

Co-precipitation of Cathode Active Materials Precursors in Lithium-ion Batteries Recycling: Experiments and Modeling

Marco Vaccari*, Federica Barontini, Antonio Bertei, Monica Puccini, Leonardo Tognotti

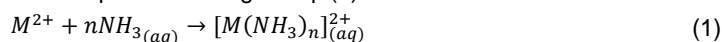
University of Pisa, Department of Civil and Industrial Engineering, Largo Lucio Lazzarino 2, 56126 Pisa (Italy)
marco.vaccari@ing.unipi.it

Recycling lithium-ion batteries (LIBs) is becoming an imperative task given the large flow of spent batteries that in the next future will have to be managed. Among the current three main recycling routes to convert spent LIBs into recycled products, that is, pyrometallurgy, hydrometallurgy, or direct recycling, the co-precipitation route lies between the last two routes: its key unit operations are the leaching of battery materials and the co-precipitation of a precursor for the re-synthesis of the cathode active material (CAM). High susceptibility to impurities in the leached solution and a strong link between high-quality CAM precursors and the composition of the dissolved metal salts, makes experimental analysis on spent LIBs a crucial step to find the best operating conditions. For this reason, we present an experimental campaign to study the co-precipitation and formation of the complex chemical compounds involved in the process. Moreover, we also exploit the support that rigorous models are giving in many industrial fields, also benefiting chemical engineering and laboratory analysis. Therefore, in this study we also present a rigorous simulation model on UniSim Design[®] with the thermodynamic package OLI[®] that enables the possibility to consider most of the different liquid-solid equilibria needed. A validation of the model is performed with experimental data and a sensitivity analysis on metal concentrations, pH, and chelating agent is performed to find the critical parameters that regulate the co-precipitation outcomes. The aim is to optimize the choice of operating conditions to limit the number of laboratory tests and complex analyses that are often expensive and time-consuming.

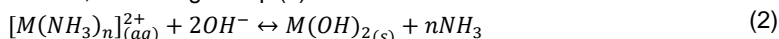
1. Introduction

The shift to electric vehicles that we are assisting in this decade will produce a large flow of spent lithium-ion batteries (LIBs) that in the next future will have to be managed. Therefore, LIBs recycling becomes a mandatory task. The currently established LIB recycling options are mainly aimed at recovering metals as alloys or individual battery-grade salts, nevertheless, processes that allow valuable materials (such as Li, Ni, Co, Cu, Al) contained in the spent batteries to re-enter the same value chain are strongly needed to obtain a closed loop, especially for critical raw materials (Latini et al., 2022b; Sommerville et al., 2021). The current three main recycling routes to convert spent LIBs into recycled products are pyrometallurgy, hydrometallurgy, and direct recycling (Latini et al., 2022a). Among them, the co-precipitation route can be classified as an hybrid one lying between the last two routes consisting of leaching of battery materials and the co-precipitation of a precursor of the cathode active material (CAM), to be directly used in the manufacturing of new batteries (Yang et al., 2017). Clearly, this route may be susceptible to impurities in the leached solution and the formation of the high-quality CAM precursors is strictly linked to the composition of the dissolved metal salts (Gerold et al., 2020). For this reason, experimental analysis on spent LIBs is crucial to find the best operating conditions to obtain a re-synthesized CAM taking into account economic and environmental constraints (Beak et al., 2022). Among the cathode materials currently used, lithium-nickel-manganese-cobalt oxides $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ (NMC) have attracted much attention (Xu et al., 2017). A transition metal hydroxide precursor is commonly synthesized during the co-precipitation process, whereas its oxidation and lithiation occur during the following sintering step. Generally, in co-precipitation tests, transition metal sulfates, complexing agents, and sodium hydroxide (NaOH) are added in a stirred reactor under a nitrogen atmosphere that remove dissolved oxygen to avoid unwanted

