

Resynthesis of NMC111 Cathodic Material from Real Waste Lithium Ion Batteries

Pier Giorgio Schiavi*, Mario Branchi, Eleonora Casalese, Pietro Altimari, Maria Assunta Navarra and Francesca Pagnanelli

^aDepartment of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro n.5, 00185, Rome, Italy
piergiorgio.schiavi@uniroma1.it

In this work, the role of the experimental conditions during the synthesis of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ cathodic material (NMC) precursor was evaluated. Precursor synthesis was carried out starting from the electrodic powder obtained from the mechanical treatment of spent lithium ion batteries. Metals were extracted by acid-reducing leaching of the electrodic powder with an extraction yield higher than 90%. Cobalt was the most concentrated metals followed by manganese and nickel. Iron, copper and aluminium, coming from battery cases and current collectors, were present as impurities in the leachate. Selective precipitation of the impurities was performed prior to precipitate the mixed hydroxide. $\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}(\text{OH})_2$ precipitations were carried out using two concentrations of NH_4OH and under nitrogen or air atmosphere. The effect of these parameters was evaluated on the NMCs structure by XRD analysis and on the electrochemical performance by the galvanostatic cycling of the NMCs when assembled in half lithium cells. XRD analysis of the NMCs have showed the obtainment of the typical layered structure of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ for any synthesized NMC and no other phases related to single oxides were found. The evaluation of the electrochemical performance has showed a significant role of the precipitation atmosphere and an improvement of the specific capacity was attained using the lowest concentration of NH_4OH . Remarkably, specific capacity values of recovered NMCs were comparable to NMCs synthesized under the same experimental conditions but using synthetic reagents.

1. Introduction

Due to the large consumption of lithium ion batteries (LIBs), a huge amount of end-of-life batteries will be disposed in the next years. In this perspective, efficient processes for LIBs recycling are required to avoid human and environmental risks represented by hazardous electrode materials contained in LIBs. In addition, the exponential increase of LIBs demand has produced a massive exploitation of the primary resources (Schiavi et al., 2019). Consequently, the main components of the LIBs electrode materials, such as graphite, cobalt, lithium and nickel, have become strategic or critical raw materials. In this perspective the recycling of the end of life LIBs is crucial to reclaim the batteries components and sustain the LIBs manufacturing chain. LIBs recycling can be carried out using pyrometallurgical processes, but electrodic materials such as lithium, aluminium and graphite are involved in secondary reactions or lost in the smelting slag (Ciez et al., 2019). Furthermore, downstream operations are generally required to separately recover cobalt and nickel (Schiavi et al., 2021). On the other hand, the possibility to feed spent LIBs together with other wastes and without any mechanical pre-treatment has led pyrometallurgical processes to be the method of choice for the treatment of spent LIBs. Another promising recycling approach involves hydrometallurgical processes. These processes are characterized by lower costs and emissions if compared with pyrometallurgical ones (Xu et al., 2020). Differently from the pyrometallurgical, the hydrometallurgical processes can ensure a complete recovery of all battery components into high purity streams (Graphite, Co, Ni, Mn and Li salts) (Meshram et al., 2020). One of the principal shortcoming of this approach regards the need of several purification stages to obtain high purity metal salts. To this purpose, several downstream operations (solvent extractions, selective precipitation, electrodeposition), that lead to a huge consumption of reactants and energy, as well as liquid and solid wastes

production, are required. In this work, a different approach for the recovery of metals contained in waste LIBs was followed. Metals extraction was reached by a consolidated acid-reducing leaching of the electrodic powder. The obtained leach liquor composed mainly by cobalt, nickel and manganese, was directly employed for the synthesis of new $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ cathodic material (NMC111) avoiding all the separation/purification steps usually employed for the recovery of cobalt, nickel and manganese as high-grade salts (Schiavi et al., 2021). The role of experimental condition during the NMC precursor synthesis ($\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}(\text{OH})_2$) starting from the leachate were investigated in order to simplify and promote the scalability of the synthesis procedure. In this view, precursor synthesis was performed following two different routes including the precipitation of mixed hydroxide in controlled inert atmosphere or by simple precipitation in air. The role of precursor synthesis conditions was evaluated by benchmarking the electrochemical performances of the different recycled NMC cathodes.

