Electronic Supplementary Information

Extraction and recovery of Co²⁺ ions from spent lithium-ion batteries using

hierarchal mesosponge γ -Al₂O₃ monolith extractors

H. Gomaa^a, M. A. Shenashen^{a,*}, H. Yamaguchi^a, A. S. Alamoudi^b, S. A. El-Safty^{a, c,}

^a National Institute for Materials Science (NIMS), Research Center for Functional Materials, 1-2-1 Sengen, Tsukuba-shi, Ibaraki-ken, 305-0047, Japan.

^b Desalination Technologies Research Institute (DTRI), P.O. Box 8328, Al-Jubail, 31951 Saudi Arabia

^c Faculty of Engineering and Advanced Manufacturing, University of Sunderland, Sunderland SR6 0DD, UK.

*E-mail: <u>sherif.elsafty@nims.go.jp</u>; <u>sherif.el-safty@sunderland.ac.uk</u> (S. A. El-Safty); <u>SHENASHEN.Mohameda@nims.go.jp</u> (M. A. Shenashen).

1. Fabrication of chelating agents (colorants)

1.1. Synthesis of (E)-4-((2-mercaptophenyl)diazenyl)-2-nitrosonaphthalen-1-ol (MPDN)

The MPDN was chemically synthesized by standard diazonium chemistry. (18.77 g, 0.15 mol) of O-aminothiophenol was dissolved uniformly in a 50 mL of 1M HCl and stirred for 1h at 0-3°C. An ice-chilled 50mL solution of sodium nitrite (10.35 g, 0.15mol) was then added drop-by-drop to the above mixture under continuous stirring for 2hs at 0-3°C. The excess nitrous acid was tested using starch–iodide paper and quenched with urea. (25.95 g, 0.15 mol) of 2-nitroso-1-naphathol was dissolved in 50mL of a 0.25% NaOH at 0-3°C. The coupling reaction was performed by adding of 2-nitroso-1-naphathol solution to the diazonium solution at 0–3°C. The reaction mixture was stirred under freezing conditions overnight and the product was observed as a yellow precipitate in the mother liquor. The solid product was filtered off and washed via hot and cold milli-Q H₂O, and then recrystallized by 70% ethanol under vacuum air at room temperature.



1.2. Synthesis of (E)-5-((1,3,4-thiadiazol-2-yl)diazenyl)benzene-1,3-diol (TDDB)

Under the same condition of synthesis of MPDN, the chromophore TDDB was synthesized by dissolving of (10.11 g, 0.10 mol) of 2-amino-1,3,4-thiadiazole in a 50mL of 1M HCl with stirring for 1h at 0-3°C. (6.9 g, 0.10mol) of sodium nitrite was then added dropwise to produce the diazonium salt. In the meantime, (11.01 g, 0.10 mol) of resorcinol was dissolved in 50mL of a 0.25% NaOH in cold conditions for 2hs and then added to the diazonium solution at 0–3°C. The yellow precipitate was continuous stirred at 0–3°C for 12 hours. The yellow product was filtered off and washed via hot and cold milli-Q H₂O, and then recrystallized by 70% ethanol under vacuum air at room temperature.







Scheme S1 Schematic design of real extraction protocol of Co^{2+} ions from the spent and scraped LIBs as follows: (A) leaching process of SLIBs and (B) extraction process of Co^{2+} ions through successive steps such as crushing of SLIBs, leaching, filtration, Fe³⁺ separation, stirring with IEs, stripping with 0.2M HCl and recycle of regenerated IEs.

3. <u>Characterization of hierarchical mesoporous γ -Al₂O₃ monolithic carriers and ionextractors (IEs)</u>

Table S1. Structure parameters such as the specific surface area, porosity and pore volume of γ -Al₂O₃, IE-1, IE-2, IE-1/Co²⁺ and IE-2/Co²⁺ solids.

