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<u>Supplementary information</u>

Leading the charge for environmentally sustainable electromobility with nanotechnology

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1. Relation of review framework to other methods and principles

The vast volume of literature focusing on nanomaterials relevant to lithium ion batteries (LIBs) and proton exchange membrane hydrogen fuel cells (PEMFCs) makes comprehensive life cycle assessments (LCAs) on all of these material candidates unrealistic. As the design phase of many products is decisive for their environmental lifecycle performance, integrating lifecycle thinking as early in the design phase as possible is important. In this review, we aim to introduce lifecycle thinking at an even earlier stage of product development. The text below describes how our framework relates to streamlined and full LCAs, the environmentally responsible product (ERP) qualitative matrix, and green chemistry.

Relation to streamlined and full life cycle assessments

The LCA standard defines a complete framework to quantify the environmental impacts associated with the production, use, and end-of-life of a product[1]. Such an approach is particularly relevant to the comparison of different products that deliver similar functions, which can serve to guide both product development and consumer choices. By quantifying multiple types of environmental burdens, such an assessment framework, minimizes the risks of problem shifting (in solving a problem, creating a new one) and unintended consequences.

The lifecycle screening method employed in this literature review is inspired by lifecycle assessment, but does not in itself constitute a full LCA.

Because LCAs strive to exhaustively inventory product systems from cradle to grave and to simultaneously cover a broad range of environmental burdens, such thorough assessments are generally considered to be data intensive, time consuming, and costly. This has raised concern as to the capacity of LCAs to guide the early design phase of products, since little data is typically available at this point and the full assessments of all possible design options would be prohibitively costly.

Such concerns are partly addressed by the iterative nature of the LCA process: it is recommended that LCAs start with a first estimate and progressively refine the assessment in dialogue with stakeholders or reviewers[1]. Several "streamlined LCA" methods have emerged to facilitate the elaboration of this first estimate, notably in the hope that it may provide timely guidance to influence product design. It has been argued that these simplified LCAs can be considered an integral part of the initial definition of the goals and the scope of a full assessment[2].

Strategies for streamlining LCAs include[2]:

1) Partly or fully ignoring upstream or downstream processes

2) Narrowing the range of environmental impacts considered

3) Limiting the constituents studied to those meeting a threshold volume

4) Using surrogate data

5) Mixing qualitative and quantitative data, depending on availability

6) Establishing "showstopper" criteria that render a certain option unacceptable and further analysis irrelevant

The present literature review of potential nanotechnological developments to LIB and PEMFC strives to synthesize what is known concerning the influence of their production, use, and end-of-life within

all spheres of protection. It therefore avoids relying on strategies 1 and 2. This review focuses on the dominant material requirements and energy inputs to nanomaterial synthesis, to the partial exclusion of other requirements (e.g., infrastructure), following strategy 3. The evaluation of the different criteria relies on previous LCA reviews and generic data, following strategy 4. What is more, it regroups quantitative estimates into broad categories, along with more qualitative estimates, in agreement with strategy 5. The present screening does not rely on explicit "showstopper" criteria (strategy 6), but a certain number of thresholds are introduced beyond which a lifecycle parameter is considered problematic (see Section 3).

Beyond these common simplifying assumptions, the current review is distinct from an actual LCA due to its qualitative and semi-quantitative nature. As such, it closely related to the Environmentally Responsible Product (ERP) matrix, a screening tool also based on lifecycle thinking.

Relation to the Environmentally Responsible Product qualitative matrix

The ERP is a screening method that enables a rapid qualitative evaluation of a product's full lifecycle[3]. It is a particularly appropriate framework for producing an overall environmental profile for a broad range of products based on a review of sparse data, as we do in this literature review.

The ERP framework evaluates five broad environmental aspects that affect every stage of the lifecycle: the choice of environmentally responsible materials, the minimization of release of residues (solid, liquid and gaseous), and the reduction in energy use. We developed a framework that reflects the priorities that emerged from the LCA literature on EVs with some elements drawn from the ERP framework.

In the case of *material choice*, the ERP method focused on the avoidance of toxic, radioactive, restricted, scarce and virgin materials[4]. We refined this list of criteria to reflect today's more abundant material LCA data and material hazard documentation. We screened the literature on the *exposure risks and hazards* of LIB and PEMFC materials, the potential *human health* and *ecosystems damages* caused by these materials' production chain, along with use of scarce resources. Together, these cover potential damage per mass of material to the three areas of protection (also called *endpoint indicators*) studied in LCAs[5], yielding an overall picture of the environmental intensity of the different materials.

Rather than focussing solely on *emissions of residues*, our analysis framework can account for all wastes and inefficient use of materials. In other words, in addition to examining waste of material through emissions, we also examined opportunities to fulfil the same function with less material, and the role that nanomaterials can play in this. Similarly, we expressed the *energy use* in terms of energy efficiency: achieving the same functionality with less energy inputs.

The ERP framework divides the lifecycle of products into five stages: *premanufacture*, *manufacture*, *packaging and transport*, *use*, and *end-of-life* (see rows in Supplementary Fig. 1). However, *packaging and transport* does not stand out as particularly relevant in recent LCAs of EVs and their powertrain devices, so this lifecycle stage was not addressed specifically in our framework. Similarly, it is difficult to distinguish between a *premanufacture* and a *manufacture* phase for nanomaterials. We therefore regrouped all three phases as the *production phase*, thereby simplifying the analysis.

For each nanomaterial, we strove to review the literature on its different lifecycle phases (rows) and lifecycle aspects (columns), presenting results in a three-category ranking (red – poor performance, yellow - intermediate, green – general improvement, as further detailed in Section 3. This is analogous to the qualitative approach by Graedel et al.[3], which ranked every parameter from 1 to 4.

	Environmental intensity of materials	Material and weight efficiency			Energy efficiency
	Materials choice	*Residues*			*Energy use*
		Solid	*Liquid*	*Gaseous*	
Premanufacture					
Product manufacture					
Packaging and transport					
Product use					
Refurbishment/ recycling, disposal					

Supplementary Figure 1 Relation between our framework (bold text, outside table) and the Environmentally Responsible Product qualitative matrix (italic text, in table). Coloured text in the first column shows how the lifecycle stages in the ERP correspond to those we consider in the review: red is production phase, dark grey is use phase and blue is end-of-life. Across the top row, the lifecycle sustainability strategies from this review and their corresponding criteria in the Environmentally Responsible Product matrix. Abbreviations: ERP - environmentally responsible product, EOL – end-of-life.

Unlike the ERP framework, we strove throughout this review to distinguish between lifecycle aspects that stem from the intrinsic properties that the nanomaterials confer to the LIB and PEMFCs (e.g., energy density, cycling efficiency, etc.) and those that stem from the production chain (e.g., synthesis material losses, toxic emissions at the mine, etc.)

