REVIEW ARTICLE

Assessing n-type organic materials for lithium batteries: A techno-economic review

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Abstract

The high demand for critical minerals such as lithium, copper, nickel, and cobalt, required for lithium-ion batteries, has raised questions regarding the feasibility of maintaining a steady and affordable supply of raw materials for their production. In the last years, researchers have shifted their attention toward organic materials, which are potentially more widely available, affordable, and sustainable due to the ubiquitous presence of the constituent organic elements. The n-type materials have a redox mechanism analogous to that of lithium-ion cathodes and anodes, hence they are suitable for a meaningful comparison with the state-of-the-art technology. While many reviews have evaluated the properties of organic materials at the material or electrode level, herein, the properties of n-type organic materials are assessed in a complex system, such as a full battery, to evaluate the feasibility and performance of these materials in commercial-scale battery systems. The most relevant cathode materials for organic batteries are reviewed, and a detailed cost and performance analysis of n-type material-based battery packs using the BatPaC 5.0 software is presented. The analysis considers the influence of electrode design choices, such as the conductive carbon content, active material mass loading, and electrode density, on energy density and cost. The potential of n-type organic materials as a low-cost and sustainable solution for energy storage applications is highlighted, while emphasizing the need for further advancements of organic materials for energy storage applications.

KEYWORDS
batteries, cost-performance analysis, lithium-ion, organic, review

1 | INTRODUCTION

One of the fundamental technologies for our society's clean energy transition is lithium-ion batteries which have enabled the use of electric vehicles and the cost-effective short-term storage of renewable energy.[1–4]

However, estimates of the required amount of critical minerals such as lithium, copper, nickel, and cobalt pose questions concerning the feasibility of maintaining a steady and affordable supply of raw materials for their manufacturing.[5] For instance, according to data from the International Energy Agency, 680 GW of grid-storage

lithium-ion batteries should be installed by 2030 to keep on track with the Net-Zero Scenario, while 16 GW were available in 2021, with an average of 80 GW per year that should be added in this timeframe.[6] Most of the commercial cathodes for lithium-ion batteries, such as nickel–manganese–cobalt oxides (NMC), rely on metals that are expensive and/or whose deposits are concentrated in very few countries. Materials such as lithium-iron phosphate (LFP) are considered to be more resilient to supply shocks, thanks to the widespread availability of iron and phosphate sources. Nevertheless, even the supply of lithium is becoming an issue since the demand for batteries is exceeding the current mining and processing capabilities of lithium-containing rocks and brines. In 2020, the supply of lithium was 77 kt, while the demand was 63 kt, of which 40 kt was for lithium-ion batteries. In 2022, the lithium demand for batteries increased to 104 kt, bringing the total to 128 kt, but the available supply only reached 126 kt.[7] The combination of this supply-demand mismatch and geopolitical instabilities has caused the lithium price to greatly increase and oscillate in the last 3 years, with peaks of +650% compared with early 2020 prices.[7–9]

Currently, research efforts are focused on novel chemistries to discover viable alternatives or complementary solutions to lithium-ion batteries, whereby the main advantages are widespread availability and greater affordability of the raw materials required for the active materials.[10–15] Due to the ubiquitous presence of organic elements (i.e., carbon, oxygen, hydrogen, nitrogen), research interest in organic materials for batteries has peaked over the past 20 years.[16–20] Other than the abundance of the precursors, organic materials are expected to be more sustainable than commercial lithium-ion battery materials, with a global warming potential that could be ∼3 to 4 times lower,[20] and the possibility of assembling biodegradable organic batteries was also demonstrated.[21] Their sustainability has yet to be proven, since to date only lab-scale life cycle assessments on non-optimized synthesis routes are available,[22,23] which usually tend to greatly overestimate the environmental impact of battery materials.[24] Another advantage of organic materials can be found in their high versatility, due to the richness of their organic chemistry. The drawbacks of organic materials include very poor electronic conductivity, requiring high amounts of conductive carbon (>30% in weight) to be added in the electrode formulation and a strong tendency to dissolve in the electrolytes commonly used for batteries, causing severe capacity fading during cycling. Moreover, their low density, when compared with inorganic materials, limits the energy density achievable with organic batteries.[25]

Conjugated conductive polymers were already intensively studied in the 80s as cathodes for lithium metal batteries, an effort that culminated in a commercialization attempt of batteries with poly(aniline) and poly(pyrrole) as active materials.[26,27] Nevertheless, the overall superior performance of their inorganic counterparts made this tentative effort short-lived, and now metal-based cathodes with graphite as anode remain the state-of-the art.[16]

Since the early 2000s, interest in organic electrode materials has re-emerged,[28–30] and in laboratory settings, various monomers and polymers capable of redox reactions have been synthesized and studied. Materials that react with cations are labeled as n-type, while those that react with anions are referred to as p-type (Figure 1). Some bipolar compounds show redox activity with both cations and anions, although at very different potentials.[31] This classification was introduced by Hünig, whose work on multistage organic redox systems originally labeled the n-type materials as B-type, and p-type materials as A-type.[32] The p-type materials are reversibly oxidized to form a positively charged species, losing electrons and with anions that balance the positive charge. Whereas, n-type materials are reduced and form a negatively charged species, with a gain of electrons which is balanced by the presence of cations.[33]

Typically, n-type materials have a lower average voltage, slower kinetics, and higher specific capacity compared with p-type materials. The p-type materials also behave differently from typical lithium-ion battery electrodes due to the fundamental role of the electrolyte as a source of anions in the redox reaction, hence they are similar to lead-acid battery electrodes.[33–35]

This review focuses on n-type materials, which have a redox mechanism analogous to that of lithium-ion cathodes and anodes, allowing for a more meaningful comparison. The n-type materials have the potential to offer an economical and sustainable solution for energy storage applications.[17,20,36] However, further insights are needed to evaluate the feasibility and performance of these materials in commercial-scale battery systems. Previous reviews have highlighted the ideal characteristics of an organic material (high electronic conductivity, capacity retention, specific capacity, density, voltage, etc.), but these properties were evaluated at the material level or at most at the electrode level, without considering them in a more complex system such as a full battery. The lack of comprehensive studies on the cost and performance of n-type material-based battery packs highlights the need for further investigation.

Herein, we present the most extensively studied, relevant cathode materials for organic batteries. Moreover, a
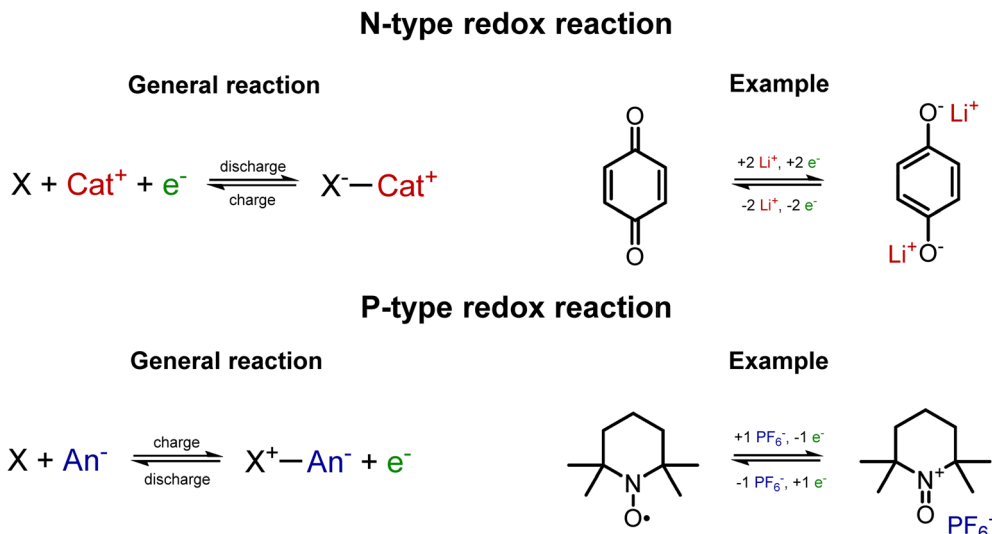
FIGURE 1 General electrochemical reactions for n-type (top left) and p-type (bottom left) organic materials and relative examples of reactions with 1,4-benzoquinone and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO).

section of this review will delve into organic anodes. We also present a detailed cost and performance analysis of n-type material-based battery packs performed with the software BatPaC 5.0.[37] Lastly, we discuss the implications of the design choices of the organic electrodes on the energy density and cost of battery packs, focusing on the influence of the conductive carbon content, the active material mass loading, and the electrode density.

2 | OVERVIEW OF N-TYPE ORGANIC ACTIVE MATERIALS

The majority of the n-type materials investigated in literature involve the reversible reduction of the oxygen atom in a carbonyl group,[38–40] but a rich chemistry of nitrogen-containing molecules is also present, involving azo, imine, sulfonamide, and nitrile redox centers.[41–43] Materials belonging to the organosulfide class are mainly characterized by the reversible breaking and reformation of a disulfide bond, the same type of reaction present in lithium-sulfur batteries[44–46]; notably, a few examples exploiting thiocarbonyl groups are also present.[47,48] These redox-active motifs can be found in small molecules as well as macromolecular structures, such as linear or cross-linked polymers,[16] covalent organic frameworks (COFs),[49,50] or metal organic frameworks (MOFs).[51,52] These two latter classes of three-dimensional, π-conjugated, crystalline coordination polymers (fully organic and metal-organic hybrids, respectively) have been widely investigated as battery materials, and their electrochemical properties are connected to the employed redox-active ligands. Some p-type materials can also undergo n-type reactions (hence correctly classified as bipolar materials), such as molecules and polymers based on the (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) moiety or other conjugated polymers.[53–55]

Organic materials are typically classified and discussed in reviews based on these different constituent elements and functional groups. However, in this review, we categorize these materials based on a practical criterion: whether or not they require a lithium-metal anode. This classification separates the materials into two categories, that is, lithium-deficient and lithium-sufficient organic materials. Most n-type cathodes require a lithium-metal anode to function in a battery, although lithium-metal batteries face challenges regarding the production and handling of thin reactive anode foils and cycle life.[1,11,56] Recent works have explored organic cathodes that contain enough lithium and are stable toward oxygen and moisture, similar to commercial inorganic cathodes.[57] These organic cathodes, synthesized in their discharged form, can be used with a conventional graphite anode or other organic anode materials, resulting in organic battery production that is potentially analogue to inorganic lithium-ion battery production. As a result, a material's lithium deficiency or sufficiency affects the production process from synthesis to assembly, as well as the performance and stability of the battery during operation. Lithium-sufficient organic materials can simplify the battery production process and eliminate the need for a lithium-metal anode; such batteries are easier to manufacture and handle. This criterion of lithium deficiency
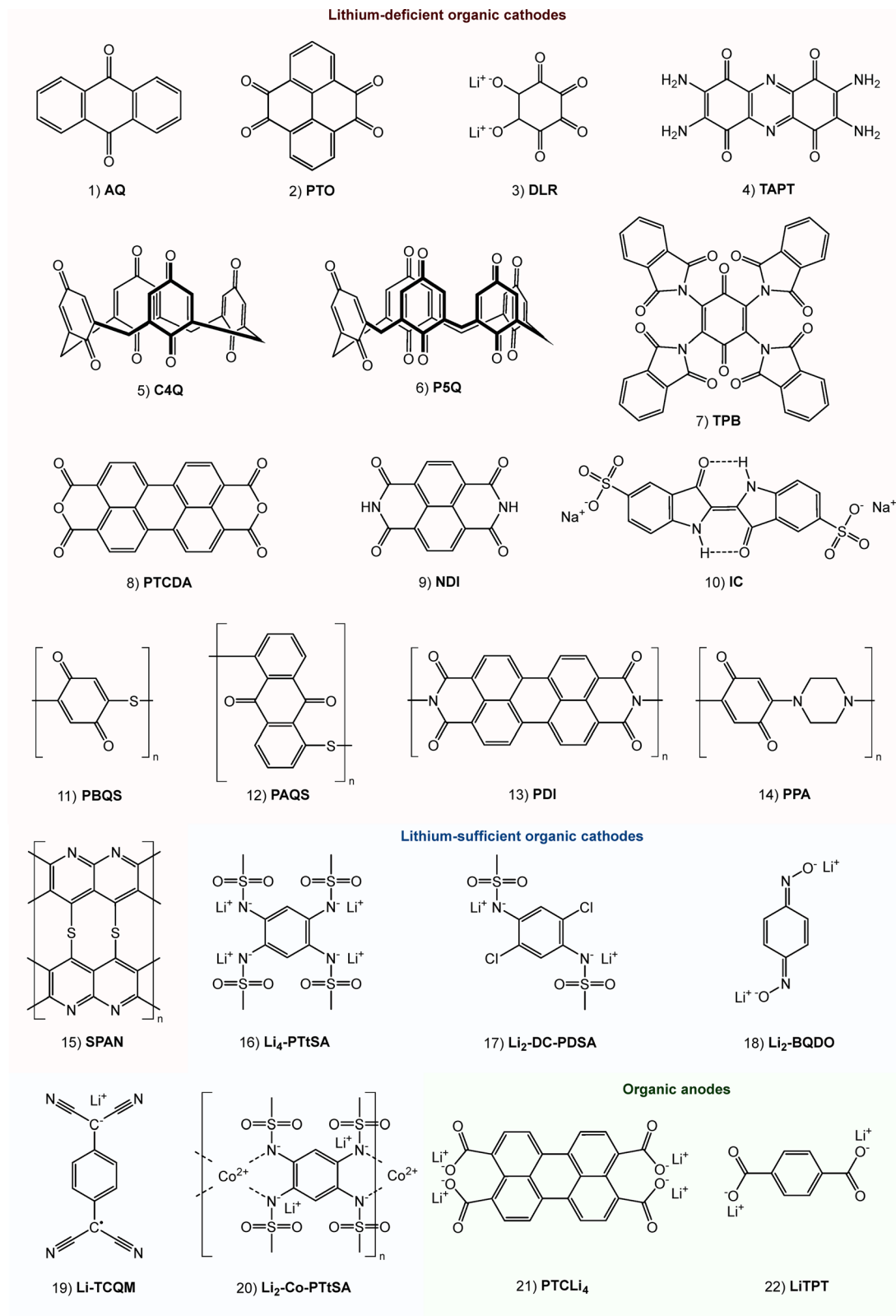
FIGURE 2 Representation of the organic materials included in the cost and performance analysis; categorized as lithium-deficient cathodes (red), lithium-sufficient cathodes (blue), and organic anode (green).

