Environmental Impact Assessment of Na$_3$V$_2$(PO$_4$)$_3$ Cathode Production for Sodium-Ion Batteries

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1. Introduction

Secondary batteries are considered key enablers in the green energy transition landscape and are destined to play a crucial role in the electrification and decarbonization of worldwide economies.[1] Electrochemically efficient, cost-effective, and environmentally sustainable batteries are gaining increased attention in the current scenario of critical raw materials (CRMs) scarcity, global warming, and environmental pollution.[2,3] Sustainable batteries can clear the way into circular economy models upon the reduction of natural resource depletion and environmental pollution associated with the uncontrolled combustion of fossil fuels.[4,5]

In spite of the current predominant role of lithium-ion batteries (LIBs) in portable electronics, electric vehicles, or stationary energy storage applications,[6] beyond-Li ion batteries are now emerging as competitive alternatives for these applications. Among the different available possibilities, sodium-ion batteries (NIBs) are of special interest given the redox potential of $E_{(Na^+/Na)} = -2.71$ V of sodium, the natural abundance of sodium (2.36% in Earth’s crust),[7] its low price of 0.15 $ kg$^{-1},[8] and the possibility of using aluminum current collectors (instead of the copper/aluminum required for LIBs).[9] In addition, a wide range of NIB cathodes relaying on Earth-abundant materials has been reported, making these batteries useful for large-scale stationary energy storage.[10] The existing mismatch between the supply and demand of raw materials in LIBs could be potentially reduced, limiting in the...
the need for CRMs such as cobalt, lithium, manganese, or graphite often needed in LIBs. Thanks to the cheaper cathode active materials and the avoidance of Cu at the current collector, NIBs at battery cell level are clearly cheaper than LIB cells.[11] This lower cost together with the chemistry and technology similarities with conventional lithium-ion-based batteries facilitates the replacement of LIBs by NIBs in the medium term. In addition, the environmental sustainability of NIBs was confirmed by Peters et al. in 2016, who used the life cycle assessment (LCA) methodology to conclude that in comparison with LIBs, NIBs present reduced impacts in global warming, fossil depletion potential, freshwater eutrophication, and human toxicity potential per 1 kWh of storage capacity.[12] In spite of these benefits, the lower theoretical capacity of 1165 mAh g⁻¹ of Na as opposed to 3829 mAh g⁻¹ of Li results in lower specific energy densities, limiting their practical implementation.[13,14]

As a critical battery component determining its electrochemical performance,[15] diverse cathode materials have been developed to make NIBs competitive against LIBs. Among them, the Na₃V₂(PO₄)₃ (NVP) cathode having a fast Na⁺-transportable NASICON framework is a popular choice given their balance between discharge capacity of 117.6 mAh g⁻¹ and platform voltage of ≈3.4 V, outperforming the electrochemical performance of many NIB cathodes reported in the literature.[16] The initial promising results obtained with Na₃V₂(PO₄)₃ have sparked notable scientific efforts aimed at improving its relatively poor electronic conductivity of 1.63 × 10⁻⁶ S cm⁻¹ and limited structural stability that result in low discharge capacities (at high rates) and poor operating lifespans.[17]

Generally speaking, these synthetic approaches have been mainly focused on the improvement of electronic conductivity and structural stability of Na₃V₂(PO₄)₃, so an efficient Na⁺ and e⁻ transference through the cathode could be obtained with limited volume changes in the process of Na⁺ extraction/insertion.[17] Notwithstanding the many different synthetic approaches reported, these can be roughly categorized into the incorporation of diverse carbonaceous materials to enhance electronic conductivity,[18–20] structural arrangement, heteroatom doping,[21–23] particle downsizing, and morphology modification to shorten transport distances of Na⁺ and electrons[24,25] or biopolymer incorporation.[26,27] Specifically, it is possible to improve the reversibility and cycling stability (at high rates specially) of the battery upon dehybridization of NVP with carbon nanostructures, which not only improve the cathode’s electronic conductivity but also its structural stability.[28,29] In addition, the presence of mesoporosity in the cathode enhances sodium storage performance in terms of achieved reversible capacity, rate performance, and cycle life.[10] However, these approaches are not designed according to green chemistry principles and often involve a synthetic process with environmentally harmful reagents and large amounts of energy. In addition, Na₃V₂(PO₄)₃ contains vanadium and phosphorus, which are CRMs due to their pressure over finite natural resources, supply chain risks, and economic relevance.[11]

Considering these issues and the circular economy actions to foster the development of environmentally sustainable battery industries,[12] the assessment of the environmental sustainability of Na₃V₂(PO₄)₃ cathode fabrication becomes necessary. The LCA methodology can be applied to that end because it enables the quantification of the environmental impacts of a given product or a service over its whole (or specific) life cycle stage, covering raw material extraction, manufacturing, distribution, use, and end-of-life.[13,14] Following widely recognized calculation methods, LCA can provide information on a wide variety of impact categories including global warming, fossil resource scarcity, ecotoxicity, eutrophication, land use, acidification, ozone depletion, or water use. The public disclosure of the LCA results enables selecting not only the environmentally preferred Na₃V₂(PO₄)₃ cathode, but also gives insights for the prospective reduction of the impacts through the implementation of eco-design strategies.[15]

Accordingly, the environmental impacts originating from Na₃V₂(PO₄)₃ cathode materials designed to show improved electrochemical performance are exhaustively quantified, analyzed, and compared. Ten representative state-of-the-art Na₃V₂(PO₄)₃ cathode materials at laboratory scale are selected to provide a representative overview of the currently available alternatives. Although the environmental competitiveness of several NIB cathodes has been recently reported, no works have been devoted to specifically analyze Na₃V₂(PO₄)₃ cathodes.[36] Using a cradle-to-gate approach, the impacts are normalized to 1 kg of cathode material. As energy storage field is a performance-driven area, the environmental impacts are then normalized to 1 kWh of (cathode-only) storage capacity. Overall, this work is aimed to provide support for battery developers and assist future advances in the development of sustainable cathodes applied into beyond-Li-ion technologies.

