Environmental Impacts of Aqueous Zinc Ion Batteries Based on Life Cycle Assessment

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Aqueous zinc ion batteries (AZIBs) are gaining widespread scientific and industrial attention thanks to their safety and potential environmental sustainability in comparison with other battery chemistries relying on organic electrolytes. AZIBs are good candidates for sustainable stationary storage, covering household energy needs or smoothing the intermittency associated with wind and solar energy. In spite of their potential as a sustainable energy storage technology, the study of their environmental repercussions remains unexplored. The environmental impacts associated with the fabrication of AZIBs are quantified using a cradle-to-gate life cycle assessment (LCA) methodology. Six laboratory-scale battery designs offering high delivered capacity, energy density and operating lifespan are selected. The contribution of different battery components to eighteen environmental impact indicators is shown. An average value of 45.1 kg CO₂ equiv per 1 kWh is obtained considering the metallic Zn anode, the cathode, the separator, the aqueous electrolyte and the electricity required for cell assembly. AZIBs are environmentally competitive with lithium-ion, lithium-oxygen, lithium-sulfur, and sodium-ion battery technologies and are attractive from a Circular Economy viewpoint given the potential of renewable materials as separators and the high recycling rates of electrodes. The obtained results prove the suitability of zinc ion batteries as a sustainable stationary energy storage solution.

1. Introduction

Energy storage technologies lie as a societal priority given their pivotal role toward decarbonization by offering a full exploitation of renewable energy sources.[1,2] Electrochemical energy storage (EES) systems can store and deliver on-demand renewable power, smoothing the intermittency associated with wind and solar energy when installed in large renewable-energy plants[3,4] Electric generation systems based on renewable resources present an environmentally and socioeconomically more sustainable alternative to those based on fossil fuels.[5] Ensuring a steady energy supply can accelerate the transition to a lower carbon economy, approaching toward the emission reductions of 30% by 2030 to meet the goals of Paris Agreement.

Thanks to their high energy density and long cycling stability,[6] lithium ion batteries (LIBs) are dominant in the portable electronics and electric vehicle (EV) markets. However, the implementation of LIBs as stationary grid storage has been constrained so far due to the fact that LIBs present several sustainability issues. The use of large quantities of scarce and toxic cathode materials (lithium, cobalt, or nickel) inevitably increases their environmental burdens.[7] Environmentally speaking, sodium ion batteries (NIBs) are emerging as a potential alternative to LIBs given the natural availability of sodium.[8] NIBs are cost-effective, offer acceptable energy densities and enable the use of bio-derived electrodes,[9–11] so they have a prominent position to next-generation batteries replacing LIBs. As for LIBs, a completely inert, oxygen...
and moisture-free atmosphere is needed for NIB assembly, typically ensured using a glove-box filled with argon for a lab-scale production or a dry room for larger production (dry room consumes up to 29.4% of total energy needed for a 32-Ah lithium manganese oxide/graphite cell production). LIBs and NIBs are characterized by the use of organic electrolytes, which seriously threatens battery safety and human and environmental health. A possible choice to reduce the environmental impact of traditional batteries bearing organic solvents is the use of highly concentrated “water-in-salt” electrolytes, where the salt-water ratio is above one. The water-in-salt configuration expands the stable operation window of traditional aqueous electrolytes, enabling their implementation into high-voltage configurations such as LIBs and NIBs. However, further sustainable battery technologies are required to meet the increasing demand of green energy storage solutions.

Aqueous rechargeable batteries (ARB) are gaining widespread attention due to their low cost, safety and potential environmental sustainability in comparison with other technologies based on organic electrolytes. Interestingly, aqueous electrolytes display ionic conductivities up to 1 S cm \(^{-1}\) in contrast with the 1–10 mS cm \(^{-1}\) shown by non-aqueous organic-based electrolytes, affording rapid (dis)charge rates. Among the different water-compatible electrochemical energy storage systems, aqueous zinc ion batteries (AZIBs) surpass other emerging technologies in terms of delivered energy densities. Contrarily to alkali-based zinc (Zn) batteries, aqueous electrolytes enable the use of Zn metal as the anode, resulting in batteries with energy densities up to 361 Wh kg \(^{-1}\) (as opposed to the classical 150–250 Wh kg \(^{-1}\) for LIBs) thanks to the theoretical capacity of 820 mAh g \(^{-1}\) (or 5855 mAh cm \(^{-3}\) provided by the Zn metal). Moreover, Zn is more abundant than Li in the earth’s crust; it is relatively harmless in comparison to other metal ions with similar chemical properties and its divalent character involves a two-electron transfer during the electrochemical process, leading to large storage capacities.

AZIBs are a perfect match for grid applications where weight is not a constraint, providing safe, low cost and non-flammable energy storage solutions. As opposed to Li\(^{+}\) or Na\(^{+}\), Zn\(^{2+}\) intercalation into classical cathodes suffer from sluggish kinetics, limiting the practical implementation of AZIBs. In this sense, several approaches are under study at the laboratory scale, including the development of cathodes offering facilitated Zn\(^{2+}\) reaction kinetics to enhance delivered capacities.