2. Materials and Methods

2.1 NMCs synthesis

Synthesis of NMCs were obtained starting from real waste electrodic powder coming from the mechanical pretreatment of spent LIBs. LIBs were collected and crushed by an Italian waste disposal company (Seval s.r.l. – Colico). Crushed batteries were lab-sieved for the separation of plastics, steel, copper and aluminium coming from battery case and current collectors. Sieving under <0.5 mm allowed the obtainment of the metal-rich electrodic powder. Electrodic powder was employed as raw material for the synthesis of NMCs. Metals were extracted by a consolidated acid-reducing leaching route. Briefly, electrodic powder was leached with 1.5 M H_2SO_4 (Sigma-Aldrich 95-97%) with a solid/liquid ratio of 1/10. Leaching was carried out at 80 ± 1 °C in a jacketed reactor for 3 h and under mechanical stirring. After 1 h, 15% v.v. of H_2O_2 (Sigma-Aldrich 30%) to respect the acid volume was added as reducing agent. Obtained leachate undergone a selective precipitation of impurity by adjusting the solution pH to 5.5. Resulting solutions was employed for the coprecipitation of $\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}(\text{OH})_2$ the precursor for NMCs synthesis. Since cobalt was the most concentrated metal in the solution, the molar ratio of Ni:Mn:Co was adjusted to 1:1:1 by adding Ni and Mn in the form of their hydrated sulphate salts ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$). Final concentration was checked analyzing the solution by atomic absorption spectroscopy (AAS – ContrAA300 Analytic Jena GBH). $\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}(\text{OH})_2$ was precipitated at 60 °C for a duration of 17 h by a co-precipitation process involving NaOH and NH_4OH as complexing agent. NaOH solution was added under vigorous and controlled stirring, until pH=11 was reached. The above-mentioned procedure is a consolidated co-precipitation method and is generally carried out under nitrogen atmosphere. To evaluate the role of nitrogen atmosphere precipitation was carried out also in air and two different NH_4OH concentrations were employed. To obtain $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, lithium carbonate was added to the hydroxide precursor with 1.1:1 molar ratio to compensate lithium evaporation. The hydroxide and lithium carbonate were grounded in mortar and the obtained mixture was first heated to 450 °C for 5 h and then sintered to 900 °C for 10 h. To benchmark the performances of the different recovered NMCs, analogous NMCs were produced by using synthetic reagents. Table 1 displays all the NMCs synthesized under the different experimental conditions.

Table 1: NMCs synthesized under the different experimental conditions

NMC	$[\text{NH}_4]^+$	Precipitation atmosphere	Precursor solution
LNS	0.044	Nitrogen	Synthetic
LNR	0.044	Nitrogen	Recovered
HNS	0.360	Nitrogen	Synthetic
HNR	0.360	Nitrogen	Recovered
HAS	0.360	Air	Synthetic
LAS	0.044	Air	Synthetic

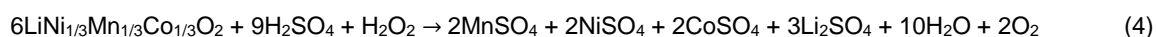
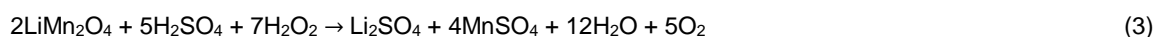
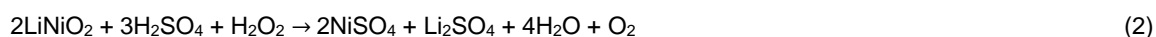
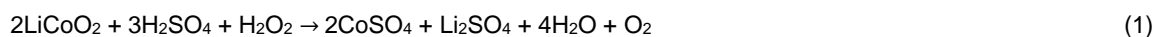
2.2 NMCs characterization

