

A contact-electro-catalytic cathode recycling method for spent lithium-ion batteries

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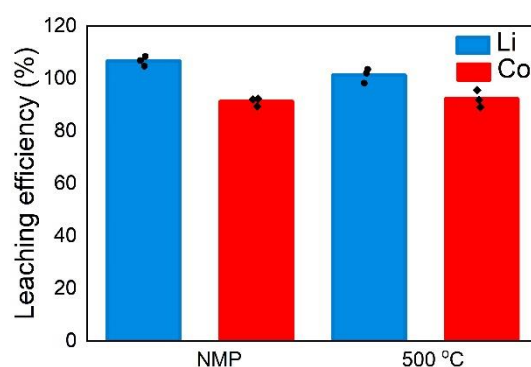
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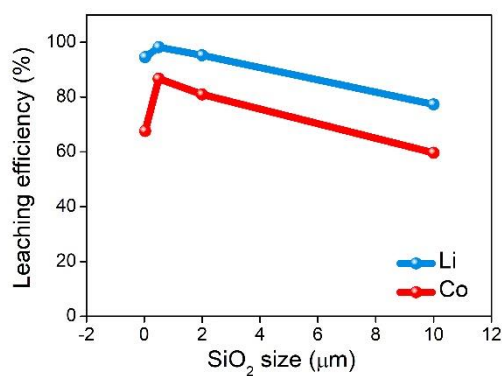
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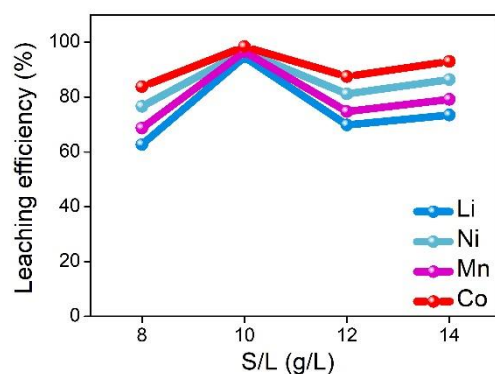
Supplementary Figure 1. Pretreatment of LIBs. Pretreatment steps of spent LIBs.



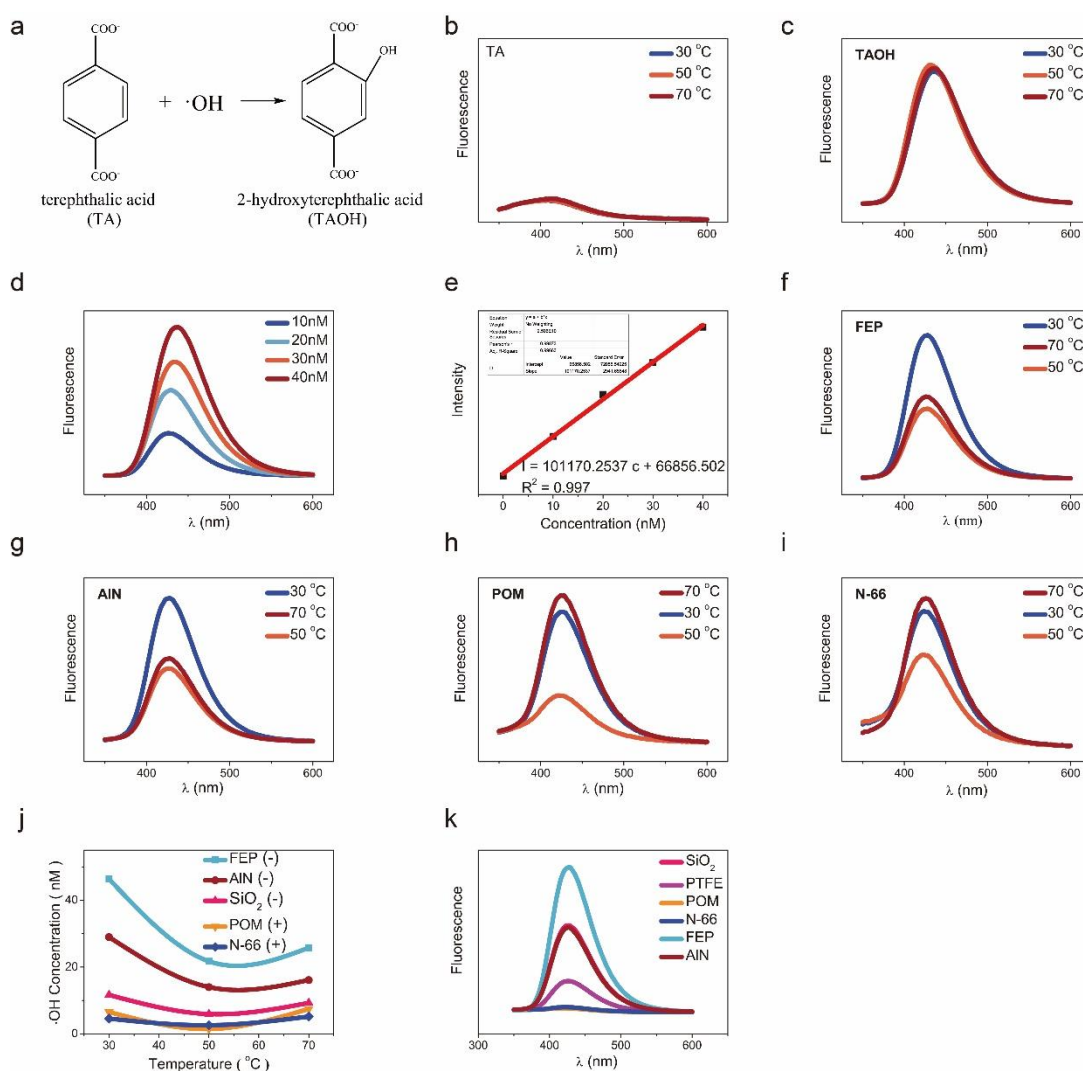
Supplementary Figure 2. Pretreatment method. The leaching efficiency by using the electrode powders with different pretreatments at 90 °C. Data are presented as mean values of three replicate data.