A priori, AZIBs should present lower environmental impacts than other intercalation battery chemistries such as LIBs or NIBs due to the fact that they could be assembled under ambient conditions (no need of inert, oxygen and moisture-free atmospheres) and rely on aqueous electrolytes. Although further technological advances are required for full industrial implementation of ZIBs, the future research should be accompanied by environmental impact assessment data to provide meaningful design strategies for the development of truly sustainable ZIBs. However, to the best of our knowledge, no works have been devoted to quantify the potential environmental benefits originating from aqueous zinc ion batteries. In this context, life cycle assessment (LCA) methodology provides a mean to quantify the environmental burdens of batteries, including raw material extraction, component processing and battery assembly. Highlighting and quantifying the environmental hotspots arising from the fabrication of AZIBs can help transitioning toward “Responsible production and consumption” (Sustainable Development Goal 12) patterns through the design of environmentally sustainable batteries. Given the well-established methodology of LCA, obtained results could support further follow-up works and would enable a comparison of this technology with mature batteries such as LIBs or more recent chemistries including NIBs or emerging battery chemistries lithium-sulfur or lithium-oxygen. The information provided by LCA can be used as a guide to design batteries that depend less on durable and toxic materials, and thus reducing their negative impact on aqueous and land environments (Sustainable Development Goals 14 and 15, “Life below water” and “Life on land”, respectively).

Here we study the cradle-to-gate environmental impacts associated to six laboratory-scale AZIBs bearing different types of cathodes facing the sluggish intercalation kinetics of Zn\(^{2+}\) into traditional inorganic hosts. Those batteries comprise cathode materials of different nature ranging from oxides to polyanionic frameworks, Prussian blue analogs, layered sulfides and organic hosts. The results here reported link laboratory-scale studies with their environmental assessment, providing a bigger picture on how the environmental impact of batteries could be mitigated.

2. Methods

2.1. Goal, Scope, and System Boundary

Here we analyze and compare the environmental impacts of six laboratory-scale aqueous zinc ion batteries using the life cycle assessment (LCA) methodology. As laboratory-scale LCA has been demonstrated an effective environmental advisory tool for emerging technologies, we aim to provide valuable information to guide future research on sustainable zinc ion batteries. LCA has been selected to evaluate the environmental impacts of batteries during their fabrication due to its successful application in related energy storage systems such as those comprising LIBs, NIBs, lithium-oxygen or lithium–sulfur batteries. The six batteries here analyzed have been selected as they serve as representative examples of the potential of oxides, polyanionic frameworks, Prussian blue analogs, layered sulfides and organic hosts, all of them specially designed to solve the sluggish Zn\(^{2+}\) insertion into traditional cathodes. Facilitating this Zn\(^{2+}\) insertion is a prime requisite to obtain zinc ion batteries with superior energy-density and long operation life spans. Environmental impacts are determined with a cradle-to-gate boundary to focus on the battery production. To that end, raw material acquisition, the synthesis or each battery component individually and their final assembly into a cell is considered.

Obtained environmental impacts are divided into eighteen impact indicator categories within the ReCiPe 2016 Midpoint method (impact indicators, from now on). These impact indicators are categorized as: fine particulate matter formation, fossil resource scarcity, freshwater ecotoxicity, freshwater eutrophication, global warming, human carcinogenic toxicity, etc.
human non-carcinogenic toxicity, ionizing radiation, land use, marine ecotoxicity, marine eutrophication, mineral resource scarcity, ozone formation (human health), ozone formation (terrestrial ecosystems), stratospheric ozone depletion, terrestrial acidification, terrestrial ecotoxicity and water consumption. The 18 impact indicators show the advantage of providing results with lower uncertainty level in comparison with endpoint indicators, which are focused to the environmental impacts at the end of the cause-effect chain (damage to human health, damage to ecosystems or damage to resource availability, for instance). To enable a cross-field comparison with further electrochemical energy storage systems (batteries and supercapacitors, for instance), an especial attention has been paid to global warming (identified by the software as global warming potential, GWP) measured in kg CO₂ equiv. With this in mind, the scope of this work and the research boundaries are schematically shown in Figure 1.

Ecoinvent 3.7 dataset (released on September 2020) together with OpenLCA software was used. As the main objective of the work is to focus on battery fabrication step, the environmental impacts of batteries are analyzed into a cradle-to-gate perspective. The scarce data regarding the end-of-life of AZIBs and its early-stage (non-mature) technology characteristics limits performing LCA studies within a cradle-to-crade perspective. Therefore, the impact indicators have not been considered. However, this should be a priority toward the full understanding of impacts arising from zinc ion batteries. 1 kWh (one kilowatt-hour) of storage capacity was used as a functional unit (FU), which is a common practice regarding LCA studies applied into battery field.[30,40,41] This standardization enables a simple yet accurate comparison with other energy storage technologies. Moreover, 1 kWh is a commonly used billing unit for consumer energy delivered by electric utilities; thus allowing an additional comparison with grid energy.