Powder X-ray diffraction (XRD, Rigaku, D-Max Ultima) employing Cu K α radiation was used to identify the crystalline phase of the prepared materials. Electrochemical characterizations were carried out using electrodes prepared by casting a dispersion of the cathodic materials on aluminium foil current collector. The dispersion was composed by 10% of carbon conducting agent (Super P, Timcal), 10% binder (PVDF Sigma-Aldrich) and 80% of cathodic materials in N-methyl pyrrolidone (NMP, Sigma-Aldrich). The resulting film was cut into disks of 10 mm diameter and dried. The prepared cathodes were assembled in a two electrode R2032 coin-type cells where lithium metal disk was used as negative electrode. The employed electrolyte was LiPF_6 1 M in an Ethylene

Carbonate - Dimethyl Carbonate, 1:1 v:v solution (LP30). Each cell was assembled in an argon-filled glove box with a content of O₂ and H₂O less than 1 ppm. Galvanostatic cycling tests at a current rate of C/10 (1C = 160 mAhg⁻¹) were carried out with a battery tester (Maccor series 4000) using a voltage range between 4.8–2.3 V. All the galvanostatic cycling experiments were carried out in triplicate. Replicas have shown a deviation on the specific capacity values within ±10%.

3. Results and discussion

Table 2 shows the composition of the metals solution resulting after the leaching of the electrodic powder. Cobalt is the most concentrated metal due to the massive use of LiCoO₂ cathodic material during the last years. Manganese and nickel content could be attributed both to their lithiated oxides (LiNiO₂, LiMn₂O₄) and to the presence of mixed oxides (NMCs). Copper and aluminium impurities come from the anodic and cathodic current collectors, respectively. Iron presence is probably related to the steel that compose the batteries case but the presence of LiFePO₄ cannot be excluded. End of life batteries are disposed with different charge state e.g. with different lithiation grade of the metal oxides that compose the cathodic materials. Depending on the lithiation grade, the oxidation state of the target metals (Co, Ni, Mn) are ranging from +2 to +4. In order to extract the metals and obtain water soluble metal salts the reduction of metals to +2 oxidation state is required. For this purpose, H₂O₂ was added as a reducing agent and the leaching mechanism can be described by the following reactions:



Using the acid-reducing leaching an extraction yield higher than 90% was reached for all the target metals as reported in Table 2. In order to remove the Cu, Al and Fe impurities that can hinder the electrochemical performances of the final NMCs a selective precipitation at pH 5.5 was performed. After filtration the purified solution was analysed and the results are reported in Table 2. Fe and Al concentrations are lower than 0.5 mg L⁻¹ while copper concentration is lower of about one order of magnitude to respect the pristine leachate. It should be noted that the concentration of the target metals decreases to respect the leachate. The lower concentration can be mainly attributed to the increase of solution volume after leachate neutralization using NaOH solution. We cannot exclude that a partial precipitation of the target metals could recur at the final purification pH of 5.5 and an optimization of the precipitation pH should be performed in order to minimize losses of target metals and maximize the abatement of impurities.

Table 2: Leachate composition resulting after electrodic powder leaching and its subsequent purification at pH 6.5.

	Co	Ni	Li	Mn	Cu	Fe	Al
Leachate (g L ⁻¹)	15.5	4.9	3.7	7.7	0.9	0.8	0.2
Extraction yield (%)	93.5	96.9	98.9	99.9	95.4	53.9	73.1
Purified leachate (g L ⁻¹)	9.8	2.3	0.9	3.6	0.1	< 5E-04	< 5E-04