oxidation reactions. When an appropriate alkaline environment is ensured, the ternary hydroxide precipitates: $Ni_xMn_yCo_{1-x-y}(OH)_2$. Our interest is in $Ni_{1/3}Mn_{1/3}Co_{1/3}(OH)_2$, which allows the recovery of the NMC111 cathode material (You et al., 2021). The formation of the precursor (ternary hydroxide) from the solution of metal sulfates involves multiple chemical-physical phenomena. NaOH, guarantees the alkaline pH to precipitate the ternary hydroxide, but can also lead to the presence of single hydroxides ($Ni(OH)_2$, $Mn(OH)_2$, $Co(OH)_2$). For this reason, ammonia is added to the solution as a chelating agent, forming complexes with the transition metals and minimizing the precipitation of individual hydroxides (Barai et al., 2019). Initially the metal cations react with this chelating agent and form metal ammonia complex according to Eq. (1):



where M^{2+} indicates the metal cations which come from the dissociation of metal sulphates ($M = Ni, Mn, Co$), and n can vary from 1 to 6. The precipitation of transition metal hydroxide occurs through the reaction between metal ammonia complex and hydroxyl anions, according to Eq. (2):



The precipitate is, therefore, the result of the dynamic equilibrium between the hydroxide and the ammonia complex (Wang et al., 2015). In general, three physical phenomena play important roles within chemical reactors during the co-precipitation process that need to be considered for setting operating conditions: nucleation, growth, and aggregation (Barai et al., 2019).

On the other hand, the development of surrogate models is becoming more and more common in many industrial fields, also benefiting chemical engineering and laboratory analysis (Plesu et al., 2018). Nevertheless, studying the co-precipitation and formation of complex chemical compounds requires laboratory tests and complex analyses that are often expensive and time-consuming. Therefore, developing a model that can forecast with sufficient reliability the outcomes of experiments (yield and composition of co-precipitated precursors) can give the opportunity to evaluate the feasibility of varying different operation parameters to assist the laboratory tests and save both time and materials. Therefore, in the following Sections the experimental campaign on LIBs co-precipitation and the correlated rigorous model developed in this study are explained.

2. Materials and methods

2.1 Experiments

Nickel sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$), manganese sulfate monohydrate ($MnSO_4 \cdot H_2O$), cobalt sulfate eptahydrate ($CoSO_4 \cdot 7H_2O$), sulfuric acid, sodium hydroxide, ammonia solution, and bidistilled water were used as the starting materials in the co-precipitation study. The transition metal sulfates were dissolved in sulfuric acid solution in a molar ratio of $Ni^{2+}: Co^{2+}: Mn^{2+} = 1:1:1$, to simulate the leachate deriving from the acid leaching step in a LIB recycling process. Sodium hydroxide was employed as precipitation agent, and ammonia as complexing agent. The co-precipitation experiments were carried out in a 500 mL four-necked glass reactor magnetically stirred placed in a temperature-controlled water bath. The reaction flask was equipped with a reagent dosing and addition system (typically a dropping funnel), a probe for inert gas purge, probes for pH and temperature measurements, and a vapor condenser to prevent water loss due to evaporation (Figure 1a).

The solutions of sodium hydroxide and ammonia were added into the reactor containing the simulated leachate solution (Figure 1b). Further NaOH solution was added until the pH reached the value of 11.1. The mixture was maintained at 60 °C with continuous stirring at 250 rpm for 5 hours, while nitrogen gas was continuously bubbled into the reactor to remove the dissolved oxygen. The pH of the solution, monitored by a pH-meter, was kept at the desired value through the addition of sodium hydroxide. Different operating conditions were explored in experimental co-precipitation tests, namely, different total metal sulfate concentration (C_M) and different ammonia concentration (C_{NH_3}) in the reaction mixture. Table 1 reports the operating conditions of the co-precipitation tests. Figure 1c shows the typical blue color of the reaction mixture just after the addition of the ammonia solution due to the formation of metal complexes, and Figure 1d the final pink colour of the mixture due to the formation of ternary hydroxide. The precipitate was vacuum-filtered, washed with deionized water, dried at 75 °C for 12 h, and weighed. To determine the chemical composition of the precipitate, the sample was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo iCAP 7400DUO) after complete dissolution in aqua regia. The Ni, Mn, and Co contents were determined using the following wavelengths: Ni 221.647 nm, Mn 257.610 nm, and Co 228.616 nm. Scanning electron microscopy (SEM) analyses of the precipitate were performed using a FEI QUANTA 450 ESEM-FEG.