2.2. Reasons behind Each Battery Selection

Similar to lithium-ion and sodium-ion batteries, the configuration of AZIBs consist of a metallic anode, a porous membrane acting as a separator soaked into an aqueous electrolyte and a cathode.[37] Based on this common design, different cathode chemistries and structures have been proposed to facilitate the intercalation of divalent Zn²⁺. In this sense, we base our studies on six different cathode designs successfully tackling the poor Zn²⁺ insertion/extraction kinetics in traditional cathodes, so enhanced performances in terms of delivered capacity, energy density and lifespan are achieved.

MnO₂ has been explored as a cathode candidate for full-cell ZIBs after the application of MnO₂ in alkaline electrolytes to develop primary Zn batteries.[17] However, bare MnO₂ suffers a notable structural transformations upon cycling, it presents a poor electronic conductivity and suffers a significant capacity fade due to Mn²⁺ dissolution into the electrolyte,[37] so a polyaniline-reinforced layered structure combined with 10 nm-sized MnO₂ cathode (phase changes are avoided and charge storage is facilitated) is selected as a representative example solving these drawbacks (delivered capacity: 125 mAh g⁻¹ for 5000 cycles at 2 A g⁻¹).[42] The fabrication of this battery results in a GWP value of 3817 kg CO₂ equiv kWh⁻¹ due to the large use of tetra-chloromethane (450 mL solvent for 9 mL of aniline). As those results can be optimized by an improved design on reacting media, we estimate they do not provide a representative mean for comparison, so the impacts arising from this MnO₂ cathode are not further commented in detail.

Accordingly, we focused our first attempt into a cobalt-based oxide as they generally enable large discharge capacities.[37] Specifically, an increased performance promoted through Zn²⁺ intercalation was achieved, where a Co(III) rich-Co₉O₄ cathode showed a specific capacity of 205 mAh g⁻¹ at 0.5 A g⁻¹ with a 92% capacity retention after 5000 cycles (battery 1, denoted as “Co(III) Rich-Co₉O₄”).[19] The aqueous electrolyte was based on 2 m ZnSO₄ with the 0.2 m CoSO₄ additive to suppress Co²⁺ dissolution during discharge and thus, enhance the cycle life. Interestingly, a specific energy of 361 Wh kg⁻¹ at a current density of 0.5 A g⁻¹ was obtained as a result of the increased cell potential up to 2.2 V, although the extensive use of Co element may a priori limit the implementation of this battery into grid storage applications. Another relevant group of intercalation oxides used in AZIBs is those based of vanadium (XV₂O₇, where X = Zn, Mg, Ca, Na…). Kundu et al. reported a vanadium oxide bronze pillared by interlayer Zn²⁺ ions and water (Zn₃V₂O₅·nH₂O nanobelts) as a cathode material to reach a reversible Zn²⁺ ion (de)intercalation storage process thanks to the large interlayer space and open tunnels for divalent Zn²⁺ intercalation (battery 2, denoted as “V₂O₅-bronze”).[43] As a result, a capacity of 300 mAh g⁻¹ at 0.3 A g⁻¹ with a specific energy of 250 Wh kg⁻¹ (volumetric energy density 450 Wh L⁻¹) and capacity retention of more than 80% over 1000 cycles was reached. Importantly, no dendrite formation was observed at the Zn electrode, making this battery ideal for long-life applications.

Not only intercalation oxides but other types of materials have also shown promising results as AZIB cathodes, where polyanionic frameworks emerge as a potential candidates. A graphene-like carbon wrapped Na₃V₂(PO₄)₃ material was applied as an intercalation host into a AZIB to obtain a capacity of 97 mAh g⁻¹ at 50 mAh g⁻¹ and capacity retention of 74% after 100 cycles (battery 3, denoted as “Nasicon – Na₃V₂(PO₄)₃”).[44]
Additionally, thanks to their tunnel structure, Prussian blue analogs (PBAs) have been extensively researched to obtain cathode materials with rapid ion migration and good mechanical stability during cycling, which is translated into good capacity retention after hundreds of cycles. In spite of their generally initially lower capacity, Hou et al. managed to obtain specific capacities of 140 mAh g\(^{-1}\) at 80 mA g\(^{-1}\) with an energy density of 170 Wh kg\(^{-1}\) and a capacity retention of 75% after 2000 cycles at 0.8 A g\(^{-1}\) using a Na\(_2\)Mn-Fe(CN)\(_6\) nanocube cathode (battery 4, denoted as “Na\(_2\)MnFe(CN)\(_6\)”).\([45]\) Layered sulfides represent another family of potential AZIB high-performance cathode materials. In this context, a transition metal layered dichalcogenide, a MoS\(_2\) host cathode with oxygen-incorporated nanosheets (MoS\(_2\)-O) was applied to enhance the interlayer gallery, enhancing Zn\(^{2+}\) diffusivity by three orders of magnitude (battery 5, denoted as “MoS\(_2\)-O”).\([46]\) As a result, a capacity of 232 mAh g\(^{-1}\) at 100 mA g\(^{-1}\) with a 68% capacity retention after 2000 cycles at 1 A g\(^{-1}\) and good rate performance in a mildly acidic aqueous ZnSO\(_4\) electrolyte was obtained.

