energies

MDPI

Article

Cryo-Mechanical Treatment and Hydrometallurgical Process for Recycling Li-MnO_2 Primary Batteries with the Direct Production of $LiMnPO_4$ Nanoparticles

Pier Giorgio Schiavi *, Flavia Carla dos Santos Martins Padoan, Pietro Altimari and Francesca Pagnanelli

Department of Chemistry, Sapienza University of Rome, P.le A. Moro 5, 00185 Rome, Italy; flaviacarla.padoan@uniroma1.it (F.C.d.S.M.P.); pietro.altimari@uniroma1.it (P.A.); francesca.pagnanelli@uniroma1.it (F.P.)

* Correspondence: piergiorgio.schiavi@uniroma1.it

Received: 2 July 2020; Accepted: 27 July 2020; Published: 3 August 2020

Abstract: In this work, an innovative hydrometallurgical recycling route for the recovery of all the materials composing Li-MnO_2 primary batteries was proposed. End-of-life batteries were mechanically treated in an innovative pilot plant where a cryogenic crushing was performed. The mechanical treatment allowed for the release of the electrodic powder contained in the batteries with the simultaneous recovery of 44 kg of steel and 18 kg of plastics from 100 kg of batteries. Electrodic powder was employed as the raw material for the synthesis of $LiMnPO_4$ nanoparticles. To obtain the synthesis precursors, selective sequential leaching of Li and Mn was performed. Li was extracted via water washing the electrodic powder and Li_2CO_3 and a purity of 99% was recovered. The black mass containing Mn oxides was leached using phosphoric acid, which gave a Mn-bearing precursor solution that was directly used for the hydrothermal synthesis of $LiMnPO_4$ nanoparticles. A preliminary materials balance of the process was presented, indicating that the proposed process should be an easy hydrometallurgical route for the recycling of primary lithium batteries. In addition, the simultaneous production of high-value-added products that could be reintroduced into the battery manufacturing chain could ensure the economic feasibility of the process.

Keywords: Li batteries recycling; $LiMnPO_4$ nanoparticles; cryo-mechanical treatment; metallic lithium

1. Introduction

The collection and recovery of batteries in Europe are regulated by the Directive 2006/66/EC, which prohibits the disposal in landfills or incineration of waste batteries and accumulators. The targets set by the legislation are to collect 65% and recover 50% by weight of the batteries [1].

Primary batteries represent about 75% of the total batteries and accumulators placed on the EU market in 2018. Among this kind of battery, alkaline represents 61%, zinc carbon represents 10%, lithium represents 3%, and silver oxide represents 1%. The residual 25% of the total batteries placed on the EU market is composed of secondary batteries (Li-ion: 16%, Ni-MH: 6%) [2]. Li-MnO_2 type, which represents 3% of primary batteries, still presents many critical issues regarding recycling. The presence of highly reactive metallic lithium and organic solvents, which compose the electrolytic solution, entail safety risks during the recycling of these batteries. Li primary batteries are currently treated along with Li-ion batteries in a few big pyrometallurgical plants in Northern EU countries [3,4]. Nevertheless, pyrometallurgical processes do not allow for the recovery of non-metals, such as graphite and carbon, and Li and Mn end up in the slag, which requires additional steps for their recovery [5]. Furthermore, this kind of processing has negative environmental impacts due to the high energy

consumption, the release of pollutant gases, and the logistics of dangerous wastes traveling throughout the EU [6]. On the other hand, the release of the electrodic materials by mechanical treatments followed by their hydrometallurgical processing can potentially ensure the integral recovery of all materials composing Li primary batteries, including ferrous metals, non-ferrous metals, light metals, graphite, plastics, and paper [7].

In the literature, very few works have been reported regarding the hydrometallurgical treatment of primary lithium batteries because the attention was mainly devoted to Li-ion batteries. Kondas et al. proposed a two-step process for the recovery of lithium, which was preceded by a roasting treatment of Li-MnO_2 coin cells [8]. The first step consists of lithium extraction in water. The second step consists of the evaporation of the leach liquor, which allows for the recovery of lithium carbonate directly. However, in this work, the treatment of the residual solid containing mainly MnO_2 was not carried out.

In another work, Paulino et al. recovered Li and Mn separately after a preliminary calcination of the sample [9]. Lithium salts were recovered via solvent extraction. For the recovery of manganese, the material previously treated with solvent was leached in sulfuric acid and hydrogen peroxide. Manganese was recovered as the sulfate salt via evaporation of the leaching solution.

Previous works have reported interesting preliminary results but the state of the art is still far from scaling up to a commercial operation. In fact, even though batteries are metal-rich secondary raw materials, their sustainable exploitation can be hindered by the complexity of operations needed for their treatment. Such complex matrices often require an intricate network of operations for the separation and purification of metals, which involves several precipitations, solvent extraction, and stripping steps [10,11]. Research efforts are currently focused on the development of recycling processes that involve the least number of hydrometallurgical operations. In addition, the direct production of high-added-value products has been included to promote the economic feasibility of the processes [12,13].