Relation to green chemistry

To ensure relevance in the daily reality of the chemistry and nanomaterial research communities, we link the various lifecycle aspects of our framework in the twelve principles of green chemistry[6,7] (see Supplementary Fig. 2).
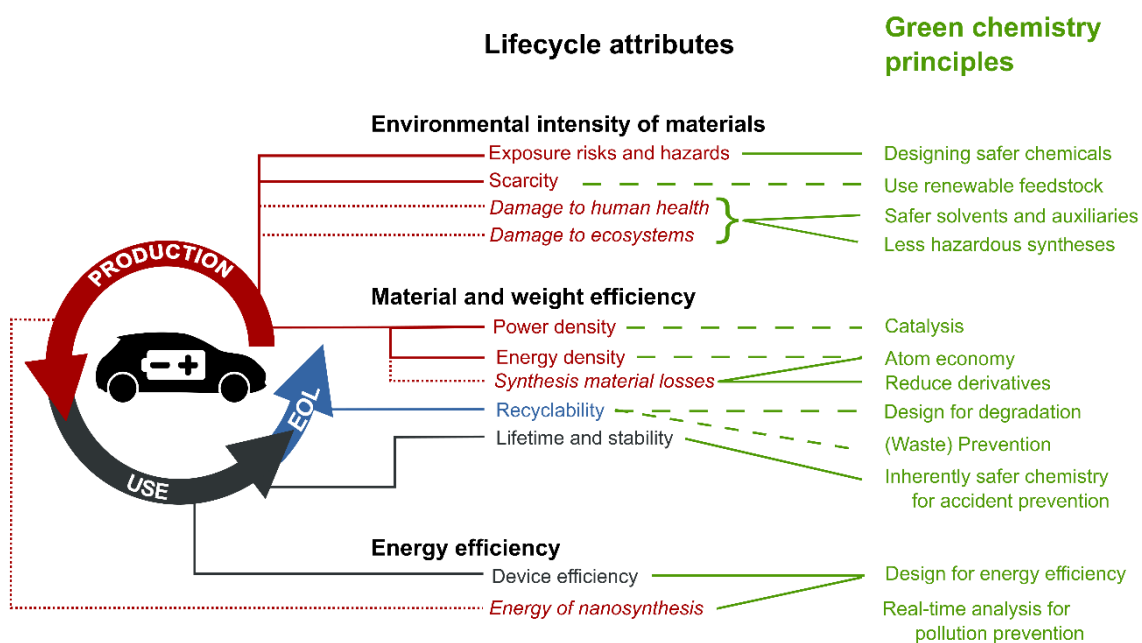
Supplementary Figure 2 Relation of lifecycle attributes to green chemistry principles. Solid green lines denote clear correspondence between our review framework and the green chemistry principles, whereas dashed green lines denote
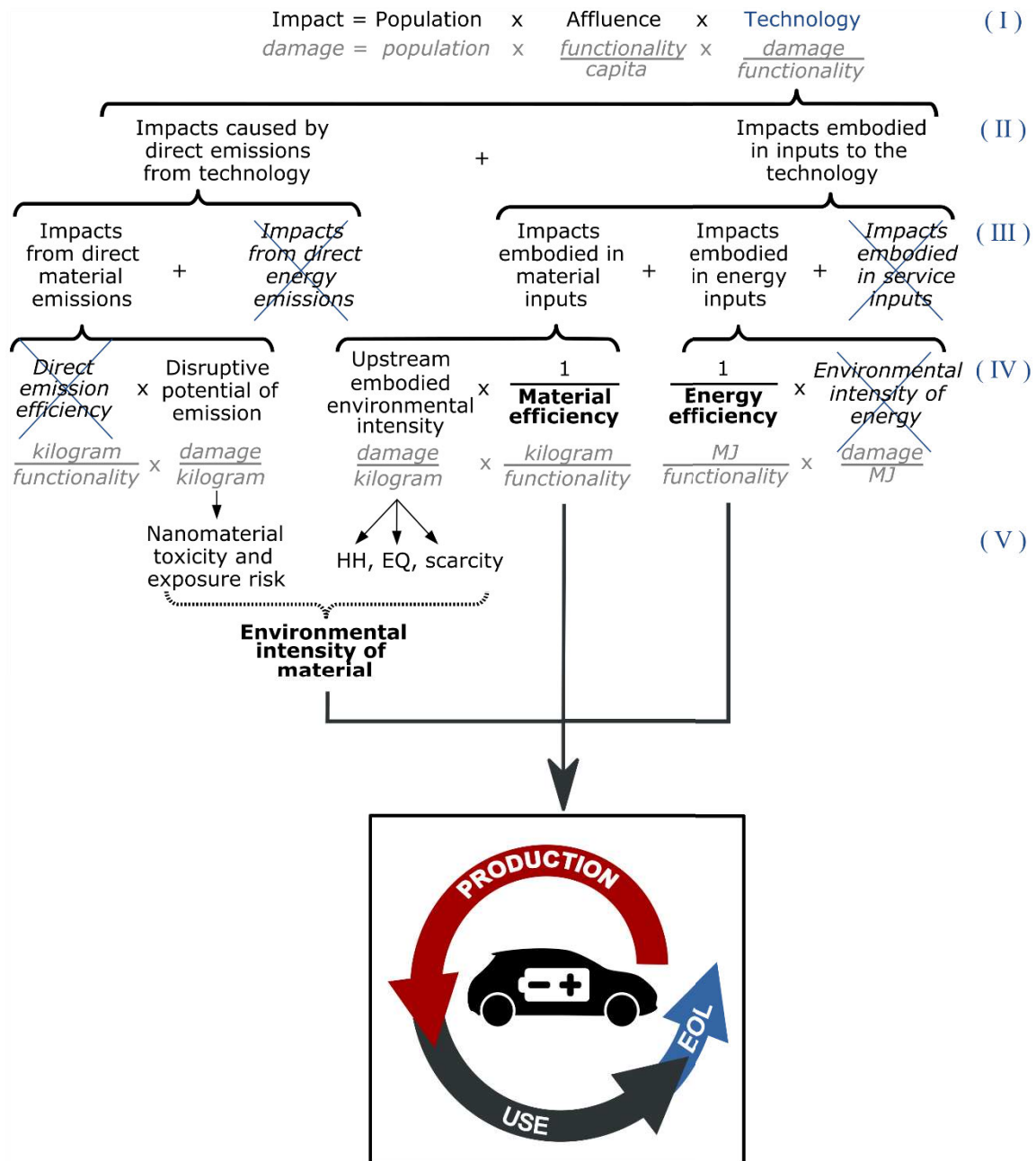
Multiple green chemistry principles are well aligned with the choice and production of materials with a lower environmental intensity. The aim of producing LIBs and PEMFCs that present lower exposure risks and hazards is in agreement with the principle of producing *chemicals that are safer by design*. Our focus on the use of less scarce resources in nanomaterial production is partly mirrored by the green chemistry goal of *using renewable feedstock*, although the use of metals is not in itself problematic if efficient recycling protocols are in place. Additionally, our focus on the human health and ecosystem damages in the materials production chain finds echoes in the search for *less hazardous syntheses* and *safer solvents and auxiliaries*.

A certain number of green chemistry principles also push for greater material efficiency, reinforcing our screening framework. Our review of synthesis material losses finds a direct counterpart in the concept of *atom economy*. By extension, the atom economy can also be understood as the aim of providing the same functionality with less mass, notably through gains in energy density in the case of LIBs. The predominant role of *catalyst development* in green chemistry is also highly relevant to the efforts to increase the power density of PEMFCs. Although none of the twelve green chemistry principles explicitly mention recyclability, the principle of *designing for degradation* and of *waste prevention* show a conscious planning for the end-of-life of the materials. Finally, the crucial question of the expected lifetime and stability of the LIB and PEMFCs finds a green chemistry counterpart with its preference for inherently *safer chemistry for accident prevention*.