Finally, organic materials represent a potentially environmentally preferable alternative to inorganic intercalation materials. Moreover, their soft molecular structure facilitates a rapid diffusion of hard divalent cations, which are accommodated with low volume change enabling thus a long-term capacity.\([23]\)

In this context, calix[4]quinone has been applied as a cathode to obtain a Zn\(^{2+}\) storage capacity of 335 mAh g\(^{-1}\) at a small voltage polarization of 70 mV and energy density of 220 Wh kg\(^{-1}\) (battery 6, denoted as “CALIX\(_4\)-C\(_4\)Q”).\([47]\) Combined with a Nafion membrane, which acted as an ion-selective separator to suppress the dissolution of active material, 87% of the initial capacity is retained after 1000 cycles at 500 mA g\(^{-1}\).

### Table 1. Material and energy input inventory for all the studied aqueous zinc ion batteries. Their electrochemical performance is also summarized.

| Aqueous zinc ion batteries | Electrochemical performance |
|---------------------------|-----------------------------|
| Theoretical capacity (mAh g\(^{-1}\)) | 205 | 300 | 194 | 160 | 232 | 335 |
| Current density (mA g\(^{-1}\)) | 50 | 100 | 100 | 100 | 100 | 200 |
| Active mass loading (mg cm\(^{-2}\)) | 1.05 | 5 | 5 | 10 | 7 | 10 |
| Charge potential (V) | 2.2 | 2.4 | 1.4 | 2 | 1 | 1 |
| Energy density (Wh Kg\(^{-1}\)) | 110 | 120 | 140 | 200 | 100 | 200 |

| CATHODE |  |
|---------|---|
| Active material (mg) | Co\(_3\)O\(_4\) nanorods | Vanadium oxide | Nasicon | Na\(_2\)MnFe(CN)\(_6\) | MoS\(_2\) | C\(_4\)Q |
| Binder | Carbon 27% | Carbon 10% | Carbon 10% | Carbon 10% | Carbon 10% | Carbon 35% |
| ANODE (mg) | Zn foil | Zn foil | Zn foil | Zn foil | Zn foil | Zn foil |
| ELECTROLYTE (mg) | 6.32 | 3.10 mg | 1.61 mg | 16.1 mg | 9.15 mg | 16.1 mg | 10.90 mg | 10.90 mg |
| Cobalt sulfate | 3.22 mg | Water | 0.10 mL | Water | 0.10 mL | Water | 0.10 mL |
| Zinc sulfate | 3.10 mg | Water | 0.10 mL | Water | 0.10 mL | Water | 0.10 mL |
| Energy Usage (kWh) | 0.000012 | 0.000012 | 0.000012 | 0.000012 | 0.000012 | 0.000012 |
| SEPARATOR (mg) | Glass fiber | Glass fiber | Glass fiber | Glass fiber | Glass fiber | Nafion |

2.3. Material and Energy Input Inventory

The laboratory-scale production of zinc ion batteries modeled using secondary data from published papers. To enable future comparison, material, water and energy input inventory for the raw material extraction, battery component production (anode, cathode, separator, and electrolyte) and final assembly of the six AZIBs above-mentioned are disclosed in Table 1. This information allows the determination of life cycle inventory (LCI) of the batteries. The material inventory shows all material flows for the production of the battery, while the energy inventory includes the energy consumed during the production process. Further disclosure of the inventory modeling is given in the Supporting Information as Tables S1 to S15 and Figures S1 to S6 (Supporting Information). It should be noticed that the
As shown in Table 1, all six batteries use a metallic Zn foil as an anode material. Between the anode and the cathode, an electrically insulating porous membrane soaked into a Zn$^{2+}$ ion conducting aqueous electrolyte is found. For zinc ion batteries, glass microfiber separator is usually applied under the Whatman trademark. Generally, the liquid electrolyte comprises an inorganic Zn salt dissolved in water, usually zinc sulfate (ZnSO$_4$) at a 2 M concentration. However, other inorganic salts such as zinc acetate Zn(CH$_3$CO$_2$)$_2$ are also found (0.5 M). Interestingly, zinc acetate is a food additive (E650), so its use may result in not-harmful batteries. 3 M zinc trifluoromethanesulfonate Zn(CF$_3$SO$_3$)$_2$ is also used as electrolyte in two of the analyzed batteries, which can cause severe burns and serious damage to eyes. In the electrolytes, other salts are incorporated at lower concentration to enhance the battery performance. For instance, 0.2 M CoSO$_4$ suppresses Co$^{2+}$ dissolution in the presence of a Co$_3$O$_4$ cathode. Its water-based nature is one of the main advantages of AZIBs, contrarily to the toxic organic electrolytes (carbonate-based) usually applied to LIBs or NIBs. Additionally, high ionic conductivities can be obtained using these solvents. The assembly of the anode, cathode, separator and electrolyte into a cell is similar for all the studied AZIBs. Interestingly, as opposed to LIBs or NIBs, no need for a moisture-free inert atmosphere is required for cell assembly, avoiding the consumption of energy and gases such as argon. To facilitate a direct comparison between different battery choices, current collectors and battery management system (BMS) are kept out of the scope of the study (their inclusion may distort our findings). The impacts arising from used metal and chemical factories infrastructure are also included, having as reference a 162 kg LIB where 7.41 × 10$^{-10}$ items of metal factory and 5.45 × 10$^{-10}$ items of chemical factory per kilogram of final battery have been used. This dataset has been used in combination with the regular processes to get the operation plus infrastructure of metal working without the machine processing. When accounting for the electricity consumed during production, specific fabrication processes was estimated (generally involving processes such as freezing, distillation, mixing, centrifugation, heating/calcination or hydraulic press).