Supplementary Figure 3. Effect of particle size. Leaching efficiency of SiO₂ with different particle size. Data are presented as mean values of three replicate data.

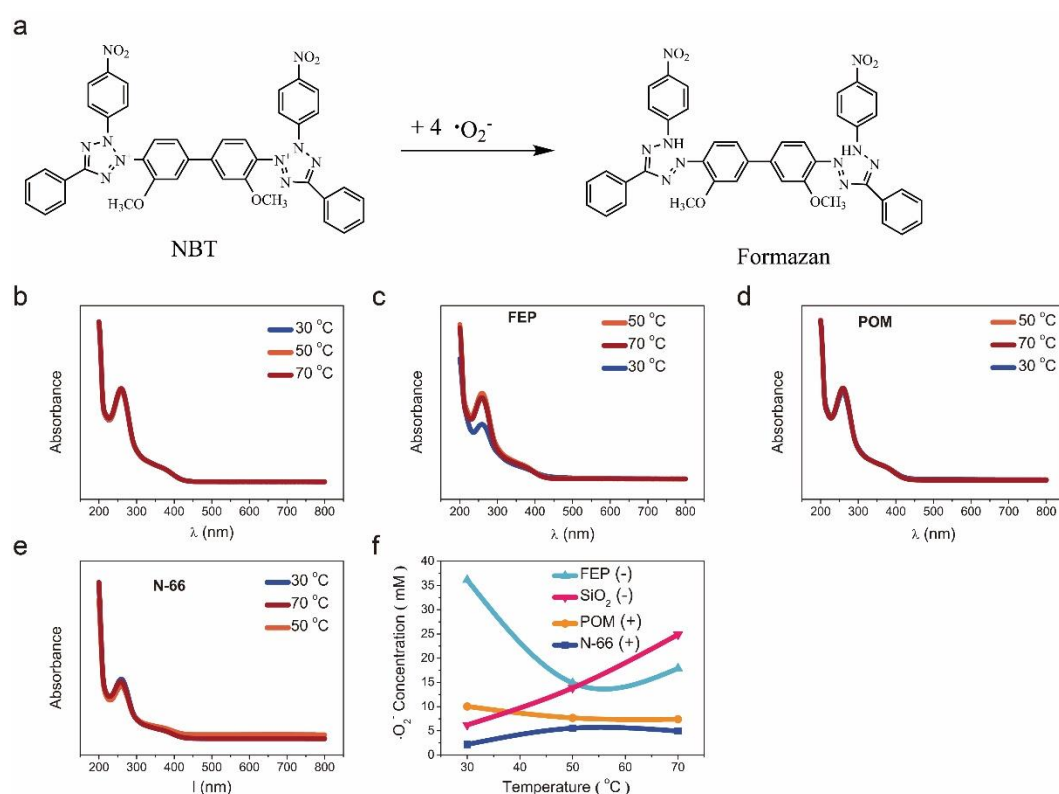


Supplementary Figure 4. Leaching efficiency of NMC powder. Data are presented as mean values of three replicate data.



