

Early-Stage Sustainability Evaluation of Nanoscale Cathode Materials for Lithium Ion Batteries

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Results of an early-stage sustainability evaluation of two development strategies for new nanoscale cathode materials for Li-ion batteries are reported: (i) a new production pathway for an existing material (LiCoO_2) and (ii) a new nanomaterial (LiMnPO_4). Nano- LiCoO_2 was synthesized by a single-source precursor route at a low temperature with a short reaction time, which results in a smaller grain size and, thereby, a better diffusivity for Li ions. Nano- LiMnPO_4 was synthesized by a wet chemical method. The sustainability potential of these materials was then investigated (at the laboratory and pilot produc-

tion scales). The results show that the environmental impact of nano- LiMnPO_4 is lower than that of the other examined nanomaterial by several factors regardless of the indicator used for comparison. In contrast to commercial cathode materials, this new material shows, particularly on an energy and capacity basis, results of the same order of magnitude as those of lithium manganese oxide (LiMn_2O_4) and only slightly higher values than those for lithium iron phosphate (LiFePO_4); values that are clearly lower than those for high-temperature LiCoO_2 .

Introduction

Batteries transform chemical energy into electricity with the support of electrochemical cells. Based on their reversibility (as a result of the use of different materials for the electrodes and electrolyte), two types of battery can be distinguished: non-rechargeable (primary) and rechargeable (secondary).^[1] According to Eurostat, the statistical service of the European Commission, six different types of non-rechargeable batteries (i.e., zinc, alkaline, button alkaline, silver–zinc, button zinc, and lithium) and 11 types of rechargeable batteries (i.e., nickel–cadmium, nickel metal hydride (NiMH), lithium-ion, lithium-ion polymer, alkaline, chargeable titanium, lead–acid, lead traction, lead stationary, nickel–iron, and nickel–zinc) are distinguished.^[2]

Within the rechargeable category, Li-ion batteries represent a particularly interesting technology because of their material-specific properties, which show a high energy density in Wh kg^{-1} and Wh L^{-1} simultaneously. These light and small batteries are, therefore, ideal for use as an energy supply in, for example, small, mobile devices for information and communication technology (ICT) or electric mobility. By comparison, other secondary batteries used commonly, such as nickel–cadmium, NiMH, and lead–acid batteries, exhibit inferior energy-

storage capabilities—explaining to a large extent their ever-diminishing relevance to the battery market.^[3]

Li-ion batteries are usually made of Li intercalation compounds that allow Li ions to be exchanged between the two electrodes. For the positive electrode, lithium cobalt oxide ($\text{LiCoO}_2 = \text{LCO}$) is the most commonly used material.^[1] However, as a result of the high cost and high toxicity of Co, the search for effective alternative Li compounds is of high importance for industry, and a variety of alternative cathode materials have been trialed in recent years, for example, layered $\text{Li-Ni}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (so-called Li-NMC) cathodes.^[4] However, as the testing and application of alternative cathode materials is typically a costly activity for industry (e.g., as a result of changes in production lines) it is important that comprehensive evaluations of potential cathode material alternatives are undertaken as early as possible in the development cycle and that these address not only technical performance but also product sustainability.

Here, we present the results of an early-stage sustainability evaluation of alternative cathode materials for Li-ion batteries that are currently in development. Classical material production activities in the laboratory for new, nanoscale electrode materials to be used in Li-ion batteries were combined and amended from a very early development stage and evaluated from a sustainability perspective using the lifecycle assessment (LCA) framework. LCA is seen currently as the most established and best developed tool to assess the sustainability of new materials and technologies.^[5] LCA comprises a comprehensive framework to quantify the potential ecological and human health impacts of a product or system over its complete life cycle. The roots of LCA can be found in the energy-related research of the 1960s and pollution prevention initiated in the 1970s.^[6] LCA has been applied in a variety of different sectors,

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which include governmental organizations and a wide range of industries, with or without support from specialized research institutes and/or consulting companies. A prominent reason for this wide application is the clear guidance of international LCA standards, ISO 14'040 and 14'044.^[7,8] LCA is not "site-specific", such as risk assessment or environmental impact assessment (EIA). Therefore, it is suitable to assess early-stage development products, such as the new cathode materials for Li-ion batteries examined here.

In the framework of this study, the following different production strategies are evaluated:

- 1) a new production pathway for the synthesis of a nanosized form of a currently in use cathode material (i.e., LCO) that is comparatively simpler than conventional production, using lower temperatures and with a shorter reaction time to produce a material with a smaller grain size, and
- 2) development of a completely new material, LiMnPO_4 (LMP), with a high structural stability in its nanoform for application as Li-ion battery cathodes.

