

Supplementary information

A novel electrochemical recycling strategy for NdFeB swarf with minimized chemical consumption

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Experimental

Reagents: Sodium sulphate (Na_2SO_4 , > 99%), sodium hydroxide (NaOH , > 99%) and sulphuric 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. NdFeB swarf was supplied by Inner Mongolia Ke Rui Xing Yun Science & Technology incubation base Co., Ltd. and pretreated by removing the grinding oil in advance as reported in our previous publication.¹

Methods

Anodic leaching of NdFeB swarf

The leaching experiments were performed in a three-chamber electrolysis cell at room temperature. The anodic chamber (4 cm × 4 cm × 5 cm, 80 mL), intermediate chamber (1 cm × 4 cm × 5 cm, 20 mL) and cathodic chamber (4 cm × 4 cm × 5 cm, 80 mL) were separated by an anion exchange membrane (AEM, AEM8040, HuamoTech, China) and a cation exchange membrane (CEM, GSCEM360, HuamoTech, China). A mixed metal oxide (30% Ta & 70% Ir) coated titanium electrode (2 cm × 2 cm, Suzhou Suertai Industrial Technology Co., Ltd, China) was used as the dimensionally stable anode (DSA) and a stainless-steel foil (2 cm × 2 cm, Innochem Science & Technology Co., Ltd, China) was used as the cathode. The DSA surface was coated by NdFeB swarf (1.0 g) with the thickness of ~1.5 mm magnetically. 0.1 mol L⁻¹ Na₂SO₄ solution and 0.1 mol L⁻¹ NaOH solution with the volume of 60 mL was used as the anolyte and catholyte, respectively. The intermediate chamber was filled with saturated Na₂SO₄ solution (20 mL). The anolyte was stirred constantly at 300 rpm using a magnetic stirrer. All experiments utilized a direct current power supply (SS-6020KD, Dongguan Bufan Electronics Co., Ltd., China). Prior to anodic leaching, a current of 0.2 A was applied between the bare anode (without NdFeB

swarf coating, resistance of 3~5 Ω) and cathode for 5 min to adjust the pH of the anolyte to approximately 2.0, preventing the hydrolysis of Fe^{3+} during the electrolysis process. Subsequently, currents ranging from 0 to 0.4 A were applied between the anode (with NdFeB swarf coating, resistance of 7~10 Ω) and cathode (initial current density of 0 to 100 mA cm^{-2} on both the anode and cathode) for 60 min to investigate the leaching efficiency, pH changes in the anodic chamber and the corresponding energy consumption.

Linear sweep voltammetry study

The electrochemical dissolution process of NdFeB swarf was evaluated in a 60 mL aqueous bath with a composition identical to that of the anolyte, containing a 0.1 mol L^{-1} Na_2SO_4 solution at a pH of 2.0. Linear sweep voltammetry (LSV) was conducted in a single-chamber electrolysis cell. The working electrodes included a bare DSA (7 mm \times 7 mm) and the DSA (7 mm \times 7 mm) coated with NdFeB swarf (0.125 g). A Pt plate (2 cm \times 2 cm) served as the counter electrode. A Ag/AgCl (3 mol L^{-1} KCl) electrode was used as the reference electrode.

Recovery of REEs

After electrolysis for 30 h, Na_2SO_4 was added to the anolyte at a molar ratio of 2:1 (Na_2SO_4 to REEs), followed by heating at 80 $^\circ\text{C}$ for 2 h to selectively precipitate REEs. While the solution was warm, the precipitates were obtained by filtration and thoroughly washed with water. After drying at 105 $^\circ\text{C}$ for 12 h, the recovered powder was then treated with the NaOH solution from the catholyte at a molar ratio of 4:1 (NaOH to REEs) at room temperature for 60 min. After filtration, the residue was washed with deionized water for 5 times and dried at 105 $^\circ\text{C}$ for 2 h. The obtained powder was calcinated at 600 $^\circ\text{C}$ for 2 h to produce the final products. The filtrate containing unreacted NaOH was collected and used in the Fe^{3+} precipitation step.

Recovery of Fe

Following the filtration of the REE precipitates, the filtrate was collected for Fe recovery. First, the filtrate was returned to the anodic chamber for the electrochemical oxidation of Fe^{2+} to Fe^{3+} . A constant current of 0.2 A was applied between a platinized titanium (Ti/Pt, 4 cm \times 5 cm, Suzhou Suertai Industrial Technology Co., Ltd, China) anode and a stainless-steel foil cathode (4 cm \times 5 cm, Innochem Science & Technology Co., Ltd, China) for 12 h. Subsequently, the filtrate containing unreacted NaOH was collected from the $\text{NaRE}(\text{SO}_4)_2$ transformation step and added to the electro-oxidized solution dropwise. Afterwards, NaOH solution collected from the cathodic chamber was added until the pH was raised to approximately 4.2. After 30 min, a sludgy solution was observed and filtered. The solid sample was washed and dried for further characterization, while the filtrate was collected and recycled back to the electrolysis cell for the next electrolysis batch.