2. Experimental Section

2.1. Goal, Scope, and Life Cycle Interpretation

LCA was applied to quantify the cradle-to-gate environmental impacts of ten representative state-of-the-art Na₃V₂(PO₄)₃ cathodes. The lack of accurate information regarding the NIB end-of-life and its nonmature character make difficult cradle-to-cradle studies. Accordingly, raw material acquisition and Na₃V₂(PO₄)₃ cathode synthesis is considered for laboratory-scale NIB cathodes. As shown in Figure 1, the laboratory-scale synthetic approaches involved different strategies to upgrade the electrochemical performance (discharge capacity, cycling stability and rate capability) of the Na₃V₂(PO₄)₃ cathodes, including the incorporation of carbonaceous structures, heteroatom doping, nanostructuring, or biopolymer incorporation (see Figure S1–S10, Supporting Information, for the followed synthetic approaches and obtained morphologies). As lab-scale LCA is recognized as an effective environmental advisory tool for emerging technologies and materials,[17] the outcome facilitates future follow-on works in the field of sustainable NIBs. In any case, we acknowledge that the obtained impacts may be considerably larger than actual industrial-scale batteries.

LCA studies were carried out with the OpenLCA software coupled with ecoinvent v3.8 dataset (released on September 2021). The environmental impacts and life cycle inventory (LCI) were provided to enable future comparison. The environmental impacts were grouped into 18 categories based on ReCiPe.
2016 Midpoint (H). As a globally accepted method, this method provides additional metrics in comparison with other approaches such as the CML-baseline. Given the relevance of greenhouse gas (GHG) emission to meet the Paris Agreement, the global warming potential (GWP) impact indicator, measured in kg·CO₂-equiv., was used for comparison. The definition of an adequate functional unit (FU) represents a challenge; while FU closer to the actual service of the battery is desired (storage capacity, for instance), additional assumptions should be made, which entail risks of increasing the level of uncertainty. Contrarily, using the mass of cathode as a FU has no direct relationship to the service of a battery but provides relevant information for straightforward comparison across multiple studies. Following the precedent established by Ellingsen et al., 1 kg of synthesized cathode was used as a FU. However, as the energy field is an electrochemical performance-driven area, a second FU focused on the energy storage capacity was also considered. This second FU was set as the gravimetric energy density (based on cathode active mass; Wh kg⁻¹ cathode⁻¹), particularly relevant toward practical implementation. This standardization facilitated a simple and accurate comparison with other electrochemical energy-storage technologies.

2.2. Life Cycle Inventory

The LCI for Na₃V₂(PO₄)₃ cathodes is shown in Table 1 (data extracted from secondary sources). This table summarizes the inventory of input and output flows for the cradle-to-gate fabrication of the cathodes. The resources of water, energy, and raw materials needed for the synthesis were computed as the inputs, while the releases/emissions to air, soil, and water originating from the fabrication process were computed as the outputs. The LCI was constructed for the specific amounts of cathode synthesized in each of the works, which ranged from ≈15 to 500 mg. When accounting for the electricity consumed upon fabrication, specific processes were estimated (generally involving stirring, heating, drying, or annealing). Additional details for the inventory are disclosed in the Supporting Information as Scheme S1–S10 and Table S1–S23, Supporting Information. The electricity mix of the European Network of Transmission System Operators (ENTSO-E) accounting for the electricity from 35 countries across Europe was used in the ecoinvent v3.8 database.

As representative state-of-the-art examples, ten Na₃V₂(PO₄)₃ cathode designs applied into NIBs were selected (all works have been published from 2015 onwards). A short description for each cathode is given hereafter. One of the first examples to upgrade the performance of Na₃V₂(PO₄)₃ was carried out by Fang et al., who wrapped the active material by a highly conductivity and interconnected hierarchical carbon framework (cathode 1, denoted as “hierarchical carbon-NVP”). The chemical vapor deposition process affords graphene-like coating layers and interconnected carbon nanoﬁbers onto highly crystallized Na₃V₂(PO₄)₃ particles, boosting e⁻ transport and accommodating volume changes upon Na⁺ insertion/extraction. As a result, the half cell delivered 110 mAh g⁻¹ at 2C (1C = 117 mAh g⁻¹) with a remarkable 54% capacity retention after 20 000 cycles at 3C rate. Following the combination of Na₃V₂(PO₄)₃ with carbonaceous structures, Na₃V₂(PO₄)₃ nanoparticles were grown in between reduced graphene oxide (rGO) layers upon the modiﬁcation of the surface charge of the gel precursor (cathode 2, denoted as “rGO-LbL NVP”). The obtained layer-by-layer structure concomitantly increased the electronic/ionic conductivity, offering a rapid Na⁺ diffusion and electron transport pathway, while the physical structure upon charge/discharge cycles was maintained. As a result, ≈110 mAh g⁻¹ at 2C with a remarkable 70% capacity retention after 15 000 cycles at 5C rate was achieved (half-cell). The simple combination of sol–gel and annealing under Ar–H₂ atmosphere rendered Na₃V₂(PO₄)₃ nanoparticles...
Table 1. Material and energy input inventory required for the synthesis of Na$_3$V$_2$(PO$_4$)$_3$ cathodes (corresponding to the amounts used in each of the analyzed works). Quantities are provided in grams if not stated otherwise. The Na$_3$V$_2$(PO$_4$)$_3$ cathode code is 1: "hierarchical carbon-NVP" 2: "rGO-LbL NVP" 3: "µPorous NVP" 4: "N-doped carbon NVP" 5: "N,B-doped carbon/NVP" 6: "La$^{3+}$-doped NVP" 7: "3D NVP nanofiber" 8: "Nanoplatelet NVP" 9: "Agarose carbon NVP" and 10: "Glucomannan NVP".