Both our framework and the green chemistry principles clearly state the importance of *energy efficiency* for the environment.

2. Scope and resolution of review framework

The present framework strives to offer early insights into the parameters that may determine the environmental profile of nanomaterials in future LIBs and PEMFCs. To this end, the literature review must be guided by a framework that strategically covers the key aspects of these materials' lifecycles. We identify these aspects and justify the scope of our framework in relation to the sequential decomposition of the total impact of a technology (as illustrated in Supplementary Fig. 3).

Impact = Population × Affluence × Technology   (I)

$$damage = population \times \frac{functionality}{capita} \times \frac{damage}{functionality}$$

Impacts caused by direct emissions from technology + Impacts embodied in inputs to the technology   (II)

Impacts from direct material emissions + Impacts from direct energy emissions   Impacts embodied in material inputs + Impacts embodied in energy inputs + Impacts embodied in service inputs   (III)

Direct emission efficiency × Disruptive potential of emission   Upstream embodied environmental intensity × $\frac{1}{Material\ efficiency}$ $\frac{1}{Energy\ efficiency}$ × Environmental intensity of energy   (IV)

$$\frac{kilogram}{functionality} \times \frac{damage}{kilogram} \qquad \frac{damage}{kilogram} \times \frac{kilogram}{functionality} \qquad \frac{MJ}{functionality} \times \frac{damage}{MJ}$$

Nanomaterial toxicity and exposure risk

HH, EQ, scarcity   (V)

Environmental intensity of material

PRODUCTION — USE — EOL

Supplementary Figure 3 Scope and resolution of review framework. Terms in bold are the lifecycle attributes in our framework. Aspects that are crossed out are not considered in our framework. Grey text indicate the units of the terms in the decomposition. Abbreviation: MJ – megajoule, HH – human health, EQ - ecosystem quality, EOL – end-of-life.

Perhaps the most famous and influential decomposition analysis is the so-called IPAT identity, which finds that our total environmental *Impact* can be understood as the product of the world *Population*, its level of *Affluence* (per-capita consumption), and the environmental intensity of the *Technologies* that satisfy this consumption (Supplementary Fig. 3, row I)[8]. The present literature review focuses on technologies that deliver a specific function (see *functional unit* in Box 1 in the main article); more specifically, that store and deliver energy for electromobility.

In analysing the total environmental impacts of a technology, it is often helpful to distinguish between, on the one hand, direct emissions released in the environment by the technology itself and, on the other hand, embodied emissions that occur in the value chains required by the technology (Supplementary Fig. 3, row II).

Pushing the decomposition further, it is common to categorize the inputs to a process, along with their embodied impacts. At a high level of aggregation, we can recognize three broad categories: material inputs (plastic, iron, etc.), energy inputs (electricity, heat), and services (transport services, infrastructure services etc.) (Supplementary Fig. 3, row III). We judged the last category to not be relevant for such early screening analysis, so impacts embodied in services were excluded from our scope, which is common practice, even in full LCAs[9]. Direct emissions can also be split between material releases in the environment and energy releases (waste heat, radiation, etc.), though the latter is not expected to be relevant to nanotechnological development.

It is common practice to decompose an environmental impact as the product between an amount and an environmental intensity[10]. Thus, the impacts embodied in a material input to a technology can be further decomposed as the product of two parameters: the amount of material needed by the technology to offer a functionality (kg of material per functionality) and the embodied environmental intensity of the material (embodied impacts per kg of material) (Supplementary Fig. 3, row IV). This is particularly relevant to nanomaterial synthesis, as nanotechnologies have the potential to change both the material efficiency of LIB and PEMFC, and the types of metals that enter in the production of these devices.

A similar decomposition can be performed for impacts embodied in energy use: it equals the amount of energy required multiplied by the upstream impacts per unit of energy (Supplementary Fig. 3, row IV). However, as most of the nanomaterials reviewed in the literature are not yet industrially produced, the locations of future industrial productions and the environmental intensity of the energy mix in these regions is not yet known. The environmental intensity of energy sources is therefore not relevant for the present analysis, only the amount of energy required (energy efficiency).

In a similar manner, impacts caused by direct emissions can be understood as the product between the amount of emissions and their capacity to cause damage in the environment per mass unit released (Supplementary Fig. 3, row IV). This early literature screening could not estimate direct material emissions during nanosynthesis or the battery use and recycling, so this was also excluded from the analysis.

The embodied environmental intensity is expressed following the three areas of protection, following common "endpoint" practice in LCA: human health, ecosystem quality, and scarcity[5]. As for direct emissions from nanosynthesis and use of nanomaterials, the literature review does not provide enough data to inventory the full range of potential emission types, and we restrict our analysis to the exposure risks and hazards of the nanomaterials themselves (Supplementary Fig. 3, row V). These four indicators for embodied and direct environmental intensities of materials are presented independently in our analysis but are thematically regrouped as describing the "environmental intensity of materials" involved in the lifecycle of nanotechnologies.

Thus, through typical decomposition of impacts and explicit scope restrictions, our analysis comes to articulate its review of nanomaterial around three lifecycle attributes (see rows in Figures 2-5 in main article). We review the literature for indications that nanomaterials might alter the material efficiency and energy efficiency of the manufacture, use, and end-of-life of LIBs and PEMFCs, along with the selection of materials with different lifecycle environmental intensities.

3. Criteria and basis for comparison

This literature review aims to cover a broad range of environmental parameters for a vast choice of potential nanomaterials that are in different stages of development. For many of these materials, the literature focuses much more on their electrochemical performance than on their overall environmental

sustainability. This leads to wild variations in the availability and type of data in the literature, from precise quantitative measurements to qualitative descriptions, and also sometimes absence of data.

To consistently manage this diversity of data, we chose to represent all parameters in a semi-quantitative and a qualitative manner. For each parameter, we regrouped the different materials and processes in three categories (green, yellow and red in the article), ranking them from best to worst. This should allow for a thorough overview of the strengths and weaknesses of the different technologies, current trade-offs, potential hotspots, and avenues for improvements.

Working with a three-category semi-quantitative indicator ('red', 'yellow', and 'green' could equally well have been 1, 2, and 3) has multiple advantages for an early screening method. First, it can serve as a common denominator for combining differing data from a broad range of sources: quantitative measurement, qualitative descriptions, etc. Furthermore, restricting ourselves to three categories better reflects the high level of uncertainty that is associated with early environmental screening of lifecycle attributes of novel nanomaterials. Reporting scores on a finer scale, e.g., from 1 to 10 or even 1 to 100, would give a false sense of quantitative precision for many of the parameters reviewed.

The definition of these colour-coded categories was performed so as to represent the range of values reviewed for each parameter. However, the definition of the boundaries between the categories is necessarily partly subjective. This is an inherent difficulty associated with the definition of any classification scheme. To some extent, the reader must accept that the definition of classification criteria will be necessary until a fully quantitative LCA analysis is performed for all competing potential nanomaterials.

In this section, we strive to present explicit, clear, and reasonable rationale behind the ranking and classification of values for each environmental parameter. For some categories of impacts, we were able to leverage established ranking schemes with a similar level of resolution as our 3-category score (e.g., HMIS ranking). For parameters where quantitative data was consistently available, categories were determined by cluster analysis. For performance data, a commercial baseline was selected relative to which the different nanomaterials were evaluated, green denoting an improvement, yellow a similar performance, and red a deterioration. In other situations, thresholds were established based on the distribution of ranked (semi-quantitative) data, aiming for a balance in the number of materials in the green, yellow and red categories. In other words, if we rank data from best to worst, we defined thresholds to between categories so as to split the distribution in roughly equal parts. Finally, as a last resort, some thresholds were based on expert judgement in a few instances, as will be justified below.