These materials have a better Li-ion diffusivity than conventional materials because of the smaller grain size. For instance, LMP in combination with carbon black could lead to a capacity up to 20% higher than that of commercially used lithium iron phosphate (LFP).^[9-11]

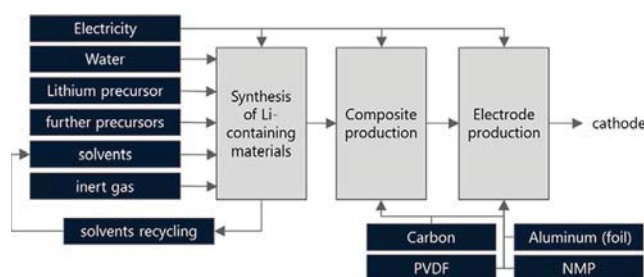
LCA of the respective production processes for the two nanomaterials investigated here (i.e., LMP and LCO) was performed on two scales: 1) laboratory scale and 2) a scaled-up theoretical pilot production line. Based on a comparison with established, commercially available cathode materials used in Li-ion batteries, the results of the LCA are then used to establish a first sustainability evaluation of an application of these new materials. The results of this type of evaluation are of a particular interest in view of current energy discussions, which are focused increasingly on the potential for local and short-term energy storage solutions.^[12]

These sustainability evaluations will enable a first estimation of the sustainability of these two different production strategies and a first opportunity to identify areas in which material and energy flows can be optimized to enhance (ecological) sustainability. Such an evaluation is important for battery producers to ensure the sustainability of their further product development. Details of the laboratory-scale synthesis of the investigated materials are provided elsewhere.^[11]

Results

LCA results of lab-scale experiments

An amount of "1 kg of produced cathode" is used as the reference flow and the so-called functional unit for all LCA calculations on the lab scale. The examined lab-scale system includes all related production steps, from the extraction of the resources that are required up to the produced cathode. Therefore, it is an example of a so-called cradle-to-gate LCA study. The examined system can be split into three distinct processes on



Scheme 1. System boundaries of the LCA of the lab-scale production of the new cathode materials (dark elements are modeled with background LCI data and bright elements with data from our own experiments).

the level of this cathode production (Scheme 1). The main data source for the three laboratory process steps shown in Scheme 1 are measured data and calculations from our own experimental work. These data were complemented with information taken from the literature to model each single process step in a consistent and comprehensive manner. A more detailed overview of this modeling of the lab-scale experiments, together with the applied data, can be found in Section 1 of the Supporting Information.

In the assessment of how the examined production process on the level of the last process step (i.e., the actual cathode production), both examined materials (i.e., LCO and LMP) show similar results, with all impact categories dominated clearly by the impact of the production of the Li-containing material (shown in Figure 1 for the case of the nanostructured LCO; the absolute values for this figure can be found in Section 4 of the Supporting Information).

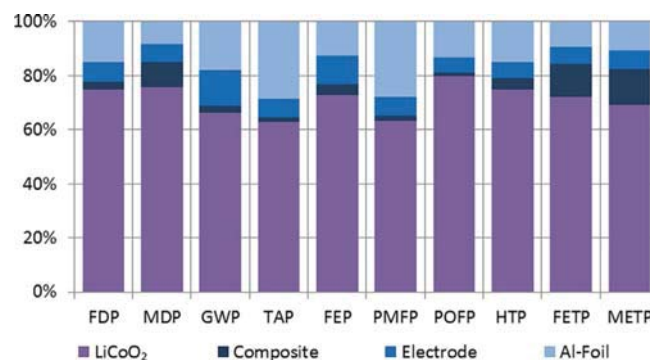


Figure 1. LCA results of 1 kg of cathode in case of the nanostructured LiCoO_2 . Results for the ReCiPe categories FDP, MDP, GWP, TAP, FEP, PMFP, POFP, HTP, FETP, and METP are shown.

The impacts related to the production of the LCO and LMP nanomaterials are shown in Figure 2 (again, the absolute values for this figure can be found in Section 4 of the Supporting Information). Apart from the respective raw materials, two further elements dominate the contributions to the various impact categories, namely, the consumption of solvents and the inert gas in the case of LCO and the solvents and the energy consumption in the case of LMP. This is a rather typical

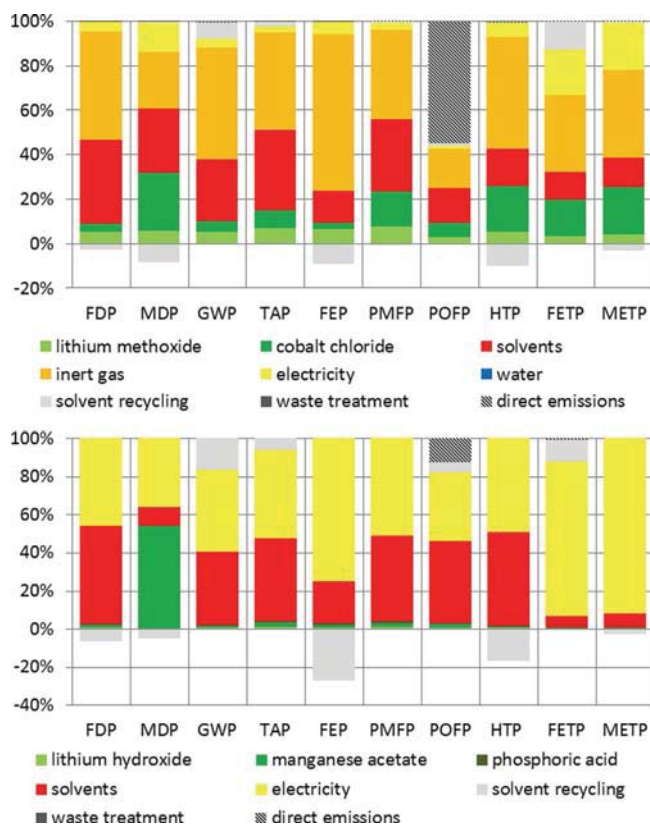


Figure 2. LCA results for the lab-scale production of 1 kg of LCO nanomaterial (top) and 1 kg of LMP nanomaterial (bottom). The same impact categories are shown as in Figure 1.

observation on the lab scale (see, for example, Piccinno and co-workers^[13]) as the objective of this level is a priori simply the proof that a process actually works. At this stage in the material development cycle, optimization measures that concern, for example, energy consumption, the use of input materials, or the use of solvents and further process-related auxiliaries have not yet been applied. The process of solvent recycling results partly in negative values because the disposal process generates small amounts of energy (electricity and heat), for which “credits” are given (more details in Section 3.7 of the Supporting Information).

