ChemElectroChem

Research Article
doi.org/10.1002/celc.202201059

Chemistry Europe
European Chemical Societies Publishing

www.chemelectrochem.org

Special Collection

Lithium and Cobalt Recovery from Lithium-Ion Battery Waste via Functional Ionic Liquid Extraction for Effective Battery Recycling

Riccardo Morina,[a] Daniele Merli,[b] Piercarlo Mustarelli,[a, c] and Chiara Ferrara*[a, c]

Sustainable management of spent lithium-ion batteries, LIBs, is an urgent and critical challenge due to the number of such devices reaching the end-of-life. Recycling can offer a path for the recovery of valuable raw materials such as lithium and cobalt, whose supply is critical. Thus, it is mandatory to develop efficient ways for the selective recovery of Li and Co from the cathode degradation processes. In this study the most updated organic acids-based processes for the degradation of $LiCoO_2$, the most common LIBs cathode, is explored to obtain a leached solution containing Li and Co. The possibility to exploit the 3-methyl-1-octylimidazolium thenoyltrifluoroacetone, Omim-TTA, ionic liquid was demonstrated to efficiently separate Li and Co. In particular it was possible to recover $>70\,\%$ of Li and separate it from Co using this ionic liquid, independently from the organic acid used for the leaching procedure and adding EDTA to the aqueous phase. The quantification was carried out through ICP analysis; the recovering of the unaltered ionic liquid was also demonstrated, to further increase the global sustainability of the process.

Introduction

The diffusion of lithium-ion batteries, LIBs, was due to their use in portable devices such as cellphones, laptops, in consumer electronics (drones, household appliance) and now is booming at even higher rates and volumes as LIBs are the device of choice for the development of electric vehicles.[1–3] The growing rate of this device is followed by the growing volumes of end-of-life LIBs, EoL-LIBs, disposed as waste. The management of this new, complex kind of waste is an open and urgent question that must be framed in a regulatory scenario. Moreover, new technologies for sustainable and efficient recycling must be developed. Up to now, in fact, only a fraction of EoL-LIBs has been collected and recycled through highly energetic processes mainly based on pyrometallurgical approaches (high temperature treatments with $T > 1000\,^{\circ}C$) followed by hydrometallurgical steps using strong mineral acids.[4–7] The result of these steps is the partial recovery of some of the metals (Co, Cu, Al, Ni), while organic components and light elements (Li, F) are inevitably lost. With the aims of limiting the environmental footprint of the recycling process, opening the range of the recoverable elements, and improving the global efficiency of the process, in the last years many studies were dedicated to new, low temperature, sustainable routes for the degradation of the mass derived from EoL-LIBs. In particular, soft hydrometallurgy exploiting organic acids and reducing agents,[8–10] solvometallurgy based on ionic liquids and deep eutectic solvents,[11–15] and biometallurgy[16–19] were presented demonstrating the possibility to fully degraded the mass derived from the pretreatment of the EoL-LIBs, and specifically the cathodic components.[7,16,20–22] In this case, the product of all the proposed treatments is a complex solution of different metals and chemical species, and further steps need to be implemented to separate and recover the metals of interest. Far less attention was devoted to this topic and often the steps presented in literature as proof-of-concept for the recovery of target metals (generally Li and Co) require many steps, huge amounts of salts and water with significant production of byproducts and wastewater. To further improve the efficiency and sustainability of the recycling scheme, new effective methods for the separation of the desired metals must be developed. In this study we propose the use of a functional ionic liquid for one-step separation of Li and Co from the leaching solution of the $LiCoO_2$, LCO, the most common cathode material, recovered from EoL-LIBs. The cathode was degraded exploiting the new approaches presented in literature proposing the use of organic acids. In particular, we explored the etching based on the use of citric, ascorbic, and tartaric

[a] R. Morina, Prof. P. Mustarelli, Dr. C. Ferrara
Department of Materials Science
University Milano Bicocca
via Cozzi 55, 20125 Milano, Italy
E-mail: chiara.ferrara@unimib.it
Homepage: https://www.unimib.it/chiara-ferrara
[b] Prof. D. Merli
Department of Chemistry
University of Pavia
Via Taramelli 16, 27100 Pavia, Italy
[c] Prof. P. Mustarelli, Dr. C. Ferrara
National Reference Center for Electrochemical Energy Storage (GISEL)
Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia Dei Materiali (INSTM)
via Giusti 9, Firenze, 50121, Italy

Supporting information for this article is available on the WWW under https://doi.org/10.1002/celc.202201059

