

Supplementary information

A cleaner strategy for efficient recovery of Sm_2O_3 and CoFeCu alloy from SmCo swarf based on an anodic leaching process

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Experimental

Reagents: Citric acid monohydrate ($\text{H}_3\text{cit}\cdot\text{H}_2\text{O}$, > 99%), sodium citrate dihydrate ($\text{Na}_3\text{cit}\cdot 2\text{H}_2\text{O}$, > 99%), sodium sulphate (Na_2SO_4 , > 99%), boric acid (H_3BO_3 , > 99%), sodium hydroxide (NaOH , > 99%) and sulfuric acid (H_2SO_4 , 98%) were analytical grade and purchased from Innochem Science & Technology Co., Ltd. All the chemicals were used without further purification. The water used throughout all experiments was purified through a Millipore system. Raw SmCo swarf was obtained during the cutting and grinding process of sintered SmCo magnets and supplied by Baotou Tianhe Magnetics Technology Co., Ltd. The raw SmCo swarf was washed 5 times with anhydrous ethanol until the filtrate was clear, dried at 60 °C, sieved (80 mesh) and stored in a sealed bottle for further use.

Methods

Anodic leaching of the SmCo swarf

Anodic leaching of the SmCo swarf was performed in a cylindrical glass electrochemical reactor with the diameter and height of 10.0 cm (Fig. 1). The volume of the electrolyte, initially consisting of $0.05 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$, $0.05 \text{ mol L}^{-1} \text{ Na}_3\text{cit}\cdot 2\text{H}_2\text{O}$ and $0.4 \text{ mol L}^{-1} \text{ H}_3\text{BO}_3$, was kept constant at 500 mL throughout the leaching experiment. Two stainless steel foils (Innochem Science & Technology Co., Ltd) with semi-cylindrical shape and an effective area of 10–80 cm^2 were dipped into the electrolyte as cathode, while the back of the foils were masked with an insulating tape. A mixed metal oxide (30% Ta & 70% Ir) coated titanium electrode (ϕ 4.2 cm \times 10 cm, Suzhou Suertai Industrial Technology

Co., Ltd) with a cylindrical shape was used as the dimensionally stable anode (DSA). A home-made magnetic ring coated with epoxy glue (ϕ 4.1 cm \times 5 cm) was placed inside the cylindrical anode. The outer surface of the cylindrical anode was covered by the SmCo swarf (10.0 g) with the thickness of around 3.0 mm and height of 3.0 cm. The anode, along with the magnetic ring and the SmCo swarf were immersed in the electrolyte with a depth of around 3.0 cm. The anode had a projected electrode surface area of around 40 cm². Currents ranging from 0.5 to 3.0 A (DC power, SS-6020KD, Dongguan Bufan Electronics Co., Ltd) were applied between the anode and cathode (initial current density from 12.5 to 75.0 mA cm⁻² on the anode, and 37.5 mA cm⁻² on the cathode, respectively) for 120 min to investigate the leaching rate of the SmCo swarf. Some 4 mol L⁻¹ H₂SO₄ was added to the electrolyte dropwise to keep the pH at around 3.5, monitored with a pH meter immersed in the electrolyte throughout the experiment. After the anodic leaching, the SmCo swarf was washed 3 times with deionized water and ethanol, respectively, followed by vacuum drying at 80 °C for further characterization.

Recovery of Sm₂O₃

After the anodic leaching process, certain amount of Na₂SO₄ with a molar ratio of Na₂SO₄/Sm³⁺ ranging from 1/1 to 4/1 was added to the electrolyte solution, followed by heating at 80 °C for 180 min to selectively precipitate Sm³⁺. While the solution was warm, the precipitate was obtained by filtration and washed thoroughly with deionized water, followed by drying at 105 °C for 120 min. Afterwards, the dried precipitate was put into a

NaOH solution with a solid-liquid ratio of 1:6 and a molar ratio of NaOH/NaSm(SO₄)₂ of 4/1. The resulting mixture was magnetically stirred at the room temperature for 60 min, followed by filtration, washing with deionized water for 3 times and drying at 105 °C for 120 min. The dried powder was calcinated in a muffle furnace (QSH-1200M-2020T, Shanghai Alarge Furnace Co., Ltd) for 120 min at 800 °C in a ceramic crucible. After cooling down, the final product was ground in an agate mortar for further use.