| Cathode 1 | Cathode 2 | Cathode 3 | Cathode 4 | Cathode 5 | Cathode 6 | Cathode 7 | Cathode 8 | Cathode 9 | Cathode 10 |
|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Material  | Quantity  | Material  | Quantity  | Material  | Quantity  | Material  | Quantity  | Material  | Quantity  |
| V$_2$O$_5$ | 0.182     | GO        | 0.009     | NH$_3$V$_6$O$_9$ | 0.293       | NH$_4$VO$_3$ | 0.228     | NH$_3$HBO$_3$ | 37.981       | V$_2$O$_5$ | 0.182     | Na$_2$CO$_3$ | 0.246       | KGM | 0.85 |
| C$_2$H$_2$ | 0.526     | V(C$_5$H$_7$O$_2$)$_3$ | 0.697 | Ar (liquid) | 46.025 | C$_2$H$_5$NO$_2$ | 0.500 | V$_2$O$_5$ | 0.720 | La(NO$_3$)$_3$ | 0.009 | Ar (liquid) | 48.168 | V(C$_5$H$_7$O$_2$)$_3$ | 0.697 | CB | 0.135 |
| CB | 0.139 | CB | 0.134 | C$_2$H$_5$O$_2$ | 0.384 | Ar (liquid) | 120.886 | CB | 0.133 | NaHCO$_3$ | 0.009 | Ar (liquid) | 74.928 | C$_2$H$_5$O$_2$ | 0.384 |
| H$_2$ | 0.199 | C$_2$H$_5$O$_2$ | 0.102 | CB | 0.030 | C$_2$H$_5$O$_2$ | 0.400 | Ar (liquid) | 40.140 | DMF | 28.320 | NH$_4$VO$_3$ | 0.333 | H$_2$ | 0.19895 | N$_2$ | 42.660 |
| H$_2$ (gas) | 0.114 | NH$_4$PO$_4$ | 0.345 | H$_2$ (gas) | 0.171 | C$_2$H$_5$O$_2$ | 0.110 | H$_2$ (gas) | 0.142 | CB | 0.136 | NMP | 40.165 | DMF | 28.320 | NH$_4$PO$_4$ | 0.34508 | NMP | 38.796 |
| NH$_4$HPO$_4$ | 0.345 | NMP | 38.716 | NMP | 42.506 | EtOH | 11.835 | N$_2$ (liquid) | 35.550 | NH$_4$HPO$_4$ | 0.345 | C$_2$H$_5$O$_2$ | 2.358 | NMP | 19.867 | NMP | 38.63983 | NaOH | 0.120 |
| NMP | 40.127 | PVDF | 0.067 | PVDF | 0.064 | NMP | 43.869 | NMP | 37.700 | NMP | 39.669 | NMP | 37.700 | PVDF | 0.070 | C$_2$H$_5$O$_2$ | 0.450 | (C$_3$H$_7$NO$_3$)$_2$ | 0.01403 | DI water | 50.066 |
| C$_2$H$_5$O$_2$ | 0.360 | Na$_2$CO$_3$ | 0.159 | NaH$_2$PO$_4$ | 0.360 | NMP | 19.867 | C$_2$H$_5$O$_2$ | 1.5000 | PVDF | 0.068 | NaH$_2$PO$_4$ | 0.360 | PVDF | 0.002 | PVDF | 0.05862 | NH$_4$VO$_3$ | 0.234 |
| PVDF | 0.070 | DI water | 40.000 | DI water | 0.551 | PVDF | 0.030 | PVDF | 0.069 | H$_2$ (gas) | 0.107 | DI water | 5.00 | Na$_2$CO$_3$ | 0.005 | DI water | 0.46767 |
| Na$_2$CO$_3$ | 0.159 | DI water | 39.495 | NaH$_2$PO$_4$ | 1.411 | DI water | 50.000 | DI water | 10.000 | |
| Energy | 25.0 kWh | Energy | 112.2 kWh | Energy | 51.0 kWh | Energy | 47.3 kWh | Energy | 41.4 kWh | Energy | 50.8 kWh | Energy | 43.6 kWh | Energy | 55.2 kWh | Energy | 56.9 kWh | Energy | 40.5 kWh |

a) CB: carbon black, NMP: N-Methyl-2-pyrrolidone, PVDF: polyvinyl fluoride, KGM: konjac glucomannan biopolymer.
being embedded into porous carbonaceous microspheres (cathode 3, denoted as “μPorous NVP”).[209] Thanks to the favored nanoparticle connectivity and improved electron transfer by the carbon phase, \( \approx 82 \text{ mAh g}^{-1} \) was achieved at 2C (half cell).

Heteroatom doping (with nitrogen, boron, sulfur, or phosphorus) is a widely pursued approach to enhance the electrochemical performance of carbonaceous materials as it introduces additional active sites for electrochemical reactions, enhances electronic conductivity, and improves surface wettability. In particular, nitrogen doping has been proven efficient to increase the intrinsic low electronic conductivity of \( \text{Na}_3\text{V}_2(\text{PO}_4)_3 \) and thus improve its cyclability and rate capability. Kim et al. used polydopamine as a nitrogen-containing source to obtain N-doped mesoporous carbon-wrapped \( \text{Na}_3\text{V}_2(\text{PO}_4)_3 \) (cathode 4, denoted as “N-doped carbon NVP”).[210] Thanks to the adhesive properties of polydopamine, intimate contact between the doped carbon and \( \text{Na}_3\text{V}_2(\text{PO}_4)_3 \) was achieved, reaching 94.8% capacity retention after 1000 cycles at 2C (half cell). In addition, dual-atom doping involving nitrogen and boron was pursued to obtain a codoped carbon-coated 3D \( \text{Na}_3\text{V}_2(\text{PO}_4)_3 \) composite (cathode 5, denoted as “N,B-doped carbon/NVP”).[22] The doping enabled a quick \( \text{Na}^+ \) and electron transport and the flower-like morphology shortens the electronic transport distance while protects the cathode structural integrity, resulting in NIB with a long cycle life as proved by \( 38 \text{ mAh g}^{-1} \) after 5000 cycles at 2C (half cell). Not only the carbon phase but also the \( \text{Na}_3\text{V}_2(\text{PO}_4)_3 \) itself was also doped to improve its electrochemical performance. In particular, lanthanum (La) was incorporated into the \( \text{Na}_3\text{V}_2(\text{PO}_4)_3 \) structure (\( \text{Na}_3\text{V}_2-\text{La}(\text{PO}_4)_3/C \)) upon a combination of sol–gel and carbon-thermal reduction methods (cathode 6, denoted as “La+-doped NVP”).[23] La+ doping expanded the lattice structure, increasing the \( \text{Na}^+ \) mobility and providing a capacity retention of 93.5% after 3000 cycles at 2C (half cell).