An invited contribution to a Special Collection dedicated to Giornate dell'Elettrochimica Italiana 2022 (GEI2022)

acids that allow to obtain >99% of dissolution of the LCO under mild conditions.[8,16,23–25] Room temperature Ionic liquids, ILs, present a series of unique properties such as low volatility, low toxicity, high solubility for metals combined with tunable hydrophobicity.[26–29] All these aspects make them appealing for many applications such as catalysts,[30] environmental contaminants removal systems,[31,32] electrolytes for energy storage devices,[33–36] and extracting agents.[37–41] Although recently many strategies have been reported to implement metals recovery and separation, such as membrane separation, ion imprinted polymers, solid phase adsorption,[42–44] liquid-liquid extraction is still appealing due to its robustness, ease of implementation, and scalability, making it exploited also at industrial scale. Traditionally liquid-liquid extraction is performed using organic solvents; large volumes of such solvents are generally needed, and this can represent a problem due to their flammability, poor environmental friendliness, volatility. A strategy to reduce the use of such solvents is to identify a deputy system eliminating these undesirable characteristics. ILs satisfy these requirements thank to their low or null flammability, low volatility, and tunable properties (such as hydrophobicity, viscosity). Generally, the extraction exploiting ILs involves the cation exchange mechanism, which implies the degradation of the initial extractant system. When one component of the IL has coordinating properties with respect to metal ion, the IL is defined as a functional ionic liquid (FIL). In this case the extraction proceeds through ion association mechanism and the extractant phase can be fully recovered.[45] 3-Methyl-1-octylimidazolium thenoyltrifluoroacetone, Omim-TTA, belongs to the class of FILs and was recently proposed for the selective Li recovery from brines presenting high concentration of Na and K.[46] The selectivity of the Omim-TTA for extraction of Li with respect to Na and K was reported for a wide range of pH ranging from acidic to basic conditions.[46] The TTA anion was also investigated in other IL systems for the selective coordination of lithium.[47] Here, we explored the extraction capability of the Omim-TTA system (0.1 M Omim-TTA in Omim-TFSI in the following labelled as Omim-TTA@TFSI) under various conditions, demonstrating the possibility to separate the Li and Co using the IL that is fully recoverable and reusable for several cycles, thus improving the global sustainability of the process.

Results and Discussion

Dissolution of LCO powders

The cathode active material was fully characterized to evaluate the composition prior the dissolution and separation steps. XRD analysis indicates the presence of LCO as the only phase, and thermal analysis showed a loss of ~6 wt% below 500 °C which is due to the presence of carbon and binder fractions (see Figure S1).

The ICP analysis showed the ~1:1 Li: Co ratio, confirming the identification of LCO as cathode material. These powders were used for dissolution without any further purification, according to the leaching protocols previously reported and summarized in Table 1.

In the recent years, a wide variety of organic acids were proposed for the degradation of cathode materials.[8,16] The variability in the experimental parameters reported in terms of holding time, temperature, and degradation yields depends on various aspects. The pKa of the acid has indeed a role, as the highest the H^+ concentration, the fastest the LCO structure is degraded; the mechanism seems to be related to the Li/H cation exchange.[8] The Co^{3+} species, present in the LCO structure, is poorly soluble in water. Therefore, the dissolution of the cathode is accelerated by a reducing agent able to convert the Co^{3+} into the more soluble Co^{2+} species. In this sense, some organic acids (e.g., citric, tartaric, and oxalic) have good reducing power, whereas for other cases it is possible to add an external reducing agent such as H_2O_2, glucose, $Na_2S_2O_3$.[8] Finally, the chelating properties of the anion of the organic acid can further promote the dissolution of the LCO structure, by stabilizing the Co^{2+} species in solution. These factors control the acidic leaching of LCO and provide a tool to rationalize the differences in the experimental parameters needed to obtain high yields. The main results from the literature are reported in Table 1.

The Omim-TTA was synthetized according to the procedure described in the experimental section; both the chemical-physical

Table 1. Review of the leaching procedures previously reported exploring the use of organic acids as leaching agents.[23–25,48–51] The main experimental parameters are reported together with a global, qualitative assessment of the process.

Leaching agent	Ref.	Acid conc. [M]	Time [min]	T [°C]	S:L ratio/g: L	Reducing agent	Yield/%	Global efficiency
Acetic acid	[48]	4	–	70	40	H_2O_2 2.5% V	75% Li; 30% Co	*
Lactic acid	[49]	1.5	20	70	20	H_2O_2 0.5% vol	97.7% Li; 98.9% Co	**
Ascorbic acid	[23]	1.25	20	70	25	none	98.5% Li; 94.8% Co	***
Tartaric acid	[24]	2	30	70	17	H_2O_2 4%	99% Li	***
Oxalic acid	[50]	3.0	90	80	50	none	99% Li, 96% Co	**
Succinic acid	[51]	1.5	40	70	15	H_2O_2 4% V	96% Li; 100% Co	**
Citric acid	[25]	1.25	30	90	15	H_2O_2 1% vol	100% Li; 91% Co	***

