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Selective extraction of nickel from acid leach solution of spent lithium-ion batteries using synergistic solvent extraction system consisting of TFCA-4PC

Li-han ZHANG[1,2], Zuo-ying CAO[1,2], Gui-qing ZHANG[1,2], Qing-gang LI[1,2],
Ming-yu WANG[1,2], Wen-juan GUAN[1,2], Sheng-xi WU[1,2], Qi DENG[3,4]

1. School of Metallurgy and Environment, Central South University, Changsha 410083, China;
2. Key Laboratory of Metallurgical Separation Science and Engineering in Nonferrous Industry, Central South University, Changsha 410083, China;
3. State Key Laboratory of Utilization of Woody Oil Resource, Hunan Academy of Forestry, Changsha 410018, China;
4. Hunan Provincial Key Laboratory of Oils and Fats Molecular Structure and Function, Hunan Academy of Forestry, Changsha 410018, China

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Abstract: A synergistic solvent extraction (SSX) system consisting of tung oil-based carboxylic acid (TFCA) and isonicotinic acid ester (4PC) was proposed to selectively extract Ni over Li and Mg from acid leach solutions of spent lithium-ion batteries (LIBs). The SSX system indicates a synergistic effect of Ni which can be mainly attributed to the multiple chelate ring structure formed between TFCA and Ni, therefore resulting in strong selectivity of Ni. With optimal conditions, the extraction of Ni reaches 97.3% in a single stage, while the extractions of Mg and Li are nil and 2.29%, respectively. Further, after scrubbing with 300 mg/L $NiSO_4$, the loaded organic solution is stripped using 0.2 mol/L H_2SO_4. The strip liquor containing 11.52 g/L Ni and only less than 6 mg/L Li is obtained.

Key words: tung oil; carboxylic acid extractant; synergistic solvent extraction; nickel; extraction mechanism

1 Introduction

The production and sales of electric vehicles (EVs) have constantly increased in recent years, driving the rapid development of the lithium-ion battery (LIB) industry [1−3]. However, the average service life of LIBs is only 3−5 years. Considering the dramatic increase in power battery production, massive amounts of scrapped LIBs are expected to be generated in the future years [4]. Without appropriate treatment, spent LIBs with hazardous electrolytes and heavy metal elements can severely damage the ecological environment and pose a significant potential threat to human health [5]. However, spent LIB cathodes contain large amounts of critical metals (Ni: 5%−12%, Co: 5%−20%, Mn: 7%−10%, and Li: 2%−5%), and their contents are much higher than those in their primary ores. Recycling these valuable metals can fill more than 40% of the gap between supply and burgeoning demand [6−8].

In the extensively adopted critical metal recovery process, spent LIBs undergo discharging, crushing, screening, acid leaching, and release of Ni^{2+}, Co^{2+}, Mn^{2+}, Li^{+} and other valuable metal cations into aqueous solutions [9]. These metal cations are then precipitated and extracted from the leach solutions to obtain compounds of Ni, Co, Mn, and Li [10,11]. Owing to their high selectivity for

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Corresponding author: Zuo-ying CAO, Tel: +86-13508479388, E-mail: caozying@sina.com

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Mn and Co, organophosphorus acid extractants (Cyanex272, PC-88A, and D2EHPA) are widely employed for extracting Mn and Co over Ni and Li [12−15]. However, owing to their insensitivity to single target cations, extensive co-extraction occurs in the individual metal element separation process. The extraction of Ni from Li involves numerous scrubbing stages, large investment, and large operational costs, leading to significant waste of valuable metal resources and imposing an operational burden of the subsequent recovery stages [16−18]. This highlights the importance of developing novel synergistic solvent extraction (SSX) system with better selectivity and higher loading capacity to achieve green and efficient recycling of critical metals from spent LIBs.

Carboxylic acid extractants are expected to extract Ni over Li. However, because of weak acidity and weak binding to metal cations, a relatively high equilibrium pH is required for extraction of transition metals [19,20]. The high equilibrium pH not only indicates higher alkali consumption in practical industrial production, but also poses a limitation on the application of carboxylic acid extractants in solutions with high metal cation concentrations. From the perspective of designing extractant structures, it is a good alternative to select a suitable skeleton and redesign the number and sites of functional groups on carboxylic acid extractants for improving the selectivity and loading capacity of Ni.

Tung oil is an ideal matrix compound for modifying carboxylic acid extractants. As a bulk renewable biological material, tung oil is environmentally friendly and cheap [21,22]. The ester group and conjugated olefin structure in its main fatty acid components endow it with excellent chemical activity that can trigger a series of chemical reactions, including ammonolysis, epoxidation, and Diels−Alder reactions [23−26].