Recycling of the electrolyte

The filtered solution after the recovery of Fe was collected. 20 mL of the filtered solution was diluted with deionized water to a total volume of 60 mL and returned to the anodic chamber for recycling. The remaining 95 mL of filtered solution was stored as a supplement for the intermediate chamber. Continuous anodic leaching of NdFeB swarf was performed for 30 h with an applied current of 0.2 A (the corresponding anodic and cathodic current density of 50 mA cm^{-2} , respectively). This recycling process was repeated 10 times to investigate the mass of dissolved NdFeB swarf, REE recovery, NaOH consumption and energy consumption associated with each cycle, in order to provide useful references for potential scaling up.

Analytical methods

The concentration of metal ions present in the solution was analyzed by optical emission spectrometry with inductively coupled plasma (ICP-OES, ICPE-9800, Shimadzu, Japan). The pH of solution was measured by a pH meter (Leici, PHBJ-260, China). The concentrations of total dissolved Fe and Fe^{2+} were determined using the 1,10-

phenanthroline method through an ultraviolet-visible (UV-Vis) spectrophotometry (U-3900, Hitachi, Japan) at a wavelength of 510 nm for the Fe-phenanthroline complexes. The phase composition of solid samples was determined with an X-ray diffractometer (XRD, PANalytical, Netherlands) using Cu-K_{α1} radiation ($\lambda = 1.5406 \text{ \AA}$). The morphology of solid samples was measured by a field emission-scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS).

Calculations

1) The total leaching efficiency (η_L) for the dissolution of the NdFeB swarf was calculated as follows:

$$\eta_L = \frac{m_0}{m_t} \times 100 (\%) \#(i)$$

where m_0 and m_t are the observed and theoretical mass loss, respectively. The observed mass loss was calculated as the mass change of NdFeB swarf before and after electrochemical leaching.

The theoretical mass loss for the NdFeB swarf (m_t) was calculated as:

$$m_t = \frac{I * t}{F * N_{EQ}} \#(ii)$$

where I is the applied current, A; F is the Faraday constant, 96485.33 C/mol; t is the time of the electrolysis, s; and N_{EQ} is the total number of equivalents obtained from dissolving a unit mass of the alloy:

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

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 alloying element.

2) The REEs recovery (γ_{REEs}) is calculated as:

$$\gamma_{REEs} = \frac{m_p}{m_D} \times 100 (\%) \#(iv)$$

where m_p is the total mass of the REEs in the RE sulfate double salts, g; m_D is the total mass of the REEs in the leached NdFeB swarf, g.

3) The net consumption of NaOH (m_{NaOH} , kg/kg) is calculated as:

$$m_{NaOH} = (m_{NaOH, RE} + m_{NaOH, Fe} - m_{NaOH, c}) / m_0 \#(v)$$

where $m_{NaOH, RE}$ is the amount of NaOH consumed by converting RE sulphate double salts to $RE(OH)_3$, kg; $m_{NaOH, Fe}$ is the amount of NaOH consumed by Fe removal process, kg; $m_{NaOH, c}$ is the amount of NaOH generated in the cathodic chamber.

4) The total energy consumption, E (kWh/kg) is calculated as:

$$E = \frac{(U_{pre} * t_{pre} + U_L * t_L + U_O * t_O) * I}{3600 * m_0} \#(vi)$$

where U_{pre} , U_L and U_O is the voltage measured between the anode and the cathode during the pre-electrolysis process, anodic leaching process and Fe^{2+} electro-oxidation process, respectively, V; t_{pre} , t_L and t_O is the duration of the pre-electrolysis process, anodic leaching process and Fe^{2+} electro-oxidation process, respectively, s; I is the applied current, A; and m_0 is the amount of the NdFeB swarf dissolved, kg. Thus the reported values are kilowatt hours per kilogram of the NdFeB swarf.