Several works have attempted to modify the \( \text{Na}_3\text{V}_2(\text{PO}_4)_3 \) morphology to enhance the rate-capacity and cycling stability. In this context, a self-sacrificed approach was followed to change the morphology of \( \text{Na}_3\text{V}_2(\text{PO}_4)_3 \) itself into a 3D connected nanofiber network (cathode 7, denoted as “3D NVP nanofiber”).[24] Such a structure combined the multichannel ion diffusion paths with continuous electronic conduction and a physically stable architecture, reaching 95.9% capacity retention after 1000 cycles at 1C when evaluated into a half cell. Similarly, Li et al. obtained highly crystalline and porous \( \text{Na}_3\text{V}_2(\text{PO}_4)_3 \) nanoplatelets via hydrothermal method and postcalcination under Ar–H₂ atmosphere (cathode 8, denoted as “Nanoplatelet NVP”).[25] The pores within the \( \text{Na}_3\text{V}_2(\text{PO}_4)_3 \) enlarged the specific surface and shortened the \( \text{Na}^+ \) and \( e^- \) diffusion path, while the thin nanoplatelet character provided easy accessibility of the electrolyte to the active sites, reaching a remarkable rate performance of 76.5 mAh g\(^{-1}\) at a rate as large as 10C (half cell).

Given the inherent polar character and carbon content of natural biopolymers (polymers originating from the cells of living organisms),[42] these macromolecules could be used to improve the electrochemical properties of \( \text{Na}_3\text{V}_2(\text{PO}_4)_3 \) cathodes. For instance, a soft templating approach using biopolymers substantially enhanced the electrochemical performance of NIBs. In this context, agarose dissolved in boiled water was applied as a carbon source to coat 20–200 nm \( \text{Na}_3\text{V}_2(\text{PO}_4)_3 \) nanoparticles with a 3D carbonaceous skeleton (cathode 9, denoted as “Agarose carbon NVP”).[26] When mounted into a half cell, the cathode obtained after Ar–H₂ sintering offered a discharge capacity of 113 mAh g\(^{-1}\) at 1C, 60 mAh g\(^{-1}\) at 5C, showing 87.5% capacity retention after 8000 cycles at 2C (half cell). From the other side, the konjac glucomannan biopolymer was applied to develop an adhesive and stable solid permeable interface in \( \text{Na}_3\text{V}_2(\text{PO}_4)_3 \) cathodes (cathode 10, denoted as “Glucomannan NVP”).[27] Developed interface did not hinder \( \text{Na}^+ \) transfer but limited the inherent oxidation of the cathode by the electrolyte at high voltages. In addition, the abundant polar groups facilitated \( \text{Na}^+ \) transport, yielding a cathode material with 74.1% capacity retention after 10 000 cycles at 5C (half cell). This strategy of surrounding the active NVP by an amorphous carbon phase acting as a binder to enhance the structural stability upon charge/discharge has been also recently reported by Zhou et al.[43]

### 3. Results and Discussion

#### 3.1. Global Warming Potential Per 1 kg of Cathode

Given its predominant relevance to meet the legally binding international treaties on climate change, we first studied the GWP impact category. The results, provided in kg CO₂-equiv., account for the emissions from GHGs on the basis of their global warming potential. To do so, a conversion is carried out to the equivalent amount of CO₂ with the same GWP. Figure 2 shows the GWP values for the fabrication of 1 kg of cathode material for ten different laboratory-scale designs (cradle-to-gate approach). Overall, GWP values ranging from 423.9 to 1380.0 kg CO₂-equiv. \( kgcathode^{-1} \) are achieved. Given the particularly striking 12810.5 kg CO₂-equiv. \( kgcathode^{-1} \) value of the “Nanoplatelet NVP” cathode arising from the low quantity of synthesized material (15.6 mg is achieved in comparison with 469–516 mg obtained in the other nine processes; see Scheme S1-S10). Supporting Information, for further information), this cathode is estimated not representative and will not be considered for discussion. In general, the cathodes bearing biopolymers (average: 548.5 kg CO₂-equiv. \( kgcathode^{-1} \)) and consisting of the simple incorporation of carbonaceous nanostructures (average: 571.5 kg CO₂-equiv. \( kgcathode^{-1} \)) are the environmentally friendlier options given the simpler character of the synthetic processes and the use of Earth-abundant materials. On the other side, nanostructuring (633.1 kg CO₂-equiv. \( kgcathode^{-1} \)) is estimated not representative and will not be considered for discussion. The GWP values for the fabrication of 1 kg of cathode material for the different laboratory-scale designs (cradle-to-gate approach) are estimated not representative and will not be considered for discussion.