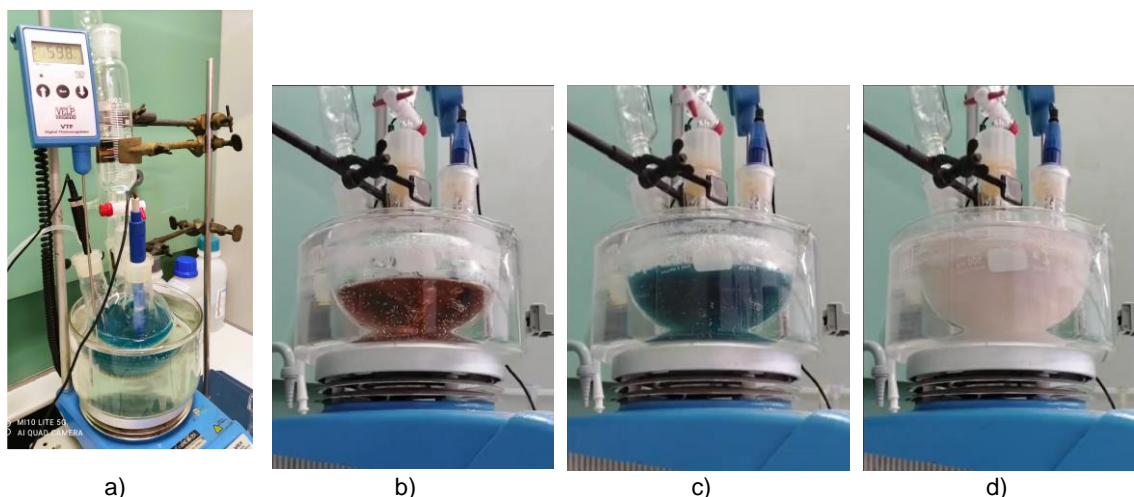


Figure 1 Experimental equipment used for co-precipitation tests (a) and reaction mixture evolution during a typical test: at the beginning (b); after the complexing agent addition (c); at the precipitation phase end (d)

2.2 Rigorous simulation model

The co-precipitation process has been modelled and simulated on UniSim Design® R470 using the OLI Engine® 10.0 package suitable for electrolytic equilibria. This model has the scope to clarify the effects of the various parameters involved in the experiments on the system. The list of components is defined using the MSE-GEMSE database as it contains most of the chemical species of interest. The schemes of the modelled experimental set-up and the one used for the sensitivity analysis are illustrated in Figure 2.