The aim of this work was the development of a hydrometallurgical recycling route for Li-MnO_2 batteries. For this purpose, all the materials composing Li-MnO_2 batteries were recovered by implementing an innovative mechanical pre-treatment and the hydrometallurgical recovery of Mn and Li as $LiMnPO_4$ (LMP) nanoparticles. To our knowledge, a mechanical pre-treatment, including the cryogenic crushing of the batteries, is reported here for the first time. Cryogenic crushing allowed for the safe release of the electrodic powder contained in the batteries and for obtaining recoverable plastics and steel streams. The electrodic powder, mainly composed of Li and Mn, was leached using a mixture of H_3PO_4 and H_2O_2, which directly gave a Mn-bearing solution that was employed as the precursor solution for the synthesis of LMP nanoparticles. This approach allowed for the simultaneous recovery of both Li and Mn in a final product with a high added value. $LiMnPO_4$ is an olivine type cathodic material that is used in the production of cathodes in lithium-ion batteries [14]. Due to its low intrinsic electronic and ionic conductivity, the most followed approach to improve the performance of the olivine material is to minimize the particle size by producing nanostructured materials [15]. Finally, it must be noted that metal lithium batteries, where metallic lithium is used as an anode, are considered to be promising candidates for next-generation batteries [16,17]. The approach reported here could be extended to these kinds of innovative batteries.

2. Materials and Methods

2.1. Mechanical Pre-Treatments

The overall proposed process is shown in Figure 1. The starting sample used in this work was made up of waste Li-MnO_2 coin-cell type batteries. Collection and mechanical pre-treatment of the batteries were carried out by an Italian waste disposal company (SEVal srl, Colico, Italy). First, the batteries were stabilized by spraying them with liquid N_2 until the temperature of the battery batch reached −100 °C. This treatment was carried out on a cryogenic conveyor belt feeding a vertical hammer mill. The crushed samples were sieved and two fractions were identified, namely, a coarse

fraction (>1 mm) and a fine fraction (≤1 mm) were obtained. The coarse fraction was mainly composed of recoverable steel, while the fine fraction was represented by the electrodic powder.

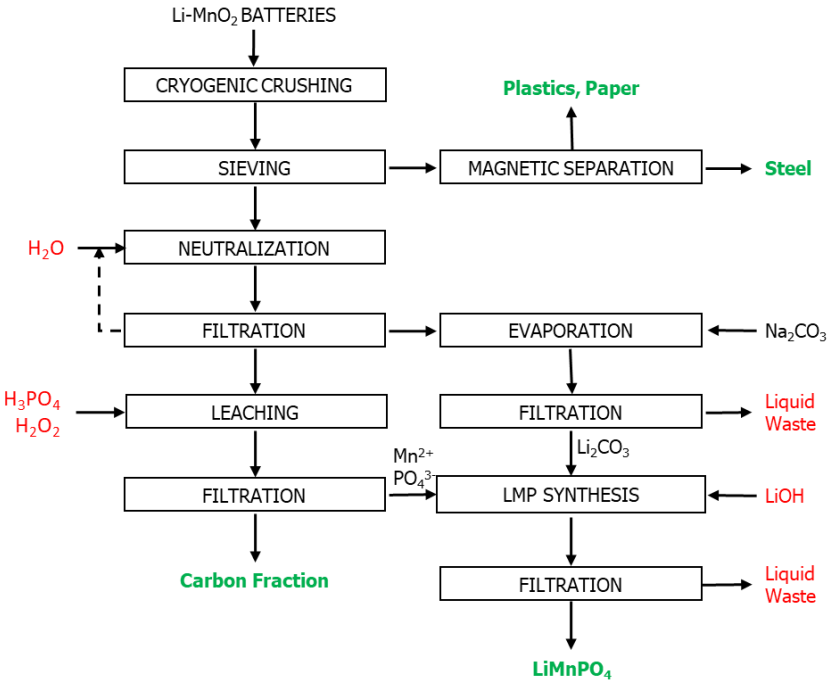


Figure 1. Scheme of the overall proposed process. LMP: $LiMnPO_4$.

2.2. Lithium and Manganese Extraction and Recovery

The electrodic powder was employed as a raw material for the synthesis of $LiMnPO_4$ nanoparticles. The electrodic powder was neutralized in a mechanically stirred reactor using water at room temperature and with a solid-to-liquid ratio equal to 1:5. The operation was performed to extract the soluble lithium coming from the metallic lithium anode and the electrolyte. After the filtration, the liquid stream was recycled for five subsequent washing operations of the electrodic powder samples. The resulting solution was employed for the precipitation of Li_2CO_3 at 95 °C; then, Na_2CO_3 was added. After two hours, the obtained suspension was filtered and oven-dried overnight at 105 °C.

The extraction of manganese from the electrodic powder was attained by leaching for 3 h under stirring at 85 °C with phosphoric acid at concentrations of 1.5 and 3.0 M. Hydrogen peroxide (35% *v*/*v*) was used as the reducing agent. A manganese-rich solution was recovered after the leachate filtration and used as the precursor solution in the LMP synthesis.