3. Results and Discussion

3.1. Global Warming of Aqueous ZIBs

The cradle-to-gate environmental impacts of AZIBs batteries per 1 kWh of storage capacity were firstly evaluated on the bases of the data disclosed in Figure 1, Table 1 and Tables S1–S15 and Figures S1–S6 (Supporting Information). For the sake of simplicity, we firstly focus our analysis on the global warming indicator, which is considered as the most relevant driver to analyze the potential environmental benefits of diverse energy storage technologies. Obtained results are summarized in Figure 2. The impacts range between 22.1 and 95.2 kg CO$_2$ equiv per 1 kWh, with an average value of 45.1 kg CO$_2$ equiv. Those results are in the range of the value recently reported by Santos et al., who found a total impact of 61.2 kg CO$_2$ equiv per 1 kWh of stored energy for a zinc-air battery. Importantly, AZIBs result environmentally competitive with other battery technologies such as Li-O$_2$ batteries (average of 55.8 kg CO$_2$ equiv) and remarkably lower to the 140.3 kg CO$_2$ equiv produced by NIBs, the average of 127.4 kg CO$_2$ equiv for Li-S batteries, and the median of 120.0 kg CO$_2$ equiv for LIBs. As these studies also consider the battery production stage, that is, a cradle-to-gate perspective, the results could be
considered comparable. However, it should be noted that the majority of these studies take into account the battery assembly up to the module or pack level because they are aimed for electric vehicle application, so further packaging and battery management system are also considered. Importantly, Dai et al. recently considered LIB pack upscaling, obtaining a cradle-to-gate global warming of 72.9 kg CO₂ equiv kWh⁻¹ for a LIB pack based on the LiNi₁/₃Mn₁/₃Co₁/₃O₂ cathode (a predominant chemistry when intended for electric vehicles). In this vein, Arvidsson et al. reported a reduction on global warming from 230.0 to 103.5 kg CO₂ equiv kWh⁻¹ upon upscaling Li-S cell production, reflecting the room for improvement of AZIB.

It can be observed that Na₂MnFe(CN)₆ and V₂O₅-bronze are the batteries with the lowest impacts, while the battery denoted as CALIX4-C4Q clearly surpasses all the others. The low CO₂ contribution of Na₂MnFe(CN)₆ and V₂O₅-bronze batteries can be explained by their high operating voltages of 2.4 and 2.0 V, respectively (while Nasicon-Na₃V₂(PO₄)₃, MoS₂-O and CALIX4-C4Q can only reach 1.4, 1.0, and 1.0 V, respectively). As a result, their active mass loading of 5 and 10 mg cm⁻² is effectively translated into large energy densities (120 and 200 Wh kg⁻¹) for Na₂MnFe(CN)₆ and V₂O₅-bronze, reducing the overall impacts. Another reason behind these results may be nature of the separator-electrolyte pair. Given the tendency of AZIBs to form large Zn morphologies causing short circuits across thin separators, these batteries require 200–900 µm thick glass fiber separators instead of the conventional 16–25 µm thick polypropylene or polyethylene separators used in LIBs. However, the CALIX4-C4Q battery uses a Nafion separator instead of the glass fiber separators (to suppress active material dissolution). This sulfonated tetrafluoroethylene (C₂₃H₂₀N₂O₂S) is obtained after the incorporation of perfluorovinyl ether groups having sulfonate groups onto a tetrafluoroethylene backbone. As a result, Nafion fabrication requires perfluorocarbons and fluorocarbons such as tetrafluoroethylene and perfluoro(alkyl vinyl ether) with sulfonyl acid fluoride. As these reagents can persist in the atmosphere for thousands of years, they have an extremely high contribution to the global warming (estimated around 5000 to 10 000 times larger than CO₂). As a result, its use encompasses larger CO₂ emissions in comparison to batteries bearing a glass microfiber separator, increasing the CO₂ equiv per 1 kWh of stored energy of the CALIX4-C4Q battery.

