

Process for Separating Li and Na Ions

The present invention relates to a process for separating Li and Na ions from sulfate-containing solutions, and a device for carrying out the process.

Vehicles with electric drives that are driven by electric power from low-emission sources are attributed the highest climate protection potential among land-based transport technologies as seen throughout their life cycle. Accordingly, electromobility is considered a key component of a sustainable and climate-friendly traffic system based on renewable powers. The focus is on lithium ion/polymer batteries as a promising storage system as the basis of electric drive, which have only a limited service life, however. In this respect, the sought degree of electrification can be achieved only in combination with a sustainable recycling concept. In particular, the planned sales ban on new cars with internal combustion engines necessitates a holistic recovery of the valuable metals contained in the consumed batteries, such as cobalt, nickel and manganese, but also lithium, which is obtainable only by lengthy processes.

The prior art describes a number of methods that deal with the recovery of the valuable metals from consumed lithium ion/polymer batteries.

US 2017/0077564 relates to a process for recycling lithium-ion batteries, comprising: (i) identifying a molar ratio for cathode materials for a new battery; (ii) forming a leaching solution by combining comminuted battery material from a lithium battery recycling stream with an acidic leaching agent and hydrogen peroxide (H_2O_2) to separate cathode materials from undissolved materials; (iii) filtering the undissolved materials from the leaching solution formed, so that the dissolved salts of the cathode materials remain in the leaching solution; (iv) determining a composition of said leaching solution by identifying a molar ratio of the salts of the cathode material dissolved therein; (v) adding Ni, Co, Mn or Al salts as sulfates (xSO_4) based on the determined composition, in order to adjust the molar ratio of the dissolved cathode material salts in the leaching solution to correspond to the identified molar ratio for the recycled battery, including the addition of a solution of aluminum sulfates and a chelating agent; and (vi)

increasing the pH of the leaching solution to at least 10 to precipitate and filter off metal ions of the cathode materials in order to form a precursor pCAM for the actual cathode active material CAM, in which the Ni, Co, Mn and Al salts remaining in the solution are present as a combined hydroxide $(\text{OH})_2$ or carbonate (CO_3) with a molar ratio as desired for the new CAM. Subsequently, the precursor is thoroughly mixed with $\text{LiOH}\cdot\text{H}_2\text{O}$ or Li_2CO_3 , and reacted to the cathode active material at temperatures of $>800^\circ\text{C}$.

US 2013/0302226 discloses a method for recycling batteries, in which a solution of aggregated battery materials is produced from consumed cells, impurities are precipitated from the solution produced, a predetermined ratio of desired materials is adjusted in the solution, and the desired material is precipitated and processed further into a cathode material for new batteries.

However, the methods described in the prior art have the disadvantage that, because of the nature of the process management, the lithium to be recovered is present as Li_2SO_4 in a solution together with Na_2SO_4 , so that it can be recovered as sparingly soluble Li_2CO_3 only towards the end of the process chain. Because of the solubility relations of Li_2CO_3 and Na_2CO_3 as well as Na_2SO_4 and Li_2SO_4 , a separation of Na and Li ions is very complicated in detail, and makes an actual quantitative recovery of lithium virtually impossible under economic aspects.

Thus, in order to achieve a sustainable and fully valuable recycling of consumed lithium ion/polymer batteries, there is still a need for a process that enables an improved recovery of lithium from Na-containing sulfate solutions. Thus, it has been the object of the present invention to satisfy this need.

Within the scope of the present invention, it has been surprisingly found that the poor separability of Li and Na ions from sulfate-containing solutions can be bypassed by a conversion to the corresponding hydroxides.

Therefore, the present invention firstly relates to a process for separating Na and Li ions, in which an aqueous solution A that includes Na_2SO_4 and Li_2SO_4 is subjected to electrolysis to obtain a solution B, and the solution B obtained is treated with a carbonate source to form Li_2CO_3 .

Those skilled in the art are aware of the fact that the compounds Na_2SO_4 , Li_2SO_4 , Na_2CO_3 , Li_2CO_3 and all the other salts are in the form of their ions in a solution. Therefore, unless designated otherwise, they are used interchangeably with the corresponding ions, and explicit mention thereof is omitted.

Surprisingly, it has been found that the larger differences in solubility between Li_2CO_3 and Na_2CO_3 as compared to the solubilities of Na_2SO_4 and Li_2SO_4 can be used to advantage, in order to achieve a more effective separation. While the solubilities of Na_2SO_4 and Li_2SO_4 differ by about a factor of only 2, Li_2CO_3 is clearly more sparingly soluble than Na_2CO_3 , which allows for a more effective separation of the two metals. Therefore, in a preferred embodiment of the inventive process, Li_2CO_3 is separated to obtain a filtrate containing Na_2CO_3 .