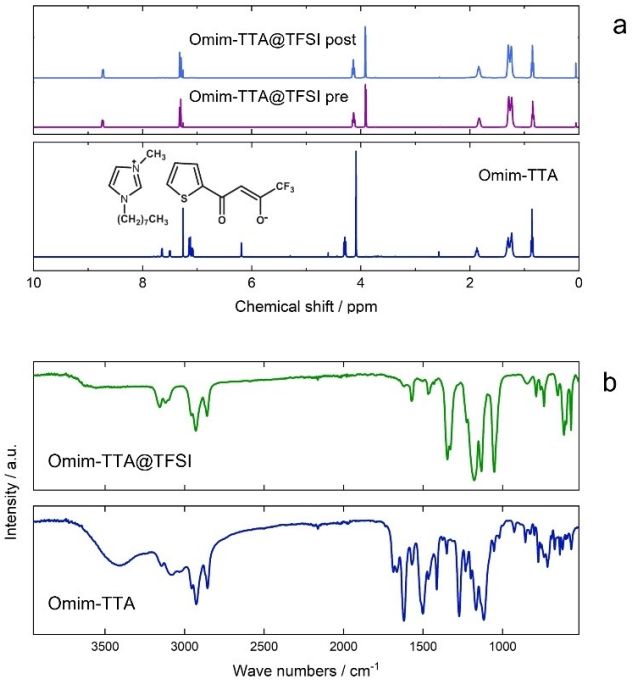

Figure 1. ^{1}H-NMR spectrum for the Omim-TTA (blue line) together with the chemical formula, the Omim-TTA@TFSI pre (purple line) and post (violet line) extraction demonstrating that the system is unaltered by the extraction and cleaning procedure (a). IR spectra (b) for the for the Omim-TTA (blue line) and Omim-TTA@TFSI (green line) ionic liquid systems.

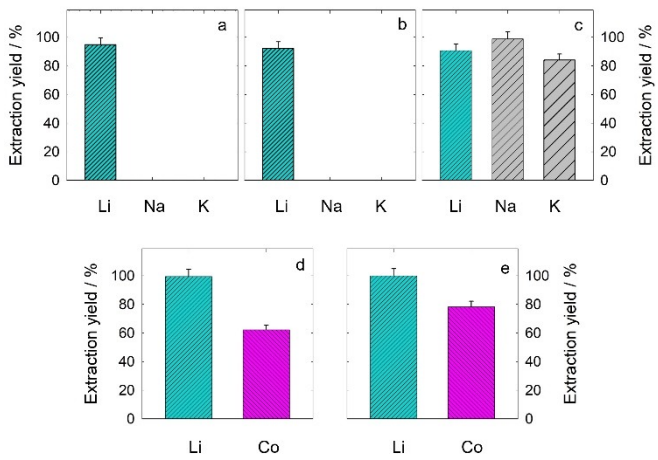

Figure 2. Extraction yields obtained for different standard solutions: solution containing 20 mg/L of Li, Na, K (a); 200 mg/L of Li, Na, K (b); 2000 mg/L of Li, Na, K (c); 200 mg/L of Li and 1600 mg/L of Co (d); 2000 mg/L of Li and 16000 mg/L of Co (e).

properties and the functional properties of the systems were checked before testing the IL on the leached solution of LCO.

The ^{1}H-NMR spectrum recorded on the as-prepared system confirms the formation and purity of the ionic liquid and its composition, as reported in Figure 1a, in good agreement with a previous report.[46] This result is confirmed also from the IR spectrum (Figure 1b), where the characteristic signals of the C=O (1500–1600 cm^{-1}), C–F (1100–1200 cm^{-1}) are present together with signals coming from moisture (3400 cm^{-1}). The preparation of the Omin-TTA@TFSI solution does not alter the structure of the Omim-TTA, as demonstrated by the ^{1}H NMR and IR spectra, where the Omim-TTA signals are still visible unaltered.

The obtained IL was considered as an extractant and diluted in 0.1 M concentration in OMIM-TFSI, the Omim-TTA@TFSI, that was already demonstrated to be the best diluent to enhance the extracting efficiency of the OMIM-TTA probably due to the strong electrophilicity.[46]

Finally, the extraction properties of the Omim-TTA@TFSI were tested with different standard solutions. The selectivity for Li extraction with respect to Na and K was demonstrated in the original work of Cai at al. for solution containing 20 mg/L of Li, Na, K and 200 mg/L of Li, 15 of Na and K to mimic the composition of natural brines.[47] Here we expanded the range of application of the ionic liquid considering standard solutions containing 20, 200, and 2000 mg/L of Li, Na, and K at pH = 3. The results of the extractions were determined via ICP analysis and reported in Figure 2. The obtained values confirm the ability of the Omim-TTA to selectively extract Li, while Na and K ions are retained in the aqueous solution for the solution containing 20 mg/L and 200 mg/L of these metals. These results overcome those presented by Cai et al., as the IL selectivity for Li extraction is high also for solutions with concentration of Na and K 10 times higher than those previously presented.[46] In contrast, no selectivity is observed for the highly concentrated solution (2000 mg/L). The mass effect can promote the favorable interaction of the different ions, independently from their dimension with the anion of the Omim-TTA@TFSI. This suggests that the IL can be used for extraction of diluted solution of Li.