2.3. Synthesis of $LiMnPO_4$

The synthesis of $LiMnPO_4$ (LMP) was adapted from the method of Ji et al. [18]. The manganese-rich solution obtained after the electrodic powder leaching was used as a starting solution for the synthesis procedure. The lithium concentration was adjusted by adding the recovered Li_2CO_3 that was previously dissolved in a sulfuric acid solution. The amounts of acid, lithium carbonate, and leaching solution used were calculated to produce a final concentration of Mn^{2+} equal to 0.1 M in a final volume of 50 mL. Keeping the system under constant stirring, commercial LiOH was added until a pH of 11–12 was reached. The yellowish suspension obtained was transferred to a Teflon vessel and microwave heated (Milestone ETHOS 900 - Milestone srl, Sorisole - Italy) for 30 min at a temperature of 180 °C. LMP was obtained after filtration and washing with water, followed by ethanol. The recovered LMP was compared with synthetic LMP produced by applying the above-described method with commercial-grade synthetic reagents.

2.4. Characterizations

The metals content in all the liquid streams emerging from the different process operations were adequately diluted and analyzed using high-resolution continuum source atomic absorption spectroscopy (AAS, contrAA 300—Analytik Jena AG, Jena, Germany). The metals contained in the solid sample were extracted via microwave-assisted leaching (Milestone ETHOS 900) using 10 mL of aqua regia and 0.5 g of the solid sample. The resulting solution was adequately diluted and analyzed using AAS.

To characterize the morphology of the recovered Li_2CO_3 and LMP, field emission scanning electron microscopy (SEM, Zeiss Auriga–Carl Zeiss, Oberkochen, Germany) was employed. The chemical composition was determined using energy-dispersive X-ray spectroscopy (EDX, Bruker QUANTAX 123 eV–Bruker Corporation, Billerica, Massachusetts). Powder X-ray diffraction (XRD, Rigaku, D-Max Ultima–Rigaku Corporation, Tokyo, Japan) employing Cu Kα radiation was used to identify the crystalline phase of the produced samples.

3. Results

3.1. Recovery of Lithium and Production of the Mn^{2+}-PO_4^{3-} Precursor Solution

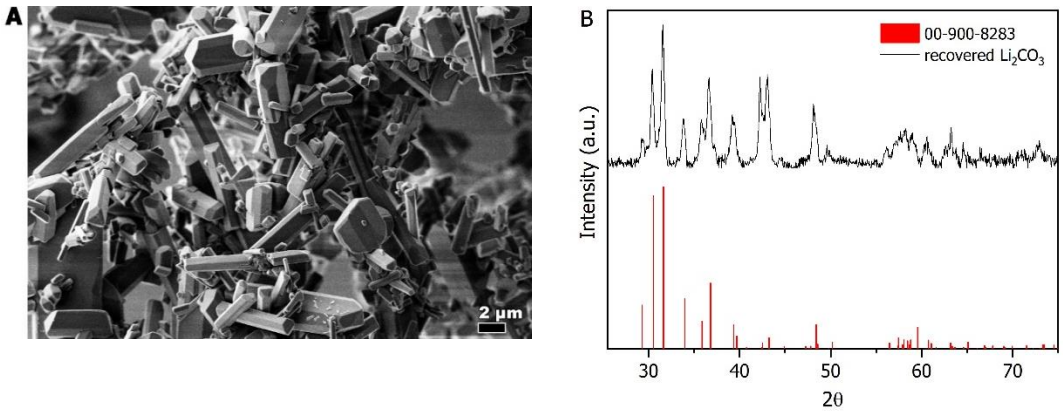
The sieving of the crushed batteries produced about a 20% fine fraction and an 80% coarse fraction. The fine fraction, which was mostly composed of electrodic powder (Figure 2A), contained 38.5 ± 0.7 and 420 ± 10 mg g^{-1} of Li and Mn, respectively. The coarse fraction was mainly composed of the steel and plastic and contained 1 ± 1 and 7 ± 2 mg g^{-1} of Li and Mn, respectively (Figure 2B). The steel content of the coarse fraction was about 45% by mass and could be directly recovered. The plastic fraction on the coarse fraction was about 18%. The electrodic powder was washed in water to extract the lithium coming from the residual metallic Li anode, the Li oxidized species formed during the crushing (LiOH, Li_2O), and from the electrolyte [19].

Figure 2. Fine (**A**) and coarse (**B**) fractions that resulted from the cryogenic crushing. The fine fraction was mainly composed of electrodic powder. The coarse fraction was composed, from left to right, of plastics, steel, and paper separators.

About half of the total Li contained in the electrodic powder was extracted. This less than quantitative extraction could be attributed to the presence of insoluble $LiMnO_2$ produced as the battery discharged ($Li + MnO_2 \rightarrow MnOOLi$) and, in a minor part, to the formation of organic lithium species generated by the lithium reaction with electrolyte solutions while the batteries discharged [20]. The recovery of lithium was attained through its precipitation as Li_2CO_3. To obtain a high Li^+ concentration and reduce the energy needed for concentrating via water evaporation, the washing solution was recycled to neutralize the fresh electrodic powder.