LCA estimation of a (future) pilot production

Based on the lab-scale data, as a second step a scale-up of a (calculated, theoretical) pilot production of the new LCO and LMP nanomaterials was established. The functional unit and system boundaries are consistent with those used for the lab-scale study. For the scale-up activity, the following general rules were applied to estimate higher and lower values:

- Starting materials: as a lower value a yield (i.e., the amount of starting material contained within the final product) of 95% was assumed, for cobalt chloride even 98%.^[14] The higher value assumes a yield of only 90% (and for cobalt chloride 95%);

- Solvents: to minimize the use of solvents, a closed system in combination with a recycling unit (by a distillation process^[15]) was modeled. It was assumed that such a closed system can be operated with 80 (higher value) to 90% (lower value) less solvent than that on the lab scale;
- Inert gas: as a lower value a reduction to 40% of lab-scale usage, as well as the abandonment of the use of multiple gases in the process, was assumed based on our expert judgment. For the higher value, a 25% higher consumption (equal to a reduction to 50% of lab-scale usage only) was investigated;
- Water: reductions of 80 and 60% compared to lab-scale usages were assumed for process water and cooling water, respectively;
- Electricity consumption: The lower values were calculated according to the engineering-based procedure described by Piccinno and co-workers^[16] (calculations behind these values are shown in detail in the Supporting Information), whereas for the higher value this amount was multiplied by a factor of 2.5;
- Heat consumption: the value reported represents the energy required to recover the used solvents in an internal distillation process;^[16]
- Waste treatment: all excess input materials are assumed to end up in an appropriate waste treatment process;^[15]
- Releases into air: all gases from the decomposed solvents and inert gases are assumed to be emitted into the air.^[16]

An overview of the resulting data for the pilot production of the new LCO and LMP nanomaterials can be found in Chapter 2 of the Supporting Information. The environmental impacts for the production of 1 kg of each type of nanomaterial on the level of a pilot plant by assuming the lower values for the various inputs and outputs, that is, to represent the maximum reduction potential are shown in Figure 3 (the absolute values behind this figure can be found in Section 4 of the Supporting Information). A dramatic change in the relative contribution of the various elements to each impact category is observed compared to the results of the lab-scale study (Figure 2). In the case of such a (theoretical) pilot plant, the greatest impacts are caused by the production of the various starting materials (i.e., cobalt chloride, lithium methoxide, phosphoric acid, manganese acetate, and lithium hydroxide combined, which represent > 60% of the total impacts) and, in the case of LMP, direct emissions to air and water (which contribute up to 80% of the total impacts). The contribution of electricity consumption is still visible for most impact categories but it is much lower compared to that of the lab-scale production. The consumption of solvents and inert gas, which are important impacts on the lab scale, are reduced considerably for the pilot plant; in particular, for nanostructured LCO their contributions are hardly visible anymore.

Upon the investigation of the influence of the key elements, that is, the amount of input materials, inert gas, solvents, and electricity for the (theoretical) pilot production, by changing from the lower to the higher value, the resulting impacts

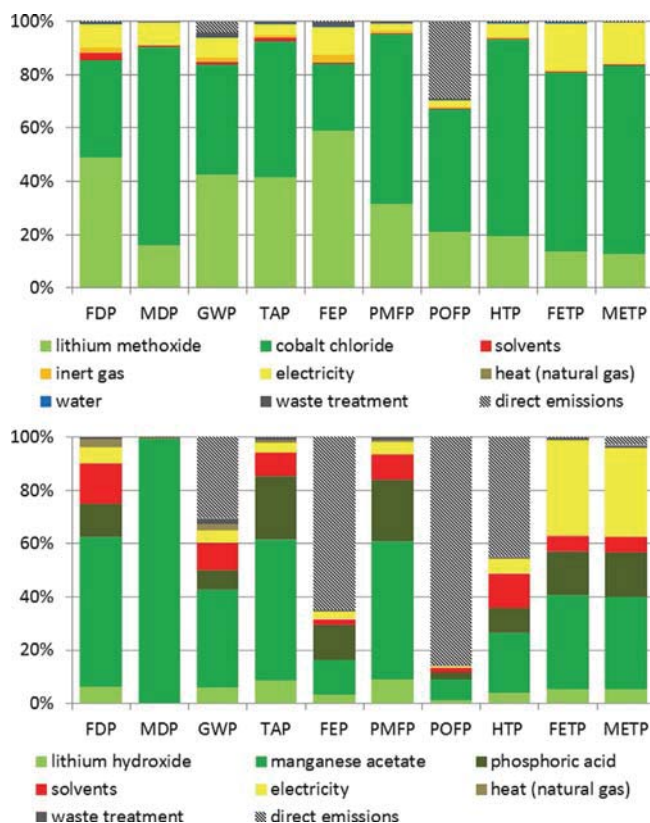


Figure 3. LCA results for a (theoretical) pilot production of 1 kg of LCO nano-material (top) and 1 kg of LMP nanomaterial (bottom) using the lower values for the various inputs and outputs. The same impact categories are shown as in Figure 1.

caused by the production of 1 kg of these nanomaterials changes (Figure 4).