Supplementary Figure 5. The ability of different materials to generate hydroxyl radicals. (a) Formation of 2-hydroxyterephthalic acid (TAOH) by the reaction of terephthalic acid (TA) with OH radical, Fluorescence spectra of (b)TA under different temperature, (c) 50 nM TAOH under different temperature shows temperature had little influence on TA and TAOH, excluding the

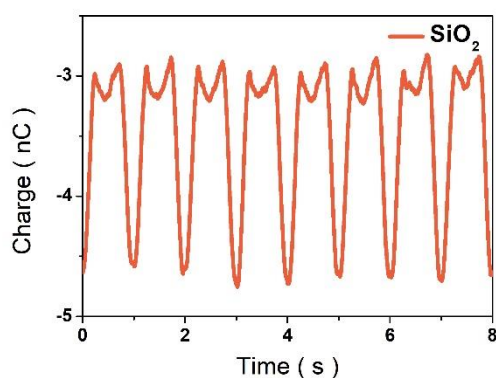
influence of temperature on reactant TA and product TAOH, (d) different concentration TAOH, (e) The linear relationship between the concentration of TAOH and the fluorescence intensity, Fluorescence spectra of TAOH in CEC for (f) FEP, (g) CEC for AlN, suggesting the content of hydroxyl radical of FEP, AlN all increased at 70°C. After liquid-solid contact, the hydroxyl radical content of negatively charged materials, such as FEP, AlN and SiO₂ at 70°C all is lower than that at 30°C, is greatly affected by temperature, Fluorescence spectra of TAOH in CEC for (h) POM, (i) N-66. The content of hydroxyl radical of positively charged materials, such as POM, N-66 at 70°C is higher than that at 30°C, and less affected by temperature. (j) The relationship between the concentration of hydroxyl radical and different materials, providing basics for the subsequent use of hydroxyl radicals generated by CEC to participate in the various catalytic reactions. (k) Fluorescence spectra of TAOH in CEC for 6 h. The intensity of SiO₂ is stronger than AlN, so the leaching efficiency of SiO₂ is higher than PTFE, AlN, POM. We do not choose FEP for leaching reaction, because FEP will undergo glass transition at 35 °C, which is not stable enough. In addition, FEP is more hydrophobic than silica, so it is not easy to disperse in solution and react with solid powder in solution.



Supplementary Figure 6. The ability of different materials to generate superoxide radical.

(a) The reaction of NBT with superoxide radical. yellow NBT changes to blue Formazan to indicate the presence of $\cdot O_2^-$, (b) UV-Vis spectra of 15 mg/L NBT under different temperature,

exclude the influence of temperature on NBT, (c) UV-Vis spectra of NBT in CEC for FEP, (d) UV-Vis spectra of NBT in CEC for POM, (e) UV-Vis spectra of NBT in CEC for N-66, showing the ability of the positively charged materials to generate superoxide radicals was less affected by temperature, (f) The relationship between the concentration of superoxide radical and different materials. Dissolved oxygen will gradually dissolve out when gradually rising temperature, and the adsorption of oxygen on silica is higher than that on FEP, which may be the reason why the ability of silica to generate superoxide free radicals is higher than that on FEP at 70°C.



Supplementary Figure 7. Electric output. Electric output of a single electrode TENG that is repeatedly immersed in DI water.

Supplementary Note 1:

Economic analysis:

Taking 1 kg spent lithium cobalt (III) oxide (LiCoO_2) powder as an example to calculate economic benefit, based on the proposed process, the recycling of LCO was economically evaluated on industrial scale. Although the technology seems to scale easily, large-scale applications allow us to be conservative in our calculations of energy/material consumption. The cost and revenues during each step are shown in Figure S19. (1\$ = 6.75 RMB, 1 kWh = 0.2 \$¹, 1 t industrial water = 0.91 \$)

1. Leaching process:

(1) Material cost:

100 L 0.2 mol/L $\text{C}_8\text{H}_6\text{O}_7 \cdot \text{H}_2\text{O}$ (0.00466 \$/g, obtained from Sinopharm Chemical Reagent Co., Ltd): 19.58 \$;