The effect of the number of washing cycles on the lithium extraction was evaluated and the results are reported in Table S1 of the supporting information file. After four washing cycles with the same solution, the lithium reached a maximum concentration of about 4 g L^{-1}. The recycling of the lithium solution beyond the fourth time resulted in no additional lithium extraction. The liquid phase obtained after the four washing cycles was used for the lithium precipitation with sodium carbonate. The solubility gap between Li_2CO_3 and Na_2CO_3 at a temperature close to the boiling point of the system allowed for the precipitation of high-purity Li_2CO_3. Crystalline Li_2CO_3 formation was confirmed, both from the SEM analysis of the solid (Figure 3A) and the XRD analysis of the produced solid. The

experimental XRD spectrum matched the Li_2CO_3 peaks when compared with a reference spectra (Figure 2B). The impurities in the obtained Li_2CO_3 were estimated after its dissolution and subsequent AAS analysis of the resulting solution (Figure 3C). Mn and Fe contents lower than 0.1% were found. Based on these data, the estimated purity of the product was higher than 99%, while about 95% of the lithium contained in the washing solution was recovered.



C

Li (mg g^{-1})	Mn (mg g^{-1})	Fe (mg g^{-1})
188.1 ± 2.8	0.10 ± 0.01	0.023 ± 0.002

Figure 3. (**A**) SEM image of recovered Li_2CO_3 crystals, (**B**) XRD powder diffraction of recovered Li_2CO_3 compared with a reference pattern, and (**C**) the composition of Li_2CO_3 estimated using atomic absorption spectroscopy (AAS).

To obtain the Mn^{2+} and PO_4^{3-} precursors for the LMP synthesis, the extraction of manganese and residual lithium was carried out by leaching the already water-leached electrodic powder with phosphoric acid. Due to the Mn^{4+} insolubility, a reducing agent to form Mn^{2+} and/or Mn^{3+} was needed. For this purpose, hydrogen peroxide was evaluated as a reducing agent by using two different concentrations of H_3PO_4. The H_3PO_4 concentrations were chosen to respect the stoichiometry of the following reaction:

$$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O. \quad (1)$$

Considering that the dissociation of H_3PO_4 was dominated by a single dissociation, two acidic solutions were employed. The first solution contained the stoichiometric amount of H^+ (1.5 M) to react with Mn, while the second solution contained a 100% excess of H^+ (3 M). Figure 4 shows the effects of the H_3PO_4 concentration and reducing agent on the Mn and Li extraction. Using 3.0 M phosphoric acid and 20% (*v*/*v*) hydrogen peroxide, the maximum yield of Mn extraction was about 75%. It is well known that Mn compounds, such as MnO_2, as well as activated carbon, can catalyze hydrogen peroxide decomposition to produce water and oxygen (Equations (2) and (3)) [21,22].

$$2H_2O_2 \overset{MnO_2}{\rightarrow} 2H_2O + O_2 \quad (2)$$

$$MnO_2 + 2H^+ + H_2O_2 \rightarrow Mn^{2+} + O_2 + 2H_2O \quad (3)$$

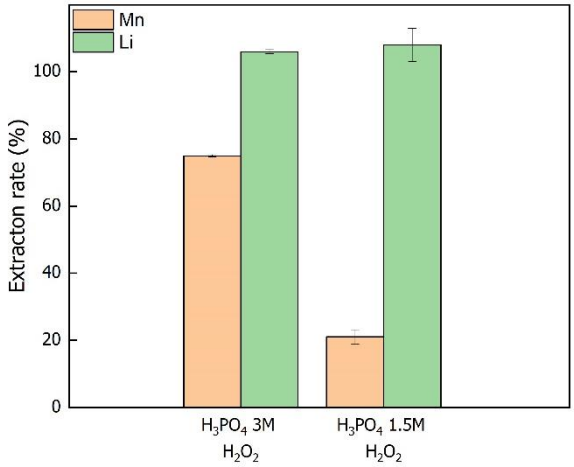


Figure 4. Extractive yields of Li and Mn after leaching for 3 h under stirring at 85 °C.

Therefore, to ensure enough reductant was added, an excess of 400% of hydrogen peroxide was employed in the leaching experiments. The use of H_2O_2 is often a critical issue for the development of a hydrometallurgical process, where its inadvertent decomposition implies a large consumption that could hinder the economic feasibility of the overall process. To avoid the use of H_2O_2, glucose was further investigated as a reducing agent. The results are reported in Figure S1. The use of glucose was already reported for the extraction of manganese using nitric acid as a leaching agent [23]. On the other hand, the obtained Mn extraction rates using glucose and phosphoric acid were lower than 10%. The H_2O_2 consumption together with the non-quantitative extraction will need to be studied further to establish more sustainable leaching conditions.