3.2. Global Warming for Each Battery Component

An analysis on how the environmental impacts are distributed for each battery component can provide guidance for future optimization. Figure 3 shows the relative contribution of the anode, the cathode, the separator, the electrolyte, the cell assembly and the electricity required for battery manufacturing to the overall global warming. Generally, the cathode, the separator, the electrolyte, the cell assembly and the electricity required for battery manufacturing are the main drivers, with average values of 37.1%, 22.6%, and 22.4%, respectively. Those results are relatively similar to the recent report on zinc/air batteries by Santos et al., who concluded that the cathode and the separator were the most impactful battery components with a CO₂ contribution of 50% and 38%, respectively. The larger contribution of the cathode (50% vs 37.1%) could be explained by the multistage fabrication process and the use of toxic and energy demanding materials such as nickel or tetrahydrofuran. In our study all the anodes are composed by a metallic zinc foil. However, the lowest contribution of 4.8% for the anode in the CALIX4-C4Q battery is due to the 13 mg cm⁻² loading used in this configuration as opposed to the 20 mg cm⁻² required for all the other batteries. Regarding the cathode, V₂O₅-bronze, CALIX4-C4Q and MoS₂-O batteries are among the options with lower contribution to the global warming (27.9%, 27.1%, and 22.4%, respectively). These results can be explained in terms of their large carbonaceous phase (27%, 35%, and 10% of the cathode, respectively) that avoids the need of energy consuming processes. In fact, Arvidsson and Sandén suggested that carbon nanomaterials could replace specific components of conventional rechargeable batteries (electrodes) with lower environmental impacts. On the other side, the multi-stage synthesis involving co-precipitation and aging of the Na₂MnFe(CN)₆ cathode contributes by 60.8% to the overall global warming. Similarly, a long hydrothermal route (180 °C, 48 h), 90 min

![Figure 3](https://www.advancedsciencenews.com/article-figures/2100308_Fig3.jpg)  
Figure 3. Relative contribution of each battery component to the global warming.
ultrasonication and inert-atmosphere post calcination at 350 °C for 5 h followed by a final sintering at 750 °C for 8 h is needed for the Nasicon-Na3V2(PO4)3, cathode, contributing by 53.3% to the overall global warming. These results highlight the relevance of Green Chemistry principles and Circular Economy concepts such as atom economy, energy efficiency, material toxicity, process simplicity, or recyclability to obtain battery cathodes with reduced impacts.

The separator is another environmental hotspot, especially considering its low contribution (<5%) in lithium-based battery chemistries. These results arise from the tendency of ZIBs to form dendritic structures, which require mechanically robust separators based on glass microfiber. As opposed to conventional polyolefin-based separators, glass fiber production requires large cumulative energy use (up to 1400 MJ kg−1) and generates considerable CO2, NOx or SOx emissions (73.1 kg kg−1, 513 and 289 g kg−1, respectively). In line with the results shown in Figure 3, particularly striking is the 55.0% contribution of the Nafton-based separator membrane to the CALIX4-C4Q battery. A possible choice to lessen the impacts in the separator category could be the implementation of biopolymer-based hydrogels, which are based on natural resources.

On average, the electricity solely contributes by 8.3%, in contrast with the results found by Dai et al. who determined the electricity consumption as a main contributor when considering a LIB having a LiNi1/3Mn1/3Co1/3O2 cathode. Similarly, our group has recently estimated that the electricity accounts for nearly 17% and 20–25% when considering the global warming of Li-O2 and Li–S batteries, respectively. This reduced impact is obtained thanks to the Nasicon-Na3V2(PO4)3, cathode, contributing by 53.3% to the overall global warming. These results highlight the relevance of reducing the impacts related to energy consumption, as potential solutions to industrial processes may include reducing the energy consumption or switching to renewable energy sources.

3.3. Environmental Impacts Categorized into 18 Indicators

The cradle-to-gate environmental impacts in 18 of the indicators provided by ReCiPe 2016 are summarized in Figure 4. The differences reach a factor exceeding 20 depending on the impact category. As a general trend, the lowest impacts are observed for the Na3MnFe(CN)6 battery, while the Co(III) Rich-Co3O4, MoS2-O and CALIX4-C4Q bear the larger impacts. Especially relevant are the water consumption, terrestrial ecotoxicity, marine eutrophication and land use of the Co(III) Rich-Co3O4 configuration. Those results are explained by the cathode design, which requires large amounts of cobalt, a critical raw material with serious supply chain risks (see European Commission report on critical raw materials 2020) and marked toxicity issues. Moreover, the synthetic process is assisted by the corrosive and toxic ammonium fluoride and the harmful urea. It is also observed that MoS2-O contributes largely to water consumption, terrestrial ecotoxicity, marine eutrophication and freshwater ecotoxicity. The thiourea used during the synthesis of the cathode is considered a carcinogen that needs to be handled with caution, while the ammonium molybdate tetrahydrate ([NH4]6Mo7O24·4H2O) causes serious eye irritation and respiratory irritation if inhaled and is harmful in contact with skin. As nanoparticles, synthesized MoS2 cathode could also create undesired toxicological effects when exposed to aquatic environments. The CALIX4-C4Q battery also encompasses considerable impacts in the categories of stratospheric ozone depletion, marine eutrophication and global warming (already commented). The fluorocarbons used to manufacture the Nafton separator play a dominant role, as they can markedly enlarge the ozone depletion. The polytetrafluoroethylene binder contributes to the categories of water consumption, terrestrial ecotoxicity, human non-carcinogenic toxicity and fine particulate matter formation. Generally, it should be taken into account that the impacts related to energy consumption could be potentially reduced if an up-scaled industrial process is considered. For example, Li–S battery cell production electricity requirement is projected to be reduced by 77% from pilot-scale facility to future industrial-scale.