or sufficiency is a crucial factor in evaluating the practicality and potential of n-type organic materials for battery applications.

We present an overview of the two classes of organic cathodes, as well as on organic anodes, with foci on the materials shown in Figure 2, which were chosen for
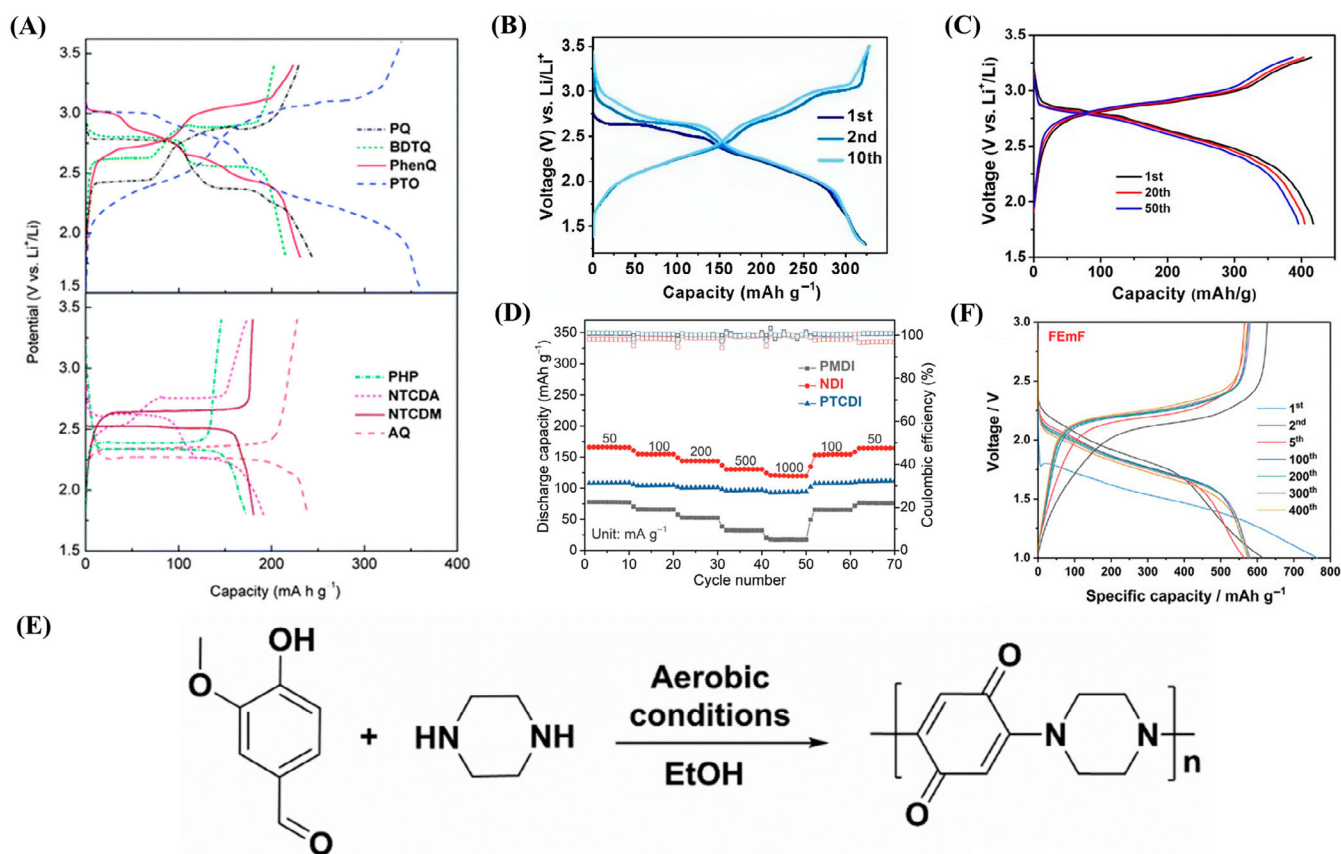
FIGURE 3 (A) Voltage/specific capacity curves of several n-type small molecule organic cathodes, among which AQ and PTO. Reproduced with permission.[59] Copyright 2013, Royal Society of Chemistry; (B) Voltage/specific capacity curve of the 1st, 2nd, and 10th cycle of a TAPT/Li metal cell in 1 M LiTFSI in DOL/DME. Reproduced with permission.[68] Copyright 2022, Wiley; (C) Voltage/specific capacity curve of the 1st, 20th, and 50th cycle of a P5Q/Li metal cell in a poly(methacrylate)/poly(ethylene glycol)-based gel polymer electrolyte. Reproduced with permission.[71] Copyright 2014, American Chemical Society; (D) Specific capacity versus cycle number for three small imide molecules as cathodes for lithium metal batteries, including NDI. Reproduced with permission.[77] Copyright 2022, American Chemical Society; (E) Reaction scheme for the synthesis of PPA from vanillin and piperazine. Adapted with permission.[101] Copyright 2021, Elsevier; (F) Voltage/specific capacity curve of a SPAN/Li metal cell in an ionic liquid-based electrolyte. Reproduced (Adapted) under the terms of the CC-BY 4.0 license.[102] Copyright 2022, Wiley.

further analysis in the energy density and cost simulations, as representative examples of the investigated n-type materials for electrochemical energy storage (Figure 2).

2.1 | Lithium-deficient cathode active materials

The n-type materials can be reversibly reduced from their neutral state to a negatively charged molecule, which then interacts with a lithium cation to store energy. In lithium-deficient cathodes, the materials are synthesized in this neutral form, and they must extract the necessary lithium from the anode; the first cycle of the corresponding battery starts with a discharge. Even though some materials described in this section may contain

lithium, the content is not sufficient to exploit the full capacity of the organic cathode and its complete removal may hinder the capacity retention of the battery.[58]

Small molecules have garnered attention as n-type cathodes because they are materials that can potentially combine several redox centers with a low molecular weight. Liang et al., demonstrated how a variety of such molecules can easily achieve >250 mAh g^{-1} as specific capacity, with a redox potential between 2.0 and 3.0 versus Li/Li$^+$ (Figure 3A).[59] Among the materials investigated in the aforementioned work, anthraquinone (**AQ**, material 1) is distinct as it is an economical chemical used in the paper and dye industry with a good theoretical specific capacity (257 mAh g^{-1}),[60,61] and it has become the foundation for a range of small molecules and polymers used as organic electrode materials. Pyrene-4,5,9,10-tetraone (**PTO**, material 2) also attracted much interest due

to a remarkably high theoretical specific capacity (409 mAh g^{-1}), owing to its four-electron redox mechanism with the four active carbonyl groups (Figure 3A).[62]

However, such ketone-based materials are prone to dissolution in the conventional organic electrolytes employed in lithium batteries, that is, mixtures of ethylene carbonate and carbonate esters with 1 M salts such as lithium hexafluorophosphate, limiting the useful life of the battery to few cycles.[63] Another promising n-type material such as dilithium rhodizonate (**DLR**, material 3) displays a theoretical specific capacity of 589 mAh g^{-1} with the lithiation of the four available ketone groups,[64] but its cyclability is extremely limited in the extended voltage range that transitions the material from $Li_2C_6O_6$ to $Li_6C_6O_6$. Interestingly, when cycled in a smaller voltage window, between $Li_4C_6O_6$ and $Li_6C_6O_6$, the cyclability improved, at the expense of the energy density.[29] Proposed reasons are the suppression of the delamination of the material by avoiding a deep charging of the cathode and the presence of intermolecular Li–O interactions that hinders the dissolution in the electrolyte.[65] In general, the presence of a high degree of intermolecular forces through hydrogen bonds and interactions with lithium ions have been found to be beneficial for the cycling stability of ketone-based molecules.[66,67] An example of the implementation of this strategy is demonstrated in the recent work of Li et al., where 2,3,7,8-tetraaminophenazine-1,4,6,9-tetraone (**TAPT**, material 4) was synthesized and tested in a battery.[68] This molecule, derived from the condensation of two tetraaminobenzoquinones, shows a six-electron redox mechanism where both the ketone oxygen and the phenazine and amine nitrogen are involved, and in the 3.5–1.5 V versus Li/Li$^+$ voltage range, reaches a capacity of ~300 mAh g^{-1} with good cycling stability (Figure 3B).

Increasing the molecular weight of the monomer together with the number of redox-active sites has been regarded as an effective strategy to suppress the molecules dissolution, since larger molecules are in principle, harder to solvate. This idea has led to the investigation of macrocyclic molecules such as calix[4]quinone (**C4Q**, material 5) and pillar[5]quinone (**P5Q**, material 6), derivations of calixarenes, a host-guest chemistry molecules class.[69] C4Q and P5Q, formed by several benzoquinones bounded by methylene groups, possess 8 and 10 ketone oxygens, respectively, resulting in a specific capacity for both molecules of 446 mAh g^{-1}. Nevertheless, their cyclability in organic electrolytes is still poor, and relatively stable cycling of these molecules has been achieved only in quasi-solid-state batteries or with ionic liquids (Figure 3C).[70–73] Instead, a successful approach with the same principle of increasing the mass of the molecule was proposed by Luo

et al., where 2,3,5,6-tetraphthalimido-1,4-benzoquinone (**TPB**, material 7) presents four rigid phthalimide groups around a benzoquinone center.[74] The increase of molecular weight is related to the aromatic functionality with the possibility of stacking, which has been shown to enhance the cyclability.[75] Each phthalimide group carries two carbonyl oxygens, for a total of 10 redox active sites, including the ones on the benzoquinone. This material, characterized by an initial specific capacity of 225 mAh g^{-1} and two plateaus at 3.1 and 2.1 V versus Li/Li$^+$, was able to cycle for at least 100 cycles at 0.2 C.