3.2. Synthesis and Characterization of $LiMnPO_4$

According to the literature, the minimum reaction time required to obtain $LiMnPO_4$ nanoparticles is only 5 min [24]. Preliminary synthetic experiments were therefore conducted for only five minutes without success. These experiments are not listed below but it was concluded that to obtain $LiMnPO_4$, a longer reaction time is required. The subsequent series of experiments were carried out with different reaction times to evaluate the effect of this parameter on the morphology and size of the obtained products. It was observed that after 30 min, parallelepiped-shaped particles with a length of about 1 micron and a width of 300 nm were obtained. EDX microanalysis (Table S2) also confirmed the presence of manganese and phosphorus, with a stoichiometric ratio close to 1:1, as expected from the theoretical stoichiometry (Li:Mn:P = 1:1:1).

The samples synthesized for 60 and 120 min were characterized in the same way as the previous sample. The resulting material showed the same morphology and dimensions (Figure 5). The Mn:P ratio data obtained from the elemental analysis was not sufficient to confirm the obtainment of $LiMnPO_4$. Therefore, X-ray diffraction analysis was performed. Since no significant effect due to the duration was found based on the SEM microscopy results, the best candidate for the analysis was the sample obtained after the lower synthesis duration of 30 min (S30). The XRD pattern (Figure 6) of sample S30 matched the reference pattern for $LiMnPO_4$ and confirmed the effective production of the characteristic crystalline phase of LMP.

Preliminary synthesis tests starting from the recovered materials were conducted by directly adding solid Li_2CO_3 to the Mn^{2+}-PO_4^{3-} precursor solution and then the pH was increased to the desired value. This procedure produced a precipitate that was probably composed of manganese carbonates that hindered the formation of LMP. The dissolution of the lithium carbonate in sulphuric acid before adding it to the solution allowed for the elimination of the CO_3^{2-} anions, causing the evolution of CO_2, and therefore the precipitation of carbonate was avoided. Figure 6 displays the SEM images of the LMP samples produced using the recovered lithium carbonate and Mn^{2+}-PO_4^{3-} solution.

Small particles of about 50 nm, with an atomic ratio Mn:P close to 0.75 (Table S2), were found in the sample with a reaction duration of 30 min (R30) (Figure 6A). Even in this case, the role of the reaction duration was investigated. The sample obtained after 60 min (R60) of reaction time showed more homogeneous particles with an average size of about 100 nm. By analyzing the areas of the sample in which the particles were clearly visible, the presence of manganese and phosphorus in a ratio close to 0.65 was verified (Table S2). EDX analysis of both the LMP produced by the recovery procedure revealed an excess of phosphorus.

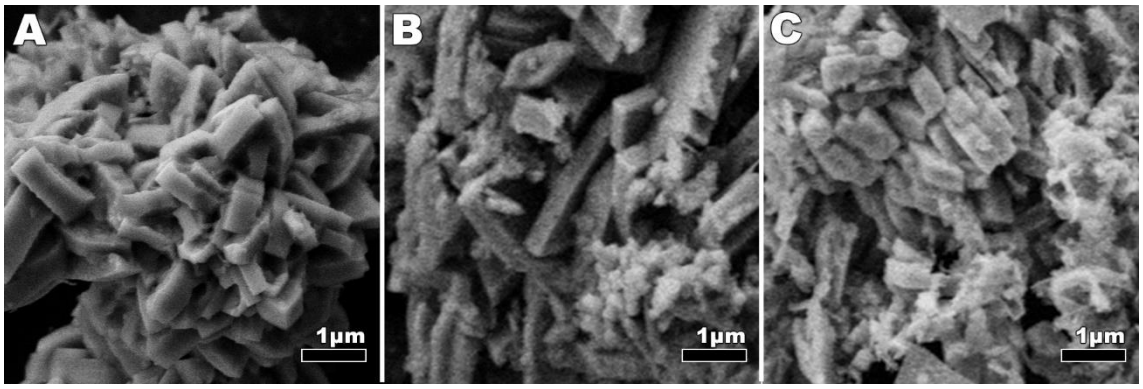


Figure 5. SEM images of LMP samples synthesized with 30 (**A**), 60 (**B**), and 120 (**C**) minutes of reaction time.

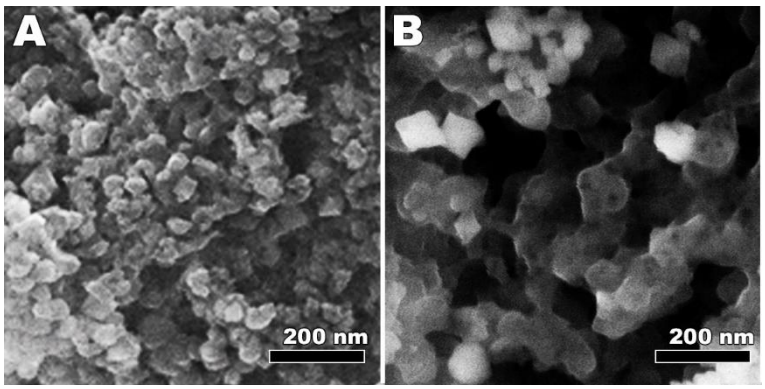


Figure 6. SEM images of the recovered R30 (**A**) and R60 (**B**) LMP.