This article's Supplementary citation data offers the interested reader all the necessary data to reorganize our review according to different classification criteria.

Environmental intensity of materials

Exposure risks and hazards

Exposure risks and hazards was assessed for materials using Material Safety Data Sheets (MSDS)[11] with the Hazardous Materials Identification System (HMIS) rating. The HMIS attempts to convey full health warning information to all employees and includes four sections: *Health, Flammability, Physical Hazard, and Personal Protection*[12]. With respect to *exposure risks and hazards,* only the *Health* section was deemed to be relevant. In the latest version of HMIS, there is an asterisk and a numeric health hazard rating. The asterisk signifies chronic health hazard, while the numeric health hazard signifies an acute health hazard. The asterisk health hazard is not always used[12]. Therefore, we use the numerical *Health* ratings, which are explained in Supplementary Table 1.

Supplementary Table 1 The numeric ranking system for the Health *according to the* Hazardous Materials Identification System (HMIS).

Health rating	HMIS health warning
4	Life-threatening, major or permanent damage may result from single or repeated overexposures.
3	Major injury likely unless prompt action is taken and medical treatment is given.
2	Temporary or minor injury may occur.
1	Irritation or minor reversible injury possible.
0	No significant risk to health.

In our review, all materials had *Health* rating below 3. Materials with a *Health* rating lower than 1 are 'green', between 1 and 2 'yellow', and 2 and higher 'red'. Carbonaceous nanostructures used as electrode materials in LIBs and catalyst support in PEMFCs were evaluated in their nanoform. HMIS health ratings were available for all of the LIB anode nanomaterials, except ruthenium oxide nanopowder. HMIS ratings of LIB intercalation cathode materials were only available for LCO and LMO. Ruthenium oxide, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC), and $0.5Li_2MnO_3 \cdot 0.5LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (LMR) have HMIS health rating 2 (red) for bulk materials. We assumed that these materials would pose no less exposure risk in nanoform and therefore also rated the nanomaterials red. For compound materials and alloys where MSDSs were unavailable, constituent compound materials (e.g. sulphur nanoparticles and graphene for sulphur-carbon nanocomposites) or alloying metals (e.g. platinum and iron powders for PtFe) were combined to make a weight percent-based evaluation. We applied a precautionary principle and therefore, if any of the constituent materials received a red on its own, the alloy or compound was rated 'red'. Nanomorphologies were evaluating using MSDS for nanoparticle morphologies of the same material (with the exception of carbon nanostructures); for nanoalloys, the weighted average approach was used with the HMIS scores of the nanoparticle component elements.
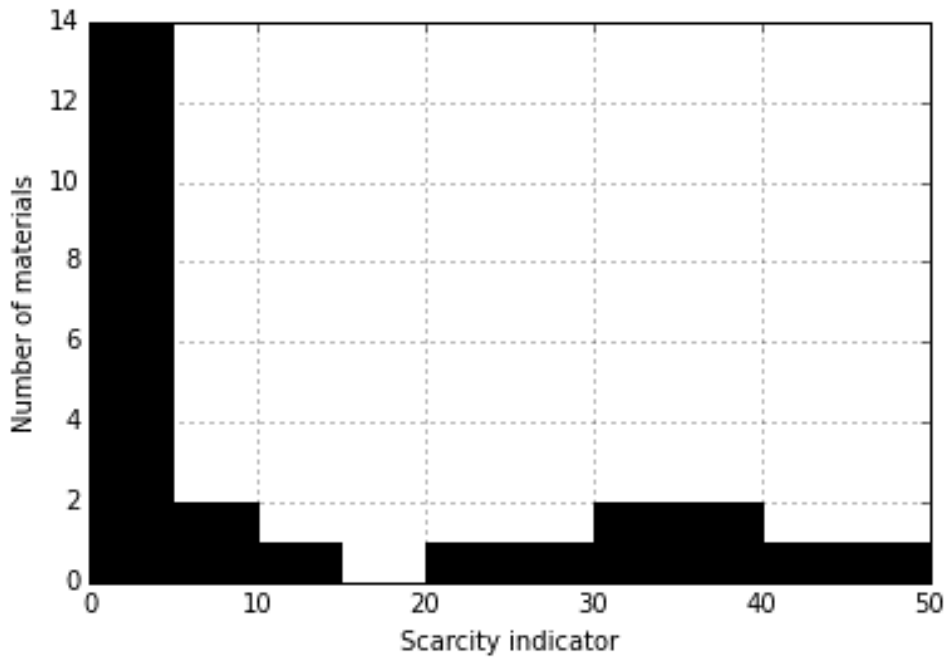
Scarcity

Scarcity was assessed based on the long-term global resource availability of metals reported in the article "Criticality of metals and metalloids" by Graedel et al.[13] This indicator, which ranges between 0 and 100, takes into account the projected ore depletion times and the companion metal fraction in exploited ores. For the different metal alloys and compounds in nanomaterials, a mass-weighted scarcity score was calculated. The different metals and alloys involved in LIBs and PEMFCs were partitioned in the 'green', 'yellow' and 'red' groups by *k*-means clustering. This algorithm divides data into groups such that it minimizes the variance around the means in these groups[14], leading to representative and robust clusters of materials with similar supply risk scores.

Two expert judgement thresholds were nonetheless introduced in the analysis of scarcity. First, the analysis by Graedel et al.[13] does not include non-metals, such as silicon, carbon, and phosphorous. Because of their high abundance in the earth crust and ecosystems, all non-metals, including polymers, were judged to not be scarce and were assigned "green" scores.

Second, some metals that are not expected to represent a supply risk by Graedel et al.[13] are nonetheless extremely rare in the earth crust. We assigned to the "red" group any metal whose mass concentration in the earth crust is inferior to 50 parts per billion, which corresponds to the concentration of the 15 least abundant elements reviewed by Nitta et al.[15]. Our approach may then be seen as a "double bottom-line"; metals are assigned to the red group if they are assigned to this group by the *k*-means algorithm, or if their concentration in the earth crust falls below a threshold, or both. This reflects the

conservative stance in view of the data uncertainty and the conceptual difficulty of defining and anticipating long-term scarcity issues[16,17].

The resulting graphs from the k-means clustering for the evaluated LIB and PEMFC materials are shown in Supplementary Fig. 4 and Supplementary Fig. 5, respectively.