Molecules belonging to the anhydride and imide classes are also characterized by four carbonyl groups as PTO, but only two of these are redox-active due to the unfavorable electronic configuration of the completely reduced structure.[59] Materials such as the organic dye perylenetetracarboxylic dianhydride (**PTCDA**, material 8) or the supramolecular chemistry compound 1,4,5,8-naphthalenediimide (**NDI**, material 9) show, respectively, 137 mAh g^{-1} at 2.4 V versus Li/Li$^+$ and 202 mAh g^{-1} at 2.3 V versus Li/Li$^+$ as theoretical capacity values.[76,77] Nevertheless, such molecules have generally higher stability in conventional organic electrolytes compared with ketone-based ones, due to the extended aromatic structure that provides strong intermolecular π–π stacking forces and the stabilization of intermediate radical species formed during the redox reaction (Figure 3D).[77] For instance, the resulting stable crystal structure of PTCDA, allows a high degree of reversibility of the de/intercalation of lithium and other monovalent and divalent metal cations.[78,79]

Other organic dyes have been proposed as energy storage materials, owing to their natural occurrence and/or high availability as widely used chemicals.[80–84] Among these, indigo carmine (**IC**, material 10) has received the most attention, being already employed as food colorant, pH indicator, and diagnostic dye. In a work from Deunf et al., where the design of indigo carmine electrodes was optimized, this material managed to achieve >100 mAh g^{-1} between 3.0 and 1.5 V versus Li/Li$^+$ with only 10% of conductive carbon, with a remarkably stable cycling even at low current rate influenced by the polar sulfonate groups that hindered the dissolution in the electrolyte.[85]

In addition to the reliance on intermolecular forces and molecule size to improve the capacity retention of n-type batteries, the polymerization of small organic molecules into macromolecules has also been extensively studied.[86] Well-designed polymers can suppress the loss of capacity due to the solvation of the electrode molecules, and they achieve a high molecular weight,[87–89] with the utilization of crosslinking agents[90–93] regarded as effective strategies.

Ketones that are unstable as molecules in lithium batteries managed to achieve good cycling stability when polymerized, at the cost of some specific capacity and a slightly lower redox potential. Polybenzoquinonyl sulfide (**PBQS**, material 11)[87,94–96] and polyanthraquinonyl sulfide (**PAQS**, material 12),[58,97,98] that is, linear polymers of benzoquinone and anthraquinone, respectively, with sulfur-based linkages, are two n-type polymers which are representative examples of this method. PAQS showed a practical specific capacity of 199 mAh g^{-1} at 2.2 V versus Li/Li$^+$, with a sloping voltage profile, while an example of AQ-based battery achieved 250 mAh g^{-1} with a potential plateau at 2.26 V versus Li/Li$^+$. Nevertheless, this decrease in energy density of the polymeric cathode when compared with the molecule-based one comes with an increase of the useful cycle life, which improves from few cycles to more than 100.[94] Whereas, PBQS achieved a specific capacity of 274 mAh g^{-1} at an average potential of 2.7 V versus Li/Li$^+$, with hundreds of stable cycles. Benzoquinone was able to cycle with 430 mAh g^{-1} at ~2.8 V versus Li/Li$^+$ in the first cycle, although the performances quickly decayed due to the dissolution of the small molecule in the electrolyte.[97]

The same polymerization approach was also extensively applied to imide molecule, and polyimides represent a widely studied class of n-type organic cathode materials.[99] A representative example belonging to this class is poly(3,4,9,10-perylenetetracarboxylic dianhydride ethylene diamine) (**PDI**, material 13), deriving from the condensation reaction of PTCDA with ethylenediamine.[100] This material exhibited a remarkably higher stability than PTCDA in the same electrolyte, with 127 mAh g^{-1} in a two-step reaction with two plateaus at 2.75 V and 2.25 V versus Li/Li$^+$, in contrast to the PTCDA that displays a single plateau at 2.45 V versus Li/Li$^+$ during charge and discharge.

The main focus of a recent work by Li et al. on n-type redox polymers was the cost of the final active material.[101] The expensiveness of the molecules, of the eventual catalysts, and the final yield of the synthesis reaction is rarely the focus of research work in this field, as demonstrated by Li et al. Poly(piperazine-altbenzoquinone) (**PPA**, material 14), a product of the condensation reaction between vanillin and piperazine (Figure 3E) resulted in a ketone-based lithium-deficient active material with a theoretical production cost of 0.48 \$ g^{-1}, which would correspond to 480 \$ kg^{-1}, and a practical specific capacity of 232 mAh g^{-1}. The cost was reported as one of the lowest among the organic materials present in the literature.

Sulfur-based polymers, exploiting a type of redox reaction analogous to the one of lithium-sulfur batteries, were also designed to achieve very high specific capacity with organic materials and contemporarily alleviate some typical issues that plague pure sulfur cathodes, such as polysulfide shuttling and poor reversibility.[44] Sulfurized polyacrylonitrile (**SPAN**, material 15) was recently employed by Liu et al. with an ionic liquid-based electrolyte and lithium metal as anode, obtaining 580 mAh g^{-1} at an average voltage of 1.8 V versus Li/Li$^+$, with stable cycling for more than 200 cycles with both thick and thin lithium metal anode foils (Figure 3F).[102]

2.2 | Lithium-sufficient cathode active materials

In contrast with the organic materials presented in Section 2.1, lithium-sufficient n-type cathodes contain enough lithium to fully lithiate the anode in a full-cell configuration, similar to commercial lithium-ion batteries. A major challenge to the development of lithium-sufficient materials is their stability toward the oxygen present in the atmosphere.[57] The air stability threshold is ~2.9 V versus Li/Li$^+$, depending on the water content in the atmosphere, but many lithium-containing materials studied in the literature tend to have redox potentials below this threshold, due to the presence of numerous electron-donating OLi groups.[103–107] The air-instability has the effect of strongly decreasing the lithium content upon oxygen exposure, decomposing the OLi groups to OH groups, hence hindering the effective use of the cathode material in a battery. Moreover, the lithiation of lithium-containing n-type materials, transpiring in liquid media through the exchanging of H by Li, requires degassed and anhydrous solvents like tetrahydrofuran or dimethylformamide, and prohibitively expensive lithium salts such as lithium hydride or methoxide in case of air-unstable cathodes.[108] Instead, the lithiation reaction can efficiently proceed in aqueous media and with lithium carbonate or hydroxide for air-stable materials, hence enabling a cost-effective and scalable synthesis. Due to the impractical production, handling, and storage conditions required for air-unstable lithium-sufficient materials, only the air-stable materials are discussed in this section.

Air-stable lithium-containing n-type cathodes have been the major focus of several works of Vlad et al. where a high redox potential is achieved in small organic molecules and coordination polymers with the use of electron-withdrawing sulphonamide groups and exploiting nitrogen as redox center.[108–112] Two relevant materials belonging to this class are tetralithium benzene-1,2,4,5-tetra-methylsulfonamide (**Li$_4$-PTtSA**, material 16) and dilithium 2,5-dichloro-1,4-phenylene-bis-methylsulfonylamide (**Li$_2$-DC-PDSA**, material 17).[108] Both materials present a flat voltage plateau upon discharge,
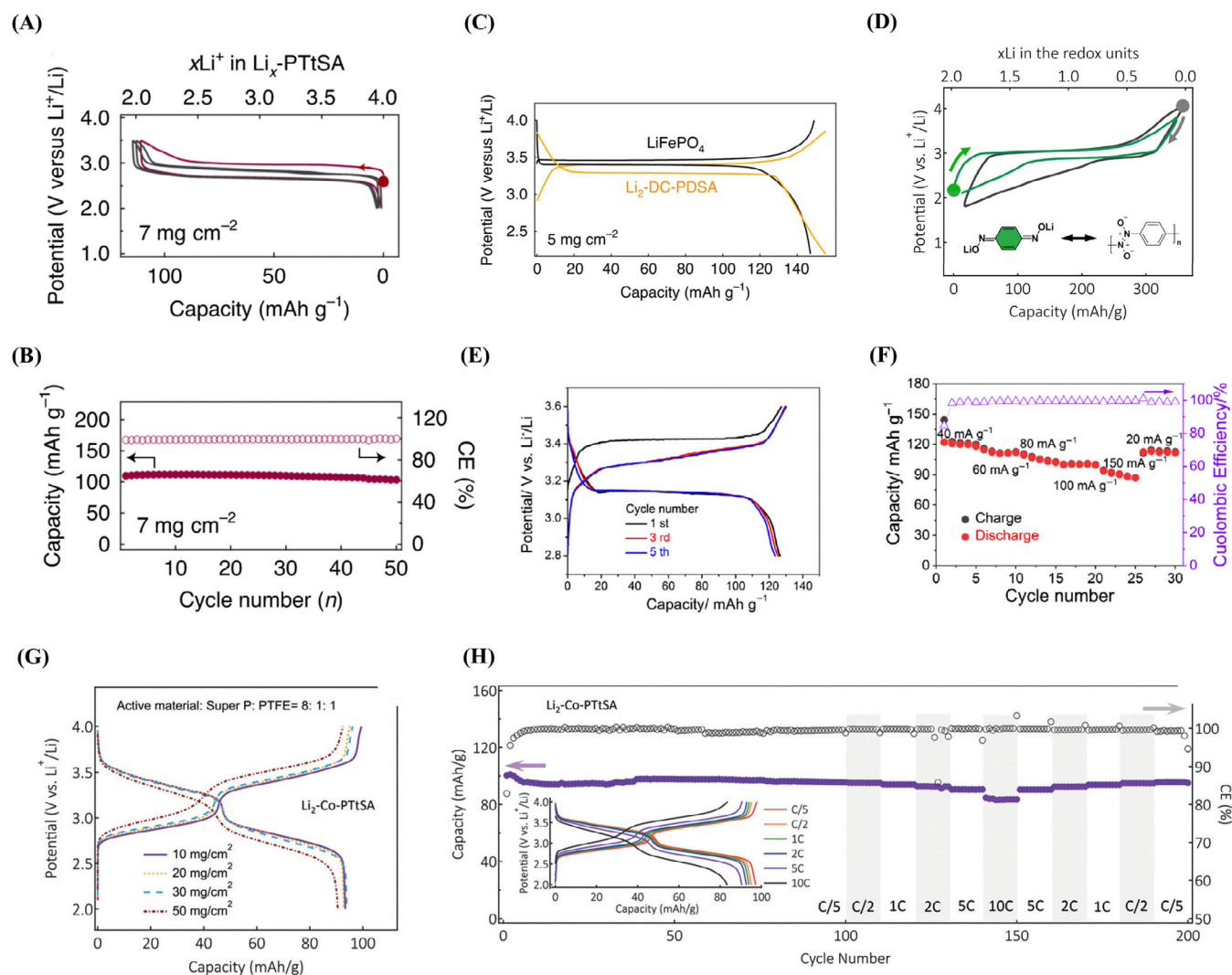
FIGURE 4 (A) Voltage/specific capacity curve for the first cycles of Li_4-PTtSA and (B) the related specific capacity versus cycle number chart. Reproduced with permission.[108] Copyright 2020, Springer Nature; (C) Comparison between the voltage and specific capacity of LFP and Li_2-DC-PDSA. Reproduced with permission.[108] Copyright 2020, Springer Nature; (D) First two cycles of Li_2-BQDO, with a depiction of the charged and discharged forms of the molecule. Reproduced (Adapted) under the terms of the CC-BY 4.0 license.[114] Copyright 2023, Science AAAS. (E) Voltage/specific capacity curve for the first cycles of Li-TCQM and (F) the related specific capacity versus cycle number chart at different current rates. Reproduced with permission.[115] Copyright 2022, Elsevier. (G) Voltage/specific capacity curve at different active material mass loadings of Li_2-Co-PTtSA and (H) the related specific capacity versus cycle number chart at different current rates. Reproduced (Adapted) under the terms of the CC-BY-NC 3.0 license.[110] Copyright 2022, Royal Society of Chemistry.

respectively, at 2.7 V versus Li/Li$^+$ and 3.3 V versus Li/Li$^+$, and the specific capacity reaches 111 mAh g^{-1} for Li_4-PTtSA and 155 mAh g^{-1} for Li_2-DC-PDSA (Figure 4A–C). As evidenced in Figure 4C, the voltage profile of Li_2-DC-PDSA resembles the one of LFP, both in terms of capacity and potential. Nevertheless, the resistance toward dissolution of these molecules in conventional organic electrolytes is low, and stable cycling was achieved with only 5 M LiTFSI in DOL/DME.