XRD analysis of samples R30 and R60 was performed and the relative patterns are shown in Figure 7. Different to sample S30, both samples R30 and R60 showed the presence of other peaks that were not related to the LMP phase. In particular, samples R30 and R60 showed some characteristics peaks that could be related to the formation of Li_3PO_4. Furthermore, the increase of the reaction time to 60 min enabled the formation of Mn_3O_4, as revealed by the XRD pattern of the R60 sample. Due to the formation of the Mn_3O_4 phase, a reaction time of 60 min could not be considered using the reported synthesis method. On the other hand, it is noted that Li_3PO_4 is a soluble salt that can be easily removed by washing the produced solid. The formation of Li_3PO_4 could be related to the excess of PO_4^{3-} and Li contained in the precursor solution. The formation of Li_3PO_4 could be avoided with the addition of synthetic reagents to reach the desired stoichiometry between Li, Mn, and PO_4^{3-}. On the other hand, the introduction of primary sources into the proposed process goes beyond the aim of this work.

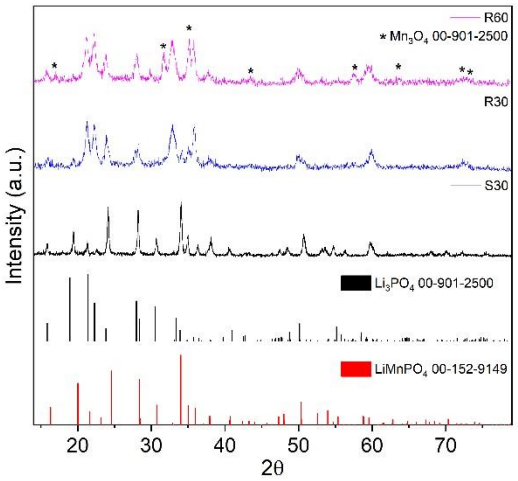


Figure 7. XRD spectra of the synthesized LMP and a reference spectra for LMP and Li_3PO_4.

3.3. Mass Balance of the Proposed Process

Data derived from the recovery of Li and Mn, together with the data obtained from the synthesis of the LMP, were employed to compose a preliminary materials balance of the whole proposed process. The amounts of the steel, electrodic powder, and plastics fractions were estimated after the crushing, sieving, and magnetic separation of 300 kg of Li-MnO_2 coin-cell batteries. The material mass balance was computed with the following considerations:

- The results of the electrodic powder washing showed about half of the total lithium contained in the batteries was present as an insoluble species. The insoluble lithium was considered to be $LiMnO_2$.
- The carbon fraction was estimated by subtracting the $LiMnO_2$ and MnO_2 amounts remaining in the fine fraction that resulted after water leaching. Here it was assumed that after water washing, the residual insoluble species were carbon, $LiMnO_2$, and MnO_2. The $LiMnO_2$ and MnO_2 amounts were estimated from the Li and Mn analysis in the washed electrodic powder.
- The remainder of the residue was considered to be made up of solvents and organic salts based on the datasheet of the most common coin-cell batteries on the market.

The inputs and outputs of the materials from the proposed process are included in the functional flow block diagram reported in Figure 8. Detailed compositions of all streams are given in Table S3. The materials' masses were computed for a batch feed consisting of 100 kg of batteries. The magnetic separation operation performed after the sieving produced for 44 kg of recoverable steel and 18 kg of a nonmagnetic fraction, which was mainly composed of the polypropylene to be separated. A total water supply of about 500 kg was needed to treat a battery batch and will become an amount of liquid waste to dispose at the end of the process. Performing the leaching with phosphoric acid allowed for a leachate precursor for the synthesis of 25 kg of LMP to be obtained. Due to the excess of PO_4^{3-} and Li^+ in the LMP synthesis streams, a solution with 6 kg of potentially recoverable Li_3PO_4 was the product at the end of the process. The proposed process, as the major part of the hydrometallurgical processes, used a large amount of water (5 kg of water per kg of treated batteries). The recycling of the water employed when processing the batteries could be advantageous for the sustainability of the process. Regarding the water needed for the neutralization (stream 7—Figure 8), recycling is currently expected. The same water stream can be used for the extraction of lithium in four consecutive batches, as illustrated in Section 2.2. After the recovery of Li_2CO_3 (stream 17—Figure 8), this solution will be rich in Na and the soluble organic electrolytes contained in the batteries. Characterization of the organic loading of the resulting solution should be addressed to evaluate possible further reuse of this stream. The wastewater coming from the LMP synthesis (stream 21—Figure 8) should contain only unreacted Li and could be recycled for the Li extraction (stream 7—Figure 8). A preliminary cost

analysis that took into account the reagents' costs and the products' revenues is reported in Table S4. Excluding the energy consumption costs, a positive economic balance of the process was found.