Most of these investigated changes from the low to the high input values influence the impacts of the two nanomaterials by 5% or even less; in particular, inert gas and solvents in the case of the LCO show hardly any influence with one exception: the photochemical oxidation formation potential (POFP) indicator shows an increase of the overall impact of more than

20% if we double the amount of lost solvents. Otherwise, the result for LCO shows for a majority of the investigated indicators the highest changes in the case of a variation of the electricity input, which is responsible for increases of the total impacts of 3% (e.g., for POFP) up to 17% (for the metal resource depletion potential; MDP). A change of the amount of the various input materials (which represent a decrease of the yield of the whole process) shows a more or less equal influence for all indicators investigated here of approximately 3–3.5%.

The results for LMP are most influenced by the amount of the various solvents, which results in an increase of the impacts of the investigated (theoretical) pilot plant of up to 80% because of the assumed doubling of the amount of lost solvents. The electricity consumption results for most factors result in an increase of approximately 4–5% with the exception of the two ecotoxicity factors (freshwater ecotoxicity potential; FETP and marine ecotoxicity potential; METP) that increase by more than 15% because of the higher electricity consumption. Again, a change of the amount of the various input materials shows a more or less equal influence along the indicators investigated here of the order of 5%.

The degree of the reduction of the total impacts of the (theoretical) pilot plant compared to lab-scale production, which takes into account all low and high values for the various elements (i.e., material input, inert gas, solvents, electricity) as described above (and listed in detail in Chapter 2 of the Supporting Information) is shown in Figure 5. The results represent the range between the use of these low and high values, respectively. As a second chemical product (i.e., LiCl) is produced in the production pathway examined here for LCO, the efforts from this process can be spread between these two products, that is, they can be allocated. To investigate the influence of this additional factor, three different allocation principles were applied: 1) all burdens allocated to LiCoO_2 (similar to the lab scale), 2) a split according to the prices of the two produced substances (LCO and LiCl), and 3) a split according to the mass amount of these two produced substances.

The third of these allocation principles results in an approximately 45% lower impact for LCO compared with the first

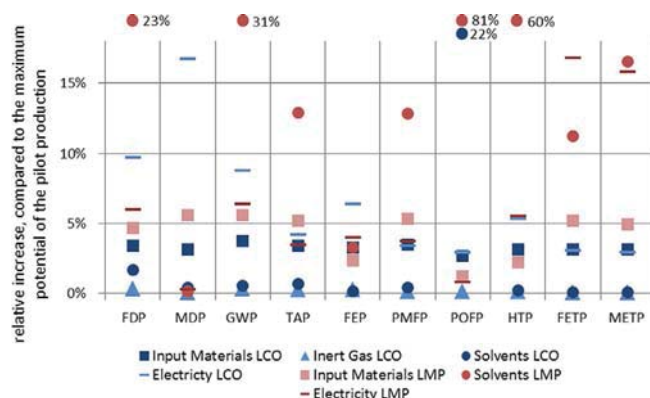


Figure 4. Relative changes of the environmental impact of the pilot production processes for LCO and LMP nanomaterials if we change the various key elements from the lower to the higher value. The same impact categories are shown as in Figure 1.

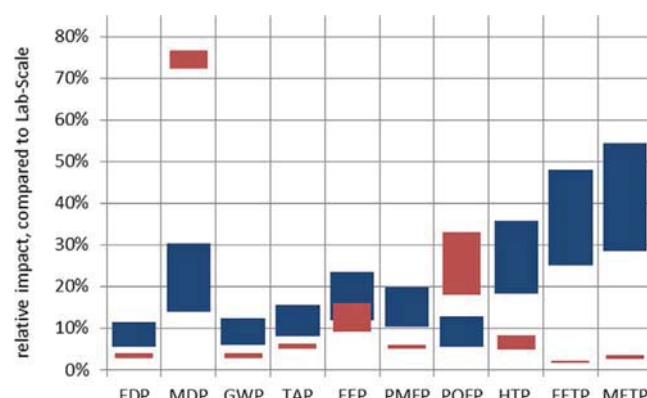


Figure 5. Relative environmental impact ranges of the pilot production processes for LCO and LMP nanomaterials in comparison to the respective lab-scale impacts (set each time 100%). The same impact categories are shown as in Figure 1.

principle, in which all impacts are allocated to this nanomaterial. Therefore, the combination of this influence of the allocation principles with the ranges for the various input values (from low to high) lead to a much broader variety of the results for LCO than for LMP with one exception: in case of the POFP indicator the strong influence of the amount of solvents (Figure 4) results in a two times higher variability for LMP than LCO despite the different allocation factors.