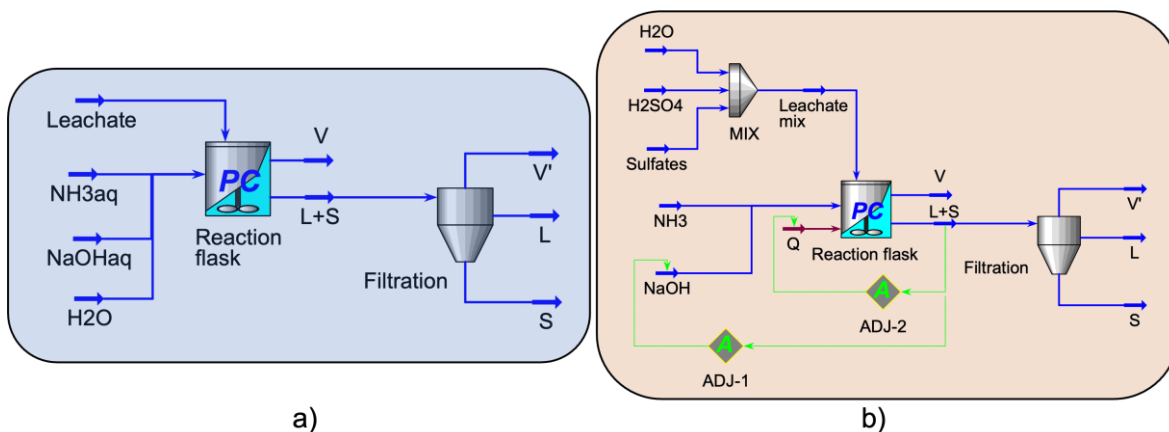


Figure 2 Experiments schemes simulated in UniSim Design®: experimental set-up on the left (a) and a support configuration for sensitivity analysis on the right (b)

The reaction flask has been modelled using the *Precipitator* unit, i.e. one of the devices that the software offers for the treatment of electrolytic systems modelling the precipitation of a selected ion in a stream entering the operation to achieve a specified target concentration in the effluent stream. Once the incoming streams are known, the calculated outputs are two (V and $L+S$ in Figure 2). The first represents a hypothetical vapor stream that could form under certain operating conditions, the second one is the solid-liquid mixture to be filtered.

The filtration is performed in a *Simple Solids Separator* unit, in which the specified parameters have been set to guarantee an ideal perfect separation. This is a simplifying choice for simulation purposes to obtain streams L and S that represent the liquid and solid flows obtained after filtration respectively. The current V' represents a vapor stream that in our case has null mass flow. The input streams to replicate the experiments (Figure 2a) are represented by the *Leachate* to be treated, the ammonia and soda solutions ($NH_3(aq)$ and $NaOH(aq)$), and water H_2O . Operative conditions of these streams are fixed at $60^\circ C$ and 1 atm.

It should be noted that the simulation model treats continuous-time processes, therefore, to convert the volumes used in the tests into mass flows, the densities of all the solutions used have been measured and a base time of 1 hour, which does not affect the simulation results, has been set. This necessary conversion prevents to evidence the impact of using different experimental procedures among the performed experiments. Subsequently, case studies are set up in which the key parameters of the process, such as the total concentration of metals, the concentration of ammonia and the pH, are varied within the limits explored in the experimental tests (Figure 2b). Each case study evaluates a single parameter at the time. In this context, the logical operation *Adjust* has been used to change the value of a variable (e.g., input soda concentration) to satisfy a specific request in another variable (e.g., pH in L+S), thus monitoring the effects of each factor on the simulated process.

3. Results

In order to carry out a model validation, the various co-precipitation tests were simulated on the developed model (Figure 2a) to compare the results with what obtained experimentally. To perform such a comparison some key aspects have to be underlined. First, being the ternary hydroxide a particular non-standard chemical compound, is not present in the selected software database, hence it is not possible to distinguish in the model results whether the precipitate contains single hydroxides or some other compound species (such as binary, ternary, etc.). A further limitation is related to the absence of ammonia complexes of cobalt and manganese among the compounds known to the software. However, the presence of the ammonia complexes of nickel makes it possible to evaluate the impact of ammonia on the process. For this reason, the sum of the molar flow rates of the formed complexes (the main contribution is from $[\text{Ni}(\text{NH}_3)_4]^{2+}$) is monitored. We underline how we can only state that nickel is “lost” and left in solution with ammonia, while cobalt and manganese apparently always precipitate as single hydroxides, thus not giving information about the real dynamics of the NMC co-precipitation. As metrics of comparison, we define two yields: the first one is the experimental co-precipitation yield ($\eta_{cp,e}$) defined in Eq. (3), i.e., the measured mass of the precipitate with respect to the theoretical one (assuming a complete precipitation reaction of transition metal sulphates as ternary metal hydroxide).