200 g SiO_2 (0.109 \$/g, obtained from Aladdin): 21.8 \$;

100 L H_2O : 0.091 \$

(2) Energy consumption:

Here, we have four ultrasound machines (10L)

Ultrasonic machine + heating: $300 \text{ W} \times 6 \text{ h} \times 4 + 400 \text{ W} \times 6 \text{ h} \times 4 = 16.8 \text{ kWh} = 3.36 \text{ $}$

$$\text{H}_2\text{O}: 5 \text{ L} * 4 * 10^{-3} * 0.91 = 0.0182 \$$$

2. Metal separation process:

(1) Material cost:

561.896 g $\text{Na}_2\text{C}_2\text{O}_4$ (0.00829 \$/g, obtained from Sinopharm Chemical Reagent Co., Ltd): 4.658 \$

saturated Na_2CO_3 (0.00474 \$/g, obtained from Sinopharm Chemical Reagent Co., Ltd): 1.766 \$

2 L H_2O : 0.00182 \$

(2) Energy consumption:

Stirring: $(0.0125 + 0.6) * 10 = 6.125 \text{ kWh} = 1.225 \$$

it takes 200 passes to process 100 L solution

Centrifugal machine: $(0.225 + 0.225) * 200 = 90 \text{ kWh} = 18 \$$

64 L H_2O : 0.058 \$

Drying oven: $800 \text{ W} * 6 \text{ h} * 2 = 9.6 \text{ kWh} = 1.92 \$$

3. SiO_2 recovery:

Centrifugal machine: $0.225 * 12 = 2.7 \text{ kWh} = 0.54 \$$

Drying oven: $800 \text{ W} * 6 \text{ h} = 4.8 \text{ kWh} = 0.96 \$$

1 L H_2O : 0.00091 \$

4. Total costs:

The total energy cost (C_E) = $3.36 \$ + 1.225 \$ + 18 \$ + 1.92 \$ + 0.54 \$ + 0.96 \$ = 26.005 \$$

The total material cost (C_M) = $19.58 \$ + 21.8 \$ + 0.0182 + 0.091 \$ + 4.658 \$ + 1.766 + 0.00182 + 0.058 + 0.00091 = 47.97 \$$

The total cost (C_4) = $C_E + C_M = 26.005 \$ + 47.97 \$ = 73.975 \$$

5. Benefits

(1) For recycle LCO, based on the concentration of Li and Co after leaching is 244.09227 mg/L and 2471.10453 mg/L as shown Fig.S18, the precipitation efficiency of Co is 78.93 %, the precipitation efficiency of Li is 53.53%.

During the precipitation process, it can obtain

605.620 g $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$: (0.110 \$/g, obtained from Sinopharm Chemical Reagent Co., Ltd)

66.618 \$

139.096 g Li_2CO_3 : (0.1175 \$/g², obtained from reference 2) : 16.343 \$

The total revenues (R_4) = $66.618 \$ + 16.343 \$ = 82.961 \$$

(2) For recycle NMC, based on the leaching efficiency of Li and Co is 94.56%, 98.39%, the assumed precipitation efficiency of Co is 78.93%, the precipitation efficiency of Li is 53.53%.

During the precipitation process, it can obtain

296.8005 g $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$: (0.110 \$/g, obtained from Sinopharm Chemical Reagent Co., Ltd) 32.65

\$

477.9335 g Li_2CO_3 : (0.1175 \$/g², obtained from reference 2) : 56.16 \$

The total revenues (R) = 56.16 \$ + 32.65 \$ = 88.81 \$

5. Profit

(1) For recycle LCO:

The profit (P) = R - C - C = 82.961 \$ - 73.975 \$ = \$8.986 /kg LCO powders

(2) For recycle NMC:

The total profit (P) = R - C - C = 88.81 \$ - 73.975 \$ = \$14.835 /kg NMC powders