The MDP indicator in the case of LMP is the only impact category that shows less than 50% reduction. This is because the Co and Mn resources (which are part of the starting materials cobalt chloride and manganese acetate for the investigated production pathways) have high impact factors in the calculation of this indicator. The four indicators fossil fuel depletion potential (FDP), global warming potential (GWP), terrestrial acidification potential (TAP), and particulate matter formation potential (PMFP), which are linked broadly to the use of fossil resources (i.e., FDP and GWP) and/or emissions to air (i.e., GWP, TAP, and PMFP), show a rather similar pattern for both materials. The values of the LMP pathway are approximately 20 times lower than that on the lab scale and are hardly affected by the variations applied between the low- and high-level options. In the case of LCO, the reduction is less and the variation, mainly because of allocation issues, is higher, but they still represent a minimum 80–85% of reduction. This high reduction is a combined effect of reduced energy consumption and solvent usage, responsible for most of the emissions to air. As soon as at least one of these effects is not so distinct, the reduction potential from the lab-scale to the pilot production diminishes considerably, which results in a much higher range between the highest and the lowest value, especially for LCO. In particular, the toxicity impact categories human toxicity potential (HTP), FETP, and METP show such a pattern in the case of LCO; but despite this, they all still show a reduction of at least a factor of 2, which ranges in most cases to a factor of approximately 5. Common to all these impact categories is the fact that the variance is much higher than that for FDP, GWP, and TAP. The LMP pathway shows clearly higher reduction potentials and almost no variability (especially for the ecotoxicity factors) because these impacts result, again, mainly from solvents and/or electricity consumption.

Comparison with other cathode materials

To evaluate the sustainability potential of the two new cathode materials, the LCA results of the pilot production described above (using the lower values from the theoretical pilot plant to evaluate the full potential of these materials) are compared with those of various types of conventional cathode materials applied currently in Li-ion batteries: HT-LCO (the high-temperature method for the production of lithium cobalt oxide, LiCoO_2), LFP (lithium iron phosphate, LiFePO_4), LMO (lithium manganese oxide, LiMn_2O_4), and Li-NMC (lithium nickel manganese cobalt oxide, $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$). The lifecycle inventory (LCI) data of these cathode materials were taken from publications by Dunn and co-workers^[17] (for HT-LCO), Majeau-Bettez and co-workers^[18] (for LFP and Li-NMC), and Notter and co-

workers^[19] (for LMO). These datasets were integrated into the LCA software tool and database used here (see the Experimental Section). A first comparison of the impacts from the production of 1 kg of each of these materials is shown in Figure 6 (for absolute values, see Section 4 of the Supporting Information).

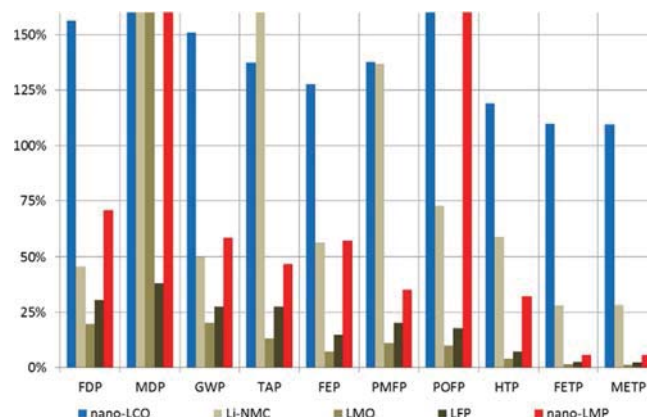


Figure 6. Relative environmental impacts for the production of 1 kg of various Li-containing cathode materials using HT-LCO as the measurement unit (i.e., HT-LCO is set as 100%). LMO = lithium manganese oxide, LFP = lithium iron phosphate, Li-NMC = lithium nickel manganese cobalt oxide and the two nanomaterials examined here are shown for the same impact categories as shown in Figure 1.

A comparison of the environmental impacts relative to those for HT-LCO (set as 100% for each of the examined environmental indicator) is shown in Figure 6. LMP nanomaterials show for most of the examined impact categories a significantly lower impact than both forms of LCO, commercial HT-LCO and the new nanoform investigated herein. Exceptions with higher values for LMP are for the POFP because of hexane release into the atmosphere (responsible for almost 70% of this impact), and the MDP because of the Mn content of the materials.

Compared to HT-LCO, the (theoretical) pilot production of LMP modeled here shows impacts that are lower by a factor of 2–3. However, the LCO nanomaterial does not show the expected advantages compared to the high-temperature option based on the pilot process. Moreover, different cathode materials result in Li-ion batteries with very different characteristics because of the differences in their capacities [Ah kg^{-1} , Ah L^{-1}], the midpoint voltage rates [V vs. Li], and the resulting energy density [Wh kg^{-1} , Wh L^{-1}], as well as the stability (number of cycles that such a battery can be recharged) of the different materials. Hence, as the battery performance is not considered, a comparison using a functional unit of 1 kg of Li-containing cathode materials is an inadequate means to designate the most “sustainable” cathode material. Typical values for the key characteristics of the examined cathode materials are summarized in Table 1.

The values for the commercial cathode materials are from recent publications and represent typical values for these materials, whereas those for the two nanomaterials developed

Table 1. Key characteristics of the various cathode materials examined in this study.