Obtained impacts are above the 22 kg CO₂-equiv. \( kgcathode^{-1} \) reported for LiFePO₄ cathode produced by hydrothermal synthesis (cradle-to-gate), the 22 kg CO₂-equiv. \( kgcathode^{-1} \) reported by Majeau-Bettez et al. for LiNiₓ₀.₅Coₓ₀.₅MnₓO₂ cathode obtained upon aqueous precipitation followed by calcination (cradle-to-gate),[44] the 21 kg CO₂-equiv. \( kgcathode^{-1} \) of the LiCoO₂ cathode when prepared by solid-state synthesis,[45] the \( \approx 32 \text{ kg CO}_2 \text{-equiv. kg}_{cathode}^{-1} \) showed by LiNiₓMnₓCoₓO₂ cathode, and the \( \approx 28 \text{ kg CO}_2 \text{-equiv. kg}_{cathode}^{-1} \) obtained for LiNiₓCoₓAlₓO₂ cathode.[46] However, it should be considered that...
the impacts of the last two cathodes (which are in the same range of the other reports) correspond to cradle-to-gate results obtained from representative manufacturers of LIBs in China. Therefore, the 13-to-45 fold increase on the GWP category shown by this work can be explained by the notably more complex synthetic approaches here analyzed, which require energy-intensive multistep processes that are not designed according to atom-efficiency principles, and use relatively hazardous chemicals with notable embodied energy and carbon impacts. For example, the production of 0.516 g of “μPorous NVP” requires 51.0 kWh of electricity (for ultrasonic treatment, stirring, evaporation, drying, grounding, heat treating, and final annealing), 0.21 g of the hazardous ammonium metavanadate (NFPA 704 190–51.0 kWh of electricity (for ultrasonic treatment, stirring, evaporation, drying, grounding, heat treating, and final annealing), 0.21 g of the hazardous ammonium metavanadate (NFPA 704 scale 4-0-0), 0.12 g of carbon black, 0.384 g of citric acid, 0.1 g of ethylene glycol, 0.17 g of H2 gas, 46 g of liquid argon, 42.5 g of the toxic NMP solvent, 0.06 g of the polyvinylidene difluoride petroleum-based polymer, 0.36 g of the inorganic monosodium phosphate salt, and 0.55 g of deionized water.

In this sense, comparing the impacts of Na3V2(PO4)3 cathode production with the synthesis of high-performance nanomaterials may be more appropriate as the involved precursors and synthetic processes have a certain similarity. Accordingly, values of 1060–2360 kg CO2 equiv. kg–1 for reduced graphene oxide production, or 217–501 kg CO2 equiv. kg–1 for graphene oxide synthesis via the Hummers and Marcano methods, have been reported.[47] Importantly, these large values do not only apply for inorganic nanomaterials but also for nanoparticles having a renewable origin such as cellulose nanofibers (190–1160 kg CO2 equiv. kg–1),[48] cellulose nanocrystals extracted from cotton (112 kg CO2 equiv. kg–1), or the cellulose nanocrystals obtained from unripe coconuts (1086 kg CO2 equiv. kg–1).[49] The underlying reasons for these impact differences will be explained in the forthcoming sections. In any case, it is worthy to note that according to the conclusions drawn by Piccinni et al., who reported that the environmental impacts of bio-based nanoparticle production can be lowered by a factor of 6.5 transitioning from the laboratory-scale (10 g) production to the industrial scale (50 kg),[50] we estimate that the carbon footprint of Na3V2(PO4)3 cathode production could be lowered in the near future.

3.2. Environmental Impacts in 18 Categories

A more detailed analysis of the environmental impacts facilitates the identification of the environmental hotspots during Na3V2(PO4)3 fabrication while enables future optimization through ecodesign approaches. Accordingly, the analysis has been expanded to all the impact categories considered by the ReCiPe 2016 Midpoint (H) LCA and the results are shown in Table 2. As occurring with the GWP value, the “Glucoammam NVP” cathode shows the lowest impacts in 16 of the 18 categories analyzed. These results may originate from the relatively simple synthetic process involving heating, stirring/evaporation, grounding, and subsequent heating at 800 °C under N2 atmosphere. In addition, Earth-abundant or organic precursors such as NaOH and citric acid have been used. However, it should be considered that all the cathode synthesis processes studied, “Glucoammam NVP” included, present highly hazardous inorganic vanadium-containing compounds as the V source for the cathode. Examples include vanadium(V) oxide (V2O5), vanadium(III) acetylacetonate (V(C5H7O2)3), or ammonium metavanadate (NH4VO3) depending on the design. Therefore, all the cathodes are subjected to certain levels of toxicity.

In spite of their multistep character involving several of the following treatments (ultrasound treatment, ball milling, stirring, autoclave heating, freeze-drying, grinding, sintering under Ar/H2 atmosphere, or heating under Ar atmosphere), the “hierarchical carbon NVP” “rGO-LbL NVP” and “μPorous NVP” cathode are the choices with intermediate impacts in most of the categories. These results highlight that the incorporation of carbonaceous (nano)structures into Na3V2(PO4)3 cathodes results in an environmentally sound alternative. Similarly, the “La3+-doped NVP” doping approach seems a sustainable alternative as solely 9 mg of the lanthanum-containing precursor (La(NO3)3) is required to obtain 484 mg of cathode material. In addition, the “3D NVP nanofiber” strategy also results in an environmentally viable alternative. Finally, “N-doped carbon NVP” “N,B-doped carbon NVP” and specially “nanoplatelet NVP” bear the largest environmental burdens.

Due to availability and price issues, certain materials applied into conventional LIBs (cobalt, lithium, graphite) are considered as CRMs by the European Union. As one of the most critical impact in the energy storage field, the “mineral resource scarcity” category is further discussed.[51] Low values in this category reflect an enhanced potential availability of the materials needed to fabricate Na3V2(PO4)3 cathodes, smoothing possible supply chain issues associated with key raw materials. In this sense, cathodes using abundant (sodium carbonate) or organic (oxalic acid, a biopolymer, citric acid) precursors, “hierarchical carbon NVP” and “glucoammam NVP” more precisely, show the lowest results with values of 2.34 and 2.43 kg Cu-equiv., respectively. In contrast, the “N-doped carbon NVP” and “N,B-doped carbon NVP” present the largest burdens (5.12 and 8.30 kg Cu-equiv., respectively). These results are explained by the relatively large quantities of reagents having vanadium (such as NH4VO3, V2O5), boron (NH2HB2O7), or phosphorus (NH4H2PO4, NaH2PO4), highlighting the notable contribution of doping processes to the “mineral resource scarcity” impact category.
Increasing the solution concentration could be one of the possibilities to reduce the resulting environmental impacts. This particularly applies to certain processes, where the generated wastewater strongly contributes to toxicity estimations. For instance, 1162 g of H₂O-waste and 1810 g of DMF-waste are generated per gram of "Nanoplatelet NVP" cathode. In addition, we encourage pursuing shorter reactions as these often require large amounts of energy (to power the furnaces) and large quantities of gases such as argon, nitrogen, or hydrogen (to ensure inert atmospheres). Cathode fabrication processes should be also designed to obtain high atom-efficiency values, which represent one of the cornerstones of the 12 Green Chemistry principles.\(^{[52]}\)

In particular, the process efficiency regarding material use (the ratio of the targeted products to the total mass of used products)\(^{[53]}\) should be as high as possible. This could be accomplished by carefully selecting the reaction stoichiometry and avoiding excess reactant from one side and the recycling of the solvents and other reagents from the other.