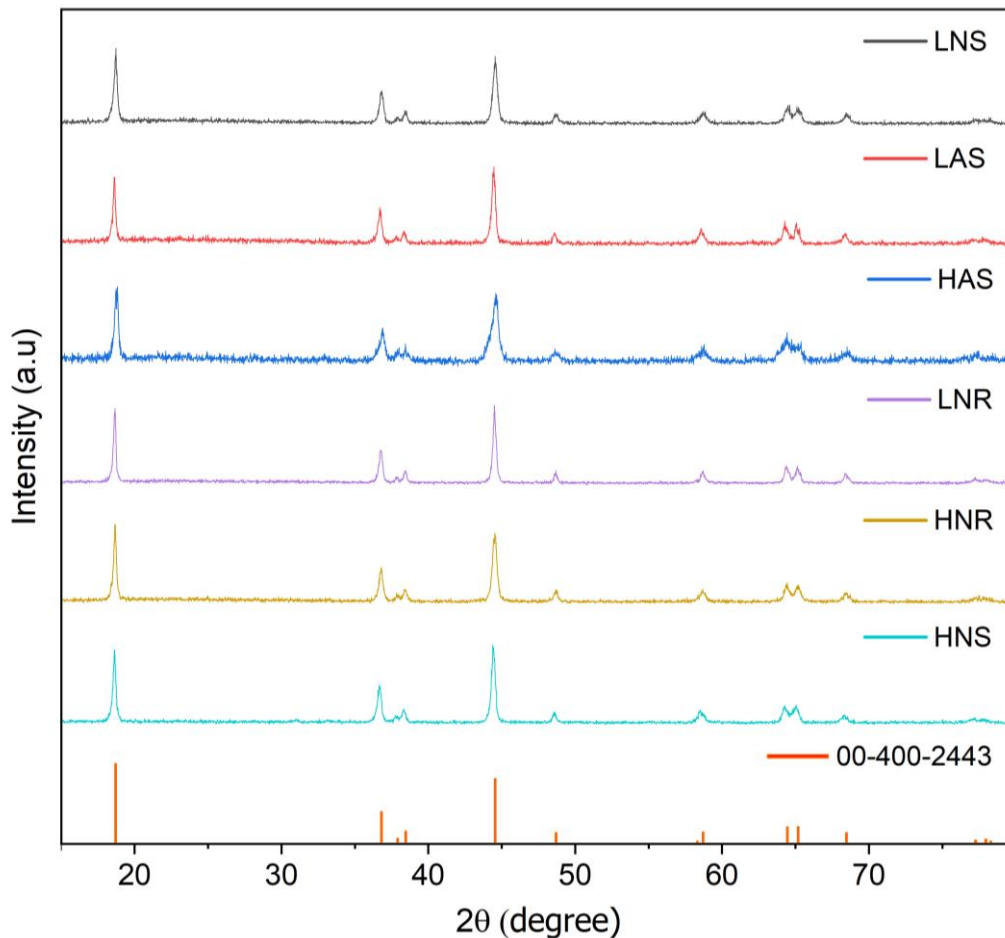


Figure 1: XRD patterns recorded for the NMCs synthesized at different operating conditions

Purified leachate was precipitated with the addition of NH_4OH as a chelating agent. As reported by Lee et al. (2004) during the precipitation of the mixed hydroxide, single $\text{Ni}(\text{OH})_2$, $\text{Co}(\text{OH})_2$ or $\text{Mn}(\text{OH})_2$ can be formed as impurity phase in the final recovered product. Furthermore, NH_4OH was also added to control the particle size, shape and tap-density of the hydroxides. For this purpose, $\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}(\text{OH})_2$ was precipitated from the purified leachate using two different NH_4OH concentrations to evaluate its role during the $\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}(\text{OH})_2$ formation. Obtained mixed hydroxides was calcined with an excess of lithium ($\text{Li}/(\text{Ni}+\text{Co}+\text{Mn}) = 1.10$) to compensate for its evaporation during the high temperature calcination. Figure 1 displays the XRD pattern recorded for any synthesized NMCs. All the synthesized NMCs showed the typical layered structure of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ and all the pattern confidentially match with the reference spectra. No other peaks attributable to single metal oxide phases were detected at any investigated condition. Rietveld method, relying on the powder diffraction step-scanned intensities, was performed to refine the crystal structure (Rietveld et al., 2014). The space group chosen was $R\bar{3}m$ and the obtained lattice parameters are showed in Table 3.

No significant differences were found on the estimated lattice parameters, while deviation on the crystallite dimension can be noted. In particular, the lower investigated concentration of NH_4OH allows the obtainment of lower crystallite dimension for both synthetic and recovered NMCs when the precipitation of their relative precursors was carried out in nitrogen. Differently, the dimension of crystallites follows the opposite trend when the synthetic precursor solutions was precipitated in air. To evaluate the effect of synthesis conditions on electrochemical performances of the NMCs, the produced cathodic materials was tested in a half lithium cell with metallic lithium as counter electrode. Galvanostatic cycling of the NMCs were carried out at 0.1 C (1 C =

Table 3: Structural parameters obtained from XRD refinement of the different NMCs obtained after precursors calcination. Values in brackets are the associated errors.