Material	Specific capacity [mAh g ⁻¹]	Midpoint voltage ^[a] [V] vs. Li	Energy density [Wh kg ⁻¹]	Average lifespan ^[b]	Ref.
nano-LCO	175	3.9	683	750	this work
HT-LCO	140	3.9	546	750	[20–24]
LMO	110	4	440	500	[20–24]
Li-NMC	165	3.8	627	1500	[20–24]
LFP	160	3.4	544	1500	[20–24]
nano-LMP	153	4.1	628	1500	this work

[a] Values calculated from the specific capacity and the midpoint voltage values.
[b] Values represent average number of cycles of the materials examined here if used in Li-ion batteries with a graphite anode.

here were obtained by us from experiments and assumptions. In detail, the following considerations are behind the values for the new materials developed here:

- nano-LCO: According to our experimental measurements, the capacity is 25 % higher than that of HT-LCO.^[9] The value for the energy density was calculated from this specific capacity by using a potential of 3.9 V,^[9] and the number of charging cycles was assumed to be similar to that of HT-LCO;
- nano-LMP: With regard to capacity, 90% of the value achieved by making nanoparticles of LMP and ball milling reported by Kwon and co-workers^[11] was assumed; the value for the energy density was calculated from this by applying a value for the potential of 4.1 V.^[11,25] For the number of charging cycles, the same value as for LFP was used as both of these materials have a similar olivine structure.

To establish an alternative basis to compare the various cathode materials is required (Figure 7). Here, energy content (top diagram; results per kWh of the totally stored energy over the indicated average number of cycles) and capacity (bottom diagram; results per Ah of the total capacity over the indicated average number of cycles) were used as such.

The patterns of these diagrams show a more or less similar picture and they are quite similar to the pattern shown in Figure 6, that is, on a per kg basis. With regard to the comparison based on the energy content and capacity, the only material for which results are at least partially higher than those of HT-LCO is the nano-form of the same material (i.e., nano-LCO). All other materials, which include nano-LMP, show, for most of the examined impact categories, values that are factors lower than those for HT-LCO. For the MDP category, the results are still dominated by the contributions of Mn, which has a high characterization factor, to lead to results of up to two orders of magnitude higher for Mn-containing cathodes. Secondly, for the POFP impacts, nano-LMP had a much lower reduction ($\approx 25\%$) because of hexane release in the modeled production process. For all other factors, the impacts from the pilot-scale nano-LMP modeled here are a factor of 4–5 smaller than the respective impacts from the HT-LCO, which are often in the same order of magnitude as the results for LMO, whereas LFP again shows lower results.

Discussion

Synthesis of nano-LCO

To date, oxide materials for cathodes have been made using solid-state, spray-drying, and, for more advanced oxides, coprecipitation methods.^[10] These represent the simplest methods for the mass production of these types of materials. By comparison, the organometallic approach described here has several advantages, most notably reductions in temperature and time requirements for the production of the desired phase of LiCoO₂ (if we take into account the annealing steps that are typically required for oxides). Furthermore, low-temperature synthesis reduces particle growth and thus enables the production of more desirable nanosized particles. As a result of the resultant short path length of Li ions, this results in faster Li ion diffusion (i.e., faster discharge–charge time). Furthermore, as the reaction is almost instantaneous, the low-temperature synthesis of nano-LiCoO₂ is a relatively fast, straightforward process that produces a high overall yield of 80–95 %. However, the process does require the use of much more expensive precursors than those used in the common synthesis route (i.e., oxides and carbonates). For the modeled pilot plant, the main contributors to

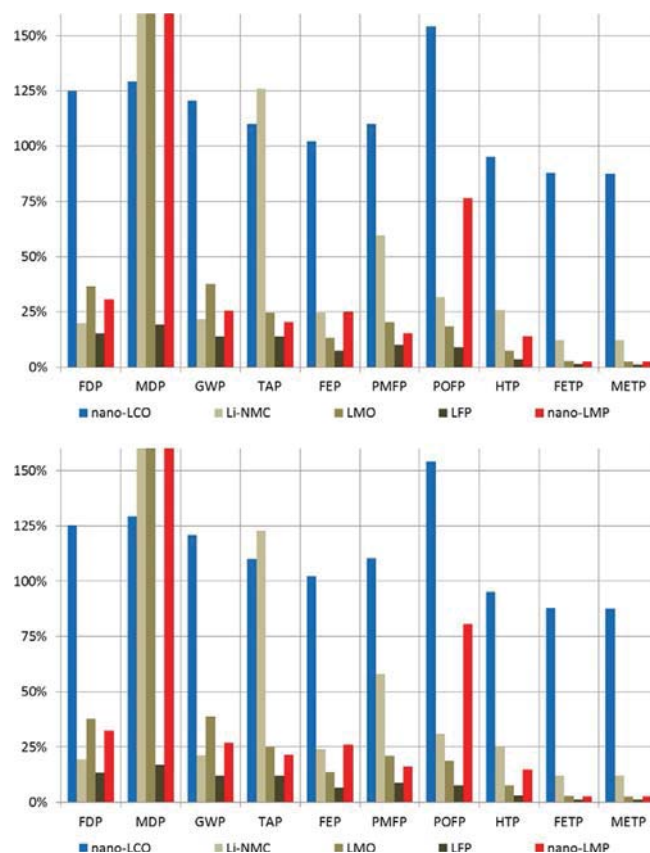


Figure 7. Relative environmental impacts for 1 kWh of stored energy (top) and 1 Ah of available capacity (bottom) of the various Li-containing cathode materials using HT-LCO as the measurement unit (i.e., set as 100%). The same impact categories are shown as in Figure 1.

the environmental impacts are the production efforts of all raw materials themselves. Hence, to improve the overall sustainability of LCO-based Li-ion batteries it is of utmost importance that an alternative source of Co than cobalt chloride is found.