The Omim-TTA@TFSI was also tested on reference solutions containing Li and Co obtained from dissolution of salts (see Experimental Section), considering 20 and 200 mg/L of Li and fixing the molar composition Li: Co 1:1 to mimic the solutions composition derived from the complete dissolution of $LiCoO_2$ as reported inthe Experminatal Section. The pH values were regulated to match the value of the solution leached with the organic acids (~3-4 as in Table 2). Results of the extraction from these reference solutions are reported in Figure 2d,e.

Table 2. Leaching agents considered in the present study for the degradation of the LCO cathode material; the most relevant parameters, such as temperature, holding time, and solid-to-liquid ratio are those reported in Table 1. The final yields of the procedure calculated as (initial powder weight – final powder weight/initial powder weight)*100 is reported together with the extraction efficiency for Li and Co.

Leaching agent	Label	Dissolution Yield [%]	Li efficiency recover [%] *	Co efficiency recover [%] *	Final pH value
Tartaric acid	TAR-LCO	94	96	98	3.0
Ascorbic acid	ASC-LCO	96	100	100	4.3
Citric acid	CIT-LCO	94	100	91	3.0

Our results show that the Omim-TTA is partially coordinating the Co ions that compete with the Li ones. While Li is completely extracted in the IL phase, Co il partially extracted resulting in a partitioning between the two phases, making the recovery unfavorable. It can be stressed that, after the extraction, the aqueous solution contains only Co, and thus can be considered for further selective recovery of this metal. However, the mixed elemental composition of the IL extractant phase would make the overall process not appealing.

Although these results may appear discouraging, it must be considered that the aim of the study is to exploit the Omim-TTA@TFSI system for the extraction of Li from leached solutions of LCO derived using different organic acids (tartaric, citric, and ascorbic), as reported in Table 2. These leached solutions TAR-LCO, CIT-LCO, ASC-LCO contain the conjugated based of the organic acid in large excess with respect to the Li and Co ions (3—5 molar excess depending on the solution). As already discussed, the presence of such coordinating species can help the dissolution process of the LCO structure and, from the point of view of the extraction of Li exploiting the Omim-TTA@TFSI system, can help in stabilizing the Co ions in the aqueous phase. For this reason, attempts to perform direct extraction of TAR-LCO, CIT-LCO, ASC-LCO using the Omim-TTA@TFSI were performed, and the results are reported in Figure 3a—c. These results show that, independently from the organic anion present in the aqueous solution, the Co ion is favorably extracted in the IL phase, whit efficiency above 88%. Contrarily, lithium extraction is strongly influenced by the nature of the starting aqueous solution. Indeed, no extraction of lithium is obtained for the TAR-LCO starting leaching, 27% is obtained for the ASC-LCO while 99% is obtained for the CIT-LCO system.

With the aim to improve the extraction efficiency with respect to lithium, EDTA was added to the aqueous solution in nearly stoichiometric ratio with the Co (1.1:1 EDTA: Co molar ratio), trying to stabilize this species in the aqueous phase. The ICP results are reported in Figure 3d—f. EDTA has been selected to be added in the aqueous phase for the stabilization of the Co ions due to its well-known complexing ability and specifically for some recent studies exploiting EDTA in separation processed for the recovery of valuable metals among with Co and Ni derived from recycling of LIBs procedures.[52—54] The coordinating effect of EDTA is immediately evident as, in all the considered cases, the Co is maintained in the aqueous solution, while lithium is extracted with efficiency equal to 70.0%, 82.4%, 70.0% for the TAR-LCO, ASC-LCO, and CIT-LCO, respectively.

Finally for the extraction of TAR-LCO, ASC-LCO, and CIT-LCO solutions with addition of EDTA, the Omim-TTA@TFSI extractant was washed with HCl: this allows to recover both Li in the washing water-based solution and the IL. The recycled Omim-TTA@TFSI was used for three other extraction cycles on the ASC-LCO solution with addition of EDTA, showing comparable extraction efficiencies, as reported in Figure 4, evidencing the stable performance with respect to the selectivity for Li extraction. At the same time the stability and integrity of the recovered Omim-TTA@TFSI after one extraction cycle is demonstrated by the ^{1}H-NMR spectra reported in Figure 1a together with the as prepared solution; the two datasets are superimposable demonstrating that the system can be recovered unaltered after the washing procedure.