Another class of molecules studied by the same group are oximates, where the electron-withdrawing N–O$^-$ group is exploited as redox center increasing the redox potential, allowing the air-stability of the lithiated oximate molecules.[113,114] An example is represented by dilithium benzoquinone dioximate (**Li$_2$-BQDO**, material 18), a small molecule resembling lithiated benzoquinone where the ketone oxygens have been substituted with oximate groups.[114] This material managed to achieve 335 mAh g^{-1}, and the cycling stability was remarkable for such a low molecular weight compound, supposedly due to the reversible formation of a polymerized form of the material upon charge (Figure 4D).
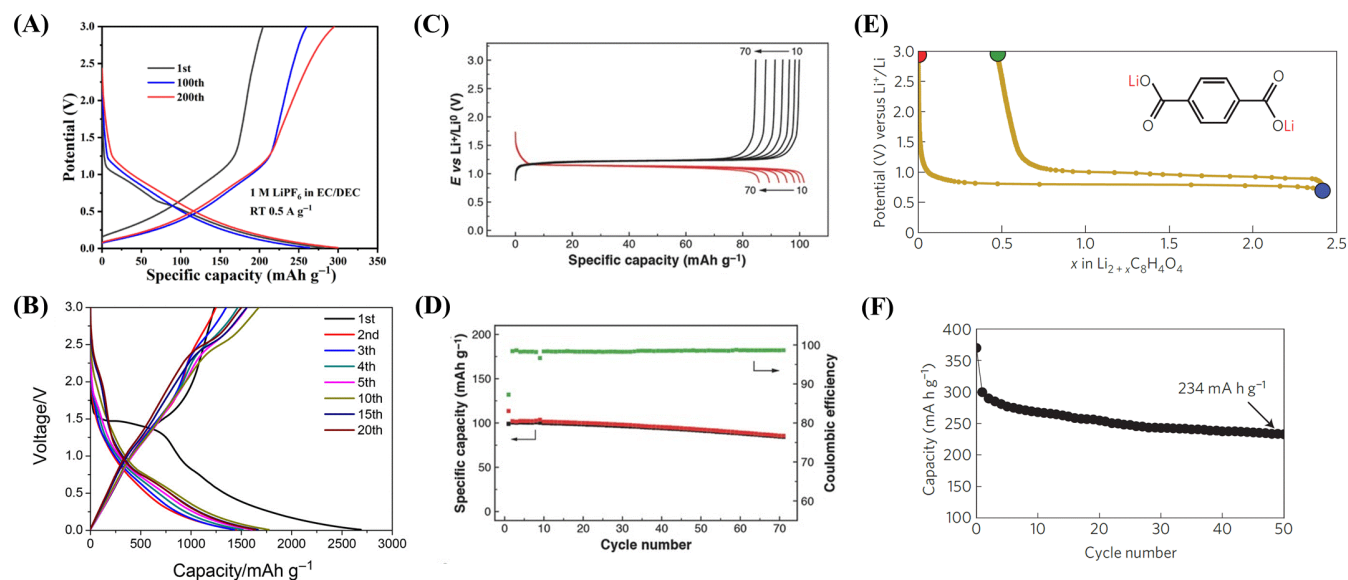
FIGURE 5 (A) Voltage/specific capacity curve of a Super P blank electrode in 1 M LiPF$_6$ in EC/DEC. Reproduced with permission.[118] Copyright 2022, Wiley; (B) Voltage/specific capacity curve of selected cycles of a maleic acid-based organic anode. Reproduced with permission.[126] Copyright 2017, American Chemical Society; (C) Voltage/specific capacity and d) cycling stability of a 12.0 mg cm^{-2} PTCLi$_4$ electrode in 1 M LiPF$_6$ in a 1:1:1 volume mixture of EC, DMC, and EMC. Reproduced with permission.[128] Copyright 2017, Wiley; (E) Voltage/specific capacity curve and (F) cycling stability of a LiTPT electrode in 1 M LiPF$_6$ in EC/DMC. Reproduced with permission.[30] Copyright 2009, Springer Nature.

Deng et al. found that the tetracyanoquinodimethane anion can also form an air-stable lithiated compound, that is, lithium tetracyanoquinodimethane (**Li-TCQM**, material 19).[115] This compound, containing a single lithium cation in the discharged form, was able to obtain 126 mAh g^{-1} with a voltage plateau at 3.15 V versus Li/Li$^+$ during discharge (Figure 4E,F). A good capacity retention was reached with the coating of the Celgard separator with a 5:5 weight ratio mixture of Nafion and Super P, which according to the authors hindered the dissolution of the Li-TCQM.

So far, the only example of air-stable lithium-containing n-type redox polymer is represented by a class of coordination polymers studied by the Vlad group, which combine the structure of the Li$_4$-PTtSA molecule with divalent transition metal coordination centers, obtaining materials which are both electronically conductive and more stable toward dissolution.[110] With cobalt as the coordination center, coordination polymers based on sodium and potassium usable as cathode for organic batteries were also obtained. Dilithium cobalt benzene-1,-2,4,5-tetra-methylsulfonamide (**Li$_2$-Co-PTtSA**, material 20) is a representative of this group of organic cathodes, with 93 mAh g^{-1} and a voltage between 3.5 and 2.7 V versus Li/Li$^+$ was achieved (Figure 4G). This material was able to cycle for almost 1000 cycles at 5 C, and at least 200 cycles at lower rates in a common LP30 electrolyte, owing to the stability afforded by the polymeric

structure, and full cells with graphite as anode reached 80% of the initial discharge capacity after ~200 cycles (Figure 4H).

2.3 | Anode active materials

The field of n-type organic anode materials has received ever-increasing attention in the last years, thanks to the plethora of possible redox-active compounds at low potential versus lithium offered by organic chemistry.[116,117] After the landmark paper of Armand et al. in 2009 on the redox activity of lithiated terephthalic acid, many researchers became interested in organic anodes, leading to a surge in research on the topic.[30] Nevertheless, there are some pitfalls in evaluating organic anode materials that make it difficult to determine whether a certain molecule or polymer exhibits good performance for practical applications.

In the majority of works in this area, the proposed materials are cycled down to almost 0 V versus Li/Li$^+$, far below the potential at which the redox reaction between lithium and the redox active groups in the molecule or polymer would occur. The great amount of conductive carbon additive when preparing electrodes for the electrochemical tests of organic anodes (usually between 20% and 60%) can then contribute to the specific capacity.

For instance, Liang et al. measured the specific capacity of Super P electrodes as blank electrode measurements, and the conductive additive can reversibly cycle between 200 and 300 mAh g^{-1} in the 0.01–3 V voltage window, depending on the current rate (Figure 5A).[118] Other conductive additives commonly employed, such as graphene or carbon nanotubes, usually display even higher capacities in the same voltage range.[119–121] Since blank electrode measurements are seldom reported in literature, it becomes difficult to evaluate the true specific capacity that can be assigned only to the organic molecule, especially if that molecule tends to dissolve in the electrolyte.

Moreover, at such low potentials, organic anodes tend to show a "superlithiation" behavior, that is, the bonding of lithium with almost all the carbon atoms present in the molecule.[122–124] This extreme lithiation state provides a very high specific capacity, but the reversibility is poor after the first cycle, requiring high overpotentials for the delithiation of the anode. With this phenomenon, impressive specific capacities can be reported (>1000 mAh g^{-1}) but the organic anode has to provide capacity at voltages up to 3 V with a sloping profile, making the final voltage of a hypothetical full cell too low to be of practical utility (Figure 5B).[125–127]

As a result, in our analysis we include only two representative anode materials belonging to this class, whose electrochemical performances can be safely attributed to the electrochemical reaction of the organic molecule, since they are characterized by a well-defined plateau at a voltage >1 V versus Li/Li$^+$, above the potential range where most of the contribution to the capacity of the conductive additive can take place.

The first one is 3,4,9,10-perylene-tetracarboxylic-dianhydride (**PTCLi$_4$**, material 21), which was proposed for the first time as anode material for lithium batteries by Iordache et al.,[128] demonstrating great stability upon cycling, and viable batteries with only 0.5% of multiwalled carbon nanotubes as conductive additive were assembled. In the same work, PTCLi$_4$ managed to achieve 108 mAh g^{-1}, a relatively low value due to the high molecular mass, with a flat potential at ∼1.20 V versus Li/Li$^+$ during charging (Figure 5C,D).

The second one is dilithium terephthalate (**LiTPT**, material 22), the lithium salt of terephthalic acid, introduced by Armand et al. as the first "modern" organic anode.[30] The molecule shows an initial specific capacity of 276 mAh g^{-1}, higher than PTCLi$_4$ due to a lower molar mass, and a voltage plateau with an average value of 0.96 V (Figure 5E,F). LiTPT is less stable than PTCLi$_4$, however, it has the advantage of being synthesized from a widely available precursor, that is, terephthalic acid, the building block of polyethylene terephthalate (PET).

3 | COST AND ENERGY DENSITY ANALYSIS

Until now, organic battery materials were not the focus of thorough techno-economic assessments, despite their cost being one of the main arguments commonly used as an advantage for this type of chemistry. The widespread availability of organic molecules as potential economical precursors to electrode materials is mainly due to the petrochemical industry, and in minor part to bio-derived resources.[17] Although, this does not translate so easily to an inexpensive battery, for two main reasons.

First, the synthesis process of the actual cathode or anode from the precursors can have a very low yield, require expensive catalysts, and/or are not scalable to an industrial production process. For instance, PTO can be theoretically obtained from the oxidation of pyrene, a sub-product of the production of coal.[129] However, the oxidation of the specific sites of the pyrene molecule to obtain the ketone oxygens in the right positions is not easily achievable, and a synthesis route with expensive catalysts and low yield has to be utilized.[130] Recent life cycle assessments on laboratory-scale organic batteries highlighted how the synthesis processes of organic molecules need to be greatly optimized to match the environmental (and cost) performance of commercial battery materials, for instance, by eliminating the use of expensive catalysts and improving the final yield.[22,23] Li et al. listed the projected cost of a variety of organic cathode materials using the data from the reactions found in the literature, and no material had a cost lower than 400 \$ kg^{-1}.[101] It should be remarked that the current cost of lithium-ion battery active materials is in the 10–60 \$ kg^{-1} range, depending on the raw material prices and the market conditions.[8,131] Currently, only a handful of n-type materials are available in large quantities and relatively low price (e.g., benzoquinone, AQ, PTCDA), being already used in other industries. This class of materials is still in its infancy, thus it is understandable that the focus is not yet on the development of large-scale and cost-effective syntheses. Very promising materials can be discovered utilizing lab-scale synthesis methods and their production process optimized to fit an industrial environment.

Second, the cathode or anode cost per unit mass has an influence on the total battery cost. The specific capacity and the average voltage of the materials are fundamental to understand how much material is needed to satisfy the energy and power requirements of the battery pack. A battery built with an organic cathode material with an extremely low cost per unit mass but very poor energy density will require a much higher quantity of active material than in a normal lithium-ion battery. Hence, multiplying mass to specific cost, the final actual

cost of the organic cathode can be higher than the inorganic cathode case. Moreover, lower energy density at the electrode level means that larger batteries have to be built, and costs that scale with the area (e.g., separators, current collectors) and the volume (e.g., electrolyte, casings) of the battery pack will also have a greater impact.