Within the scope of the process according to the invention, a number of compounds can be employed as the carbonate source. Preferably, the carbonate source is selected from the group consisting of Na_2CO_3 , CO_2 , NaHCO_3 , $(\text{NH}_4)_2\text{CO}_3$, $(\text{NH}_4)\text{HCO}_3$, and mixtures thereof. The use of CO_2 as a carbonate source has proven particularly advantageous and thus preferable. It can be recovered, for example, from exhaust gases of other processes, and thus directed to sustainable utilization, whereby the emission of CO_2 can be reduced.

The process according to the invention provides that a solution of the sulfate salts of Na and Li is subjected to electrolysis, where it is considered that the sulfate salts are thus converted to the corresponding hydroxides, which can be separated more easily. In this respect, a membrane electrolysis is preferred, especially an electrodialysis and more particularly an electrodialysis with bipolar membranes. Particularly preferred is a multicompartment electrolysis with a cation exchange membrane and an anion exchange membrane.

Within the scope of the process according to the invention, the lithium is recovered as Li_2CO_3 , which can be withdrawn from the solution as a solid in a further step. Preferably, the Li_2CO_3 is separated by at least one method selected from the group consisting of sedimentation, filtration, and centrifugation. The separation may include a short washing process, in which the washing liquors can be recycled into the overall process at suitable places.

The process according to the invention allows for an effective separation of Na and Li. If the degree of purity of the Li_2CO_3 obtained should be felt insufficient, the Li_2CO_3 can be subjected to further purification steps. In a preferred embodiment, the Li_2CO_3 obtained is converted to soluble LiHCO_3 in a further step by treating with CO_2 . Highly pure Li_2CO_3 can be obtained from this solution by heating the solution containing LiHCO_3 . Therefore, an embodiment is preferred in which the solution containing LiHCO_3 is heated to form Li_2CO_3 . This purification step offers the advantage that the mother liquor obtained in the separation of Li_2CO_3 and the CO_2 obtained in the formation of the Li_2CO_3 and driven out of the reaction mixture can be recycled into the process, so that a sustainable cycle is formed.

The starting solution A of the process according to the invention can be obtained in a number of methods as applied in recycling processes. The sulfate-containing aqueous solution A is preferably obtained by treating a solution X, wherein said solution X includes Li_2SO_4 and at least one compound MSO_4 in which M is a transition metal, preferably selected from the group consisting of Ni, Co, Mn, Al, and mixtures thereof. For example, this treatment may be performed by using NaOH and optionally further additions of H_2SO_4 . It is considered that the metal M is converted to its hydroxide by treating the solution X with NaOH to form Na_2SO_4 as a by-product. Alternatively, the metal can be transferred into the organic phase at first by reactive extraction in the presence of an organic extractant, and subsequently extracted from the organic phase as MSO_4 back into the aqueous phase with sulfuric acid, and thus recycled into the further value-added cycle.

Preferably, within the scope of the process according to the invention, solution X is obtained by treating a suspension Y, which includes at least a compound LiMO_2 , with H_2SO_4 and a reducing agent, in which M is a transition metal, preferably one selected from the group consisting of Ni, Co, Mn, Al, and mixtures thereof. Preferably, the reducing agent is selected from the group consisting of H_2O_2 and SO_2 .

The process according to the invention aims, in particular, at the recovery of Li from lithium ion/polymer batteries. Therefore, an embodiment is preferred in which the suspension including LiMO_2 is obtained from consumed lithium ion

batteries and/or production waste from the production thereof. In this way, the process according to the invention provides a comprehensive recycling cycle that allows for an efficient recovery of the lithium built into lithium ion/polymer batteries, and thus is a valuable contribution to the success of the sought concept of electromobility.

Within the scope of the comprehensive approach to recycling, the transition metal hydroxide obtained in the treatment of solution X can also be processed further, for example, for further use as a cathode active material in new batteries. Therefore, in a preferred embodiment of the process according to the invention, the treatment of solution X is carried out in such a way that a transition metal mixed hydroxide $\text{Ni}_x\text{Co}_y\text{Mn}_z(\text{OH})_2$ is still obtained by adjusting the stoichiometry of the transition metals and precipitation with NaOH. Said adjusting of the stoichiometry can be achieved, for example, by selectively separating or selectively adding one or more of the components of said transition metal mixed hydroxide. In this way, the ratio of Ni:Co:Mn desired in the later cathode material can be adjusted already in the transition metal mixed hydroxide. Within the scope of the current turnaround to nickel-enriched cathode active materials, adjusting the stoichiometry by selectively separating one or more of the components of the transition metal mixed hydroxide is preferred. In a preferred embodiment, the ratio of Ni:Co:Mn in the transition metal mixed hydroxide is 1:1:1, alternatively preferably 8:1:1.