In our previous studies, multifunctional extractants were synthesized and novel SSX systems were constructed to selectively extract metal ions from complex aqueous solutions [27,28]. In this study, a novel tung oil-based extractant with a chelating carboxylic acid group was synthesized. The chemical structure of the synthesized product, tung oil-based carboxylic acid (TFCA), was characterized by Fourier transform infrared (FT-IR) spectroscopy and high-resolution mass spectrometry (HRMS). The extraction performance of the novel SSX system (TFCA and 4PC) was investigated systematically. To clarify coordination modes of the Ni extraction complex, the reaction mechanism was investigated using the slope method and FT-IR spectroscopy.

2 Experimental

2.1 Materials

The tung oil used in this study was provided by Chenzhou Guosheng Bioenergy Technology Co., Ltd. (China). The synergistic extractant, 4PC, was provided by Hunan Hongbang Material Technology Co., Ltd. (China). Sulfonated kerosene and isooctanol (99% in purity), provided by Shanghai Utop Chemical Technology Co., Ltd. (China), were used as the diluent and modifier, respectively. The sulfuric acid leachate of spent LIBs (NCM cathode material) was provided by Guangdong Fangyuan New Materials Group Co., Ltd. (China). All other reagents used in this study were of analytical grade.

2.2 Synthesis of methyl ester of tung oil fatty acids

Tung oil (100 g, 0.11 mol), anhydrous methanol (40 g, 1.2 mol), and KOH (1 g, 0.018 mol) were mixed in a 500 mL round bottom flask, stirred, and reacted in a water bath at 60 °C for 4 h. After the reaction was completed, the reaction mixture was distilled to remove excess methanol, and the components were separated using a separatory funnel to obtain upper layer fatty acid methyl esters (TME). The crude product was scrubbed three times with de-ionized water until the washing water was neutral. The residual water in the organic phase was removed using a rotary evaporator under vacuum at 95−99 °C to obtain clear and transparent light yellow TME (92.6% yield).

2.3 Synthesis and purification of TFCA

TME (100 g, 0.34 mol), fumaric acid (40 g, 0.34 mol), and methyl valerate (40 g) were added to a flask, stirred, and refluxed in an oil bath at 135 °C for 30 h in a nitrogen atmosphere. After the reflux solvent, methyl valerate, was removed using a rotary evaporator, excess fumaric acid was precipitated by adding dichloromethane to the residue and removed by filtration. Then, crude TFCA was further purified to remove other fatty acid methyl esters that were not involved in the reaction. Due to the polarity difference between TFCA and impurities, fatty acid methyl esters were extracted with petroleum ether, a low-polarity solvent. The highly pure yellow viscous TFCA was obtained by removing the residual petroleum ether using a rotary evaporator under vacuum (75.2% yield).

2.4 Extraction experiments

Extraction experiments were carried out using separatory funnels in a thermostatic shaker, at room temperature (25 °C) and 220 vibration per minute for 10 min. Equilibrium pH was adjusted by controlling the initial pH value.

The key parameters, namely, extraction efficiency (*E*), distribution ratio (*D*), and synergistic coefficient (*R*) were calculated by the following equations:

$$E=\frac{V_{\text{org}}\cdot C_{\text{org}}}{V_{\text{f}}\cdot C_{\text{f}}}\times 100\% \tag{1}$$

$$D=\frac{C_{\text{org}}}{C_{\text{r}}} \tag{2}$$

$$R=\frac{D_{\text{SSX}}}{D_{\text{TFCA}}+D_{\text{4PC}}} \tag{3}$$

where V_{org} and V_{f} are organic and feed solution volumes, respectively. C_{org}, C_{f}, and C_{r} are the metal concentrations of the organic, feed solution and raffinate, respectively. D_{SSX}, D_{TFCA}, and D_{4PC} are the distribution ratios of each metal in the SSX, TFCA, and 4PC systems, respectively.

2.5 Analysis and characterization

The concentrations of metal cations in the aqueous solution were determined by inductively coupled plasma optical emission spectroscopy (ICAP7400 Thermo Electron Corporation, USA). The chemical structures of TFCA and the metal extraction complex were characterized by FT-IR spectroscopy (Nicolet iS20, Thermo Scientific, USA) and HRMS (Agilent 6550 QTOF, Thermo Fisher-QE, USA).

3 Results and discussion

3.1 Synthesis of TFCA

On comprehensive consideration of the number of functional groups and the overall carbon chain structure, an unsaturated long-chain structure of methyl eleostearate was used as a framework, and a pair of chelating carboxylic acid groups was introduced at the conjugated olefin through Diels−Alder reaction to enhance the selectivity of the carboxylic acid extractant for divalent metal cations. The synthetic scheme of TFCA is shown in Fig. 1.

Purified TFCA was characterized by FT-IR spectroscopy (Fig. 2, Table 1) and HRMS (Fig. 3; characteristic peak located at *m*/*z*=407.2469). All key groups and their corresponding characteristic peaks in the FT-IR spectrum of TFCA are listed in Table 1. The main peak is clearly visible in the mass spectrum (Fig. 3). Only a few miscellaneous peaks are detected in the mass spectrum, indicating the high purity of TFCA.