Recycling of the electrolyte

Continuous anodic leaching of the SmCo swarf for 20 h under the conditions of the applied current of 3.0 A (the corresponding anodic and cathodic current density of 75.0 and 37.5 mA cm⁻², respectively) and maintained pH of around 3.5 was carried out. The solution after the recovery of Sm was sent back to the electrolysis cell for recycling. This recycling process was repeated 10 times to investigate the composition change of the electrolyte, the mass of dissolved SmCo swarf and deposited CoFeCu alloy, acid consumption, base consumption and energy consumption associated with each cycle, in order to provide useful references for potential scaling up.

Analytical methods

The chemical composition of the solid samples that were thoroughly dissolved in dilute hydrochloric acid in advance and the liquid samples were measured with inductively coupled plasma optical emission spectrometry (ICP-OES, ICPE-9800, Shimadzu, Japan). X-ray diffraction (XRD, PANalytical, Netherlands) was used for phase analyses of

samples. The morphologies of samples were observed by scanning electron microscope (SEM, S-4800, Hitach, Japan).

Calculations

The formation rate of H⁺ during OER process

The formation rate of H⁺ ($\gamma(\text{H}^+)$) via OER (reaction 1) was calculated based on Faraday's law without considering H⁺ mass transfer:

$$\gamma(\text{H}^+) = \frac{c(\text{H}^+)}{t} = \frac{j}{d * F} \#(i)$$

where $c(\text{H}^+)$ is the H⁺ concentration, mol L⁻¹; t is the time of the electrolysis, s; j is the applied current density, A m⁻²; d is the perpendicular distance to the surface of DSA anode, m; F is the Faraday constant, 96485.33 C mol⁻¹. Clearly, $\gamma(\text{H}^+)$ increases with increasing applied current density under a constant d . In the case of $j = 10 \text{ mA m}^{-2}$, $d = 0.1$ and $1 \text{ }\mu\text{m}$, then $\gamma(\text{H}^+)$ was calculated to be 10.36 and 1.03 mol L⁻¹ s⁻¹, respectively.

The theoretical volume of acid usage

The added volume of acid to maintain the pH of the electrolyte around 3.5 can be theoretically calculated by considering two processes: the release of H⁺ into the electrolyte via OER from the anode and the use of H⁺ via HER from the cathode. When current is applied to the anode, the SmCo swarf is electrochemically dissolved, consuming a part of the current. Consequently, the remaining current can be attributed to the OER process,

which results in the release of H^+ into the electrolyte. The amount of released H^+ ($n_A(H^+)$) from the anode can be calculated according to Faraday's law:¹

$$n_A(H^+) = \frac{I * t}{F} - m_{SmCo} * N_{SmCo} \#(ii)$$

where I is the applied current, A; F is the Faraday constant, 96485.33 C mol⁻¹; t is the time of the electrolysis, s; m_{SmCo} is the observed mass loss of the SmCo swarf, g; and N_{SmCo} is the total number of equivalents obtained from dissolving a unit mass of the SmCo swarf:²

$$N_{SmCo} = \sum \frac{f_i * n_i}{a_i} \#(iii)$$

where f_i , n_i , and a_i are the mass fraction, the number of electrons exchanged, and the atomic weight, respectively, of the i th element of the SmCo swarf.

Similarly, the cathodic current was divided with a portion being utilized for the deposition of CoFeCu alloy and the remaining portion being consumed by HER. The amount of consumed H^+ ($n_c(H^+)$) on the cathode can be calculated as:

$$n_c(H^+) = \frac{I * t}{F} - m_{CoFeCu} * N_{CoFeCu} \#(iv)$$

where m_{CoFeCu} is the mass of the deposited CoFeCu alloy, g; and N_{CoFeCu} is the total number of equivalents obtained from a unit mass of the CoFeCu alloy:

$$N_{CoFeCu} = \sum \frac{f'_i * n'_i}{a'_i} \#(v)$$

where f_i' , n_i' , and a_i' are the mass fraction, the number of electrons exchanged, and the atomic weight, respectively, of the i th element of the CoFeCu alloy. Therefore, the theoretical acid usage (V) can be calculated as:

$$4 * c_{H_2SO_4} * V = n_C(H^+) - n_A(H^+) = m_{SmCo} * N_{SmCo} - m_{CoFeCu} * N_{CoFeCu}$$

This equation can be expressed as:

$$V = \frac{m_{SmCo} * N_{SmCo} - m_{CoFeCu} * N_{CoFeCu}}{4 * c_{H_2SO_4}} \#(vi)$$

where $c_{H_2SO_4}$ is the concentration of H_2SO_4 , mol L^{-1} .