$$\eta_{cp,e} = \frac{\text{measured mass of precipitate}}{\text{theoretical mass of precipitate}} \quad (3)$$

On the other hand for the model results, considered the above mentioned limitations, we consider the modeled nickel precipitation yield that counts the moles of $\text{Ni}(\text{OH})_2$ in stream S with respect to the moles of NiSO_4 entering the reaction flask as defined in Eq. (4).

$$\eta_{Ni,m} = \frac{\text{moles of Ni(OH)}_2 \text{ in S}}{\text{moles of NiSO}_4 \text{ in Leachate}} \quad (4)$$

Therefore, Table 1 collects the results of the first 20 test performed and simulated comparing the two metrics.

Table 1 Results comparison between experimental tests and simulated model

test ID	C_{NH_3} [M]	C_M [M]	$\eta_{cp,e}$ [%]	$\eta_{Ni,m}$ [%]	test ID	C_{NH_3} [M]	C_M [M]	$\eta_{cp,e}$ [%]	$\eta_{Ni,m}$ [%]
1	0.88	0.06	100.0	98.9	11	0.98	0.07	94.8	99.5
2	0.88	0.06	99.8	98.9	12	0.83	0.10	94.0	99.7
3	0.86	0.06	93.6	99.5	13	0.59	0.07	97.6	99.8
4	1.56	0.07	64.2	78.0	14	0.58	0.07	93.4	99.9
5	1.43	0.15	85.2	91.1	15	0.59	0.07	100.0	99.9
6	0.86	0.06	95.8	99.7	16	0.43	0.07	95.0	100.0
7	0.54	0.06	98.6	100.0	17	0.53	0.06	96.5	99.9
8	0.55	0.06	100.0	99.9	18	0.57	0.09	99.1	99.9
9	0.88	0.13	97.5	100.0	19	0.56	0.09	95.7	100.0
10	0.57	0.07	97.3	99.9	20	0.57	0.09	96.4	99.9

It is underlined that the molar flow rates of cobalt and manganese entering and leaving the system are equal, indicating that the precipitation yields of these metals are equal to 1 in the simulations. This is probably still due to the absence of their complexes as previously explained. As observed in Table 1, $\eta_{Ni,m}$ is almost always near to 100% with a minimum value of 98.9 when excluding tests 4 and 5; in fact, part of Ni remains in solution in the form of a tetra-ammonia complex ($[\text{Ni}(\text{NH}_3)_4]^{2+}$). Experimental results give a co-precipitation yield value that is almost always very high and in fair agreement with the simulated results.

For tests 4 and 5, featuring a high concentration of ammonia, it is evident that the sum of the molar flow rates of the complexes is greater than that of the other tests. This is in agreement with the results of the experimental activity; in fact, the solution obtained after filtration had a bluish color typical of the nickel-ammonia complex and the results of the ICP-OES analyses indicated that the solid had a lower content of nickel. This is reflected onto such different values of the two metrics in Table 1. Also the yield of the precipitated solid (very different from the other ones) shows that tests 4 and 5 have operating conditions which do not allow the precipitation of the ternary hydroxide and, therefore, which are not to be employed. In addition, even with the given limitations, the model is also able to classify these two sets of operating conditions as inefficient ones.

After the model validation a sensitivity analysis was performed to study the effect of some parameters on the precipitation yield. In particular, varying the ammonia concentration (C_{NH_3}) in the solution from 0 to 2 M, the total concentration of metals (C_M) and the pH of stream L+S (pH_{L+S}) are varied individually evaluating different case studies as shown in Figure 3. As already explained, the absence of the aforementioned compounds in the software database only allows meaningful evaluations of the precipitation yield of nickel and not that of the other metals. Therefore, it is possible to identify the ammonia concentration above which the process efficiency for nickel decreases. For the same reason, however, it is not possible to determine the minimum quantity of ammonia for the hydroxide to precipitate as a ternary and not individually.