Supplementary Figure 4 Distribution of LIB materials by scarcity indicator score as in Graedel et al.[13].
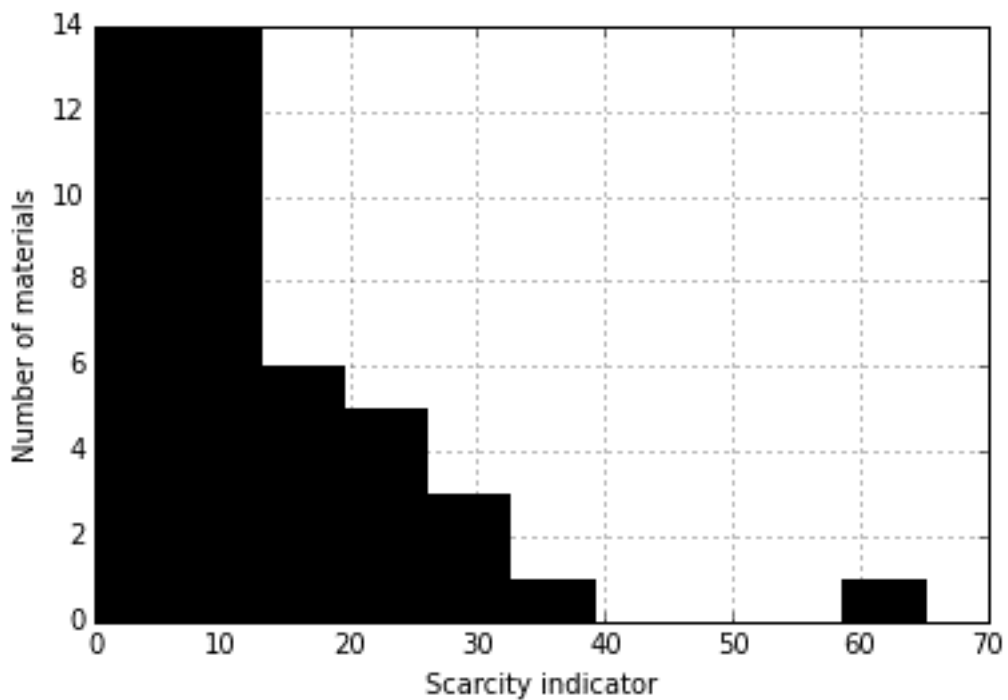
Supplementary Figure 5 Distribution of PEMFC materials by scarcity indicator score as in Graedel et al.[13].
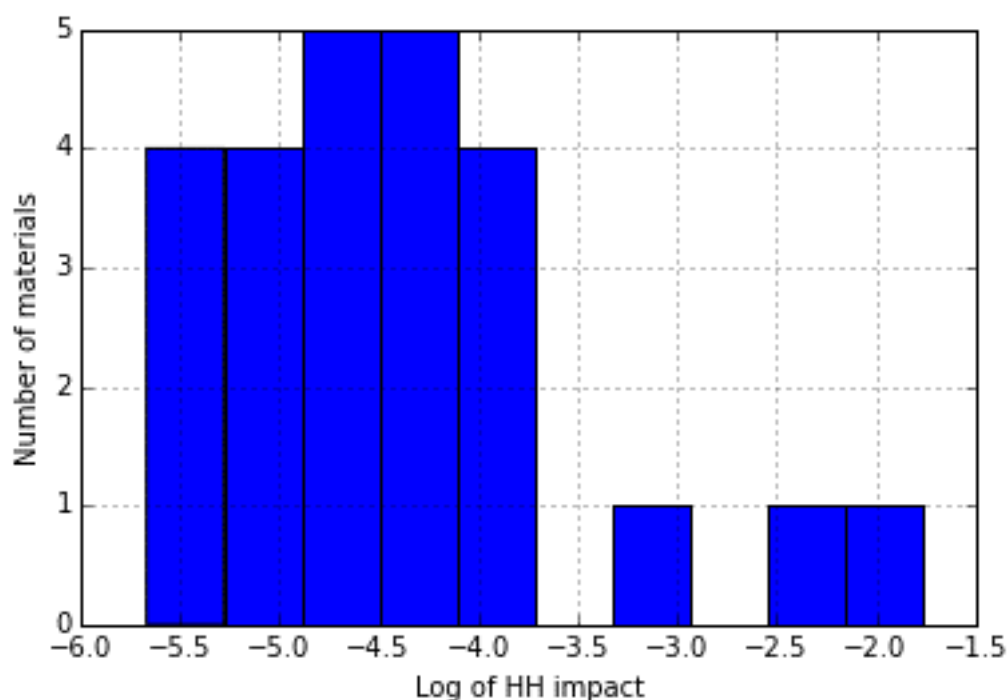
Damage to human health and to ecosystems

Graedel et al.[13] evaluate *damages to human health* and *ecosystems* using *ecoinvent 2.2* and *ReCiPe 1.10* endpoint indicators from a hierarchical perspective for the production process of metals. In this review, we updated the results by using *ecoinvent 3.2* end *ReCiPe 1.11* and included non-metal materials used in LIBs and PEMFCs. For alloys and heterogeneous chemical compounds, the indicators were adjusted to match the stoichiometric composition of the alloy or compound, and presented per kg of alloy/heterogeneous compound.

As few metal oxides are represented in Graedel et al.[13] or in the *ecoinvent* database[18], all metals were compared based on the lifecycle impacts of their reduced form, for greater consistency across nanomaterials. Zirconium constitutes the only exception to this, as damage estimates were only available for the metal oxide.

In a similar manner as for the scarcity indicator, we employed *k*-means clustering to define the red, yellow and green material groups for embodied human health and ecosystem damages. However, the clustering was complicated by the large spread of impacts for the different materials, ranging over five orders of magnitude, from 10^{-6} to 10^{-1} DALY/kg in the case of embodied potential human health for fuel cell materials. This large spread lead to the quasi-totality of metals to be considered 'green', essentially because platinum and ruthenium have such disproportionately large impacts. Regrouping metals whose impacts range over orders of magnitude in the same (green) group would have been counterproductive. To regroup materials whose production impacts have a similar order of magnitude, we applied the *k*-means clustering to the $\log_{10}$ of the impacts. This allowed for the distinction not only of materials with extremely high impacts in the red group, but also materials with extremely low impacts in the green group.

The resulting graphs from the *k*-means clustering to the $\log_{10}$ of damages to human health and ecosystems caused by battery materials are shown in Supplementary Fig. 6 Supplementary Fig. 7, respectively.
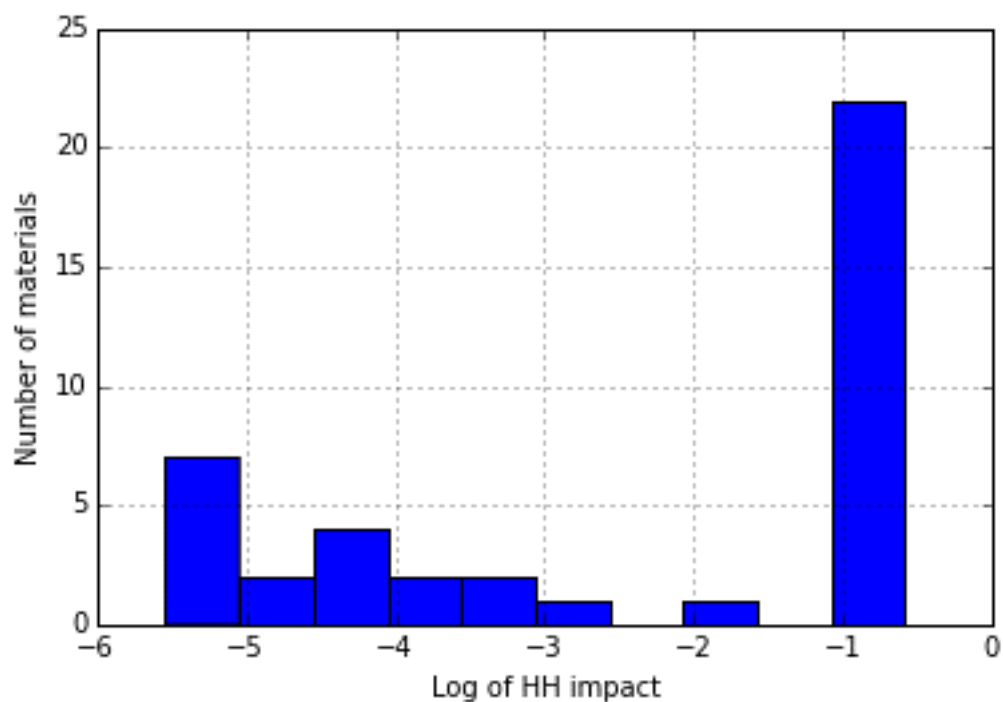