### 3.3. Environmental Impacts and Electrochemical Performance

As the energy storage is a performance-driven field, the environmental impacts cannot be fully understood without the analysis of the electrochemical behavior. Accordingly, LCA studies have been completed considering the Na₃V₂(PO₄)₃/Na half-cell configuration. Although full-cell configurations (i.e., NVP||carbon) result closer to practical implementation, most of the works have focused on half cells as it provides further information on the working electrode (NVP cathode in this case). Thereby, the discharge capacity and gravimetric energy density are considered for the half-cell configuration. In fact, the impacts are normalized to 1 kWh of (cathode-only) storage capacity defined as

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\text{Gravimetric energy density (Wh · kg}^{-1}\text{)} = \frac{\text{nominal voltage} \times \text{discharge capacity}}{\text{cathode weight} \times \text{kg}}
\]

Given that the information provided by the published works does not provide enough information on cell weight, 1 kWh of cathode-only storage capacity is considered as the FU. This standardization allows considering the electrochemical performance for environmental impact analysis and avoids uncertainties associated with the lack of information (the exact amount of cathode material is provided in the form of mass loading and cell size). The gravimetric energy density values have been extracted from the published works, while a C-rate of 0.5C (a 2 h discharge) has been selected for all the batteries to provide a common ground for comparison. For the sake of clarity, characteristic galvanostatic charge-discharge curves of Na₃V₂(PO₄)₃/Na half cells are shown in Figure 3a.\(^{[54]}\)

![Figure 3a](image-url)
cathode presents a flat plateau centered at nearly 3.4 V versus Na⁺/Na during sodiation/desodiation processes (Na₃V₂(PO₄)₃ ↔ NaV₂(PO₄)₃ reaction),[16] which coupled with a discharge capacity of up to 117.6 mAh g⁻¹ (theoretical value)[55] renders gravimetric energy densities exceeding 300 Wh kg⁻¹.

To evaluate the impacts of the cathodes when implemented into Na₃V₂(PO₄)₃/Na cells, new LCA studies have been conducted considering the material, and energy requirements to process the cathode, the separator, the liquid electrolyte, and the metallic Na anode have been considered. As summarized in the Table 3, the cathode is composed of the active Na₃V₂(PO₄)₃.

![Figure 3. a) Characteristic galvanostatic charge/discharge profiles of Na₃V₂(PO₄)₃/Na cells. The orange shadowed area shows the graphical calculation of the gravimetric energy density, which is the area under the voltage versus specific capacity curve. b) GWP of Na₃V₂(PO₄)₃/Na cells standardized to 1 kWh of (cathode-only) storage capacity.](image)

Table 3. Electrochemical performance of synthesized Na₃V₂(PO₄)₃ cathodes in a Na₃V₂(PO₄)₃/Na half-cell configuration.

| Cathode                     | Binder     | Additive | Solvent     | Separator | Electrolyte                | Anode       | Cycle capacity [mAh g⁻¹] | Capacity retention [%] | Cycle [°C] |
|-----------------------------|------------|----------|-------------|-----------|---------------------------|-------------|--------------------------|------------------------|------------|
| "Hierarchical carbon-NVP"[18] | 10 wt% PVDF | 20 wt% CB | N.R. Glass fiber | EC/DEC (1:1 vol.) | 1 M NaClO₄ in | Na metal | 115 @ 0.2C | 73% after 10 000 @ 30C | @ 30C |
| "rGO-Lbl NVP"[19]           | 10 wt% PVDF | 20 wt% CB | NMP Glass fiber | EC/DMC (1:1 vol.) | 1 M NaClO₄ in | Na metal | 117 @ 1C | 77% after 10 000 @ 50C | @ 50C |
| "µPorous NVP"[20]            | 10 wt% PVDF | 10 wt% CB | NMP Glass fiber | EC/PC (1:1 vol.) | 1 M NaClO₄ in | Na metal | 116.5 @ 0.2C | 90% after 400 @ 1C | @ 1C |
| "N-doped carbon NVP"[21]    | 10 wt% PVDF | 10 wt% CB | NMP Glass fiber | EC/PC/DEC (1:1:1 vol.) | 1 M NaClO₄ in | Na metal | 103 @ 0.5C | 95% after 1000 @ 20C | @ 20C |
| "N,B-doped carbon/ NVP"[22] | 10 wt% PVDF | 20 wt% CB | N.R. Glass fiber | NMP | 1 M NaClO₄ in PC with 5% FEC | NVP/NVP configuration | 112 @ 1C | 96% after 1000 @ 50C | @ 50C |
| "La³⁺-doped NVP"[23]         | 10 wt% PVDF | 20 wt% CB | NMP Glass fiber | EC/DC (1:1 vol.) with 5% FEC | 1 M NaClO₄ in | Na metal | 104.5 @ 1C | 77% after 5000 @ 50C | @ 50C |
| "3D NVP nanofiber"[24]       | 10 wt% PVDF | 20 wt% CB | NMP Glass fiber | EC/PC (1:1 vol.) with 5% FEC | 1 M NaClO₄ in | Na metal | 113 @ 1C | 96% after 1000 @ 10C | @ 10C |
| "Nanoplatelet NVP"[25]       | 10 wt% PTFE | 20 wt% CB | NMP Glass fiber | EC/PC (1:1 vol.) with 5% FEC | 1 M NaClO₄ in | Na metal | 112 @ 0.5C | 83% after 10 000 @ 50C | @ 50C |
| "Agarose carbon NVP"[26]     | 10 wt% PVDF | 10 wt% CB | NMP Polypropylene | EC/DMC (1:1 vol.) with FEC | 1 M NaPF₆ in | N.R. | 113 @ 1C | 88% after 8000 @ 2C | @ 2C |
| "Glucomannan NVP"[27]        | 10 wt% KCM in H₂O (1.25 wt%) | 20 wt% CB | Water Glass fiber | EC/DC (1:1 vol.) with 5% FEC | 1 M NaClO₄ in | Hard carbon | 109 @ 0.5C | 74% after 10 000 @ 50C | @ 50C |