Synthesis of nano-LMP

Wet chemistry often results in the formation of nanoparticles because homogeneous and stoichiometric reactions take place at a relatively low temperature.^[25] However, yields from such synthetic methods are typically extremely low because of low concentrations in the solution. Advantages of the synthesis described here for LiMnPO_4 nanomaterials are, through the appropriate selection of adequate surfactants and starting materials, its comparatively higher yields and ability to control nanoparticle shape (rod, sphere, cubic, needle).^[11,25] As all subsequent electrode production and assembly processes were adopted from methods used commonly, they can be considered as convenient for industrial scale-up as they require no major changes to existing procedures and processes. However, the use of surfactants and organic solvents increases the environmental impact and cost, although we expect that these can be reduced by the recycling of the organic solvents.

Sustainability potential analysis

The comparative LCA of the new nanomaterials investigated here (i.e., nano-LCO and nano-LMP) with conventional, commercial cathode materials shows that the potentials of the two new nanomaterials are quite different. Although the modeled pilot production of nano-LMP results in impacts that are in the range of those of the commercial materials, the results from the scale-up of nano-LCO do not lead to lower impacts. Rather, the chief contributors to the environmental impacts for the theoretical pilot production processes for both nanomaterials were the starting materials and, albeit it to a much lower extent, energy consumption during the synthesis process. In particular, the starting materials dominate the impacts from the production of nano-LCO clearly and are responsible for over 80 % of the total impacts for all impact categories. A similar result is observed for manganese acetate, one of the starting materials for the production of nano-LMP, and it is responsible for 30–50 % of the total impacts. Further investigation into the effect of the use of alternative starting materials, if such materials can be found, on the sustainability potential of the materials is, therefore, required.^[14]

Further work is also required to obtain the technical measurements of the new cathode materials, whereas their development is expected to continue through, for example, their application in actual battery compositions. With regard the sustainability potential analysis, the approach and results presented are currently limited to and valid only for the cathode materials considered. If possible, eventual increases in the energy storage capacity (per kg and/or m^3 of battery) or battery lifetime would further add to the (ecological) advantages and sustainability of these new, alternative materials compared to conventional, commercial materials. Hence, the LCA analysis

should be repeated after prototype Li-ion batteries that incorporate these new materials have been developed and tested. In particular, our analysis suggests that the nano-LMP shows considerable promise from a technical and sustainability perspective that warrants further investigation.

Conclusions

The environmental impacts of the modelled pilot production of the two new nanomaterials are clearly dominated by the impacts related to the applied materials, that is, cobalt in case of nano- LiCoO_2 (nano-LCO), and manganese for nano- LiMnPO_4 (nano-LMP). The (upscaled) process for the latter shows that the thereby resulting environmental impacts relative to the specific capacity or energy content are in the same order of magnitude as today's used cathode materials (such as lithium nickel manganese cobalt oxide or lithium iron phosphate), whereas the here performed upscaling for the nano-LCO form does not allow reduction of the related environmental impacts in a similar manner. Especially the nano-LMP pathway shows rather high promises from a technical and a sustainable perspective in view of the next generation of Li-ion battery chemistry. Once these new materials are used in (new) types of Li-ion batteries, the here described investigations need to be repeated to verify whether these current promises could be maintained or ideally even further exceeded.

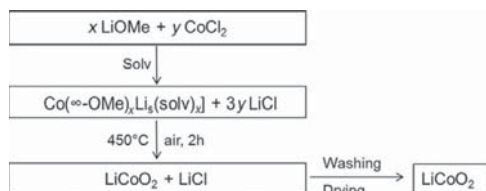
Experimental Section

Typically, currently used rechargeable Li-ion batteries use the so-called high-temperature form of LiCoO_2 (HT-LCO) as a positive electrode material.^[10,26] HT-LCO is produced mainly by stirring and heating a solid-state mix (of carbonates and oxides) between 600 and 900 °C for several hours in an oxidant atmosphere.^[10] This process is considered as rather energy intensive and results in the formation of micrometric particles. However, the obtained high-temperature phase of LiCoO_2 shows good electrochemical properties (a low self-discharge rate and stable cycling properties) for use as a cathode material, whereas the low-temperature form appears to possess weaker electrochemical properties.^[26]

Strategy 1: A new production pathway for LiCoO_2

Nanosized particles of LCO, obtained by a new pathway, showed improved properties as, because of the smaller grains, they had a higher Li-ion diffusivity and, consequently, a higher reversible capacity.^[10] The precursors used for the formation of these nanosized LCO particles were lithium alkoxides and/or aryloxides, THF, methanol, and cobalt chloride (a source of Co ions). Lithium pheoxide (1 M in THF), lithium isopropoxide (2 M in THF), methanol (technical and analytical grade), and cobalt chloride (dry or hydrated with two H_2O , 99 %) were purchased from Sigma-Aldrich. Lithium *tert*-butoxide (1 M in THF), lithium methoxide (1 M in methanol) and THF (dry and over molecular sieves, ≥ 99.9 %) were purchased from Acros Organics (Belgium). THF and methanol were both used as solvents and ligands within this process. A variety of different lithium alkoxides and/or aryloxides were used as a starting material on the lab scale (an overview of all used starting materials can be found in Table S1 of the Supporting Information). Here, only the pathway using lithium methoxide as a starting material is consid-

ered further. Lithium methoxide is considered the most promising of all examined starting materials because of its economic advantages (e.g., low cost and decomposition temperature) and low carbon content. The synthesis reaction of LCO is shown in Scheme 2.