3.2 Extraction performance

The metal extraction pH isotherms with the TFCA system alone and the SSX system consisting of TFCA and 4PC were conducted and compared in Fig. 4. With 0.2 mol/L TFCA alone, the extractions of metals follow the order of Cu > Zn > Ni > Co > Mn > Ca > Mg > Li. In comparison with the extraction pH isotherms of other carboxylic acid

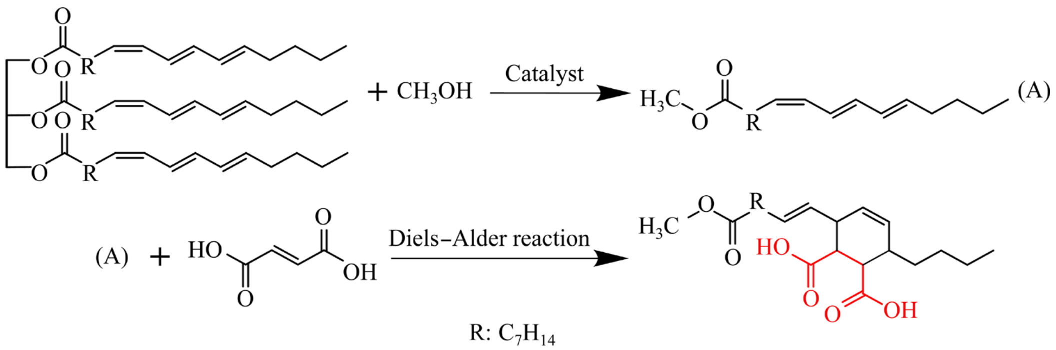

Fig. 1 Synthetic scheme of TFCA

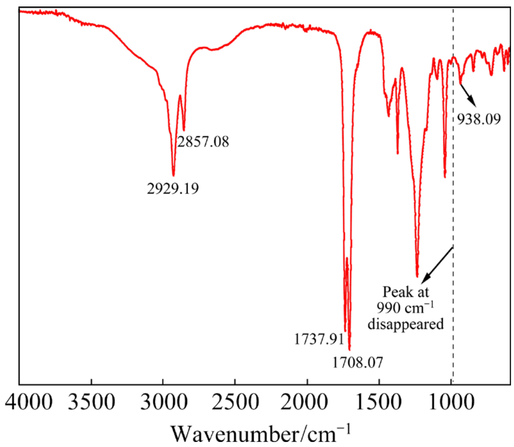

Fig. 2 FT-IR spectrum of TFCA

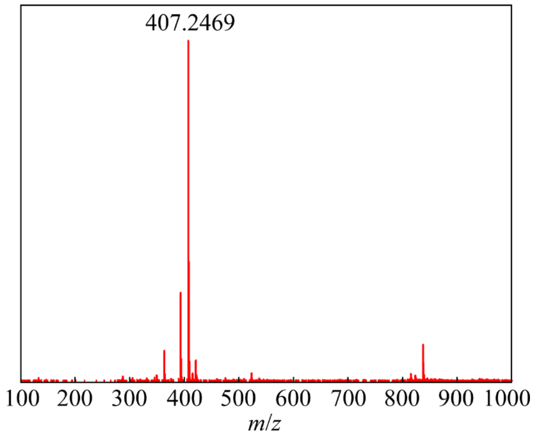

Fig. 3 HRMS spectrum of TFCA

Table 1 Infrared frequencies and assignment of TFCA peaks

Vibrational mode	Theoretical characteristic frequency/cm^{-1}	Characteristic frequency/ cm^{-1}
$\nu_{\text{—OH(—COOH)}}$	3550−2500	3500−2500
$\nu_{\text{—CH}_2}$	~2925, ~2850	2929.19, 2857.08
$\nu_{\text{—C═O(—COOCH}_3\text{)}}$	1750−1735	1737.91
$\nu_{\text{—C═O(—COOH)}}$	1760−1700	1708.07
$\delta_{\text{—OH(—COOH)}}$	955−915	938.09

extractants like Versatic 10 [29], it is found that they have exactly the same extraction order on metals and similar curves of these metal cations, which can be mainly attributed to the commonality of the carboxylic acid functional group.

Both TFCA and Versatic 10 are carboxylic acid extractants, but different from monoacid, TFCA contains a pair of chelating carboxylic acid groups. During the extraction process, except for the cation exchange reaction, a more stable multivariate ring structure between TFCA and divalent metal cations can be formed. The pH$_{50}$ value of TFCA for Ni^{2+} is 5.67, as listed in Table 2, whilst the pH$_{50}$ value of Versatic 10 for Ni^{2+} is 6.34, indicating a stronger complex ability of TFCA.

When 4PC was added into TFCA, the SSX system exhibits significant synergistic effect on Ni and reasonable synergistic effect on Cu, Zn and Co, but anti-synergistic effect on Ca, Mg and Li. The extraction curve of Mn remains almost same. The ΔpH$_{50}$ of Ni over Mg and Ni over Li reaches 2, indicating that the separation of Ni over Mg and Li in acid leach solutions of spent LIBs can be easily achieved using the SSX system.