The systems can be thus reused several times to further improve the sustainability of the EoL-LiBs management.

Conclusion

In this study we proposed the use of an already reported ionic liquid, the 3-methyl-1-octylimidazolium thenoyltrifluoroacetone,

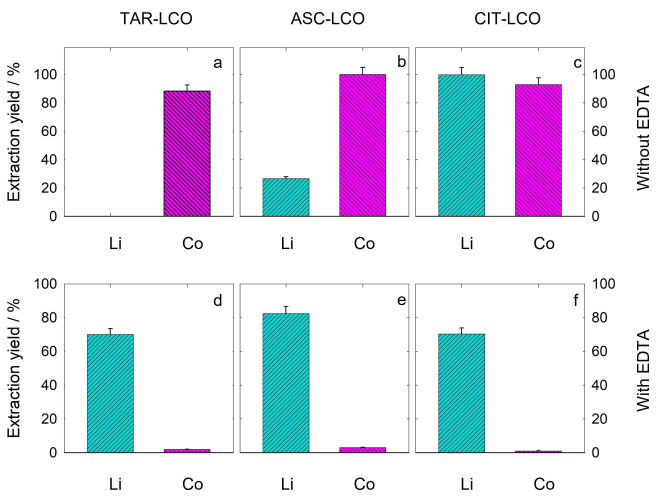

Figure 3. ICP results from extraction from TAR-LCO (a), ASC-LCO (b), CIT-LCO (c) as prepared and TAR-LCO (d), ASC-LCO (e), CIT-LCO (f) with the addition of EDTA to the aqueous solution.

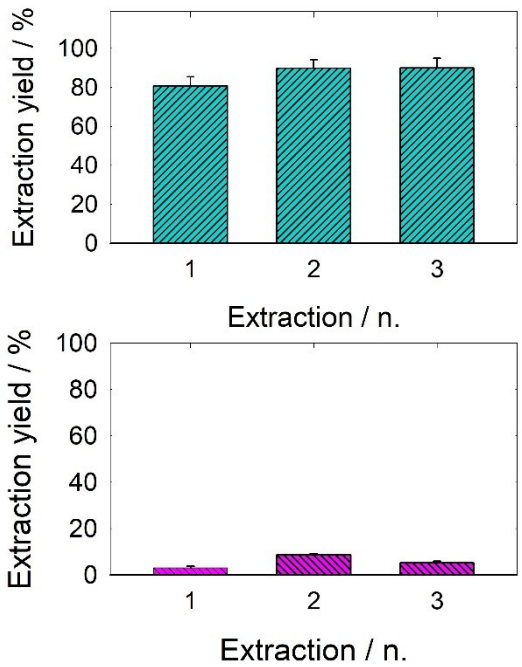

Figure 4. ICP results from three sequential extractions for the ASC-LCO (f) with the addition of EDTA.

Omim-TTA, for the selective recovery of lithium and cobalt from the leached solution of $LiCoO_2$, LCO, cathode derived from end-of-life batteries. The degradation of the cathode was performed considering the most updated and sustainable processes exploiting organic acids, recently reported in literature, i.e., those employing the tartaric, ascorbic, and citric acids. The selection of Omim-TTA ionic liquid was based on the recent report on its efficiency for the selective extraction of Li from solutions containing Na and K. While we were able to reproduce the synthesis of the Omim-TTA system and widen the field of concentration for the recovery of Li vs Na and K, the preliminary tests performed on the leached solutions of $LiCoO_2$ demonstrated that no selectivity for Li coordination could be achieved, despite the presence of good coordinating anions such as the conjugated base of the considered organic acids. Interestingly, high selectivity was obtained for the extraction of cobalt from the solution obtained with the use of tartaric acid, as ~80% of the cobalt was extracted in the IL phase while lithium was retained in the aqueous phase. This unexpected behavior could be exploited for the direct recovery of cobalt. On the contrary, for the leached solutions with addition of EDTA high selectivity of Li extraction could be obtained thanks to the stabilization of Co ions in EDTA aqueous solutions. This allowed for the subsequent separation of Li and Co through precipitation and/or washing procedure. Finally, the ionic liquid could be fully recovered via simple washing with HCl solution, allowing for the reuse of the ionic liquid for subsequent extraction cycles.