Sample name	S_{BET} , m ² /g	Pore size, nm	Pore volume, cm ³ /g
γ-Al ₂ O ₃	419	13.9	1.3115
IE-1	395	12.1	0.9586
IE-2	399	12.2	0.9598
IE-1/Co ²⁺	330	12.05	0.8503
IE-2/Co ²⁺	332	12.1	0.8515



Fig. S1 SEM-EDX mapping of Al₂O₃ (A), IE-1(B), IE-2 (C), IE-1/Co²⁺ (D), and IE-2/Co²⁺ (E).



Fig. S2 FT-IR spectra of of γ -Al₂O₃, IE-1 and IE-2.



Fig. S3 TG analysis of γ -Al₂O₃, IE-1 and IE-2.

4. <u>Colorimetric determination of Co²⁺ ions</u>



Fig. S4 (A) The spectral absorbance of $Co^{2+}/IEs-1$ and 2 complexes at wide range of pH 1~10 (conditions: λ_{max} = 370 and 410 nm, 20mg of IEs-1 and 2 stirred with 20mL of Co²⁺solution [1ppm] for 15 min at 25±2°C). (B) The effect of spectrophotometrically response time on the detection process of Co²⁺ ions using IEs-1 and 2 at pH 5 and 4, respectively. (C) The effect of contact time on the uptake efficiency of Co²⁺ ions using IEs-1 and 2 at pH 5 and 4, respectively (ICP-MS data).

5. Quantitative measurements of Co²⁺ ion concentrations



Fig. S5 Quantitative measurements using a wide range of standard Co²⁺ ion concentrations under the optimum pH conditions using IE-1 (A) and IE-2 (B) including the calibration curves of IE-1 and IE-2 at pH 5 and 4, and wavelength λ_{max} = 370 and 410 nm, respectively. The LOD values of Co²⁺ ions were determined from the linear part of the calibration curve (Inserts), where the LOD values of IE-1 and IE-2 are 4.5×10^{-8} and 3.05×10^{-8} M (i.e., equivalent to 2.7 and 1.8 ppb or µg/L), respectively.

6. <u>Representative Co²⁺-selective-profile during the addition of anions</u>



Fig. S6 Representative selective-profile of [2ppm] Co^{2+} optical-adsorption/extraction among other competitive anions using IE-1 and IE-2. The optical signalling of IEs in the presence of interfering anionic species were recorded at wavelength λ_{max} = 370 and 410 nm and pH 5 and 4, respectively. Results indicated the high selective-extraction of Co^{2+} ions and the interfering anions. This finding indicates that no effect of the anions to be interfered during the Co^{2+} extraction process in SLIBs.

7. <u>Co²⁺ ion removal/adsorption isotherms</u>



Fig. S7 (A) Effect of initial Co^{2+} ion concentration [0.01-500ppm] on the amount of adsorbed/extracted Co^{2+} under the optimum adsorption conditions. (B) The linear form of the Langmuir isotherm model using IEs-1 and 2. (C) Linear form of the Freundlich isotherm model using IEs 1 and 2. (stirring-time of 30min; 20 mg of IEs-1 and 2; 20mL of Co^{2+} solution; pH 5 and 4 and temperature of $25\pm2^{\circ}C$).

8. Evaluation of the kinetic adsorption mechanism of Co²⁺ ions



Fig. S8 (A, B) Linear form of pseudo-first and (C, D) second order models of IEs-1 and 2 (where, 20 mg of IEs-1 and 2; 20mL of Co^{2+} solution; pH 5 and 4 and temperature of $25\pm2^{\circ}C$).

9. Evaluation of Co²⁺ ion-releasing experiment



Fig. S9 (A) Effect of HCl eluent /striping agent concentration (M) and (B) stripping time (minutes) on the recovery/releasing efficiency of adsorbed Co^{2+} ions from $[Co^{2+}/IE-1]^{n+}$ and $[Co^{2+}/IE-2]^{n+}$ solids.