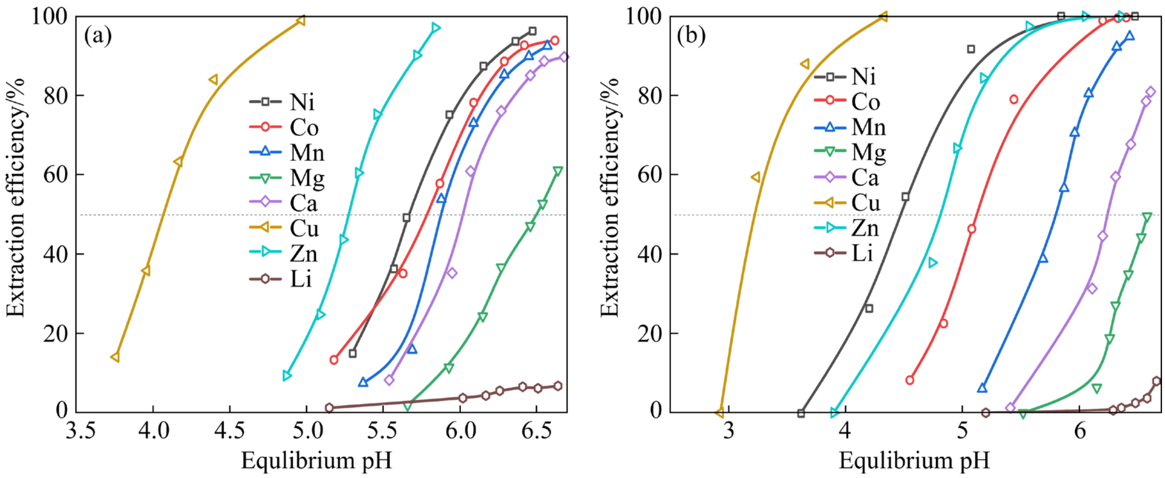

Fig. 4 Extraction−pH isotherms of TFCA (a) and TFCA+4PC (b) for metal cations (Aqueous solution: 0.02 mol/L M^{2+} and 0.2 mol/L Na_2SO_4; Organic solutions: 0.2 mol/L TFCA, 0.4 mol/L 4PC; Phase ratio (O/A) of 1:1; Temperature: 25 °C)

Table 2 Extraction pH_{50} values of TFCA/TFCA+4PC for metal cations

System	Cu^{2+}	Zn^{2+}	Ni^{2+}	Co^{2+}	Mn^{2+}	Ca^{2+}	Mg^{2+}	Li^{+}
TFCA	4.07	5.27	5.67	5.78	5.88	6.02	6.50	−
TFCA+4PC	3.23	4.81	4.47	5.12	5.80	6.24	6.60	−
Synergistic coefficient, *R*	16.98	7.46	30.77	7.90	1.12	0.37	0.44	0.40

3.3 Separation of Ni from Mg/Li using SSX system

3.3.1 Effect of equilibrium pH

The authentic solution containing 11.55 g/L Ni, 0.31 g/L Mg and 3.22 g/L Li provided by Fangyuan Company (China) was used as feed, which was the same feed in subsequent experiments. The effect of equilibrium pH on the extraction of metals are shown in Fig. 5.

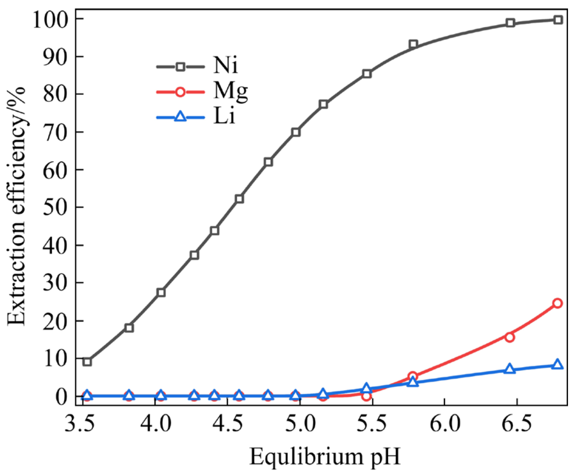

Fig. 5 Effect of equilibrium pH on extraction process (TFCA: 0.3 mol/L; 4PC: 0.6 mol/L; Time: 10 min; O/A ratio: 1:1; Temperature: 25 °C)

The extraction efficiency of Ni increases from 9.18% to 83.36% with the increase of equilibrium pH from 3.5 to 5.5, while the extraction efficiencies of Mg and Li maintain stable below 3%. Further increase in equilibrium pH results in slight increase of Ni extraction efficiency but large increase of Mg and Li extraction efficiencies, which decreases the separation coefficient of Ni, Mg and Li. Therefore, the equilibrium pH of 5.5 is selected as optimum for subsequent tests.