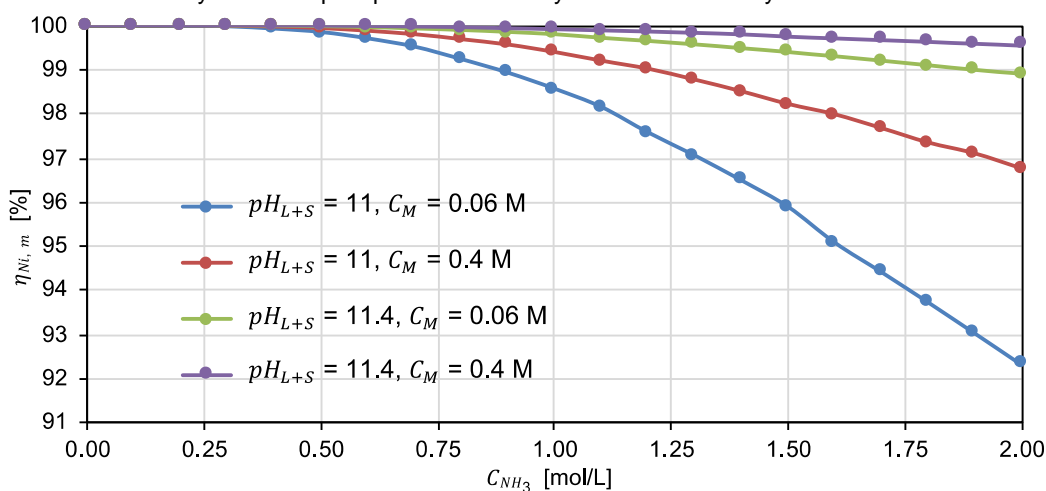


Figure 3 Sensitivity analysis on nickel precipitation yield varying C_{NH_3} , C_M , and pH_{L+S} .

As shown in Figure 3 for any of the tested fixed values of pH_{L+S} and C_M , a higher ammonia concentration leads to a decrease in the nickel yield. In fact, increasing C_{NH_3} implies a greater quantity of complex in solution and, therefore, a lower availability of nickel for the formation of the ternary hydroxide (as also evident in experiments 4 and 5). An opposite trend can be noted for fixed values of pH_{L+S} and C_{NH_3} : a higher concentration of metals corresponds to a higher yield of nickel. Since the amount of ammonia is fixed, the nickel that can be linked in complexes is also approximately constant overall. For this reason, a higher flowrate of incoming nickel leads to an increase in the metal in the solid. On the other hand, for fixed values of C_M and C_{NH_3} , a higher pH_{L+S} leads to a higher yield. Referring to Eq. (2), the increase of OH^- ions involves the shift of the reaction equilibrium towards the formation of solid hydroxide, increasing the nickel recovery yield. Finally, it must be commented that the model simulates only the equilibrium conditions and for this reason and the aforementioned limitations, a lower limit under which the concentration of ammonia is not sufficient to aid the formation of the trioxides compound cannot be calculated, i.e., Figure 3 shows a maximum of $\eta_{Ni,m}$ at $C_{NH_3} = 0$. Furthermore, a good co-precipitation must also consider the size of primary grains, their aggregation and homogeneity, all depending on pH_{L+S} and C_M (Barai et al., 2019).

4. Conclusions

The closed-loop regeneration of cathode materials is one of the highest value-added directions in lithium-ion battery (LIB) recycling. The co-precipitation process can be classified as a recycling route lying between hydrometallurgy and direct recycling because it employs the leaching step while targeting the re-synthesis of cathode active materials (CAM), thus involving complex chemical equilibria.

