; S/L, 25 g L$^{-1}$; temperature, 323 K; stirring speed, 500 rpm.
Table S7: Kinetic parameters during the leaching process of valuable metals from the fine ground LiBs powder with different H₂O₂ concentration by residue layer diffusion control model. Conditions: citric acid, 1.5 mol L⁻¹; S/L, 25 g L⁻¹; temperature, 323 K; stirring speed for oil bath, 500 rpm.

| H₂O₂ (vol%) | Li 1st stage | Li 2nd stage | Mn 1st stage | Mn 2nd stage | Co 1st stage | Co 2nd stage | Ni 1st stage | Ni 2nd stage |
|-------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
|             | k3 × 10⁻⁴ (min⁻¹) | R² | k3 × 10⁻⁴ (min⁻¹) | R² | k3 × 10⁻⁴ (min⁻¹) | R² | k3 × 10⁻⁴ (min⁻¹) | R² | k3 × 10⁻⁴ (min⁻¹) | R² |
| 0           | 15.3         | 0.9916       | 3.52         | 0.9913       | 5.42         | 0.9929       | 4.32         | 0.9994       | 4.60         | 0.9939       | 3.68         | 0.9993       | 5.25         | 0.9933       | 4.25         | 0.9984       |
| 0.5         | 12.9         | 0.9977       | 3.99         | 0.9765       | 7.11         | 0.9976       | 4.19         | 0.9894       | 6.68         | 0.9979       | 3.69         | 0.9958       | 6.66         | 0.9971       | 3.99         | 0.9975       |
| 1           | 13.9         | 0.9885       | 3.51         | 0.9773       | 9.08         | 0.9897       | 4.77         | 0.9911       | 8.96         | 0.9837       | 4.44         | 0.9952       | 8.56         | 0.9891       | 4.70         | 0.9952       |
| 1.5         | 17.5         | 0.9418       | 3.53         | 0.9744       | 12.2         | 0.9988       | 4.81         | 0.9789       | 12.6         | 0.9560       | 4.57         | 0.9957       | 12.1         | 0.9521       | 4.87         | 0.9906       |
| 2           | -            | -            | 3.10         | 0.9694       | -            | -            | 4.21         | 0.9443       | -            | -            | 5.56         | 0.9817       | -            | -            | 4.72         | 0.9759       |

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