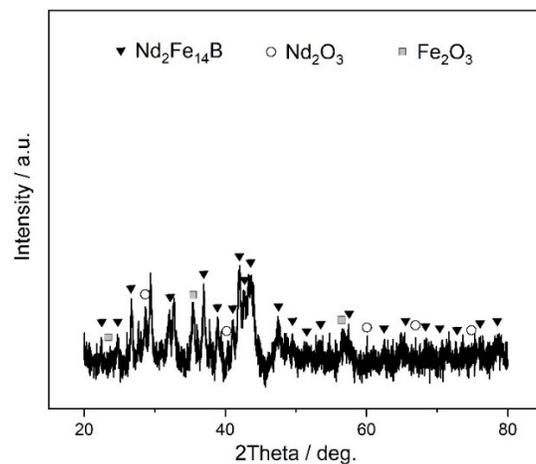


Fig. S1 XRD pattern of the NdFeB swarf after removing the grinding oil.

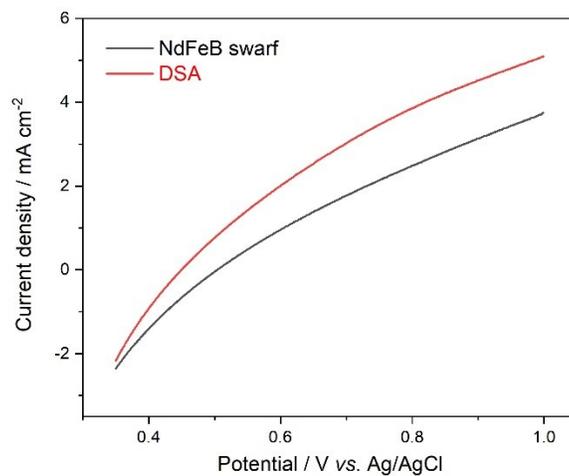


Fig. S2 LSV curves of the DSA and the DSA coated with NdFeB swarf in the anolyte at a scan rate of 20 mV s^{-1} .

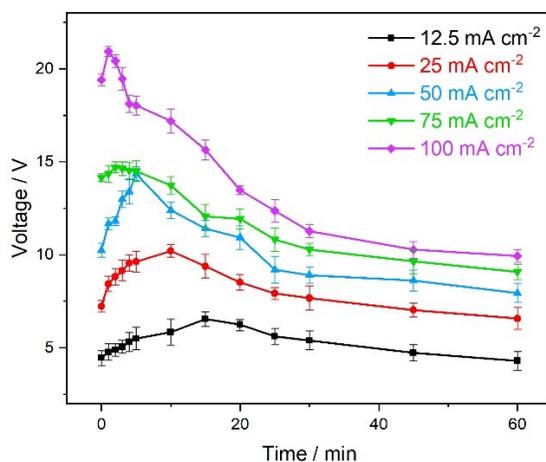


Fig. S3 Effect of current density on the total cell voltage between the anode and cathode.

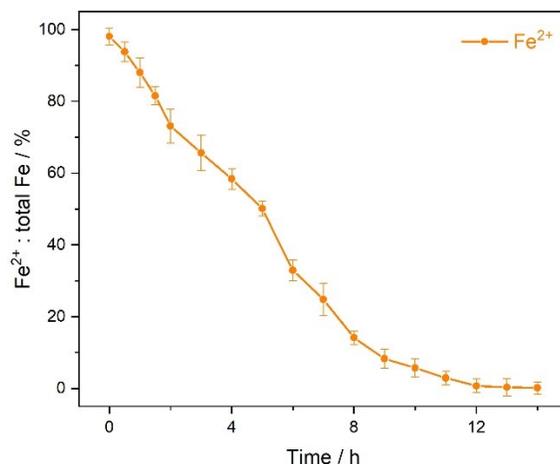


Fig. S4 Influence of electro-oxidation time on the Fe²⁺ content in the anolyte with the applied current of 0.2 A.

Table S1. Elemental composition of the NdFeB swarf in wt.%.

Element	Content (wt.%)	Element	Content (wt.%)
Fe	67.82	Co	1.29
Nd	16.83	Cu	0.28
Pr	9.51	Al	0.17
Ga	0.58	B	1.13
Dy	0.88	Others	1.51

Table S2 Effect of current density on the NdFeB swarf dissolution, total leaching efficiency and energy consumption of the anodic leaching step.

Anodic current density (mA/cm ²)	Mass of magnet dissolved (g)	Total leaching efficiency (%)	Energy consumption (kWh/kg)
12.5	0.056	99.51	4.71
25	0.111	98.93	7.63
50	0.223	98.99	9.92
75	0.331	98.11	11.46
100	0.428	95.23	14.85

References

1. X. Xu, X. Jia, P. Jing, Y. Zhang, J. Cui, K. Zuzek, S. Saso, B. Liu and J. Zhang, *J. Rare Earths*, 2024, DOI:10.1016/j.jre.2024.02.001.