Experimental Section

Omim-TTA synthesis

IL synthesis was performed following the procedure described in the literature. [46] Briefly, the TTA was dissolved in CH_2Cl_2 with addition of ammonia solution to obtain the NH_4-TTA salt as a white powder. An equivalent with small excess of Omim-Cl was added to the former solution and heated at 40 °C under stirring overnight. The product recovered after rotary evaporation is the Omim-TTA IL, appearing as a viscous orange liquid, as already reported. The product was characterized by NMR, IR, and thermal analysis. The final Omim-TTA was used in 0.1 M concentration in Omim-TFSI solution (99.9%, Solvionic with <10 mg/L Li) that has already been demonstrated to be the system with the highest extraction efficiencies. In the text the pure Omim-TTA IL will be named "Omim-TTA" while the 0.1 M Omim-TTA in Omim-TFSI will be referred as "Omim-TTA@TFSI".

Cathode powder from EoL-LIB

The cathodic powder was recovered from spent 18650 batteries with no indication of chemistry. The batteries were cycled and completely discharged in NaCl saturated water solution for 48 hours, then opened by manually cutting the metallic case. The jelly roll was recovered and unfolded, the cathodic compartment was withdrawn for further processing and characterization. Powders were recovered after a mild shredding process allowing to fragment the current collector and detach the active material. The obtained powders recovered through sieving (1 mm and 500 um) were characterized through XRD, TGA, and ICP analysis. These results combined with the electrochemical profiles confirm the $LiCoO_2$ composition of the powders (LCO in the text).

Leaching using organic acids

The cathode powders were degraded by exploiting the previously reported procedures involving citric, tartaric, and ascorbic acids.[23–25] The optimal conditions for the complete dissolution of the cathode and reported in Tables 1 and 2. Complete dissolution of the LCO powders with yields >94% were obtained for all the considered organic acids. The small fraction of solid residue is due to the carbon content of the cathodic powders' formulation.

All the solutions were diluted prior the extraction with the IL. As the Omim-TTA@TFSI extractant demonstrate good selectivity for Li in the 20–200 mg/L range as discussed in the next section and previously reported,[46] the leached solutions were diluted ~1:10 with the aim to reach this range of concentration for the Li ion. For the selected samples, the EDTA was added in 1.1:1 molar ratio with respect to Co.

Extraction procedure

The initial aqueous solutions were extracted using the IL based on 0.1 M Omim-TTA in Omim-TFSI in volume ratio 1:3 under vigorous magnetic stirring at room temperature for 120 minutes. The two fractions were recovered and analysed. Finally, for selected extraction batches, the extractant phase was recovered by washing with HCl to recover the extracted lithium as LiCl, following the procedure reported before.[46] The recovered IL was analysed through NMR and reused for 3 extraction cycles. The extraction yields have been calculated in analogy with the previous study on the Omim-TTA@TFSI work [Eq. (1)] to facilitate comparison among the data:[46]

$$\text{Extraction yield } \% = (1 - [M]_e/[M]_0)^*100 \quad (1)$$

With $[M]_e$ concentration of the M species in the aqueous phase at the equilibrium and $[M]_0$ the concentration of the M species in the aqueous phase before the extraction.

Reference solutions

Aqueous solutions containing Li, Na, K in 20, 200, and 2000 mg/L concentrations were prepared by dissolution of LiCl, NaCl, KCl. Aqueous solutions with 200 mg/L Li and the resulting Co mg/L needed to respect the 1:1 molar ratio derived from the $LiCoO_2$ degradations were prepared by the dissolution of LiCl and $Co(NO_3)_2$*$6H_2O$ salts. pH values were controlled with adding of HCl and NH_4OH.

Characterisation

^{1}H-NMR spectra were acquired for Omim-TTA in CDCl3 on a Bruker 400 MHz with 64 scans and delay time of 2 seconds. Data obtained for the ^{1}H spectrum of the Omim-TTA are: ^{1}H NMR (400 MHz, CDCl3, mg/L, δ): δ 0.88 (t, 3H), δ 1.26 (m, 10H), δ 1.86 (m, 2H), δ 4.08 (s, 3H), δ 4.28 (t, 2H), δ 6.15 (s, 1H), δ 7.07 (m, 1H), δ 7.15 (d, 2H), δ 7.35 (m, 1H), δ 7.50 (m, 1H), 10.01 (s, 1H).

X-ray Diffraction (XRD) patterns were acquired by a powder diffractometer Rigaku Miniflex 600, equipped with a Cu source (1.54 Å) in the 2θ range of 20—80.

Inductively coupled plasma optical emission spectrometry (ICP-OES) was performed by a Thermo Scientific CAP7400Duo, equipped with a quartz torch, a charge injection detector and a CetacASX-560 autosampler. The ICP analysis have been based on preliminary

calibration of the instrument, the instrumental measurement uncertainty is 5 %.

Fourier Transformed Infrared (FTIR) Spectroscopy was performed in the Attenuated Total Reflectance (ATR) mode on a Thermo Fisher Scientific Nicolet iS20 in the wavenumber range 4000–550 cm^{-1} (resolution spectra 4 cm^{-1}, 32 scans).