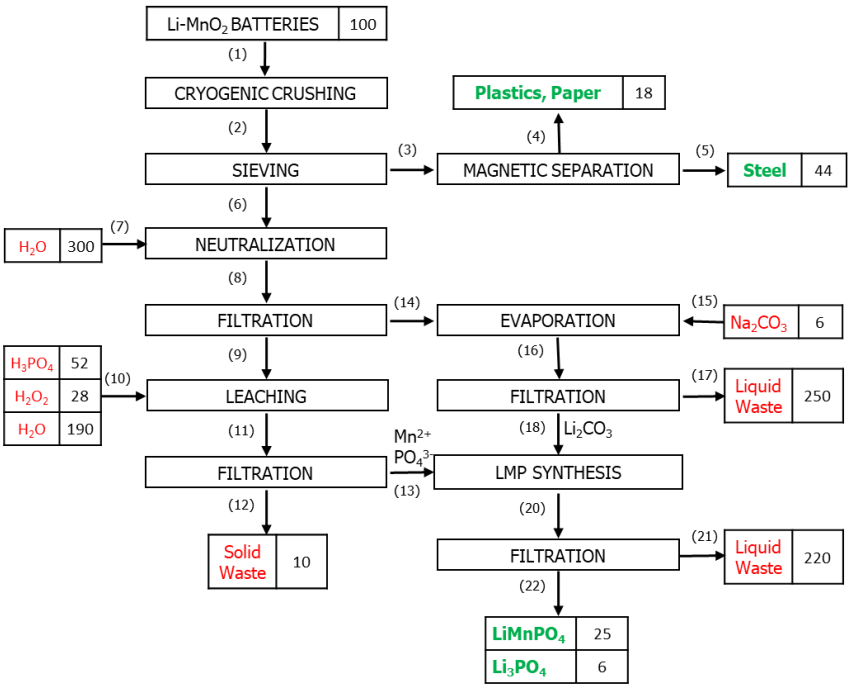


Figure 8. Functional flow block diagram including the materials balance in kilograms.

4. Conclusions

The proposed process is an attractive solution for the treatment of primary Li-MnO_2 batteries. These kinds of batteries are not treated with a dedicated process but instead are fed into a pyrometallurgical process with other wastes, resulting in the subsequent loss of Li and Mn. The cryogenic crushing of the batteries has allowed for their mechanical treatment without concern for the safety risks caused by the presence of metallic lithium and flammable electrolytes. Sieving 100 kg of crushed materials resulted in 44 kg of recoverable steel, 18 kg of plastics, and electrodic powder. The electrodic powder was employed as the raw material for the synthesis of $LiMnPO_4$ nanoparticles. Li_2CO_3 with a purity of 99% was recovered after its precipitation from the lithium-rich solution, which resulted from the washing of the electrodic powder. Leaching the electrodic powder with H_3PO_4 produced a Mn-bearing solution, which was directly employed for the synthesis of $LiMnPO_4$. The obtained data were employed to compose the materials balance of the process. After treating 100 kg of batteries, 25 kg of LMP and potentially 6 kg of Li_3PO_4 could be produced. The easy process configuration, together with the production of high-value-added products, could pave the way for the development of a dedicated process for the treatment of Li primary batteries.

Supplementary Materials: The following are available online at http://www.mdpi.com/1996-1073/13/15/4004/s1. Figure S1: Extractive yields of Li and Mn after leaching for 3 h under stirring at 85 °C. Table S1: Lithium concentration trend due to recycling the washing solution. Table S2: Mn, P, and O amounts in the produced LMP samples as estimated using EDX analysis. Table S3: Materials balance in kilograms of the proposed process. Table S4: Preliminary economic analysis of the process considering the operative costs excluding the costs associated with the energy consumption.

Author Contributions: Conceptualization, P.G.S. and F.P.; methodology, F.C.d.S.M.P. and P.G.S.; data curation, P.G.S.; writing—original draft preparation, P.G.S.; writing—review and editing, P.G.S., F.P. and P.A.; funding acquisition, P.A. All authors have read and agreed to the published version of the manuscript.

Funding: Mechanical treatment operations were carried out within the LIFE-LIBAT project (LIFE16 ENV/IT/000389).