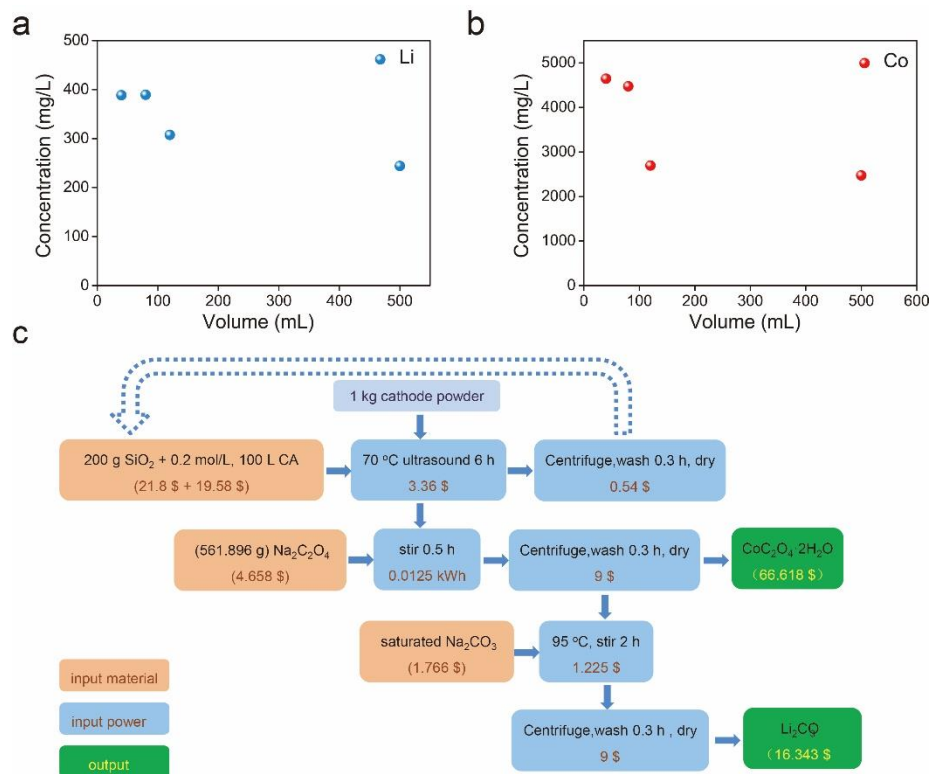
In addition, if we use Co_3O_4 as final product: $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ is burned at 650 °C, 3h³ in muffle furnace,

muffle furnace: 2.5kW * 3h * 0.2 \$ = 1.5 \$

Here, we assume that 90% of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ produces Co_3O_4 , 239.09 g Co_3O_4 : 59.8684

\$ (0.2504 \$/g, obtained from Sinopharm Chemical Reagent Co., Ltd)

The profit ($P_{\text{Co}_3\text{O}_4}$) = 76.21-73.975-1.5 = 0.735 \$



Supplementary Figure 8. Economic analysis. (a) Concentration of Li and (b) Co after leaching for different volume of CA solutions, (c) Flow of the energy consumption and chemical reagents during the CEC recovery of Co and Li proposed in this study.

Supplementary Table

Supplementary Table 1

The main metal elements contained in leaching solution		
Metal elements	Li	Co
Content (wt%)	6.029	54.87

Supplementary Table 2

Comparison of profit of various techniques for metal extraction in LIBs recycling.						
cathode	Technique	Conditions	Cost	Revenues	Profit	Refs
			(\$/kg)	(\$/kg)	(\$/kg)	
NMC	acid leaching + electrodeposition	10 M HCl, 4 g/30 mL, 2 h	2.0273	2.23	0.2	1
NMC	subcritical reaction	1.53 M acetic acid, 1.67 g/g glucose, 5.19 g/ L, 185 °C, 67 min	7.146	8.161	1.015	4
NMC	Acid leaching	1 M H ₂ SO ₄ , 0.6 M malonic acid, 5 vol. % of 30% H ₂ O ₂ , 61 g/L, 70 °C, 60 min			8.69	5
NMC	Acid leaching + CEC	80 mg SiO ₂ , 0.2M CA, 10 g/L, 70 °C, 360 min	73.975	87.405	14.835	This work
LFP	Ball mill+acid leaching+precipitati on	500 rpm, milling time:2 h, 1:1 LFP : oxalic acid, 20:1 ball : powder, 30 min	43.14	100.75	57.61	6
LFP	Oxidation leaching	10 g/L, 15 vol % H ₂ O ₂ , 50 °C, 30 min	2.07	1.776	0.295	7
LFP	Direct Recycling	0.2 M LiOH, 0.08 M CA, 90 °C	2.1	3.2	1.1	8
LCO	Acid leaching + CEC	80 mg SiO ₂ , 0.2M CA, 10 g/L, 90 °C, 360 min	73.975	82.961	8.986	This work

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