Acknowledgements

C.F. acknowledges financial support from the Fondazione Cariplo through the grant "Cathode Recovery for Lithium Ion Battery Recycling – COLIBRI". P.M. and C.F. acknowledge financial support from Regione Lombardia (Regional Hub for Circular Economy, R²BAT Laboratory).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Critical Raw materials · Ionic Liquids · Liquid-liquid extraction · Lithium-Ion Batteries · Recycling

[1] Y. Ding, Z. P. Cano, A. Yu, J. Lu, Z. Chen, *Electrochem. Energy Rev.* **2019**, *2*, 1–28.
[2] X.-W. Wang, Y.-M. Cao, N. Zhang, *Energy Policy* **2021**, *151*, 112163.
[3] F. Wu, J. Maier, Y. Yu, *Chem. Soc. Rev.* **2020**, *49*, 1569–1614.
[4] S. Jiang, H. Hua, L. Zhang, X. Liu, H. Wu, Z. Yuan, *Sci. Total Environ.* **2022**, *811*, 152224.
[5] Y. Miao, L. Liu, Y. Zhang, Q. Tan, J. Li, *J. Hazard. Mater.* **2022**, *425*, 127900.
[6] H. Pinegar, Y. R. Smith, *J. Sust. Metal.* **2019**, *5*, 402–416.
[7] C. Ferrara, R. Ruffo, E. Quartarone, P. Mustarelli, *Ad. En. Sust. Res.* **2021**, *2*, 2100047.
[8] R. Golmohammadzadeh, F. Rashchi, E. Vahidi, *Waste Manage.* **2017**, *64*, 244–254.
[9] B. Musariri, G. Akdogan, C. Dorfling, S. Bradshaw, *Miner. Eng.* **2019**, *137*, 108–117.
[10] P. Meshram, A. Mishra, Abhilash, R. Sahu, *Chemosphere* **2020**, *242*, 125291.
[11] M. J. Roldán-Ruiz, M. L. Ferrer, M. C. Gutiérrez, F. del Monte, *ACS Sustainable Chem. Eng.* **2020**, *8*, 5437–5445.
[12] M. K. Tran, M. T. F. Rodrigues, K. Kato, G. Babu, P. M. Ajayan, *Nat. Energy* **2019**, *4*, 339–345.
[13] J. Yu, Q. Tan, J. Li, *J. Cleaner Prod.* **2020**, *255*, 120269.
[14] H. Zheng, J. Huang, T. Dong, Y. Sha, H. Zhang, J. Gao, S. Zhang, *Chin. J. Chem. Eng.* **2022**, *41*, 246–251.
[15] R. Morina, D. Callegari, D. Merli, G. Alberti, P. Mustarelli, E. Quartarone, *ChemSusChem* **2022**, *15*, DOI 10.1002/cssc.202102080.
[16] G. Harper, R. Sommerville, E. Kendrick, L. Driscoll, P. Slater, R. Stolkin, A. Walton, P. Christensen, O. Heidrich, S. Lambert, A. Abbott, K. Ryder, L. Gaines, P. Anderson, *Nature* **2019**, *575*, 75–86.
[17] T. Huang, L. Liu, S. Zhang, *Hydrometallurgy* **2019**, *188*, 101–111.
[18] M. Sethurajan, S. Gaydardzhiev, *Resour. Conserv. Recycl.* **2021**, *165*, 105225.
[19] M. P. Do, J. Jegan Roy, B. Cao, M. Srinivasan, *ACS Sustainable Chem. Eng.* **2022**, *10*, 2634–2644.
[20] X. Zeng, J. Li, N. Singh, *Crit. Rev. Environ. Sci. Technol.* **2014**, *44*, 1129–1165.
[21] X. Zhang, L. Li, E. Fan, Q. Xue, Y. Bian, F. Wu, R. Chen, *Chem. Soc. Rev.* **2018**, *47*, 7239–7302.
[22] J. Ordoñez, E. J. Gago, A. Girard, *Renewable Sustainable Energy Rev.* **2016**, *60*, 195–205.
[23] L. Li, J. Lu, Y. Ren, X. X. Zhang, R. J. Chen, F. Wu, K. Amine, *J. Power Sources* **2012**, *218*, 21–27.
[24] L.-P. He, S.-Y. Sun, Y.-Y. Mu, X.-F. Song, J.-G. Yu, *ACS Sustainable Chem. Eng.* **2017**, *5*, 714–721.
[25] F. Meng, Q. Liu, R. Kim, J. Wang, G. Liu, A. Ghahreman, *Hydrometallurgy* **2020**, *191*, 105160.
[26] T. Welton, *Biophys Rev.* **2018**, *10*, 691–706.