Sm recovery

Sm recovery is calculated as:

$$\eta_{Sm} = \frac{m_p}{m_D} \times 100 (\%) \#(vii)$$

Where m_p is the total mass of Sm in the sulphate double salts, g; m_D is the total mass of Sm in the dissolved SmCo swarf, g.

Energy consumption

The energy consumption, E (kWh kg^{-1}) of the electrolysis process is calculated as:

$$E = \frac{U * I * t}{3600 * m_{SmCo}} \#(viii)$$

Where U is the voltage measured between the anode and cathode, V; I is the applied

current, A; t is the duration of the electrolysis, s; and m_{SmCo} is the amount of the dissolved SmCo swarf, kg. Thus the reported values are kilowatt hours per kilogram of the SmCo swarf.

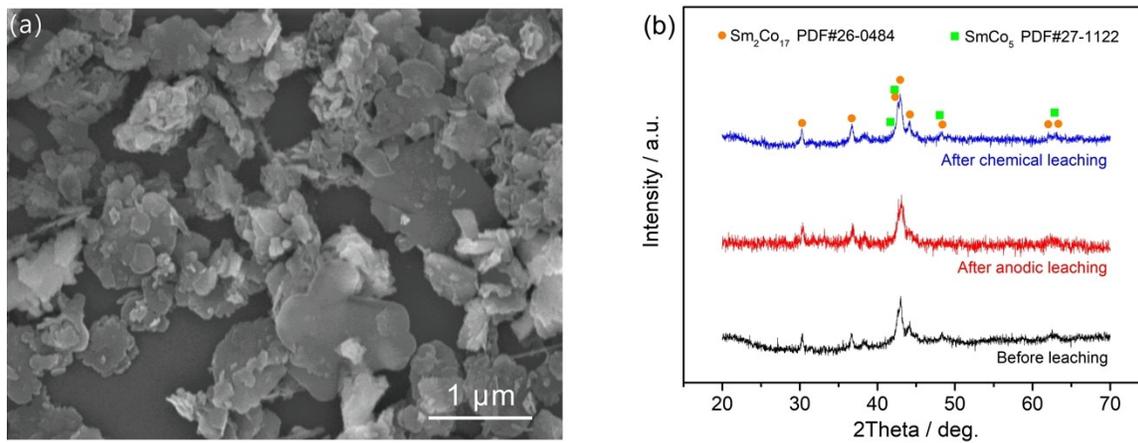


Fig. S1 (a) SEM image of the SmCo swarf after pretreatment. (b) XRD patterns of the SmCo swarf before leaching, after electrochemical leaching and after chemical leaching.

Table S1. Elemental composition of the SmCo sludge in wt.%.

Element	Sm	Co	Fe	Cu	Others
Content (wt.%)	24.2	46.9	16.4	5.3	7.2

Table S2 Energy consumption of the electrolysis step with (a) and without (b) placing a filter paper between the DSA anode and the SmCo swarf at the current density from 12.5 to 75.0 mA cm⁻² for 120 min.

Current density (mA cm ⁻²)	(a) Energy consumption (kWh kg ⁻¹)	(b) Energy consumption (kWh kg ⁻¹)
12.5	6.37	5.11
25.0	7.94	6.38
37.5	8.99	7.96
50.0	10.45	9.03
75.0	12.61	10.96

Table S3 Acid consumption of different time periods during the electrolysis of the SmCo sludge.

Time periods	0–4 h	4–8 h	8–12 h	12–16 h	16–20 h
Acid consumption (mL)	22.5	5.0	2.1	1.5	1.1

Table S4 The content of metal ions in the leachate before and after the removal of Sm³⁺.

Elements	Before the removal of Sm ³⁺ (mg mL ⁻¹)	After the removal of Sm ³⁺ (mg mL ⁻¹)
Sm ³⁺	23.4	0.20
Co ²⁺	5.0	4.9
Fe ²⁺	1.5	1.45
Cu ²⁺	0.15	0.15

Table S5 The composition of the electrolyte after electrolysis over the 10 recycling cycles.

Elements (mg mL ⁻¹)	Sm ³⁺	Co ²⁺	Fe ²⁺	Cu ²⁺
Fresh	23.4	5.0	1.5	0.15
1st	24.55	5.18	1.44	0.19
2nd	24.74	5.11	1.59	0.23
3rd	24.33	5.09	1.55	0.17
4th	25.07	5.29	1.67	0.23
5th	24.61	5.17	1.62	0.22
6th	25.45	5.67	1.87	0.23
7th	24.39	5.14	1.59	0.21
8th	23.97	4.98	1.54	0.2
9th	25.17	5.33	1.75	0.24
10th	24.55	5.12	1.67	0.22

References

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