NMC	Crystallite dimension (Å)	a (Å)	c (Å)
LNS	971.53(6)	2.867(0)	14.243(2)
LNR	870.77(5)	2.865(9)	14.250(4)
HNS	992.73(5)	2.869(4)	14.254(2)
HNR	965.49(1)	2.866(2)	14.244(8)
HAS	840.79(1)	2.865(9)	14.248(0)
LAS	990.40(1)	2.866(1)	14.247(4)

160 mAh g⁻¹) the discharge specific capacities recorded during cycling are reported in Figure 2. Synthetic NMCs obtained with the highest concentration of NH₄OH show a great influence of the precipitation atmosphere. HNS NMC has a discharge capacity on the second cycle of 140 mAh g⁻¹ while the electrode obtained in air atmosphere displays a discharge capacity of 80 mAh g⁻¹ (Figure 2a). Remarkably, a slight higher specific capacity was found for the electrode synthesized starting from the recovered metals (HNR - Figure 2a) to respect the analogue NMC produced with synthetic solution (HNS - Figure 2a). The same effect of the precipitation atmosphere was found using the lowest concentration of NH₄OH. In fact, LAS electrode displays the lower specific capacity of 78 mAh g⁻¹ at the second cycle while LNS electrode displays the highest recorded capacity of 157 mAh g⁻¹ among all the tested NMCs. Most important, the recovered electrode coming from the synthesis of precursors in nitrogen atmosphere and with the lowest concentration of NH₄OH (LNR - Figure 2b) display a capacity trend close to the same electrode obtained using the synthetic solution (LNS - Figure 2b). Regarding the low capacities attained for the electrodes precipitated in air, further characterization of the NMC materials should be performed. In fact, the nitrogen atmosphere during the precipitation of the mixed hydroxide precursor should avoid the oxidation of the metals during the precipitation with the consequent formation of single metal oxides. On the other hand, from the XRD analysis no other phases were detected after the calcination of the precursors. To better clarify this effect, an in depth characterization of the produced NMCs such as tap density and particle size distributions could be helpful. In addition, it should be highlighted that the synthesis of the mixed hydroxide precursor was carried out with a concentration of metals (0.16 M) about one order of magnitude lower respect to the conventional concentration (2 M) reported through the literature for the synthesis of NMCs (Gratz et al., 2014). The metals concentration has a key role during the formation of the precursor particles in the co-precipitation stage (Lai et al., 2019) but the concentration employed in this work is dictated by the recovery process and strictly depends on the solid/liquid ratio employed during the leaching of the electrodic powder.

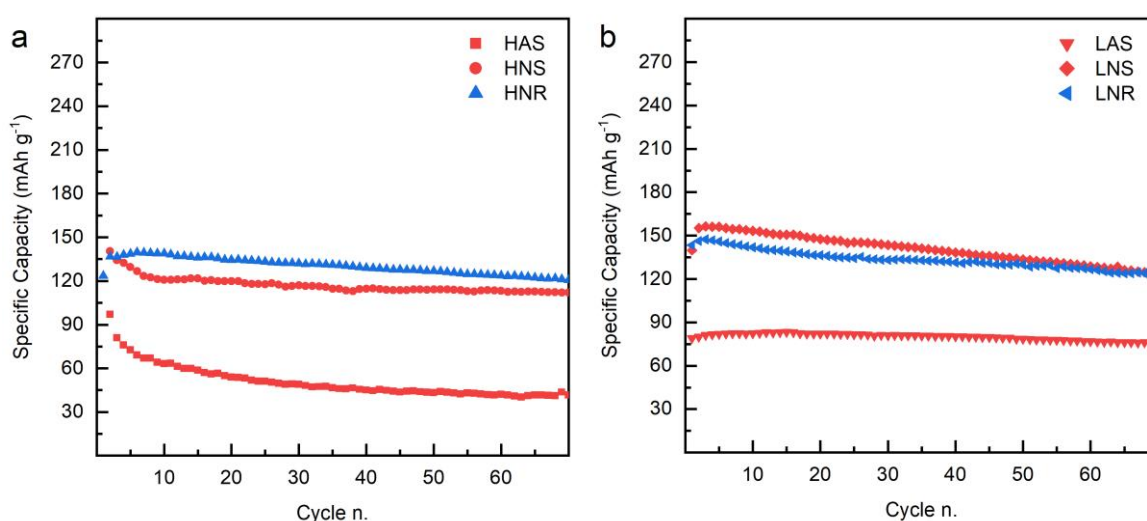


Figure 2: Galvanostatic cycling of the recovered and synthetic NMCs produced under different experimental conditions