[27] M. Petkovic, K. R. Seddon, L. P. N. Rebelo, C. Silva Pereira, *Chem. Soc. Rev.* **2011**, *40*, 1383–1403.
[28] R. F. Rodrigues, A. A. Freitas, J. N. Canongia Lopes, K. Shimizu, *Molecules* **2021**, *26*, 7159.
[29] N. v. Plechkova, K. R. Seddon, *Chem. Soc. Rev.* **2008**, *37*, 123–150.
[30] K. C. Badgujar, V. C. Badgujar, B. M. Bhanage, *Curr. Opin. Green Sustain. Chem.* **2022**, *36*, 100621.
[31] S. Roy, Md. Ahmaruzzaman, *J. Environ. Manage.* **2022**, *315*, 115089.
[32] R. Goutham, P. Rohit, S. S. Vigneshwar, A. Swetha, J. Arun, K. P. Gopinath, A. Pugazhendhi, *J. Mol. Liq.* **2022**, *349*, 118150.
[33] S. Ferrari, E. Quartarone, C. Tomasi, D. Ravelli, S. Protti, M. Fagnoni, P. Mustarelli, *J. Power Sources* **2013**, *235*, 142–147.
[34] P. Stigliano, C. Ferrara, N. Pianta, A. Gentile, L. Mezzomo, R. Lorenzi, V. Berbenni, R. Ruffo, G. B. Appetecchi, P. Mustarelli, *Electrochim. Acta* **2022**, *412*, 140123.
[35] S. Ferrari, E. Quartarone, P. Mustarelli, A. Magistris, S. Protti, S. Lazzaroni, M. Fagnoni, A. Albini, *J. Power Sources* **2009**, *194*, 45–50.
[36] M. Armand, F. Endres, D. R. MacFarlane, H. Ohno, B. Scrosati, *Nat. Mater.* **2009**, *8*, 621–629.
[37] L. Xu, X. Zeng, Q. He, T. Deng, C. Zhang, W. Zhang, *Sep. Purif. Technol.* **2022**, *288*, 120626.
[38] X. Guo, W. Yao, Y. Chen, J. Fan, Y. Zhao, J. Wang, *J. Mol. Liq.* **2017**, *236*, 308–313.
[39] K. Wang, H. Adidharma, M. Radosz, P. Wan, X. Xu, C. K. Russell, H. Tian, M. Fan, J. Yu, *Green Chem.* **2017**, *19*, 4469–4493.
[40] P. A. Yudaev, E. M. Chistyakov, *ChemEng.* **2022**, *6*, 6.
[41] A. P. Paiva, C. A. Nogueira, *Waste Biomass Valorization* **2021**, *12*, 1725–1747.
[42] A. J. Whitworth, J. Vaughan, G. Southam, A. van der Ent, P. N. Nkrumah, X. Ma, A. Parbhakar-Fox, *Miner. Eng.* **2022**, *182*, 107537.
[43] A. Brewer, J. Florek, F. Kleitz, *Green Chem.* **2022**, *24*, 2752–2765.
[44] X. Zhou, B. Wang, R. Wang, *Sep. Purif. Technol.* **2022**, *298*, 121469.
[45] C. Shi, H. Li, B. Liu, Y. Qin, G. Song, *J. Mol. Liq.* **2020**, *304*, 112756.
[46] C. Cai, T. Hanada, A. T. N. Fajar, M. Goto, *Desalination* **2021**, *509*, 115073.
[47] J. Wang, S. Yang, X. Zhang, Y. Wang, D. Wang, W. Li, M. A. Ashraf, A.-H. A. Park, X. Li, *Energy Fuels* **2020**, *34*, 11581–11589.
[48] H. Setiawan, H. T. B. M. Petrus, I. Perdana, *Int. J. Min., Metal., and Mater.* **2019**, *26*, 98–107.
[49] G. Santhosh, G. P. Nayaka, *Clean Eng Tech.* **2021**, *3*, 100122.
[50] A. Verma, G. H. Johnson, D. R. Corbin, M. B. Shiflett, *ACS Sust. Chem. Eng.* **2020**, *8*, 6100–6108.
[51] L. Li, W. Qu, X. Zhang, J. Lu, R. Chen, F. Wu, K. Amine, *J. Power Sources* **2015**, *282*, 544–551.
[52] S. Gupta, K. K. Pant, G. Corder, *Chem. Eng. J.* **2022**, *446*, 137397.
[53] Z. Li, B. Onghena, X. Li, Z. Zhang, K. Binnemans, *Ind. Eng. Chem. Res.* **2019**, *58*, 15628–15636.
[54] M. Golmaei, T. Kinnarinen, E. Jernström, A. Häkkinen, *J. Environ. Manage.* **2018**, *212*, 219–227.

Manuscript received: October 20, 2022
Revised manuscript received: November 19, 2022