PVDF, polyvinylidene difluoride; PTFE, polytetrafluoroethylene; KGM: konjac glucomannan biopolymer; CB: carbon black, NVP, N-methyl-2-pyrrolidone; N.R., not reported, EC, ethylene carbonate, DEC, diethyl carbonate, DMC, dimethyl carbonate, FEC, fluoroethylene carbonate, PC, propylene carbonate. 1C = 117.6 mA g⁻¹.
material (ranging from 70 to 80 wt%), a carbonaceous additive such as carbon black aimed to increase the electronic conductivity, and a polymeric binder (polyvinylidene difluoride, polytetrafluoroethylene, or konjac glucomannan). The cathode is processed using a solvent such as N-methyl-2-pyrrolidone or water. The amount of the cathode has been estimated based on the cathode mass loading and cell diameter reported in the analyzed manuscripts except for the “N-doped carbon” and “Agarose carbon NVP”, where an average mass loading of 1.5 g cm\(^{-2}\) is set (due to data unavailability). A metallic Na foil (200 mg for our calculations) is used as an anode material in most of the cases. An electrically insulating but ionically conducting physical separator is placed between the anode and the cathode. To that end, a glass fiber (Whatman trademark) or a polypropylene (Celgard trademark) membrane is soaked into an organic electrolyte (100 µL for our calculations) having dissolved Na salts. NaClO\(_4\) is the preferred salt, while mixtures of ethylene carbonate, diethyl carbonate, dimethyl carbonate, fluoroethylene carbonate, or propylene carbonate are used as solvents. A moisture-free inert atmosphere is required for the assembly of the half cell, so argon and additional energy inputs are also considered. Current collectors and the battery management system are kept out of the inventory.

With GWP values ranging from 539.8 to 1622.1 kg CO\(_2\)-equiv. kWh\(_{\text{cathode}}\)\(^{-1}\) (see Figure 3b, the full impact analysis is provided in Table S24, Supporting Information), the lowest carbon footprint is obtained by the “µPorous NVP.” The “3D NVP nanofiber” cathode also scores low (966.6 kg CO\(_2\)-equiv. kWh\(_{\text{cathode}}\)\(^{-1}\)), while the “La\(^{3+}\)-doped NVP” and “Nanoplatelet NVP” present the largest impact (1622.1 and 6137.3 kg CO\(_2\)-equiv. kWh\(_{\text{cathode}}\)\(^{-1}\), respectively). Comparing these results with those previously shown for 1 kg of cathode, it remains apparent that the environmentally friendlier choice by weight does not necessarily translate into the most adequate design when considering battery performance. For example, although the GWP impacts of “hierarchical carbon-NVP” “rGO-LbL NVP” and “µPorous NVP” are roughly equal in terms of mass, the greater energy density and cathode mass loading can halve the GWP value, from 1102.5 kg CO\(_2\)-equiv. kWh\(_{\text{cathode}}\)\(^{-1}\) of the “hierarchical carbon-NVP” cathode to 539.8 kg CO\(_2\)-equiv. kWh\(_{\text{cathode}}\)\(^{-1}\) of the “µPorous NVP” cathode when considering 1 kWh of storage capacity as FU.

Considering the notably 13–45 larger CO\(_2\) footprint of the cathodes here analyzed in comparison with the impacts originating from the industrial-scale fabrication of Na\(_2\)V\(_2\)(PO\(_4\))\(_3\) cathodes [46] and the fact that the discharge capacity differences during the initial charge/discharge cycles are below 20% in most of the cases (see “cycle capacity” column in Table 3), the following dilemma appears: how worthwhile results, environmentally speaking, are improving the electrochemical performance at the expense of multistep, energy-consuming, and toxic processes? Nowadays this question remains open to debate, although future work may help to clarify this matter. As recently considered by Prozio and Scown, [49] performing LCA studies focusing on the battery use phase is highly recommended, where parameters such as cycle capacity, rate capacity, Coulombic efficiency, or operation lifespan should be considered. The cathodes containing graphene (“hierarchical carbon-NVP” and “rGO-LbL NVP”) are among those showing the largest discharge capacity values at 1C, so graphene results in a suitable additive to provide superior electronic conductivity to the cathode and enhance the rate capability (which is consistent with the literature). [96,57] Moreover, the “nanoplatelet NVP” cathode delivers 76.5 mAh g\(^{-1}\) at 10C, meaning that it will only take 36 s to charge/discharge the battery. So this design, in spite of its large environmental impacts, may be useful and environmentally efficient for fast charging electric buses.