4. Conclusion

The role of precursor synthesis conditions was evaluated on the electrochemical performance of the NMCs synthesized starting from waste LIBs. In particular, the role of NH_4OH concentration and precipitation atmosphere was evaluated. XRD analysis of the NMCs displays the obtaining of the typical layered structure of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ for any synthesized NMC and no other phases related to single oxides were found. The evaluation of the electrochemical performance by galvanostatically cycling the NMCs, has shown a significant role of the precipitation atmosphere and an improvement of the specific capacity using the lowest concentration of NH_4OH . Remarkably, using the same experimental conditions, specific capacity values of recovered and synthetic NMCs were comparable. The obtained results highlight as the attained electrochemical performances are lower if compared with commercial grade NMCs materials. This can be explained by the lower concentration of metals employed for the synthesis of the mixed hydroxide precursors. On the other hand, this lower concentration, of about one order of magnitude to respect the concentration used in the works reported in the literature, is dictated by the metals extraction process. In order to obtain more concentrated leachate an optimization of the leaching procedure should be assessed allowing for the evaluation of the role of metals concentration during NMC resynthesis.

Acknowledgments

Mechanical treatment operations were carried out within the transferability activities of LIFE-LIBAT project (LIFE16 ENV/IT/000389). Optimization of NMCs synthesis conditions was carried out within LIFE-DRONE project (LIFE19 ENV/IT/000520)

References

- Ciez, R. E., & Whitacre, J. F., 2019., Examining different recycling processes for lithium-ion batteries. *Nature Sustainability*, 2(2), 148-156.
- Lai, W.-H., Wang, Y.-X., Wang, Y., Wu, M., Wang, J.-Z., Liu, H.-K., Dou, S.-X., 2019, Morphology tuning of inorganic nanomaterials grown by precipitation through control of electrolytic dissociation and supersaturation. *Nature Chemistry*, 11(8), 695-701.
- Lee, M. H., Kang, Y. J., Myung, S. T., & Sun, Y. K., 2004, Synthetic optimization of Li [Ni_{1/3}Co_{1/3}Mn_{1/3}] O₂ via co-precipitation. *Electrochimica Acta*, 50(4), 939-948.
- Gratz, E., Sa, Q., Apelian, D., & Wang, Y., 2014, A closed loop process for recycling spent lithium ion batteries. *Journal of Power Sources*, 262, 255-262.
- Meshram, P., Mishra, A., Abhilash, R., Environmental impact of spent lithium ion batteries and green recycling perspectives by organic acids – A review, 2020, *Chemosphere*, 242, 125291.
- Rietveld, H., M., The rietveld method, 2014, *Physica Scripta*, 89, 98002.
- Schiavi, P. G., Altimari, P., Zanoni, R., & Pagnanelli, F., 2021, Full recycling of spent lithium ion batteries with production of core-shell nanowires//exfoliated graphite asymmetric supercapacitor. *Journal of Energy Chemistry*, 58, 336-344.
- Schiavi, P.G., Altimari, P., Branchi, M., Zanoni, R., Simonetti, G., Navarra, M.A., Pagnanelli, F., 2021, Selective recovery of cobalt from mixed lithium ion battery wastes using deep eutectic solvent, *Chemical Engineering Journal*, 417, 129249
- Schiavi, P. G., Farina, L., Zanoni, R., Altimari, P., Cojocariu, I., Rubino, A., Navarra M.A., Panero S., Pagnanelli, F., 2019, Electrochemical synthesis of nanowire anodes from spent lithium ion batteries. *Electrochimica Acta*, 319, 481-489.
- Xu, C., Dai, Q., Gaines, L., Hu, M., Tukker, A., Steubing, B., 2020, Future material demand for automotive lithium-based batteries, *Communications Materials*, 1, 99.