Supplementary Figure 6 Distribution of LIB materials by damages to human health indicator ($\log_{10}$ scale). Abbreviation: HH – human health.
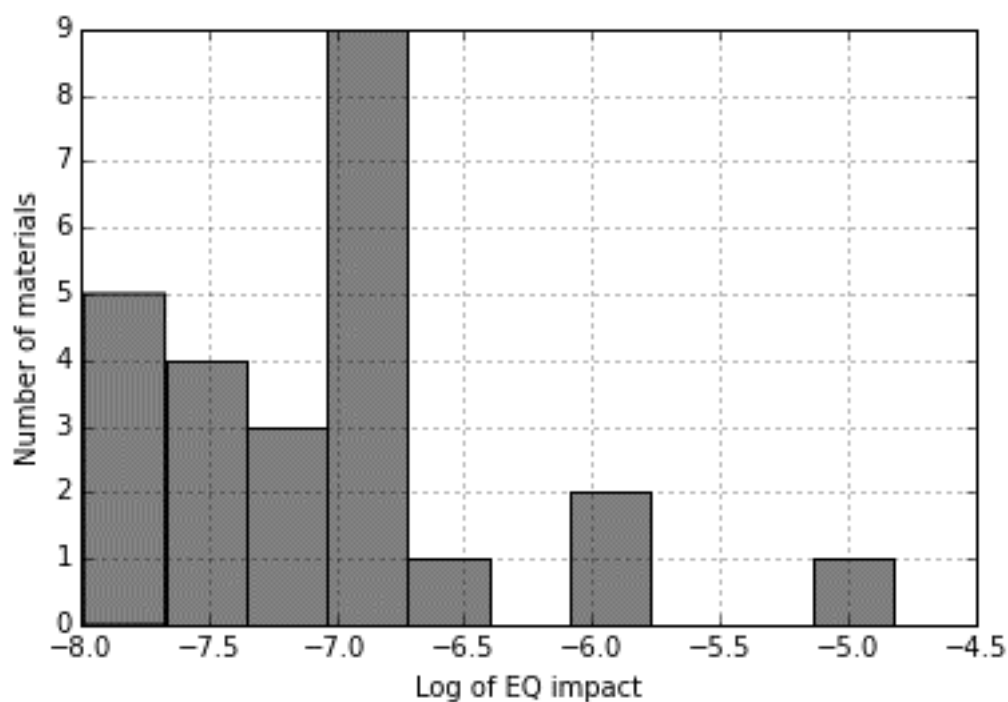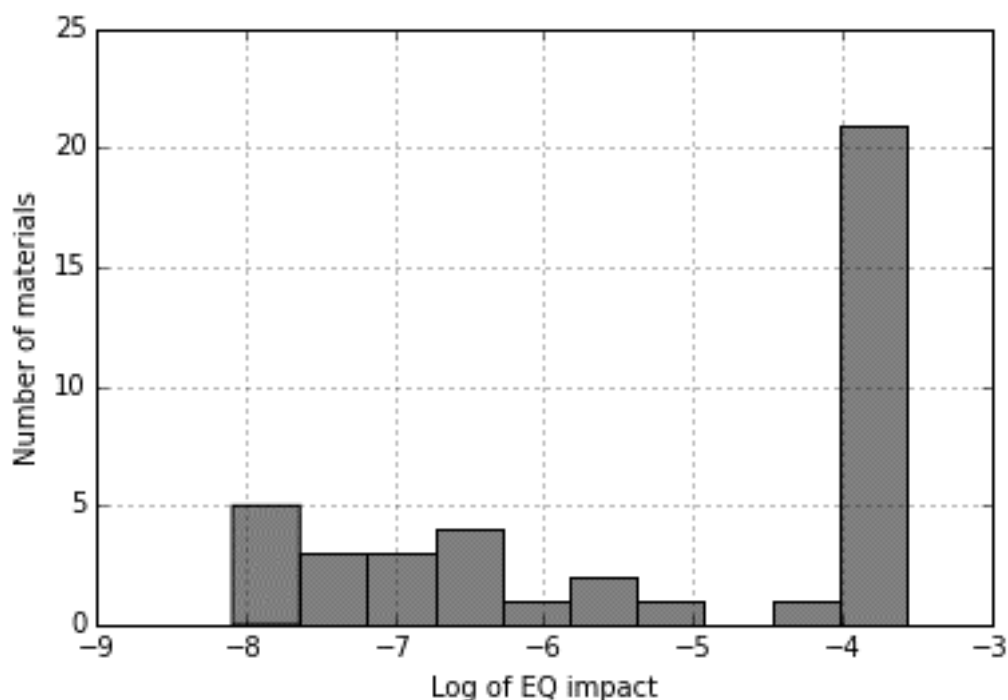
Supplementary Figure 7 Distribution of LIB materials by damages to ecosystem quality (log$_{10}$ scale). *Abbreviation: EQ - ecosystem quality.*

The resulting graphs from the *k*-means clustering to the log$_{10}$ of damages to human health and ecosystems caused by fuel cell materials are shown in Supplementary Fig. 8 and Supplementary Fig. 9, respectively.

Supplementary Figure 8 Distribution of PEMFC materials by damages to human health indicator (log$_{10}$ scale). *Abbreviation: HH – human health.*

Supplementary Figure 9 Distribution of PEMFC materials by damages to ecosystem quality (log$_{10}$ scale). Abbreviation: EQ - ecosystem quality.

Material and weight efficiency

Energy density, power density, and lifetime and stability

To assess *energy density*, *power density*, and *lifetime and stability* aspects, we reviewed LIB and PEMFC literature. The abovementioned aspects were evaluated relative to the commercial "baseline", i.e. graphite (anode) and lithium nickel cobalt aluminium oxide (cathode) bulk materials for LIBs and nanoparticle platinum (catalyst) and high surface area carbon (catalyst support for PEMFCs. A general improvement is rated green, similar performance yellow, and poorer performance red. Supplementary Table 2 and Supplementary Table 3 list the performance parameters used to evaluate the *material and weight efficiency* criteria for LIBs and PEMFCs, respectively.