In particular, capacity retention should be considered as one of the primary drivers toward sustainability (both economic and environmental) because it ensures the reuse strategy, the tightest loop in the circular economy diagram. The right column in Table 3 summarizes the capacity retention (%) after a given number of charge/discharge cycles. The comparison however is complex because of the different C-rates used. Overall, the majority of the cathodes show large capacity retention values, with specially remarkable values for “rGO-LbL NVP,” “N-doped carbon NVP” “N,B-doped carbon/NVP,” “3D NVP nanofiber” and “Nanoplatelet NVP”, which keep more than the ≈80% of their initial discharge capacity after more than 5000 cycles at very high C rates. These cathodes are encouraged for longlasting applications where conventional Na\(_2\)V\(_2\)(PO\(_4\))\(_3\) cathodes fail. Conversely, the “µPorous NVP” cathode seems to have the poorest cyclability, so in spite of its lower GHG emission per 1 kWh, it could bear larger environmental burdens when considering use phase. Conventional cathodes fail in these two specific applications (long operation lifespan and high charge), so the increased environmental footprint may be offset as conventional Na\(_2\)V\(_2\)(PO\(_4\))\(_3\) cathodes can hardly function beyond 100 cycles at 2–3C rate. [58]

In any case, it should be also considered that these values remain notably above when comparing with the GWP values (for the whole cell) obtained for other electrochemical energy storage systems such as lithium–O\(_2\) batteries (average of 55.8 kg CO\(_2\)-equiv. kWh\(^{-1}\)), [59] lithium-sulfur (average of 127.4 kg CO\(_2\)-equiv. kWh\(^{-1}\)) [60] and LIBs (average of 120 kg CO\(_2\)-equiv. kWh\(^{-1}\)). [61] In addition, Na\(_2\)V\(_2\)(PO\(_4\))\(_3\)/Na half cells also surpass the 140.3 kg CO\(_2\)-equiv. kWh\(^{-1}\) reported by Peters et al. for batteries composed of a hard carbon anode, Na\(_2\)Ni\(_0.3\)Mn\(_{0.5}\)Mo\(_{0.1}\)Se\(_{0.05}\) cathode, an organic solvent with NaPF\(_6\) electrolyte, and a polyethylene/polypropylene separator. [12] The prime cause for these larger impacts is that the laboratory-scale synthetic processes here studied have been not optimized in regard with their environmental performance, requiring both large amounts of reagents and energy. In addition, certain cathodes present remarkable capacity retention values, a critical aspect as it directly affects the durability of the batteries. In times when enduring goods can keep the material and energy resources in the loop for longer, the search for cathodes combining low GHG emissions, high energy density, and durability is encouraged.

### 3.4. Sensitivity Analysis

Overall, the synthetic approaches here analyzed have not been designed following green chemistry principles. Particularly relevant is the contribution of electricity to diverse environmental impacts including GWP, air pollution, water pollution, or solid waste disposal. In fact, the manufacture energy requirements have been highlighted as a major cause of GWP in battery
To evaluate the potential for the environmental impact reduction of the proposed cathodes, a sensitivity analysis is performed by shifting from a standard energy mix (high voltage | electricity, high voltage | Cutoff, U - ENTSO-E) to a fully renewable electric power supply. A new electricity source has been modeled considering the current renewable source proportion from Germany, Denmark, and the Netherlands and further modifying the ecoinvent 3.8 electricity mix to convert it to 100% renewable (76% wind, 12% biomass, 7% biogas, and 5% hydro-power), so representative values over the European renewable energy mix are reached (see Figure S11, Supporting Information). The “μPorous NVP” cathode is selected as a representative design comprising common synthetic steps (ultrasonic treatment, stirring, evaporation, drying, grounding, heat treatment, and annealing) and average energy and material inputs. As summarized in Figure 4, when considering 1 kWh of storage capacity as an FU, the environmental impacts could be reduced by 16.9 to 38.0% depending on the category, where the GWP value is lowered from 539.8 to 341.7 kg CO₂-equiv. kWh⁻¹. However, renewable energy is time dependent, so a realistic scenario may give intermediate results. However, it remains clear that additional efforts should be carried out to optimize reaction conditions (temperature and time) so the energy consumption could be reduced and environmentally sound Na₃V₂(PO₄)₃ cathode fabrication processes can be established.

4. Conclusion

The cradle-to-gate environmental impacts originating from the fabrication of Na₃V₂(PO₄)₃ cathodes are quantified, analyzed, and compared using LCA. Ten different cathode designs aimed to enhance the energy density, operation lifespan, and rate capability of sodium-ion batteries are selected to provide a representative overview in the sodium-ion battery landscape. The analysis of laboratory-scale batteries provides insights during the early-design step and subsequent practical implementation for future research on environmentally friendlier cathodes in particular and sodium-ion batteries in general. The impacts of 1 kg cathode production are accounted for 18 indicators. Global warming values from 423.9 to 1380.0 kg CO₂-equiv. kg⁻¹ are obtained, where cathodes using biopolymer precursors or those incorporating carbonaceous structures bear the lowest impacts. On the contrary, doping approaches present larger impacts. To get the bigger picture, the analysis has been expanded to Na₃V₂(PO₄)₃/Na half cells. When considering the impacts per 1 kWh of cathode-only storage capacity, the global warming contribution was found to be 539.8–1622.1 kg CO₂-equiv. kWh⁻¹. A sensitivity analysis demonstrates the potential to reduce the environmental impacts by 16.9–38.0% by transitioning to a renewable energy mix. According to the electrochemical performance in Na₃V₂(PO₄)₃/Na half-cell configuration, the “μPorous NVP” cathode shows the lowest carbon footprint per 1 kWh of storage capacity. However, when considering the use phase, heteroatom doping and morphology modification are good alternatives. However, considering the larger impacts of the cathodes here analyzed against industrial Na₃V₂(PO₄)₃ cathodes, the use of electrochemically enhanced cathodes is recommended for specific cases requiring long operation lifespans or fast charging applications. In the future, LCA studies could be accompanied by life-cycle costing analyses to evaluate the economics of battery cathodes and shed further light on the industrial feasibility of sodium-ion batteries. Overall, this
work highlights that not only material weight or storage capacity but also further operating features (C-rate, lifespan, and discharge capacity) should be considered to design truly environmentally sustainable batteries.

5. Data Availability

Table 1 summarizes the material and energy input inventory obtained for secondary data. The Supporting Information provides additional flowcharts for each cathode, together with a brief explanation to guide the reader. The materials and energy inventory modeling according to the ecoinvent v3.8 database is also provided. Additional calculations conducted to evaluate the environmental impacts of the cathodes into Na$_3$V$_2$(PO$_4$)$_3$/Na cells are available from the corresponding author upon reasonable request.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

cathodes, circular economy, life cycle assessments, Na$_3$V$_2$(PO$_4$)$_3$, sodium-ion batteries

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