3.3.2 Effect of TFCA concentration

The effect of TFCA concentration (0.15−0.45 mol/L) on the extraction of metals are shown in Fig. 6. The extraction of Ni is improved significantly with increasing TFCA concentration, while the extractions of Mg and Li remain constant. The continuously increasing difference between the extraction of Ni and the extractions of Mg/Li favors the selective recovery of Ni from complex aqueous solutions. The extraction efficiencies of Ni, Mg, and Li are 97.35%, 0%, and 3.38%, respectively, at a TFCA concentration of 0.4 mol/L, and are not significantly improved upon further increase in the TFCA concentration. Considering the separation factor of Ni and Mg/Li, and the utilization ratio of extractant, an extraction system containing 0.4 mol/L TFCA and 0.8 mol/L 4PC is considered to be optimal.

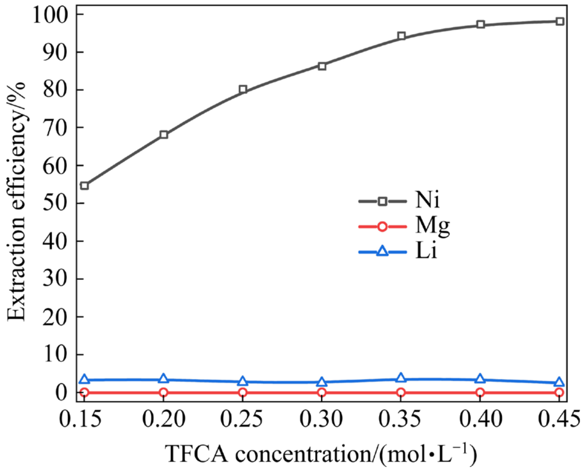

Fig. 6 Effect of TFCA concentration on extraction process (Equilibrium pH: 5.5; *n*(TFCA)/*n*(4PC)=1:2; Time: 10 min; O/A ratio: 1:1; Temperature: 25 °C)

3.3.3 Effect of 4PC concentration

Synergistic experiments with fixed TFCA concentration (0.4 mol/L) and varying concentrations of 4PC were conducted at equilibrium pH values of 3.4−6.6 (the neutral extractant 4PC alone cannot extract any metal from sulfate solutions).

As demonstrated in Fig. 7, a relatively high equilibrium pH (pH_{50}=5.53) is still required for the extraction of Ni using TFCA alone, and this is also accompanied by slight co-extraction of Mg and Li. The Ni pH isotherm shows a large shift towards lower pH with increasing 4PC concentration. A $pH_{50(Ni)}$ of 4.93, 4.51, 4.32, and 4.17 is required at a

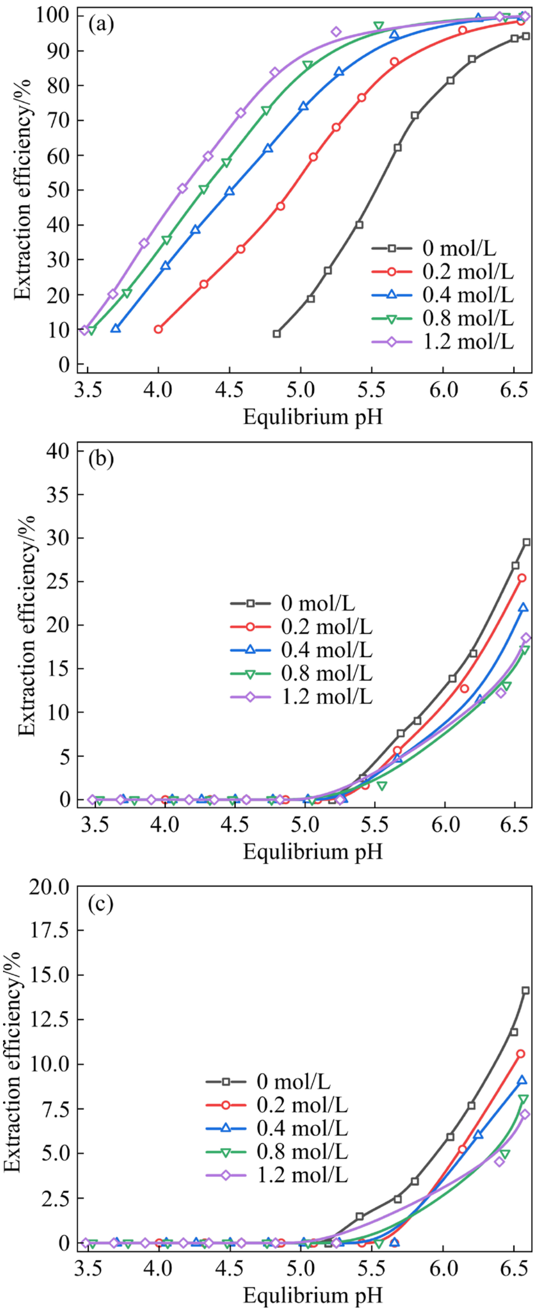

Fig. 7 Effect of 4PC concentration on extraction of Ni (a), Mg (b) and Li (c) (TFCA: 0.4 mol/L; Time: 10 min; O/A ratio: 1:1; Temperature: 25 °C)

4PC concentration of 0.2, 0.4, 0.8, and 1.2 mol/L, respectively, indicating significant enhancement of the selectivity of Ni with the SSX system. Figures 7(b, c) show that the separation coefficients of Ni, Mg and Li increase because 4PC inhibits the extraction of Mg and Li. Considering that the synergistic effect of the SSX system for Ni and the anti-synergistic effect for Mg and Li cannot be significantly enhanced when the 4PC concentration is higher than 0.8 mol/L, the optimal extraction concentration of 4PC for subsequent experiments is determined to be 0.8 mol/L.