Supplementary Table 2 **Material and weight efficiency** *criteria for lithium ion batteries. Abbreviations: mAh g^{-1} – milliampere-hour per gram, V – voltage, kWh kg^{-1} – kilowatt-hour per kilogram.*

LIBs	Energy density	Power density	Lifetime and stability
Cathode and anode materials	• Capacity (mAh g^{-1}) • Voltage (V) • Energy density (kWh kg^{-1})	• Rate capability/ performance/characteristics • Rate of lithium intercalation/deintercalation • Conductivity • Impedance	• Calendar/cycling life • Capacity fade/loss • Stability (thermal, structural, and cycling) • Performance degradation • Failure • Fade in charge storage • Reaction with the electrolyte • Number of cycles • Cyclability • Cycling performance • Coulombic efficiency

PEMFCs	Power density	Lifetime and stability
Cathode catalyst & support	• Current density (A cm^{-2}, A mg^{-1}$_{Pt}$, A mg^{-1} $_{catalyst}$) • Generated voltage (V) • Power density (W cm^{-2}) • Oxygen reduction reaction kinetic rate • Onset voltage • ECSA	• ECSA retained after accelerated durability testing • H$_2$O$_2$ evolution rate • Polarization shift • Loss of current, power density

The relevant literature are referred to in the text and the caption of Figures 2-5 in the main article and in greater detail in the *Supplementary citation data*.

Recyclability and disposal

The recyclability of the studied LIB electrode materials and PEMFC materials was assessed based on current recycling practices as described in the literature[19–24] and through personal communication with commercial recylers[25,26] of these devices. Materials that can be reused or recycled receive a green ranking, materials that are unproblematic for disposal or have "imperfect" recycling processes receive a yellow ranking, and materials that may pose issues at the end-of-life processing receive a red ranking. N/A was assigned to materials where recycling is not a priority, e.g., for materials where there is no foreseeable shortage, such as sulphur or renewables. Material and energy inputs required for the various recycling processes were not assessed. For LIBs, the recyclability of nanoscale materials was assumed to be similar to that of the bulk materials.

Synthesis material losses

Synthesis material losses were evaluated based on synthesis protocols available in the literature, as well as synthesis reviews describing environmentally significant aspects[27–30]. Because bottom-up methods allow for the customized design of reactions and processes at the molecular level and thereby minimizing unwanted waste, it is generally believed that top-down techniques are more waste-producing than bottom-up techniques[29].

The solvothermal synthesis methods are environmentally advantageous, as rates of reactions are increased (closed system) and reagents are recycled[29]. The method is called hydrothermal if the used solvent is water[27]. Sonochemical synthesis is also environmentally advantageous, with yields as high as 90-95% due to ultrasonic irradiation[29,31]. Milling is said to be a highly efficient and low emission method[30]. The solid state synthesis method has high economic efficiency[30], suggesting low use of costly solvents and high production yields resulting in low synthesis material losses. Electrospinning is said to be a "green" and facile route that can easily be scaled up and is a low cost process[30], again suggesting low material losses.

Utilization efficiency of a plasma enhanced chemical vapour deposition (CVD) chamber ranges from 5% to 62%, depending on what perfluorocarbon is used[29]. It is environmentally preferable to thermal CVD as it operates at lower temperatures and has a higher production yield[27]. Yield values of carbon nanotubes production by the CVD method vary from 20% to 100%[29]. Although carbon nanotubes can be produced via four major synthesis routes (arc discharge, CVD, laser ablation, and the high pressure carbon monoxide process)[32], CVD is the only promising synthesis method for large scale production[27].

In this review, it was assumed that carbon nanotubes is synthesised through the CVD method with mediocre synthesis yield. Laser ablation synthesis yield range up to 70%[29].

Nanoparticles extracted from solution by precipitation must be washed repeatedly with organic solvents and ultrapure water until the products are isolated from solvents, surfactants, or reagents[29]. The precipitation method employs heavy chemical usage pre- and post-synthesis for purifying the product and accompanying wastewater generation from centrifugation or other separation techniques[29]. Sol-gel offers control over purity, composition, homogeneity and temperature, but it also requires large amount of organic solvents and reagents[30] and has low yield[29]. Metal organic CVD is a high cost route[30] that has a low precursor utilization efficiency of only 1 to 20% and at least 50% of the precursor gases becomes waste[29]. Wet etching use strong acids, metal salts, and generates acidic or organic waste, whereas dry etching uses greenhouse gases with low utilization efficiency[29]. Arc discharge synthesis has low yields hovering around 30%[29].

Supplementary Table 4 shows a general evaluation of *synthesis material losses* for nanosynthesis methods reviewed in this article.

Supplementary Table 4 Overview of **Synthesis material losses** *for nanomaterials synthesis routes reviewed in this article. Abbreviation: CVD - chemical vapour deposition.*

	Green	Yellow	Red
Synthesis material losses (nanomaterial purity, yield)	• Solvothermal/hydrothermal • Sonochemical • Milling • Solid state • Electrospinning	• Plasma enhanced CVD • CVD for carbon nanotubes • Laser ablation	• Precipitation • Sol-gel • Metal organic CVD • Etching • Arc discharge

Energy efficiency

Device efficiency

The device efficiency was evaluated relative to the commercial "baseline", i.e. graphite and lithium nickel cobalt aluminium oxide (NCA) bulk electrode materials for LIB and Nafion® membrane for PEMFCs. In LIBs, device energy efficiency was evaluated based on Coulombic efficiency and cycling (charge-discharge) efficiency. Vehicle batteries must have a Coulombic efficiency exceeding well over 99.5% if their effective lifetime is to exceed five years. LCA studies analysing LIBs apply charge-discharge cycling efficiencies of 90%[33–36] and 95-96%[37]. The cathode material cycling efficiency can be nearly 100%, whereas the carbonaceous (graphite) anode shows initial efficiency of 95% and lower[38]. In addition to stated cycling efficiencies, the efficiency was evaluated based on voltage hysteresis and factors contributing to internal resistance, such as phase transition, material polarization, electrical conductivity, and structural change. In PEMFCs, device energy efficiency is evaluated on the basis of internal resistance in the cell, and (for the components considered in the review) is determined by the electrical conductivity of the catalyst supports.

Energy of nanosynthesis

Energy of nanosynthesis is a measure of how much energy was required to produce a certain nanomaterial. Similar to the evaluation of *synthesis material losses*, *energy of nanosynthesis* was evaluated based on synthesis protocols and synthesis reviews describing environmentally significant aspects[27–30]. In some cases, the nanosynthesis method in itself may not be particularly energy demanding, but can require subsequent drying heat for annealing or calcination, which may be

significant. Therefore, energy of nanosynthesis evaluations are seen as combination of synthesis methods and temperatures. The text below describes relevant energy use for some synthesis processes.

Despite long synthesis times, sonochemical synthesis is a low-energy synthesis route as it takes place at room temperature[31] and only requires energy for ultrasonic irradiation and any baths or probes that are used[29]. Chemical etching can be performed near room temperature[39]. Wet etching requires energy for agitation, whereas plasma etching requires energy for plasma and vacuum system[29].

Plasma-enhanced CVD requires energy for the plasma generator and vacuum system and requires significantly lower temperature than the CVD process[27]. Hydrothermal and solvothermal are low-temperature synthesis routes and may be preferred as they are not as energy intensive as other methods[27,29,40,41] and do not require post-annealing treatments[29]. The hydro- and solvothermal operation temperatures are usually between 100-280 °C[41] for 5-10 hours[28]. Calcination temperatures are lower (e.g. 400-750 °C for 0.5-12 hours[28]) compared to the solid-state methods. Energy use for electrospinning itself is associated only with high-voltage power supply and syringe pump[29] as it may be performed at room temperatures[42], but the subsequent calcination requires high temperatures of about 500-900 °C[42,43]. Even though the mechanical milling process only requires energy for the milling equipment and can work at low temperatures[27], high-energy mechanical milling requires high temperatures for calcination (e.g. 400-700 °C for silicon-carbon composites)[29,30]. It is therefore considered as a rather energy intensive process[44].