Hence, understanding the actual gravimetric and volumetric energy density that can be obtained in a full-scale battery with n-type organic materials such as cathodes or anodes is fundamental to assess their cost-effectiveness. Thus far, the most detailed energy density assessment of organic batteries was made by Judez et al., where cells were simulated with an in-house algorithm and the influence of binder content, carbon content, electrolyte quantity, N/P ratio, and areal capacity was studied.[132] They used four model organic materials belonging to different chemistries with the specific capacity, one average discharge voltage value, and the density as material properties. They identified the electrolyte/active material ratio as the most important parameter to achieve high energy density organic batteries, but they did not discuss the projected cost of such batteries. A recent review on organic materials from Kim et al. recognized how the potential practical application of such materials should be the main priority.[20] Hence, they reported the electrochemical performances of organic batteries found in literature referring to the whole electrode composition and the related experimental data, and not theoretical values or material-level quantities. Another review from Lu and Chen included a small analysis of the energy density and cost of a 100 kWh, 150 kW battery pack with benzoquinone and dilithium rhodizonate (material 3) as cathodes and lithium metal as anode, as well as with dilithium terephthalate (material 22) and a polydopamine-derived polymer as anodes for NMC 622 batteries.[18] It was found that the polymer-based anode materials have the poorest performance compared with graphite with NMC 622 as cathode, in terms of both the energy density and the cost. Alternatively, comparing a NMC 622-Li battery with benzoquinone and dilithium rhodizonate lithium metal batteries, the former would still be advantageous from every aspect except the cathode active material cost, even when considering the theoretical capacity values for the small organic molecules. The analysis performed in this work uses the BatPaC model software, considering only four materials, no lithium-sufficient cathodes, and the influence of the electrode design on the final results was not assessed.

Herein, we present a detailed cost and energy density analysis of battery packs built with the 22 molecules and polymers represented in Figure 2, dividing between lithium-deficient and lithium-sufficient cathodes. Lithium-deficient cathodes will be simulated with lithium metal as anode and compared with lithium metal batteries with NMC 622 and LFP as cathode. For the organic molecules, the N/P ratio is set to 1.1, while for the inorganic cathodes the same parameter has a value of 0.3.[1] Lithium-sufficient materials will be coupled to graphite, DLT, and PTCLi$_4$ as anodes and compared with lithium-ion batteries with NMC 622 and LFP as cathode and graphite as anode, setting an N/P ratio of 1.1 for all the simulated materials. All the organic batteries will be simulated with two configurations, one with high active material mass loading (96%), similar to the loading of commercial lithium-ion batteries, and one with a lower active material loading (65%), to represent a typical loading of lab-scale studies where a large amount of conductive carbon is usually added. The specific capacity and the voltage profile were obtained from experimental data in relevant publications, while the density values were estimated.

Moreover, in the cost analysis, two additional scenarios will be considered, that is, low and high cost of lithium, to compare the resulting batteries both with the current prices of raw materials and with pre-2022 ones. The cost associated with all the lithium-deficient cathode materials is assumed to be 10 \$ kg^{-1}, while the one for the lithium-sufficient cathode materials and the lithium-containing anodes is 10 \$ kg^{-1} in the low lithium cost scenario, and 20 \$ kg^{-1} in the high lithium cost scenario. Making estimates based on lab-scale synthesis yields and prices for reactants would not be representative of an industrial production scenario for these materials.[60] Hence, we decided to assume a standard, low cost for all the organic materials, slightly lower than the one of LFP pre-2022.

A brief overview of the properties of all the active materials can be found in Table 1, with additional details in Table S1. The summary of the simulation (model, methodology, and assumptions) conditions can be found in Table S2. The employed metrics to evaluate the cost and the performance of the batteries are the pack cost per kWh, in \$ kWh^{-1}, the pack gravimetric energy density, in Wh kg^{-1}, and the pack volumetric energy density, in Wh kg^{-1}. These three pack-level metrics offer a theoretical but comprehensive way to assess the cost, the weight, and the size of the battery packs resulting from the simulations.

We would like to remark that we are using the most optimistic conditions to simulate the organic battery packs, as we assume that the n-type cathodes and anodes would be able to work in the same conditions of commercial lithium-ion batteries (e.g., electrolyte type and quantity, cathode thickness, active material loading, separator type and thickness, pulse resistance). Hence, the following analysis should be interpreted as a best-case scenario for the implementation of such materials in actual battery packs for grid storage.

TABLE 1 List of the organic and inorganic materials included in the cost and energy density analysis.

Type of material	Material code	Classification	Specific capacity (mAh g)	True density (g cm^{-3})	Average potential (V vs. Li/Li$^+$)	Reference(s)
Organic materials	AQ	Lithium-deficient	250	1.31	2.26	[87]
	PTO	Lithium-deficient	362	1.67	2.55	[59]
	DLR	Lithium-deficient	503	1.80[a]	2.18	[29]
	TAPT	Lithium-deficient	306	1.60[a]	2.43	[68]
	C4Q	Lithium-deficient	442	1.30[a]	2.59	[70]
	P5Q	Lithium-deficient	418	1.30[a]	2.60	[71]
	TPB	Lithium-deficient	231	1.60[a]	2.28	[74]
	PTCDA	Lithium-deficient	134	1.71	2.43	[76]
	NDI	Lithium-deficient	167	1.55	2.29	[77]
	IC	Lithium-deficient	97	1.78	2.19	[80,85]
	PBQS	Lithium-deficient	274	1.20[a]	2.68	[97]
	PAQS	Lithium-deficient	199	1.20[a]	2.19	[87]
	PDI	Lithium-deficient	127	1.20[a]	2.46	[100]
	PPA	Lithium-deficient	232	1.20[a]	2.58	[101]
	SPAN	Lithium-deficient	580	1.20[a]	1.78	[102]
	Li$_4$-PTtSA	Lithium-sufficient	111	1.60[a]	2.69	[108]
	Li$_2$-DC-PDSA	Lithium-sufficient	155	1.60[a]	3.24	[108]
	Li$_2$-BQDO	Lithium-sufficient	335	1.30[a]	2.80	[114]
	Li-TCQN	Lithium-sufficient	126	1.60[a]	3.13	[115]
	Li$_2$-Co-PTtSA	Lithium-sufficient	93	1.50[a]	3.09	[110]
	PTCLi$_4$	Anode	108	1.70[a]	1.20	[128]
	LiTPT	Anode	276	1.55	0.96	[30,133]
Inorganic materials	NMC 622	Lithium-sufficient	187	4.65	3.82	[37]
	LFP	Lithium-sufficient	157	3.45	3.40	[37]
	Graphite	Anode	360	2.27	0.14	[37]

[a]Assumed density. When the superscript is not present, the true density is obtained from relevant publications or other available sources.

3.1 | Lithium-deficient cathode materials with lithium metal anode

The summary of the simulation results on the lithium-deficient cathode materials is shown in Figure 6, where the NMC and LFP batteries are indicated in red, and the organic materials in shades of blue. The darker blue shows the low active material content case, while the lighter blue indicates the high active material content case.

The volumetric energy density (Figure 6A) is notably low for all the organic batteries, mostly owing to the low density of the cathode materials (between 1.2 and 1.78 g cm^{-3}), especially when compared with the ones of NMC 622 (4.65 g cm^{-3}) and LFP (3.45 g cm^{-3}). Comparing IC and PDI, despite IC having lower electrochemical performances than PDI in terms of specific capacity and voltage profile, the former's higher density (1.78 vs. 1.2 g cm^{-3}) makes it possible to obtain a pack volumetric energy density of 123 Wh l^{-1} in the high active material content case, while PDI achieves only 117 Wh l^{-1}.

Moreover, the lithium-deficient organic materials require an amount of lithium equal to 110% of the cathode capacity (N/P = 1.1), the latter being completely delithiated. Instead, NMC 622 and LFP already have lithium inside the crystal structure, hence the lithium anode is set to only 30% of the capacity (N/P = 0.3), to act as reserve in case of irreversible lithium loss. Hence, the relatively thick, low density lithium anode required by the organic cathodes further decreases the volumetric energy density.

The gravimetric energy density of the n-type organic batteries is nearer to the inorganic battery performances (Figure 6B), and some small molecules like DLR (200 Wh kg^{-1}) and P5Q (197 Wh kg^{-1}) are at the level of
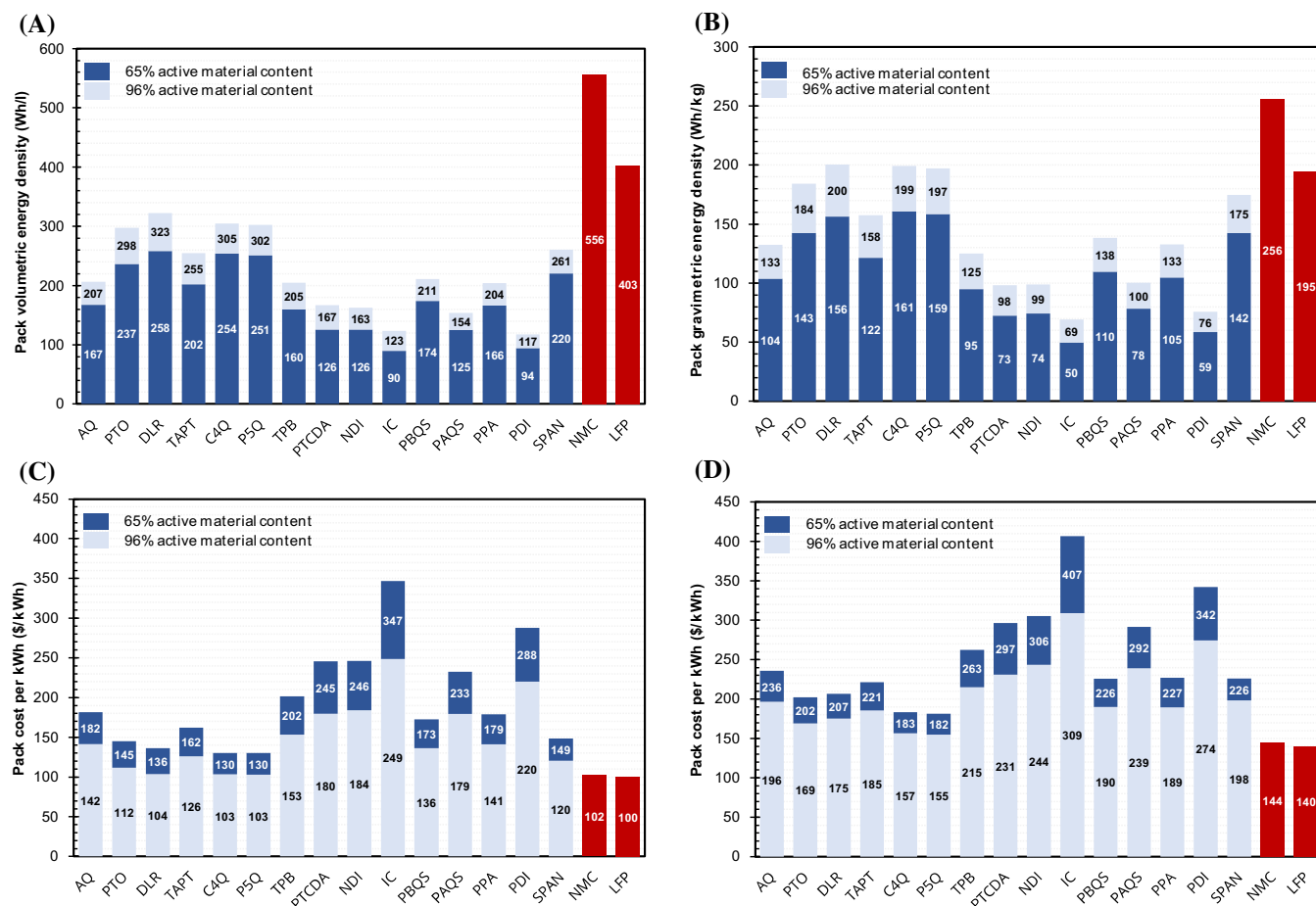
FIGURE 6 Comparison of the (A) pack volumetric energy density, (B) pack gravimetric energy density and pack cost per kWh in the (C) low lithium cost scenario and (D) high lithium cost scenario for the lithium-deficient organic cathode materials (in shades of blue) and inorganic cathodes (in red), both with lithium metal anode.

an LFP lithium metal battery (195 Wh kg^{-1}). Small molecules with lower capacity and/or lower voltage perform poorly, as well as the majority of the polymers, since polymerization of the redox-active monomers usually results in more inactive mass and a decrease of the redox potential. Only the SPAN manages to achieve a relatively high gravimetric energy density (175 Wh kg^{-1}) thanks to the very high specific capacity provided by the reaction between lithium and sulfur. However, when considering a lower, standard active material content in the electrode, these values decrease between 19% and 28%, according to the specific organic compound. Therefore, achieving the highest possible amount of active material in the electrode is crucial to maximize energy density and remain competitive with inorganic systems.