3.3.4 Effect of time and temperature

The effects of reaction time (1−15 min) and reaction temperature (15−40 °C) on the extractions of metals were studied. As demonstrated in Fig. 8, the extractions of metal cations remain stable with increasing reaction time and temperature. The optimal extraction conditions can be determined by mixing the aqueous solution with organic solvent for 10 min at 25 °C.

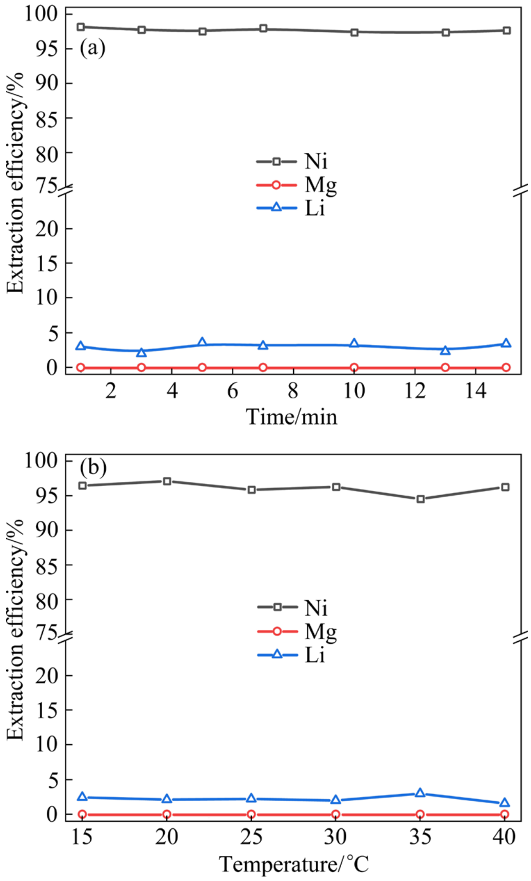

Fig. 8 Effect of time (a) and temperature (b) on extraction of metals (Equilibrium pH: 5.5; TFCA: 0.4 mol/L; 4PC: 0.8 mol/L; O/A ratio: 1:1)

3.3.5 Scrubbing and stripping

To minimize co-extraction of Li, diluted $NiSO_4$ solution was used to scrub the loaded organic phase containing 11.75 g/L of Ni and 0.06 g/L of Li. The results are shown in Fig. 9(a). It is found that ~75% of Li is scrubbed out by de-ionized water, indicating that most of Li is entrained in the organic solution. With the increase of $NiSO_4$ concentration to 300 mg/L, more than 90% of Li is scrubbed out in a single stage, which further improves the Ni−Li separation effect.

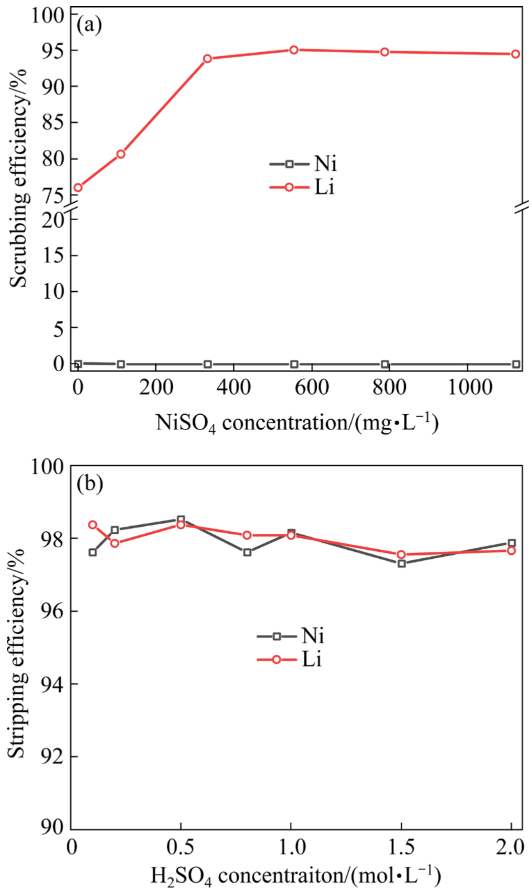

Fig. 9 Effect of $NiSO_4$ concentration on scrubbing efficiency (a) and H_2SO_4 concentration on stripping efficiency (b) (O/A ratio: 1:1; Time: 10 min; Temperature: 25 °C)

After scrubbing with 300 mg/L $NiSO_4$, the scrubbed organic phase was stripped using diluted H_2SO_4 solution. As depicted in Fig. 9(b), the strip of Ni and Li keeps stable with the increase of H_2SO_4 concentration, and ~98% of loaded metals can be stripped with 0.2 mol/L H_2SO_4, implying that the chelating structure formed between TFCA and Ni does not inhibit the strip reaction. Finally, a strip liquor containing 11.52 g/L Ni and only less than 6 mg/L Li is obtained.