In this work, the co-precipitation process of NMC111 precursor was studied experimentally by varying the main parameters affecting the system, namely the chelating agent (ammonia) concentration, the total concentration

of metals, as well as the pH, and the reaction time. Experimental tests have been also modeled on rigorous simulation software (UniSim Design® with OLI® Interface) to possibly optimize the operative conditions. Given that the selected model database does include neither the ternary hydroxide nor the ammonia complexes of Co and Mn, the model results were analyzed employing the nickel complexes in the solution. A sensitivity analysis was also performed to address the Ni precipitation yield varying the operative parameters and evidencing a maximum value of ammonia concentration above which the co-precipitation performance decayed sensibly. A comparison of model results and the co-precipitation yields obtained in the various laboratory tests showed a quite satisfactory match. Although it was possible to identify suitable operating conditions, a proper optimization procedure of those was not carried out given the lack of information in the model database and the derived number of uncertainties.

Furthermore, it is worthwhile noting that the developed model cannot include kinetic aspects or other aspects linked to the morphology of the final particles. However, it is well known that operative reaction conditions, such as reaction time, are key factors influencing the aggregate morphology and particle size distribution, which in turn affect the electrochemical performance of the material. Experimental investigations on the effect of operating conditions on particle morphology are currently in progress.

Acknowledgments

This research was supported by the University of Pisa through the funding program “Progetti di Ricerca di Ateneo PRA 2020–2021”, project no. PRA_2020_48.

References

- Barai P., Feng Z., Kondo H., Srinivasan V., 2019. Multiscale Computational Model for Particle Size Evolution during Coprecipitation of Li-Ion Battery Cathode Precursors. *The Journal of Physical Chemistry B* 123, 3291–3303.
- Beak M., Park J., Park S., Jeong S., Kang J., Choi W., Yoon W.S., Kwon K., 2022. Understanding the effect of nonmetallic impurities in regenerated cathode materials for lithium-ion battery recycling by tracking down impurity elements. *Journal of Hazardous Materials* 425, 127907.
- Gerold E., Luidold S., Antrekowitsch H., 2020. Selective precipitation of metal oxalates from lithium-ion battery leach solutions. *Metals* 10, 1–15.
- Latini D., Lagnoni M., Brunazzi E., Mauri R., Nicoletta C., della Posta P., Tognotti L., Bertei A., 2022a. Recycling of Lithium-Ion Batteries: Overview of Existing Processes, Analysis and Performance. *Chemical Engineering Transactions* 96, 25–30.
- Latini D., Vaccari M., Lagnoni M., Orefice M., Mathieux F., Huisman J., Tognotti L., Bertei A., 2022b. A comprehensive review and classification of unit operations with assessment of outputs quality in lithium-ion battery recycling. *Journal of Power Sources* 546, 231979.
- Plesu V., Bonet J., Bonet-Ruiz A.E., Chavarria A., Iancu P., Llorens J., 2018. Surrogate model for carbon dioxide equilibrium absorption using aqueous monoethanolamine. *Chemical Engineering Transactions* 70, 919–924.
- Sommerville R., Zhu P., Rajaeifar M.A., Heidrich O., Goodship V., Kendrick, E., 2021. A qualitative assessment of lithium ion battery recycling processes. *Resources, Conservation and Recycling* 165, 105219.
- Wang D., Belharouak I., Ortega L.H., Zhang X., Xu R., Zhou D., Zhou G., Amine K., 2015. Synthesis of high capacity cathodes for lithium-ion batteries by morphology-tailored hydroxide co-precipitation. *Journal of Power Sources* 274, 451–457.
- Xu J., Lin F., Doeff M.M., Tong W., 2017. A review of Ni-based layered oxides for rechargeable Li-ion batteries. *Journal of Materials Chemistry A* 5, 874–901.
- Yang Y., Xu S., He Y., 2017. Lithium recycling and cathode material regeneration from acid leach liquor of spent lithium-ion battery via facile co-extraction and co-precipitation processes. *Waste Management* 64, 219–227.
- You B., Wang Z., Shen F., Chang Y., Peng W., Li X., Guo H., Hu Q., Deng C., Yang S., Yan G., Wang J., 2021. Research Progress of Single-Crystal Nickel-Rich Cathode Materials for Lithium Ion Batteries. *Small Methods* 5, 2100234.