This latter statement can be confirmed when looking at the cost comparison. The same small molecules cited above have the potential of reaching an equal or lower cost than inorganic lithium metal batteries in the low lithium cost scenario and with high active material content, especially considering that

their actual cost could be even lower than the 10 $ kg^{-1} assumed here (Figure 6C). Nevertheless, such small molecules are also the ones that suffer the most from dissolution problems in common electrolytes, and their number of cycles before the end-of-life is two-three orders of magnitude lower than NMC 622 and LFP. A scenario with high lithium cost (Figure 6D) seems to impact organic and inorganic batteries with the same magnitude (+41.2% for NMC 622, +40% for LFP, between 25% and 50% for the organic materials). Despite not containing any lithium in the cathode, and hence not incurring cost increases for the positive electrode, the organic batteries contain more lithium metal in the anode, due to their higher N/P ratio, hence they can be severely affected by a lithium price hike.

In synthesis, DLR, C4Q, and P5Q are the best-performing materials, at the LFP level concerning the gravimetric energy density and the cost per kWh. However, this holds only for the high active material loading case and for the low-lithium cost scenario.
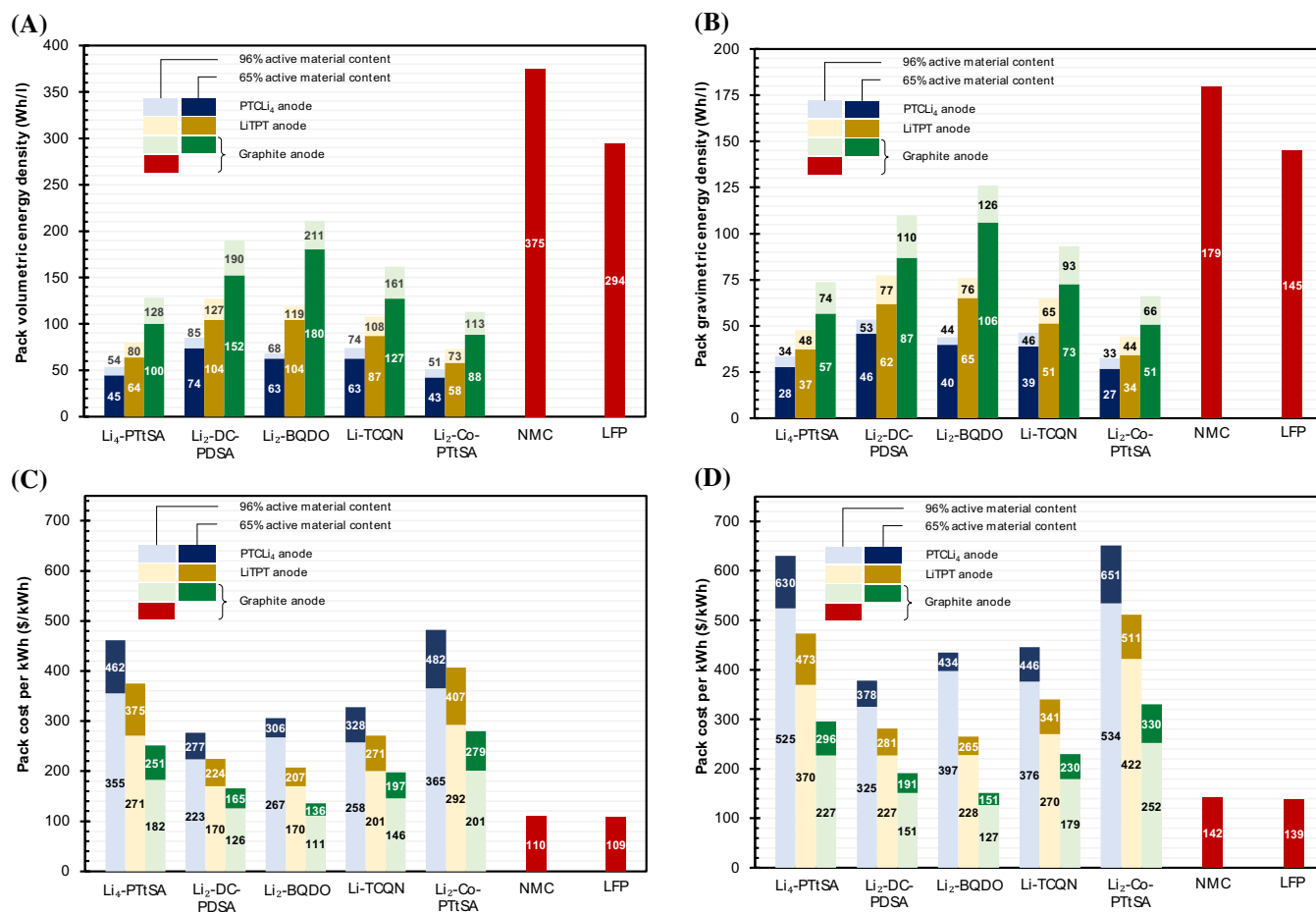
FIGURE 7 Comparison of the (A) pack volumetric energy density, (B) pack gravimetric energy density and pack cost per kWh in the (C) low lithium cost scenario and (D) high lithium cost scenario for the lithium-sufficient organic cathode materials (in shades of blue, yellow, and green) and inorganic cathodes (in red), with different anode materials.

3.2 | Lithium-sufficient cathode materials with graphite and organic anodes

The simulation results for the lithium-sufficient organic cathode batteries are reported in Figure 7, with the NMC and LFP batteries in red. The organic batteries with PTCLi$_4$ as anode are indicated in shades of blue, the ones with LiTPT as anode in shades of yellow, and the ones with graphite as anode in shades of green. The lighter colors represent the high-active material content case, while the darker ones indicate the low-active material content case.

The first comparison can be done between the performance of the different anodes. In all the cases, PTCLi$_4$ displays the poorest performance, LiTPT lies in between and graphite is the superior material. The most straightforward reason can be found in the relatively high average potential of PTCLi$_4$ (1.20 V vs. Li/Li$^+$) and of LiTPT (0.96 V vs. Li/Li$^+$) when compared with the one of graphite (0.14 V vs. Li/Li$^+$). A higher anode potential results in a lower full cell voltage, hence requiring more cathode

and anode active material to achieve the same stored energy of a cell with a higher voltage. Moreover, both organic materials show a lower specific capacity than graphite (360 vs. 108 mAh g^{-1} for PTCLi$_4$ and 276 mAh g^{-1} for LiTPT), another factor that increases the mass of anode needed for the final battery to balance the cathode capacity. Finally, the density of graphite is 50% higher than that of PTCLi$_4$ and 50% higher than LiTPT, which has an influence on the final volumetric energy density and on the cost and weight of the casing required by cells, modules, and pack. The cost of the battery pack is in the first approximation inversely related with the energy density of the pack, evidenced in Figure 7C,D.

Focusing on the performance of the lithium-sufficient cathodes, we can rank the analyzed materials as Li$_2$-BQDO > Li$_2$-DC-PDSA > Li-TCQN > Li$_4$-PTtSA > Li$_2$-Co-PTtSA. Similar to the lithium-deficient materials analysis, the volumetric energy density of the organic batteries is much inferior compared with those of the inorganic batteries (Figure 7A), due to the low density of the organic materials.

Li_2-BQDO possesses a very high specific capacity (335 mAh g^{-1}) and a good average voltage when discharging (2.80 V vs. Li/Li$^+$, thus achieving 126 Wh kg^{-1} when coupled with graphite, which is still much lower than NMC 622 (179 Wh kg^{-1}), but near to LFP (145 Wh kg^{-1}; Figure 7B). Remarkably, the projected cost per kWh of a Li_2-BQDO/graphite battery in the high active material content case and the high lithium cost scenario is lower than the cost of both NMC 622 and LFP batteries (127 vs. 142 \$ kWh^{-1} for NMC 622 and 139 \$ kWh^{-1} for LFP). Also, in the low lithium cost scenario, the cost of the organic battery is similar to the inorganic ones. These numbers should not be interpreted as a unequivocal superiority of this material over commercial lithium-ion batteries, but as an indication that Li_2-BQDO (or a material with similar/superior properties) could be a promising candidate for a cost-effective organic battery, especially in situations of lithium price hike.

Li_2-Co-PTtSA displays the highest cycling stability among the lithium-sufficient ones, possesses the lowest energy density and cost per kWh in all the scenarios and configurations. Nevertheless, its performances are only slightly inferior than the corresponding monomer Li_4-PTtSA.

Overall, graphite could be the best choice as anode for the lithium-sufficient organic materials, since it ensures higher volumetric and gravimetric energy density and could enable cost-competitive organic batteries with high capacity, high voltage molecules as Li_2-BQDO, especially in the case of a high-cost lithium scenario.

4 | ORGANIC ELECTRODE DESIGN

To study the influence of specific electrode design parameters in relation to the results of the energy density and cost modeling, we simulated with BatPaC four organic battery configurations: one lithium-deficient cathode (P5Q) with lithium metal anode and one lithium-sufficient cathode (Li_2-BQDO) with three anode materials (graphite, LiTPT, and PTCLi$_4$). The simulations were made by varying three design parameters, that is, the amount of conductive additive, the active material mass loading, and the electrode density.

4.1 | Influence of the conductive additive content in the electrode

As demonstrated in the results reported in Section 3 in Figures 6 and 7, maximizing the weight fraction of active material in the positive electrode is fundamental to achieve the highest energy density and lowest cost for the organic battery packs, to be competitive with lithium metal and lithium-ion batteries based on inorganic cathodes. However, since organic materials are usually poor electronic conductors, a high amount of conductive carbon is usually added to the electrode to obtain a working electrode.[134]

Lu and Chen reported the electronic conductivity of a variety of organic materials, which was found to vary widely between 10^{-15} and 10^{-3} S cm^{-1}, but the vast majority of the analyzed n-type materials had a conductivity in the 10^{-11}–10^{-7} S cm^{-1} range.[18] Lithium metal oxides usually display an electronic conductivity >10^{-6} S cm^{-1}, and a small amount of carbon is normally necessary to ensure good performance (2%–4% of the weight of the electrode). Some inorganic lithium compounds are characterized by much lower conductivities, such as lithium titanium oxide (10^{-13} S cm^{-1}) or lithium iron phosphate (10^{-9} S cm^{-1}), but strategies such as carbon coating and nanosizing of the electrode particles enable these materials to be viable for commercial applications with the same amount of carbon as the other metal oxides.[135,136]

For organic materials, using conductive additives with high aspect ratios such as carbon nanotubes or high surface area such as graphene, graphene oxide, and reduced graphene oxide has been reported to be an effective strategy to decrease the amount of necessary carbon in the electrode.[91,137–139] The optimization of the electrode preparation, often overlooked in fundamental studies on new materials, was also beneficial.[85,128,140]