In addition to the recovery of the materials employed, especially the valuable metals, another aspect of a sustainable recycling strategy is the environment-friendly treatment of resources. Among other things, this means that, if possible, chemicals required for the recycling process are also recovered, or recirculated. In the present process, this applies, in particular, to the sulfuric acid, which is necessary for obtaining the solution X. Therefore, an embodiment of the process according to the invention is preferred in which the sulfuric acid obtained in the electrolysis is used at least in part for preparing solution X.

The present invention further relates to a device for carrying out the process according to the invention. The device includes at least one electrolytic unit having at least one supply for introducing solution A and at least one drain for draining solution B.

The present invention is further explained by means of the following Examples, which should by no means be understood as limiting the idea of the invention.

Figure 1 schematically shows the concept of the process according to the invention, according to which a solution A obtained during the recycling of lithium ion/polymer batteries and containing Li_2SO_4 and Na_2SO_4 is subjected to electrolysis, whereby the sulfates are converted to the corresponding hydroxides, and the Li is separated off as Li_2CO_3 by treatment with CO_2 as a carbonate source, while Na_2CO_3 remains in solution.

Figure 2a schematically shows how solution A is obtained from a suspension Y obtained during the processing of lithium ion/polymer batteries that contains Li in the form of a lithium/transition metal oxide LiMO_2 . The lithium/transition metal oxide is converted to Li_2SO_4 and the corresponding transition metal sulfate MSO_4 (solution X) by treatment with H_2SO_4 and a reducing agent, preferably H_2O_2 or SO_2 . The transition metal sulfate can be converted to the corresponding hydroxide $\text{M}(\text{OH})_2$ by treating the solution X with NaOH , and separated off, whereby a solution is obtained that contains Na_2SO_4 and Li_2SO_4 and serves as a starting solution A for the process according to the invention.

According to the scheme shown in Figure 2b, solution X can further be treated with H_2SO_4 to obtain the transition metal in the form of its sulfate.

Figure 3 shows the schematic procedure of the process according to the invention, in which a solution A of Li_2SO_4 and Na_2SO_4 is subjected to electrolysis to obtain solution B, from which Li_2CO_3 can then be separated by treating with a carbonate source. In this way, an effective separation of the two ions can be achieved.

C L A I M S :

1. A process for separating Na and Li ions, characterized in that an aqueous solution A that includes Na_2SO_4 and Li_2SO_4 is subjected to electrolysis to obtain a solution B, and the solution B obtained is treated with a carbonate source to form Li_2CO_3 .
2. The process according to claim 1, characterized in that the carbonate source is selected from the group consisting of Na_2CO_3 , CO_2 , NaHCO_3 , $(\text{NH}_4)_2\text{CO}_3$, $(\text{NH}_4)\text{HCO}_3$, and mixtures thereof.
3. The process according to at least one of the preceding claims, characterized in that said electrolysis is a multicompartment electrolysis with a cation exchange membrane and an anion exchange membrane, especially electrodialysis, preferably electrodialysis with bipolar membranes.
4. The process according to at least one of the preceding claims, characterized in that the Li_2CO_3 formed is separated by at least one method selected from the group consisting of sedimentation, filtration, and centrifugation.
5. The process according to at least one of the preceding claims, characterized in that the Li_2CO_3 obtained is converted to soluble LiHCO_3 in a further step by treating with CO_2 .
6. The process according to at least one of the preceding claims, characterized in that the aqueous solution A is obtained by treating a solution X, wherein said solution X includes Li_2SO_4 and at least one compound MSO_4 , in which M is a transition metal, preferably selected from the group consisting of Ni, Co, Mn, Al, and mixtures thereof.
7. The process according to claim 6, characterized in that solution X is obtained by treating a suspension Y, which includes at least a compound LiMO_2 , with H_2SO_4 and a reducing agent, in which M is a transition metal,

preferably one selected from the group consisting of Ni, Co, Mn, Al, and mixtures thereof.

8. The process according to claim 7, characterized in that the compound including LiMO_2 is obtained from consumed lithium ion/polymer batteries and/or production waste from the production thereof.
9. The process according to at least one of claims 6 to 8, characterized in that a transition metal mixed hydroxide $\text{Ni}_x\text{Mn}_y\text{Co}_z(\text{OH})_2$ is further obtained when solution X is treated, by adjusting the stoichiometry of the transition metal and precipitating with aqueous sodium hydroxide.
10. The process according to claim 9, characterized in that said adjusting the stoichiometry of the transition metal is effected by selectively separating or adding one or more of the components of the transition metal mixed hydroxide.
11. The process according to at least one of the preceding claims, characterized in that the sulfuric acid obtained in the electrolysis is used at least in part for preparing solution X.
12. A device for carrying out a process according to at least one of the preceding claims, comprising an electrolytic unit having at least one supply for introducing solution A and at least one drain for draining solution B.