The “mineral resource scarcity” impact category deserves a special mention as it relates to the use of key raw materials considered one of the bottlenecks in the battery industry. According to the Committee for Mineral Reserves International Reporting Standards, mineral resource is defined as “a concentration or occurrence of solid material of economic interest in or on the Earth’s crust in such form, grade or quality, and quantity that there are reasonable prospects for eventual economic extraction. The location, quantity, grade or quality, continuity, and other geological characteristics of a mineral resource are known, estimated, or interpreted from specific geological evidence and knowledge, including sampling.” The abundant organic fraction in the CALIX4-C4Q battery and the large abundance of cathode components in the Na3MnFe(CN)6 (NaCl represents ~96% of the reagents for cathode manufacturing) yield mineral resource scarcity values of nearly 0.53 and 0.44 × kg Cu equiv, respectively. On the contrary, Co(III) Rich-Co3O4 largely relies on key raw materials (Mn, Co) whose demand is expected to grow by more than 100% by 2050 under a 2 °C scenario compared to a business as usual scenario, which yields a value of 3.3 × kg Cu equiv.

3.4. Future Improvement Measures

Environmentally speaking, the use of aqueous electrolytes together with the possibility of ambient-atmosphere battery assembly is the most remarkable unparalleled advantage of AZIBs. This is in sharp contrast with both the toxic and non-degradable organic electrolytes used in most of the battery technologies. However, AZIBs also present relevant disadvantages that need to be solved in the near future. One of the most striking drawbacks is the lower volumetric energy density...
of AZIBs in comparison with other battery technologies such as lithium-oxygen or lithium-sulfur, which yields larger (in size) battery cells for a given storage capacity and increases the amount of raw materials required for packing. This matter encompasses increased environmental impacts associated with the extraction and processing of raw materials. In Figure 5 we envision possible alternatives toward the development of sustainable zinc ion batteries. One possible strategy to achieve zinc ion batteries with reduced environmental impacts is the development of cathode materials able to operate at higher voltages (∼1.3 V for MnO₂, ∼0.7 V for MXnVoₘ, ∼1.7 V for PBAs, ∼1.1 V for organics), reducing the overall battery volume.[66] Another approach to reduce battery size is the increase of cathode mass-loadings up to 10 mg cm⁻² as opposed to from the common 2 to 3 mg cm⁻², affording larger energy densities.[67] However, the limited Zn²⁺ ion diffusion and poor electrical conductivity at high mass loadings should be solved for practical implementation. Additionally, the use of additives or electrostatic filters that can inhibit cathode dissolution should be also pursued in order to avoid the quick capacity fade suffered by AZIBs and enhance battery lifespan, a prime requisite toward sustainability.[32] The dissolution of organic materials, especially pronounced in the case of organic-based cathodes,[47] could be avoided using environmentally preferred options based on renewable materials such as cellulose nanocrystals (CNCs).[23]
Figure 5. Scheme showing possible future improvement steps toward AZIBs with reduced environmental impacts.

One of the main challenges facing ZIBs toward commercialization is their rapid capacity fade. Several efforts are being made to obtain batteries offering long operation life spans, which would display reduced environmental cradle-to-grave impacts considering their use phase (kWh of lifetime energy throughput as a Functional Unit). For example, a K_{0.86}V_{0.5} cathode (interlayer space of 0.95 nm) was designed to obtain a mechanically bendable battery (energy density of 268.2 Wh kg^{-1}) able to offer a capacity retention of ≈97% after 2800 cycles. A Bi_{2}S_{2} cathode having weak van der Waals interactions between layers offers an improved cyclic stability and fast diffusion of Zn^{2+}, achieving a cyclic performance of 80.3% over 2000 cycles at 1 A g^{-1}. Metal-organic frameworks could be applied to obtain a ZIB with a 92% capacity retention after 900 cycles at 1000 mA g^{-1}. Not only inorganic cathodes but also organic materials can be used to obtain long-lasting batteries. For instance, Glatz et al. developed a novel organic cathode (1,4 bis(diphenylamino)benzene) paired with a cellulose membrane to obtain a 75% capacity retention after 1000 cycles at 6C rate.

Designing AZIBs within a Circular Economy perspective could also improve their environmental performance. Two main strategies may be envisaged. The first one deals with the use of electrolytes/separators (relative average contribution to the global warming of 22.7%) based on renewable-materials rather than the common petroleum-based separators. In this context, polysaccharides and their derivatives result good candidates as their hydrophilic character enables the development of hydrogels (3D cross-linked porous networks having large water contents). Importantly, hydrogel electrolytes combine adequate mechanical properties and good electrochemical performance, so their implementation can lower environmental impacts as they can be synthesized via simple and environmentally-benign physical cross-linking processes (reducing abiotic raw material depletion arising from conventional separators). offer extended operating lifespans (promoting the reuse strategy), and enable the application of renewable materials from plants, animals and micro-organisms (promoting bioeconomy concepts). It is worthy to note that biomass-derived carbons can also be used as cathodes for intercalation batteries.