3.4 Extraction mechanism

The slope method was employed to investigate the extraction mechanism of nickel with the new SSX system. The derivation of the formula for slope method has been discussed in our previous paper [30,31].

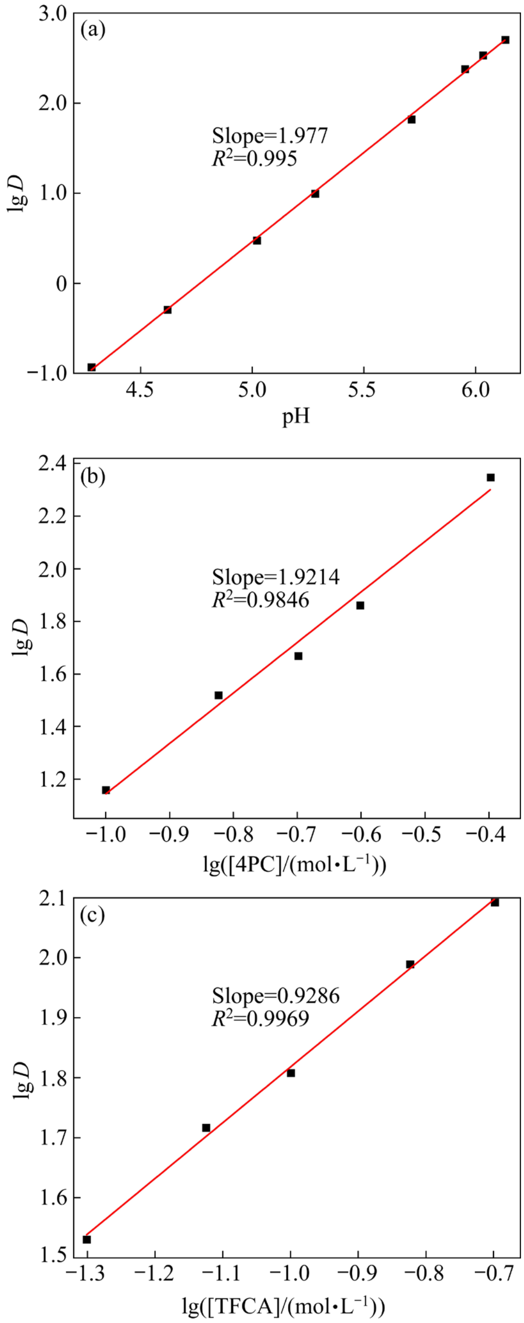

Fig. 10 Relationship between lg D and pH (a), lg D and lg [4PC] (b) and lg D and lg [TFCA] (c) (Ni^{2+}: 100 mg/L; O/A ratio: 1:1; Time: 10 min; Temperature: 25 °C)

As shown in Fig. 10, the slopes of lg D–pH, lg D–lg [4PC] and lg D–lg [TFAC] were 2, 2 and 1, respectively. Therefore, the extraction mechanism for the synergistic extraction of Ni by SSX system can be expressed by Eq. (4):

$$Ni^{2+}(aq)+\overline{H_2A(org)}+\overline{2L(org)} \rightleftharpoons \overline{NiAL_2(org)}+2H^{+}(aq) \tag{4}$$

By comparing the FT-IR spectra of the blank organic phase with that of the loaded organic phase in Fig. 11, several significant changes are observed: (1) The intensity of stretching vibration peak of —OH in the —COOH functional group at 3500–

2500 cm^{-1} decreases significantly, which can be attributed to the cation exchange between TFCA and Ni^{2+}, and the hydrogen of —OH is removed when the Ni extraction complex is formed. (2) Two weak absorption peaks of the pyridine ring are observed at 1607.11 and 1408.51 cm^{-1}, whereas the two peaks corresponding to the Ni extraction complex shift to higher frequencies of 1622.77 and 1420.80 cm^{-1}. Apart from the blue shift, all the peaks of the blank organic and loaded organic are identical.

The above results suggest that both TFCA and 4PC are involved in the coordination of the Ni extraction complex, which is consistent with the results obtained using the slope method. The most probable structure of the metal extraction complex is deduced, as shown in Fig. 12.