Metal organic CVD takes place at higher temperatures than plasma-enhanced CVD; its primary energy consumption is associated with the vacuum system (low to medium vacuum pressure range: 0.5 to 760 Torr), gas handling system, purifiers, heat treatment of reactants before deposition, and high deposition temperatures (500-1200 °C)[27,29]. Nanosynthesis through precipitation and co-precipitation requires energy for heating treatments[28], such as drying and calcination[29]. Calcination temperatures of 500-800 °C for 12 hours under N_2 or argon flow is required for the crystalline LFP powders[28], but higher temperatures have also been reported[45,46]. Sol-gel is a long established industrial process for producing nanoparticles[27] and is often used for the preparation of metal oxides[28]. The sol-gel process itself can be performed at low temperatures, but requires drying and subsequent furnace treatment (e.g. LTO is calcined at 700-800 °C[30]) under an inert or reducing atmosphere[40]. Solid state synthesis is a technique used to produce chemical structures by reactions carried out at extreme conditions, such as high temperature and pressure. Prepared mixtures are often heated in two steps. For LFP, the first step is carried out at 250-350 °C and the second step at 400-800 °C[28]. In general, the appropriate sintering temperature range is 650–700 °C[28]. Calcination temperatures as high as 800-1000 °C are also used[30]. Arc discharge is a very high energy synthesis route, employing processing temperatures above 4000 °C. Spray pyrolysis typically starts with the pumping (or spraying) of a solution of mixed precursors into a pyrolysis furnace at moderate temperatures ranging between 100–600 °C in the form of droplets by a carrier gas[28,47]. The collected precursor powders are then annealed at temperatures typically ranging between 400–800 °C[28,47]. As there is such a great span in temperature ranges, the energy requirements of spray pyrolysis may be moderate or high.

Synthesis and processing routes for nanomaterials were roughly evaluated qualitatively considering the required processing temperature input as described specifically in the synthesis protocols or more generally regarding synthesis methods. Due to large variation in temperature, pressure, and duration of treatment, the evaluation of energy of nanosynthesis is more prone to uncertainty than other aspects evaluated in this review. Furthermore, as the nanomaterials may be synthesized through different synthesis routes, the evaluation was limited to the synthesis routes reviewed in this article. As previously mentioned, carbon nanotubes can be manufactured using various synthesis methods. Carbon nanotubes manufacturing is energy intensive regardless of synthesis method, but arc discharge

and laser ablation are more energy intensive than CVD and the high pressure carbon monoxide process[32]. Production of carbon nanotubes was therefore always rated as red.

Supplementary Table 5 shows a general evaluation of *energy of nanosynthesis* for nanosynthesis methods reviewed in this article.

Supplementary Table 5 Energy of nanosynthesis evaluation for some synthesis routes. Abbreviation: CVD - chemical vapour deposition.

	Green	Yellow	Red
Energy of nanosynthesis	• Sonochemical • Etching	• Plasma enhanced CVD • Solvothermal/hydrothermal • Electrospinning • Milling • Spray pyrolysis (low temperatures)	• Metal organic CVD • Precipitation • Sol-gel • Solid state • Arc discharge • Spray pyrolysis (high temperatures)

4. Review of bulk polymer matrices for electrolyte membranes

The following is a review of the main groups of polymer electrolyte membranes for PEMFCs. These polymers are bulk materials whose main functionality (i.e., proton conduction) occurs on the nanoscale. Since the main article reviews nanotechnology modification to these polymers, the bulk materials are briefly evaluated here using the lifecycle attributes to provide relevant background information to be considered in parallel with the main text. Keeping in mind our lifecycle sustainability attributes, we differentiate between two main membrane material categories: fluorinated and non-fluorinated membranes.

Fluorinated membranes may be fully fluorinated, such as Nafion (poly(perfluorinated sulfonic acid); PFSA), or partially fluorinated polymers. To date, these membranes have the best technical performances in operating PEMFCs, but device efficiency (proton conductivity) decreases at higher temperatures and in anhydrous conditions[48]. Work has therefore aimed at finding materials and means of improving existing materials under these conditions. Promising low equivalent-weight PFSA membranes such as perfluoroimide acids have greater ionic conductivity per gram of polymer and thus provide increased power density than Nafion. These materials also show improved device efficiency and lifetime over conventional Nafion in hot and dry operating conditions, through greater proton conductivity and stability, respectively[49]. Partially fluorinated membranes based on polymers such as polyvinylidene fluoride and poly(ethylene-*co*-tetrafluoroethylene) lack the durability and tolerance to fuel impurities to be considered in transport PEMFCs, despite their oxidative stability[50].

The specific toxicological effects, bioaccumulation and biomagnification tendencies and exposure risk of the fluorinated polymers being explored as PEMFC membranes do not appear to have been studied. Similar fluorinated polymers such as perfluoroalkyl carboxylic and sulfonic acids, however, are found to be persistent and bioaccumulative, and, in some cases, biomagnified[51,52]. Furthermore, chemical degradation of fluorinated membranes during PEMFC operation result in the release of corrosive and toxic hydrofluoric acid[48,53], which is also a precursor to the fluorinated polymers. Tetrafluoroethylene, another precursor to fluorinated polymers, is also of toxicological concern[54]. As such, from the perspective of material impacts, it is highly recommended to focus research on the pursuit of non-fluorinated PEMFC membranes.

Non-fluorinated membranes include acid and hydrocarbon membranes such as poly(arylene ether)s, polyimides, styrene and derivatives, as well as inorganic or solid acid membranes (e.g., $CsHSO_4$, $Rb_3H(SeO_4)_2$ and heteropolyacids such as $H_3PW_{12}O_{40}.nH_2O$, etc). These membranes have generally fallen short of the technical goals for PEMFCs for transport applications; they have lower device efficiency due to their lower ionic conductivity, or are unstable and lack the robustness required for an adequate device lifetime relative to Nafion membranes[50,55]. However, as discussed above, their lack of fluorine atoms generally makes these materials less environmentally intensive than fluorinated membranes and modifications such as covalent attachment of proton-conductive compounds, cross-linking and nanostructure are being explored as methods to overcome weaknesses[49,56–60]. An exception to the technical performance of this category of membranes are phosphoric acid-doped polybenzimidazole-based membranes. These membranes perform well in high temperatures with low humidity levels and are robust against fuel impurities. However, they also have reduced device lifetime due to lower mechanical strength and due to damage caused by phosphoric acid leachate formed under normal operating conditions; acid leaching also decreases the energy efficiency of the membrane via losses in proton conductivity[58,61]. Beyond the attributes considered here, phosphoric acid-PBI membranes may have issues with cold start due to poor device efficiency performance at lower temperatures.

Composite membranes have been researched as a synergetic means to boost the performance of two or more different polymers. In addition to the composite electrospun membranes discussed in the main manuscript, polytetrafluoroethylene-reinforced PFSA membranes demonstrate improved lifetime characteristics and device efficiency over benchmark Nafion membrane[48]. The mechanical strength provided by the polytetrafluoroethylene matrix improves material efficiency by allowing thinner membranes, which also improves the device energy efficiency by reducing ionic resistance.

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