The second strategy should be focused toward improving the recycling and recovery of raw materials from used AZIBs. Within a Circular Economy approach, closing the loop through recycling avoids the generation of undesired waste streams and reduces the need for the extraction of primary raw materials. Environmentally speaking, recycling may be advantageous in the cases where the new environmental impacts during the recycling can be outweighed by the corresponding environmental credits from the recovered materials. Recycling enables a second life of the battery, resulting in an amortization of the emissions resulting from the manufacture of the cell and optimizing the use of resources. For example, Mayordomo et al. recently showed that the fabrication of a second life LIB can achieve a reduction of 75% in CO_{2} emissions in comparison with the new battery. However, as battery recycling involves a series of chemical and physical processes, their energy consumption and emissions generated (CO_{2} and others) need to be disclosed. Rajaeifar recently showed that depending on the NMC111 lithium-ion battery recycling process (involving pyrometallurgy and/or hydrometallurgy), GWP changes by a factor of 5 could be obtained.

In spite of these studies on LIBs, the recycling technology ZIBs is still in its infancy. However, there are some studies that provide promising results in this direction. In contrast with the LIB technology, metallic zinc recovery efficiencies >99% can be recovered from used batteries by methods such as evaporation and separation with controlled oxidation, and the recovered material can be recycled indefinitely with no changes in its physical properties. Although separators based on glass fiber and Nafion are difficult to recycle and dispose (those used in analyzed batteries), the biocompatibility of biopolymer electrolytes enable environmentally friendly end-of-life approaches. Similarly, many cathodes used in AZIBs (manganese oxides, for example) can also be recycled by thermal treatment at 900 °C, which economically feasible. Binders such as SBR or PVDF are difficult to recover, and their presence often makes difficult the recovery of cathode materials. Moreover, their degradation yields harmful halogenated compounds that should be treated to avoid their release to the air or water. Additionally, the salts used in AZIBs such as ZnSO_{4} can be separated and recycled through membrane distillation integrated with crystallization. Those advantages highlight the need of LCA implementation to quantify the environmental impacts of diverse battery recycling approaches as the environmental burdens originating from these procedures remain undisclosed. Moreover, all hydrometallurgical, pyrometallurgical and direct recycling seem to have environmental pros and cons, so selecting the appropriate procedure seems a complex task.

4. Conclusions

This work shows a cradle-to-gate life cycle assessment on the environmental impacts of aqueous zinc ion batteries. Six laboratory-scale batteries with facilitated Zn^{2+} intercalation
are selected so enhanced performances in terms of delivered capacity, energy density and lifespan are achieved, providing valuable information to guide future research on sustainable zinc ion batteries. Life cycle inventories depicting energy and material inputs required for the raw material extraction, component fabrication and cell assembly are disclosed to facilitate future follow-up works. Environmental impacts are classified into 18 standardized ReCiPe 2016 midpoint impact indicators, allowing their study by categories such as freshwater ecotoxicity, global warming, human toxicity (carcinogenic and non-carcinogenic), marine eutrophication, stratospheric ozone depletion or water consumption. Global warming values in the range of 22.1–95.2 kg CO₂ equiv per 1 kWh of storage capacity are achieved, representing improved values over lithium-based batteries. Those impacts remain below the median 120, 140.3, and 127.4 kg CO₂ equiv 1 kWh of storage capacity reported for LIBs, NIBs or Li-S batteries, respectively. Overall, batteries based on V₂O₅-bronze and Na₂MnFe(CN)₆ cathodes show an improved environmental performance over the CALIX₄-C₄Q cathode, with a four-fold reduction in the global warming. With average contributions of 37.1% and 21.2%, the cathode and the anode are the main contributors, respectively. A relative average contribution of 22.6% is obtained for the separator, revealing the importance of the glass microfiber. In this sense, particularly striking is the 55.0% contribution of the Nafion separator membrane to the CALIX₄-C₄Q battery.

Although this work represents a first effort to quantify the environmental impacts of zinc-ion batteries, consolidated LCA results may be useful to guide the path from laboratory-scale research to practical implementation of ZIBs. Results here shown emphasize the environmental suitability of ZIBs, providing cues for the future ecosdesign of green stationary energy storage technologies. As zinc ion batteries fulfill Circular Economy concepts related to material toxicity (aqueous electrolytes) and process simplicity, low environmental impacts are obtained. Importantly, those impacts might become decreased in the near future given the potential for upscaling battery manufacturing, the prospective substitution of petroleum-based separator membranes by biopolymer-hydrogel electrolytes and the recycling of metallic zinc and zinc-based salts.

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.

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Research data are not shared.

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