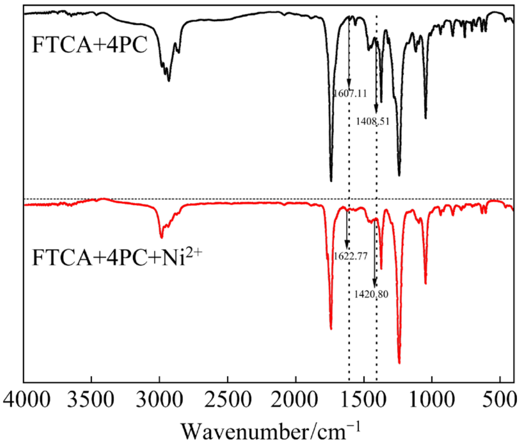

Fig. 11 FT-IR spectra before and after extraction using SSX system

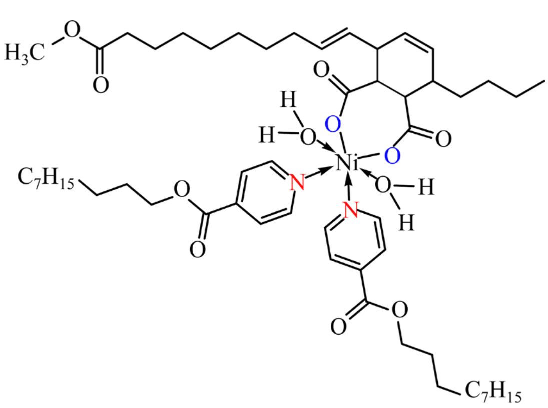

Fig. 12 Plausible structure of Ni extraction complex

4 Conclusions

(1) A new chelated carboxylic acid extractant is synthesized with tung oil as raw material and a novel SSX system consisting of TFCA and 4PC is thus developed to selectively extract Ni from Li in acid leach solutions of spent LIBs.

(2) The extraction experiments indicate that a multiple chelate ring is formed between TFCA and divalent metal cations, thereby enhancing the binding ability of TFCA and improving the stability of the metal extraction complexes. The extraction operations were systematically investigated, and the following conditions are determined to be optimal: equilibrium pH 5.5, *c*(TFCA) 0.4 mol/L, *c*(4PC) 0.8 mol/L, O/A ratio 1:1, reaction time 10 min, and reaction temperature 25 °C. More than 97% of Ni^{2+} in the aqueous solution is extracted through a single stage, and meanwhile, the extraction of Li is within 3%. A high purity nickel sulfate solution is obtained after the loaded organic solution is scrubbed by $NiSO_4$ solution and stripped with 0.2 mol/L H_2SO_4. The excellent extraction performance of this novel SSX system indicates promising applications in authentic solutions.

(3) The results of the slope method and spectroscopic analysis reveal that Ni^{2+} is extracted from the leach solution in the form of "$Ni(C_{23}H_{34}O_6)(C_{16}H_{25}NO_2)_2 \cdot 2H_2O$", and extraction mechanism involves cation exchange and coordination reaction.

CRediT authorship contribution statement

Li-han ZHANG: Writing − Original draft preparation, Validation, Investigation, Formal analysis, Data curation; **Zuo-ying CAO:** Supervision, Writing − Reviewing and editing, Project administration; **Gui-qing ZHANG:** Supervision; **Qing-gang LI:** Supervision; **Ming-yu WANG:** Supervision; **Wen-juan GUAN:** Supervision; **Sheng-xi WU:** Supervision, Funding acquisition; **Qi DENG:** Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

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采用 TFCA-4PC 协同萃取体系
从废旧锂离子电池酸浸液中选择性萃取镍

张立涵 1,2，曹佐英 1,2，张贵清 1,2，李青刚 1,2，王明玉 1,2，关文娟 1,2，巫圣喜 1,2，邓 奇 3,4

1. 中南大学 冶金与环境学院，长沙 410083；
2. 中南大学 冶金分离科学与工程重点实验室，长沙 410083；
3. 湖南省林业科学院 木本油料资源利用国家重点实验室，长沙 410018；
4. 湖南省林业科学院 油脂分子构效湖南省重点实验室，长沙 410018

摘　要：采用一种由桐油基羧酸(TFCA)与异烟酸酯(4PC)组成的协同溶剂萃取(SSX)体系，从含 Mg/Li 的废旧锂离子电池(LIBs)酸浸液中选择性萃取 Ni。SSX 体系对 Ni 表现出较强的协同作用，这主要归因于 TFCA 可以与 Ni 形成较为稳定的多元螯环结构，因此，体系对 Ni 的选择性得到增强。在优化条件下，经过单级萃取，Ni 的萃取率达到 97.3%，而 Mg 和 Li 的萃取率分别为 0 和 2.29%。随后，负载有机相经过 300 mg/L $NiSO_4$ 洗涤后采用 0.2 mol/L H_2SO_4 反萃，获得的反萃液中含有 11.52 g/L 的 Ni 和<6 mg/L 的 Li。

关键词：桐油；羧酸萃取剂；协同溶剂萃取；镍；萃取机理

(Edited by Bing YANG)