From the results of the simulations (Figure 8), we observe that, in all the battery configurations, as the amount of conductive additive in the organic electrodes increases, the decrease in gravimetric and volumetric energy density, as well as the increase in pack cost, become more pronounced. Keeping the fraction of binder constant, when the conductive additive fraction increases, the active material fraction decreases, and with a fixed thickness of the electrode, this results in a decrease of the active material loading. Hence, the areas of the electrodes must increase to achieve the design capacity, and all the costs directly related to the area of the battery (separators, current collectors) will also rise. The electrode preparation becomes more expensive too, since a bigger area has to be coated, and the costs for binders, conductive additives, and solvent for the slurry will have a greater impact. For the P5Q/Li metal battery and the Li_2-BQDO/graphite battery (Figure 8A,B), an increase of 5% of the weight fraction of carbon in the cathode corresponds to an average cost increase of ∼4%, and an average decrease of volumetric and gravimetric energy density, respectively, of ∼3.5% and 3%.
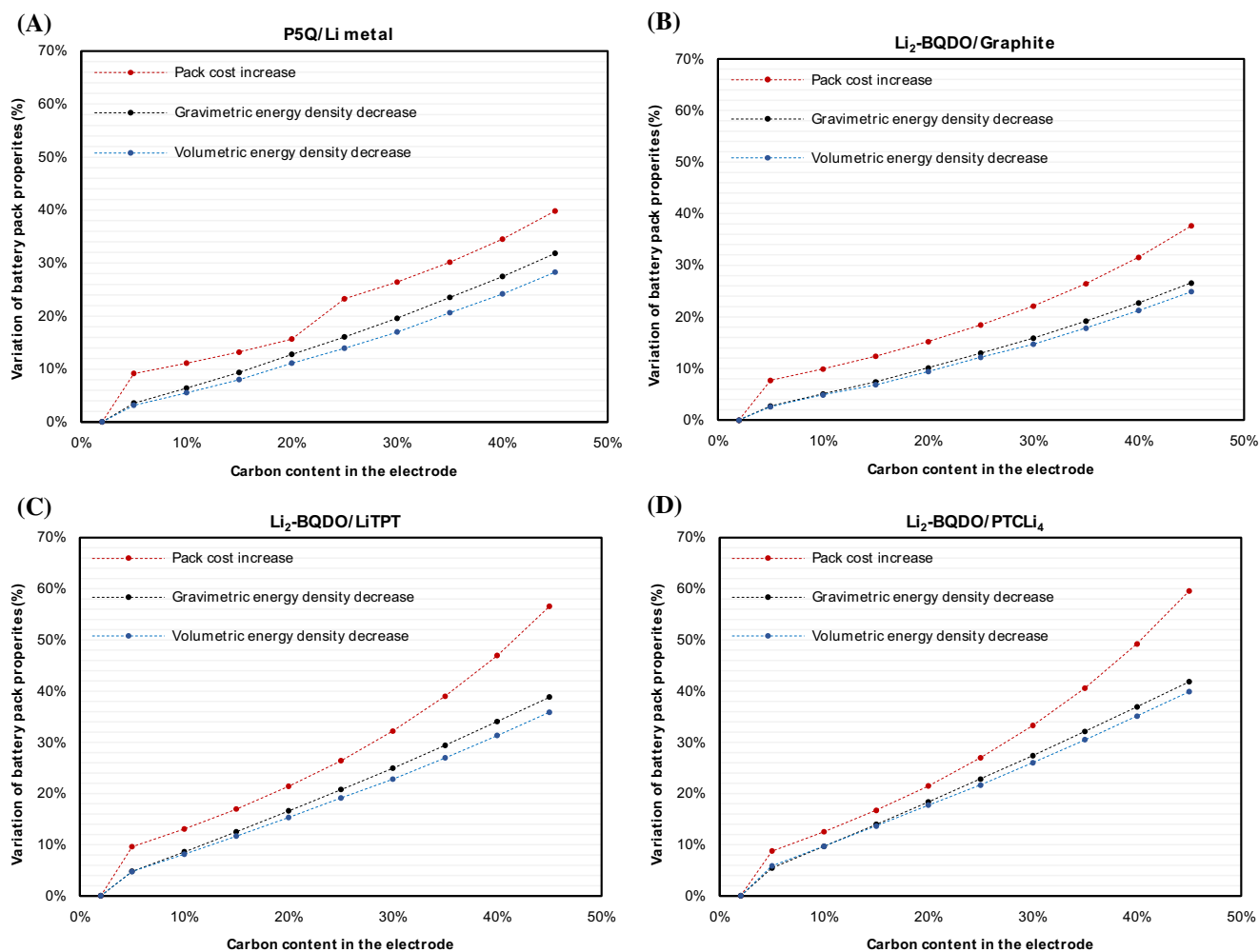
FIGURE 8 The influence of the carbon content in the electrode(s) on the battery pack properties for (A) a P5Q/Li metal battery, (B) a Li$_2$-BQDO/Graphite battery, (C) a Li$_2$-BQDO/LiTPT battery, and (D) a Li$_2$-BQDO/PTCLi$_4$ battery. The percentage variation of the battery pack properties refers to the case with the lowest amount of carbon. For the Li$_2$-BQDO/LiTPT battery and the Li$_2$-BQDO/PTCLi$_4$ battery, the carbon content is also increased in the negative electrode.

We identify how the fully organic batteries, that is, Li$_2$-BQDO/LiTPT and Li$_2$-BQDO/PTCLi$_4$, are greatly affected by a higher amount of conductive additive in the electrodes (Figure 8C,D). For these two configurations, we considered that both anode and cathode are affected by the carbon addition. Hence, for a full organic cell, the average cost increment for each 5% step increase of conductive additive is ~6%, while the volumetric and gravimetric energy decreases are around 4.5% and 4%, respectively.

4.2 | Influence of the active material mass loading

Maximizing the weight fraction of active material in the electrode is not the only means to obtain practical batteries, since a high active material mass loading is also necessary to optimize the utilization of the available space in the battery pack. Electrodes with a thickness between 30 and 90 μm are standard for commercial lithium ion batteries, according to the application and the specific material, corresponding to mass loadings between 5 and 20 mg cm^{-2}.[141,142]

For organic battery materials, active material mass loadings found in the literature are often below 1 mg cm^{-2}, but to achieve high energy densities, the target should be higher than 10 mg cm^{-2}, to achieve areal capacities similar to those of inorganic materials. However, due to the low density of organic materials, such a mass loading results in a relatively high electrode thickness. For example, in the four battery configurations shown in Figure 9, the highest mass loading is 11.37 mg cm^{-2}, corresponding to a cathode thickness of 120 μm, yet such thick electrodes incur problems related to the severely increased mass transport resistance in the porous electrode.[143]
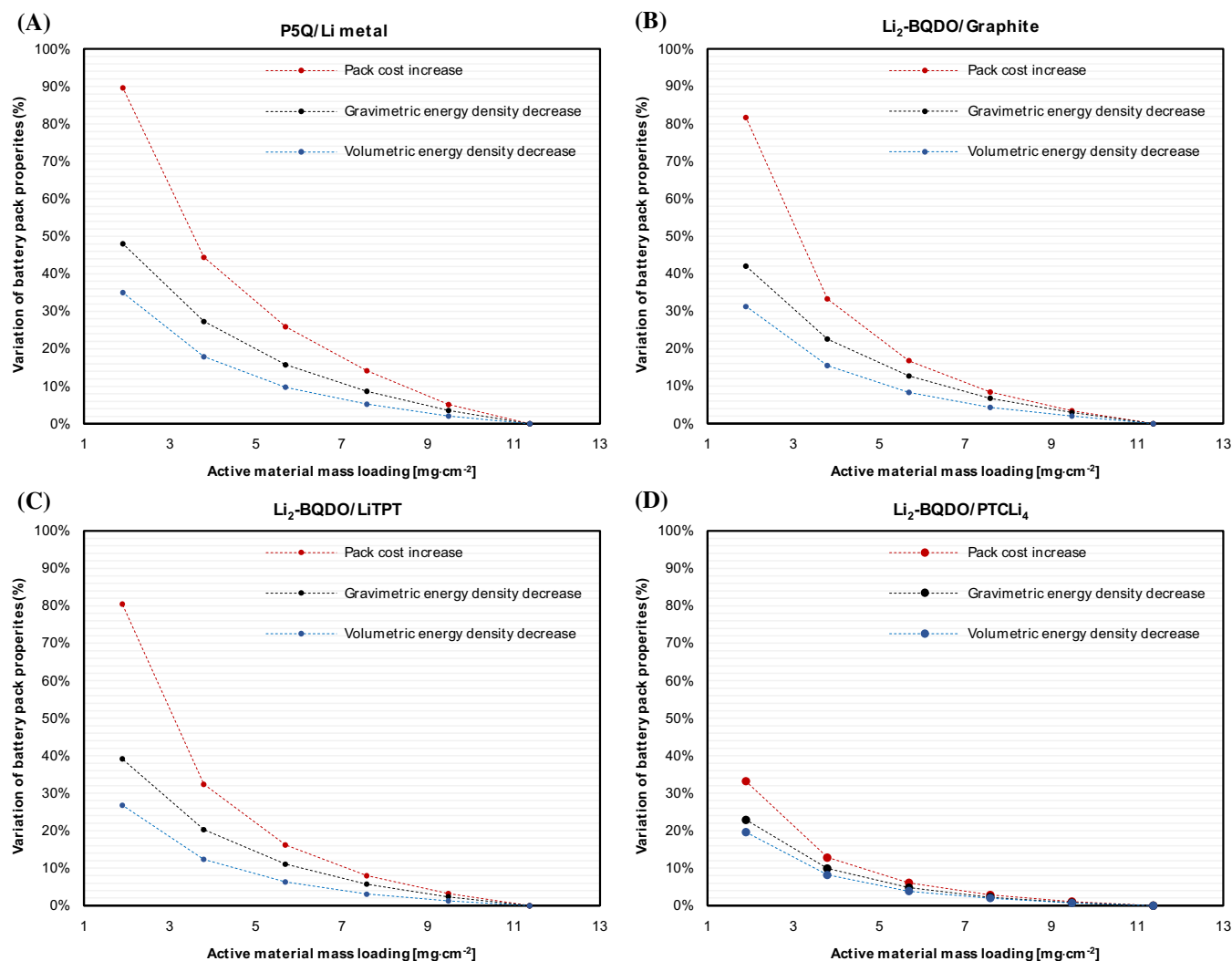
FIGURE 9 The influence of the active material mass loading of the cathode on the battery pack properties for (A) a P5Q/Li metal battery, (B) a Li_2-BQDO/Graphite battery, (C) a Li_2-BQDO/LiTPT battery, and (D) a Li_2-BQDO/PTCLi$_4$ battery. The percentage variation of the battery pack properties refers to the case with the highest active material mass loading.

The importance of the mass loading, and hence of the areal capacity, to compete with commercial technologies was recognized by Molina et al., which developed a conjugated microporous n-type polymer as cathode for lithium batteries and engineered the cathode to achieve mass loadings between 9 and 60 mg cm^{-2}, using single-walled carbon nanotubes and reduced graphene oxide as conductive additives.[91] Iordache et al. studied PTCLi$_4$ and reported electrodes with an active material mass loading up to 12 mg cm^{-2}, obtained by minimizing the quantity of multiwalled carbon nanotubes used as electronically conducting agent.[128] Also, the works from the Vlad group on lithium-sufficient organic materials showed the possibility of constructing viable batteries with mass loadings up to 50 mg cm^{-2}.[108,110]

By decreasing the maximum cathode thickness, we simulated the decrease of the active material mass loading in the four organic battery configurations, and the effect that this design parameter has on the energy density and the cost of the battery pack (Figure 9). For all cases, the result is an overall worsening of the battery pack properties, which becomes more intense when the mass loading decreases further. The cause of the decrease of volumetric and gravimetric energy density and the rise in cost are similar to the one of the carbon content in the electrode, that is, the electrode surface needs to increase to meet the design requirements due to the lower capacity per unit area.