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Directive, B. Directive 2006/66/EC of the European Parliament and of the Council of 6 September 2006 on batteries and accumulators and waste batteries and accumulators and repealing Directive 91/157/EEC. *Off. J. Eur. Union* **2006**, *266*, 1–14.
2. Stahl, H.; Baron, Y.; Hay, D.; Hermann, A.; Mehlhart, G.; Baroni, L.; Rademaekers, K.; Williams, R.; Paha, S. *Study in Support of Evaluation of the Directive 2006/66/EC on Batteries and Accumulators and Waste Batteries and Accumulators*; Final Report; European Commission: Rotterdam, The Netherlands, 2018.
3. Espinosa, D.; Bernardes, A.M.; Tenório, J. An overview on the current processes for the recycling of batteries. *J. Power Sources* **2004**, *135*, 311–319. [CrossRef]
4. European Commission. *Study on the Calculation of Recycling Efficiencies and Implementation of Export Article (Art. 15) of the Batteries Directive 2006/66/EC*; Final Report; European Commission: Brussels, Belgium, 2009.
5. Liu, C.; Lin, J.; Cao, H.; Zhang, Y.; Sun, Z.H. Recycling of spent lithium-ion batteries in view of lithium recovery: A critical review. *J. Clean. Prod.* **2019**, *228*, 801–813. [CrossRef]
6. Sattar, R.; Ilyas, S.; Bhatti, H.N.; Ghaffar, A. Resource recovery of critically-rare metals by hydrometallurgical recycling of spent lithium ion batteries. *Sep. Purif. Technol.* **2019**, *209*, 725–733. [CrossRef]
7. Huang, T.; Liu, L.; Zhang, S. Recovery of cobalt, lithium, and manganese from the cathode active materials of spent lithium-ion batteries in a bio-electro-hydrometallurgical process. *Hydrometallurgy* **2019**, *188*, 101–111. [CrossRef]
8. Kondás, J.; Jandová, J.; Nemeckova, M. Processing of spent Li/MnO2 batteries to obtain Li2CO3. *Hydrometallurgy* **2006**, *84*, 247–249. [CrossRef]
9. Paulino, J.F.; Busnardo, N.G.; Afonso, J.C. Recovery of valuable elements from spent Li-batteries. *J. Hazard. Mater.* **2008**, *150*, 843–849. [CrossRef]
10. Atia, T.A.; Elia, G.; Hahn, R.; Altimari, P.; Pagnanelli, F. Closed-loop hydrometallurgical treatment of end-of-life lithium ion batteries: Towards zero-waste process and metal recycling in advanced batteries. *J. Energy Chem.* **2019**, *35*, 220–227. [CrossRef]
11. Yi, X.; Huo, G.; Tang, W. Removal of Fe(III) from Ni-Co-Fe chloride solutions using solvent extraction with TBP. *Hydrometallurgy* **2020**, *192*, 105265. [CrossRef]
12. Schiavi, P.G.; Farina, L.; Zanoni, R.; Altimari, P.; Cojocariu, I.; Rubino, A.; Navarra, M.A.; Panero, S.; Pagnanelli, F. Electrochemical synthesis of nanowire anodes from spent lithium ion batteries. *Electrochim. Acta* **2019**, *319*, 481–489. [CrossRef]
13. Gratz, E.; Sa, Q.; Apelian, D.; Wang, Y. A closed loop process for recycling spent lithium ion batteries. *J. Power Sources* **2014**, *262*, 255–262. [CrossRef]
14. Hu, X.; Sun, X.; Yang, M.; Ji, H.; Li, X.; Cai, S.; Guo, R.; Hou, F.; Zheng, C.; Hu, W. Sandwich nanostructured LiMnPO 4/C as enhanced cathode materials for lithium-ion batteries. *J. Mater. Sci.* **2017**, *52*, 3597–3612. [CrossRef]
15. Drezen, T.; Kwon, N.-H.; Bowen, P.; Teerlinck, I.; Isono, M.; Exnar, I. Effect of particle size on LiMnPO4 cathodes. *J. Power Sources* **2007**, *174*, 949–953. [CrossRef]
16. Wang, R.; Cui, W.; Chu, F.; Wu, F. Lithium metal anodes: Present and future. *J. Energy Chem.* **2020**, *48*, 145–159. [CrossRef]
17. Shen, X.; Li, Y.; Qian, T.; Liu, J.; Zhou, J.; Yan, C.; Goodenough, J.B. Lithium anode stable in air for low-cost fabrication of a dendrite-free lithium battery. *Nat. Commun.* **2019**, *10*, 900. [CrossRef] [PubMed]
18. Ji, H.; Yang, G.; Ni, H.; Roy, S.; Pinto, J.L.; Jiang, X. General synthesis and morphology control of LiMnPO4 nanocrystals via microwave-hydrothermal route. *Electrochim. Acta* **2011**, *56*, 3093–3100. [CrossRef]
19. Wang, W.; Chen, W.; Liu, H. Hydrometallurgical preparation of lithium carbonate from lithium-rich electrolyte. *Hydrometallurgy* **2019**, *185*, 88–92. [CrossRef]
20. Salomon, M. Solubility problems relating to lithium battery electrolytes. *Pure Appl. Chem.* **1998**, *70*, 1905–1912. [CrossRef]
21. Huang, H.-H.; Lu, M.-C.; Chen, J.-N.; Lee, C.-T. Catalytic decomposition of hydrogen peroxide and 4-chlorophenol in the presence of modified activated carbons. *Chemosphere* **2003**, *51*, 935–943. [CrossRef]
22. Petlicki, J.; Palusova, D.; Van De Ven, T.G.M. Physicochemical Aspects of Catalytic Decomposition of Hydrogen Peroxide by Manganese Compounds. *Ind. Eng. Chem. Res.* **2005**, *44*, 2002–2010. [CrossRef]

23. Pagnanelli, F.; Furlani, G.; Valentini, P.; Veglio, F.; Toro, L. Leaching of low-grade manganese ores by using nitric acid and glucose: Optimization of the operating conditions. *Hydrometallurgy* **2004**, *75*, 157–167. [CrossRef]
24. Fang, H.; Li, L.; Yang, Y.; Yan, G.; Li, G. Carbonate anions controlled morphological evolution of LiMnPO4 crystals. *Chem. Commun.* **2008**, *9*, 1118–1120. [CrossRef] [PubMed]