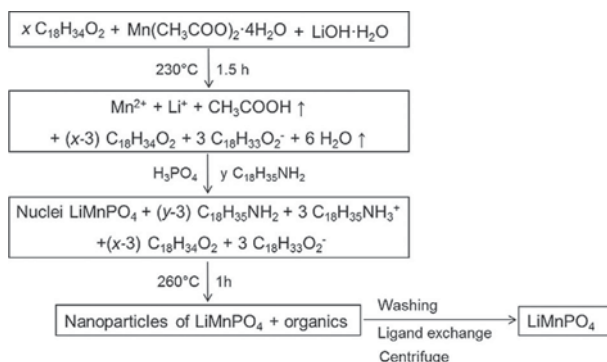
Scheme 2. New production pathway for LiCoO₂.

The synthesis consisted of the addition of the lithium methoxide to a THF solution of CoCl₂ under Ar or N₂. This suspension was heated for 30 min under reflux followed by the removal of the solvent by evaporation. The obtained powder was decomposed thermally in air at 450 °C and annealed at 600 °C in an oven under air flux. The total production time by this new production pathway was less than 6 h (compared to 36 h for the solid-state reaction at 850–900 °C). Finally, the obtained black powder was washed several times with water and then dried with ethanol under vacuum conditions. The complete synthesis procedure for this new cathode material has been described in more detail by Brog et al.^[9]

Strategy 2: New cathode material (nano-LiMnPO₄)

The second cathode nanomaterial, LiMnPO₄ (LMP), was obtained through thermal decomposition. The precursors of LMP in this process were LiOH·H₂O (Sigma-Aldrich, ≥ 99.0%), Mn(CH₃COO)₂·4H₂O (Alfa Aesar, 98 %), and H₃PO₄ (Sigma-Aldrich, 85 wt % in H₂O). Benzyl ether ((C₆H₅CH₂)₂O, Sigma-Aldrich, 98 %) was used as a solvent, and oleic acid (C₁₈H₃₄O₂, Sigma-Aldrich, ≥ 93 %) and oleylamine (C₁₈H₃₅NH₂, Sigma-Aldrich, technical grade) were used as surfactants. The synthesis of LiMnPO₄ is shown in Scheme 3. The synthesis was performed at 120–260 °C for 4–5 h. The obtained material was rinsed with hexane and ethanol to remove the organics before the remaining surfactants of oleic acid and oleylamine were removed by ligand exchange at 70–80 °C.

LMP nanoparticles were obtained in various shapes, which included elongated spheres, thin rods, thick rods, needles, and cubes. The sizes and the shapes of the LMP nanoparticles varied depending on the synthesis temperature and the ratio of the surfactants



Scheme 3. Synthesis of LiMnPO₄ by thermal decomposition.

and precursors. The complete synthesis procedure for this new cathode material was described by Kwon et al.^[11]

Electrode preparation with LiCoO₂ and LiMnPO₄

Both LCO and LMP were ball milled with carbon to produce a homogenous composite powder. Pastes were prepared subsequently by mixing this powder with polyvinylidene fluoride (PVDF) binder and *N*-methyl-2-pyrrolidone (NMP) solvent. The pastes were then deposited onto aluminum foil (used as the current collector) to produce the two different types of cathodes. More details were presented by Kwon and Fromm.^[25]

LCA calculations

LCA was performed by using the software tool OpenLCA with background LCI data taken from v3.3 of the ecoinvent database,^[27] using the system model “allocation based on recycled-content”. For the background materials for which the ecoinvent database does not contain any specific data, relevant existing datasets were chosen as proxies or new rough, gate-to-gate datasets were established (Supporting Information). For the life cycle impact assessment step, one of the most up-to-date methods in this area, the ReCiPe method,^[28] as implemented by ecoinvent in its database version 3.3, was applied. The large choice of impact categories in this method ensured the fulfillment of the requirements of the ISO 14040 and 14044 standards,^[7,8] which require that impact categories are selected such that a broad set of environmental issues related to the product system studied are taken into account and with consideration for the goal and scope of the study. Here, the following assessment factors are reported, which were identified as relevant in a detailed analysis of the normalized results on the level of the lab-scale production processes: fossil fuel depletion potential (FDP), metal resource depletion potential (MDP), global warming potential (GWP), terrestrial acidification potential (TAP), freshwater eutrophication potential (FEP), particulate matter formation potential (PMFP), photochemical oxidation formation potential (POFP), human toxicity potential (HTP), freshwater ecotoxicity potential (FETP), and marine ecotoxicity potential (METP).

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Conflict of interest

The authors declare no conflict of interest.

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