The Li_2-BQDO/PTCLi$_4$ battery suffers the mildest consequences from the decrease of the active material mass loading of the cathode (Figure 9D). At the lowest simulated mass loading (1.90 mg cm^{-2}), the cost of the battery pack increases only 33% compared with the base case at 11.37 mg cm^{-2}, compared with the +91% of the P5Q/Li metal battery, +84% of the Li_2-BQDO/graphite battery, and +82% of the Li_2-BQDO/LiTPT battery
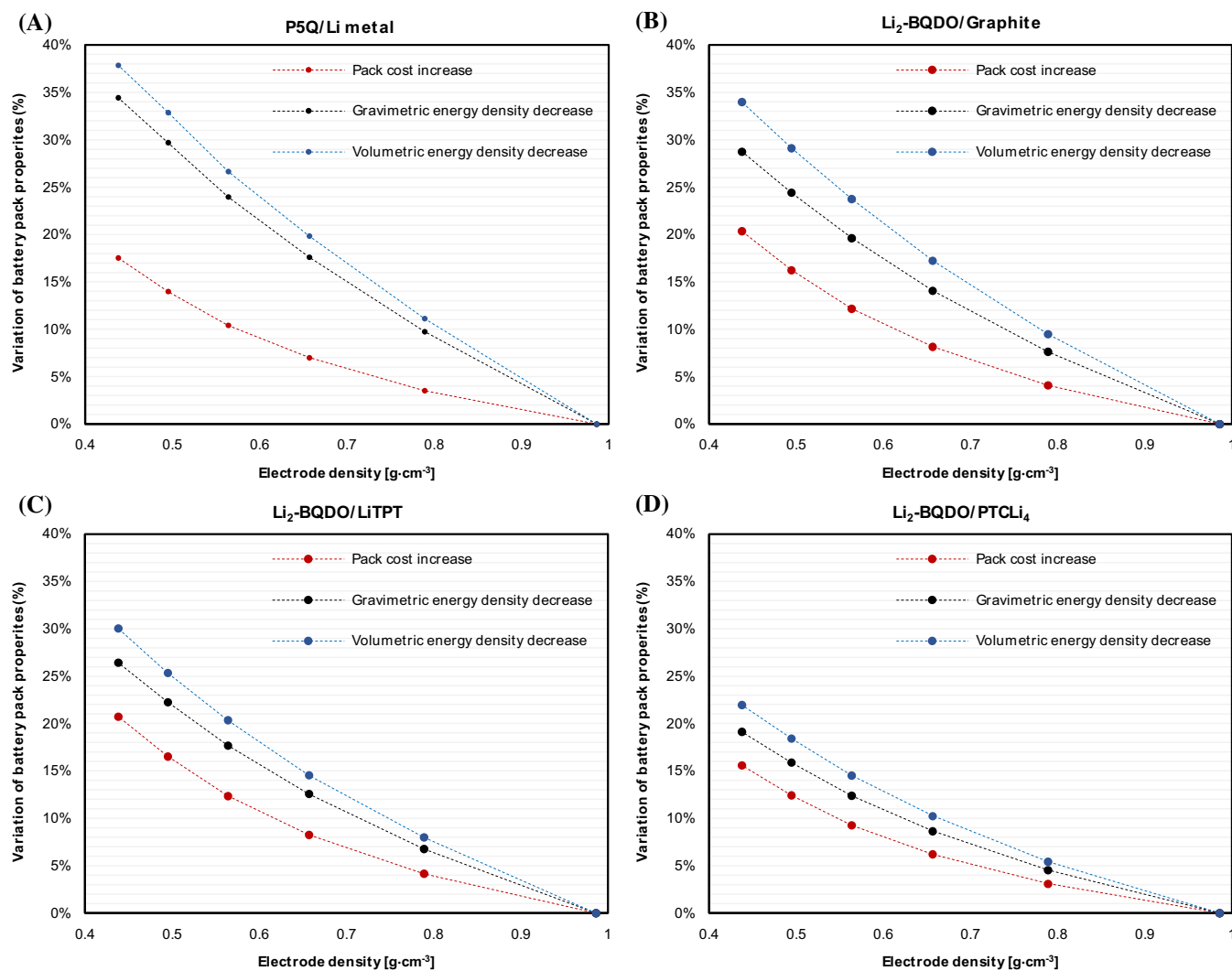
FIGURE 10 The influence of the cathode density on the battery pack properties for (A) a P5Q/Li metal battery, (B) a Li_2-BQDO/graphite battery, (C) a Li_2-BQDO/LiTPT battery, and (D) a Li_2-BQDO/PTCLi$_4$ battery. The percentage variation of the battery pack properties refer to the case with the highest cathode density.

(Figure 9B–D, respectively). The reason for the relatively small cost increase (and energy density decrease) for the Li_2-BQDO/PTCLi$_4$ battery is that together with the cathode, the anode thickness also decreases, due to the lower capacity that must be balanced. Since the low-density PTCLi$_4$ anode has a modest specific capacity compared with the other anodes and to Li_2-BQDO (Table 1), its thickness decreases far more than the cathode, partially offsetting the detrimental effects of the cathode active material loading reduction.

4.3 | Influence of the electrode density

Finally, the density of the organic electrodes plays a pivotal role in the optimization of the energy density and cost of the battery. Organic materials tend to have intrinsically lower density than inorganic ones,[18] due to the light elements they are composed of, thus placing them at a disadvantage when considering the size of the battery pack. The density of the final electrode obtained from the organic active material also takes into account the densities of the conductive carbon and binder, as well as the porosity of the electrode. This last parameter is fundamental to achieve the best performance of the final battery: the porosity is the necessary empty space required to hold the electrolyte in the electrode, a space that could theoretically be filled with active material, thereby increasing the energy stored in the same volume of electrode. Hence, a high porosity results in an overall lower energy density of the cell, but it assures a good wetting of the electrode with the electrolyte. A low porosity is good to maximize the energy density and to improve the electronic

conductivity, but it can affect the rate performance in case of insufficient electrolyte quantity.[144]

For instance, in the study from Molina et al. the density of the organic cathode obtained with the buckypaper technique was estimated to be 0.2 g cm^{-3}, resulting in electrodes thicker than 3 mm and with a porosity of ∼70% to achieve 60 mg cm^{-2} active material loading.[91] However, commercial lithium-ion battery cathodes are usually limited to maximum 120 μm of thickness for high-energy configurations,[37] to avoid an excessive increase of the mass transport resistance and the cracking of the electrode after coating and drying, and the porosity is usually in the 20%–30% range. High thickness and porosity could cause manufacturing problems and the need for an excessive quantity of electrolyte to fill the electrode void space. Lombardo et al. studied the influence of the electrode porosity for disodium biphenyl-4,4′-dicarboxylate, a n-type organic anode for sodium-ion batteries, by varying the compression ratio of the electrode after calendering.[145] They found that the higher the compression ratio (i.e., the lower the porosity), the higher the specific capacity at all current rates, which they interpreted as a result of the improvement of the electronic conductivity of the electrode.

To understand the impact of the electrode density on the cost and energy density results, the same four organic batteries were simulated increasing the cathode porosity while keeping the same active material loading, hence increasing the thickness of the positive electrode (Figure 10). In this case the volumetric energy density is the parameter most affected by a decrease of the electrode density, followed closely by the gravimetric energy density. The evident effect of a lower electrode density is to increase the volume of the whole battery pack, jeopardizing the volumetric energy density. The gravimetric energy density decreases too, because of the increased weight caused by the additional electrolyte required to fill the porosity of the cathode and from the bigger metal casings of cells, modules, and pack.

The cost per kWh increases the least in the P5Q/Li metal battery, but this configuration also experiences the largest decrease of both energy densities with the electrode density (Figure 10A). Since the lithium metal anode is a thin and compact layer, if the density of the cathode decreases, the overall energy density will be more affected than the other organic batteries (Figure 10B–D), where the contribution to the size and the mass of the cells is shared equally between the two porous electrodes.

5 | CONCLUSIONS

The n-type organic materials have emerged as a promising alternative to inorganic materials for energy storage applications, especially considering the high demand and limited supply of critical minerals required for lithium-ion batteries. They are widely regarded as a low-cost solution due to the abundance of organic elements and molecules, but for the determination of the actual cost in a battery, other factors such as specific capacity, voltage profile, density, and electrode design also play a fundamental role in determining the practicality and potential of n-type organic materials for battery applications. Organic materials are typically classified based on their constituent elements and functional groups, however, we have proposed a practical criterion for categorizing them, that is, whether they require a lithium-metal anode.

To assess the cost-effectiveness of n-type organic materials, it is crucial to understand the actual energy density that can be obtained in a full-scale battery. The analysis made using BatPaC has demonstrated that maximizing the amount of active material in the electrode is crucial to achieving performances that can compete with inorganic systems. The best-performing materials were found to be small molecules, that usually exhibit the lowest capacity retention, highlighting the need for further research efforts in terms of the stabilization during the cycling of such molecules in batteries, through molecular engineering and/or electrolyte formulation. Air-stable, lithium-sufficient materials, despite being inferior from the energy density point of view, could become cost-effective materials competing with inorganic chemistries.

The study of the electrode design highlighted the importance of obtaining an extremely dense high active material mass loading electrode to maximize the organic battery energy density. Relatively small deviations from the optimal configuration are not so impactful (for instance, using 90% active material instead of 96% in the electrode), and they could be necessary to obtain viable organic-based cathodes and anodes. However, efforts are required to avoid the use of double-digit weight fractions of conductive carbon.

Overall, while n-type organic materials have potential as a low-cost and sustainable solution for energy storage, further research is necessary to optimize the synthesis process and the electrode design, as well as to improve their energy density and stability during operation. We would like to stress that an abundancy in the raw materials cannot be automatically translated in an inexpensive active material, and there is a need for a more holistic view when assessing the scalability of new (organic) materials for batteries that target large-scale commercial application. We recommend implementing the evaluation of the practicality and cost-effectiveness of organic materials in full-scale battery packs using detailed energy density and cost simulations, with optimistic assumptions for their potential scale-up in a commercial setup. This practice can provide pivotal insights into the viability of organic materials for future battery technologies.

CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

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REFERENCES

1. Schmuch R, Wagner R, Hörpel G, Placke T, Winter M. Performance and cost of materials for lithium-based rechargeable automotive batteries. *Nat Energy*. 2018;3(4):267-278.
2. Cano ZP, Banham D, Ye S, et al. Batteries and fuel cells for emerging electric vehicle markets. *Nat Energy*. 2018;3(4):279-289.
3. Zhu Z, Jiang T, Ali M, et al. Rechargeable batteries for grid scale energy storage. *Chem Rev*. 2022;122(22):16610-16751.
4. Tian Y, Zeng G, Rutt A, et al. Promises and Challenges of Next-Generation "Beyond Li-ion" Batteries for Electric Vehicles and Grid Decarbonization. *Chem Rev*. 2021;121(3):1623-1669.
5. Greim P, Solomon AA, Breyer C. Assessment of lithium criticality in the global energy transition and addressing policy gaps in transportation. *Nat Commun*. 2020;11(1):4570.
6. IEA. Grid-Scale Storage. Accessed June 8, 2023. https://www.iea.org/reports/grid-scale-storage
7. IEA. *Trends in Batteries – Global EV Outlook 2023 – Analysis*. Accessed May 28, 2023. https://www.iea.org/reports/global-ev-outlook-2023/trends-in-batteries
8. Zuo W, Innocenti A, Zarrabeitia M, Bresser D, Yang Y, Passerini S. Layered oxide cathodes for sodium-ion batteries: storage mechanism, electrochemistry, and techno-economics. *Acc Chem Res*. 2023;56(3):284-296.
9. Rudola A, Sayers R, Wright CJ, Barker J. Opportunities for moderate-range electric vehicles using sustainable sodium-ion batteries. *Nat Energy*. 2023;8:215-218.
10. Whittingham MS. Special editorial perspective: beyond Li-ion battery chemistry. *Chem Rev*. 2020;120(14):6328-6330.
11. Duffner F, Kronemeyer N, Tübke J, Leker J, Winter M, Schmuch R. Post-lithium-ion battery cell production and its compatibility with lithium-ion cell production infrastructure. *Nat Energy*. 2021;6(2):123-134.
12. Tapia-Ruiz N, Robert Armstrong A, Alptekin H, et al. 2021 roadmap for sodium-ion batteries. *J Phys Energy*. 2021;3(3):031503.
13. Maroni F, Dongmo S, Gauckler C, Marinaro M, Wohlfahrt-Mehrens M. Through the maze of multivalent-ion batteries: a critical review on the status of the research on cathode materials for Mg^{2+} and Ca^{2+} ions insertion. *Batter Supercaps*. 2021;4(8):1221-1251.
14. Elia GA, Kravchyk KV, Kovalenko MV, Chacón J, Holland A, Wills RGA. An overview and prospective on Al and Al-ion battery technologies. *J Power Sources*. 2021;481:228870.
15. Zhu K, Wang C, Chi Z, et al. How far away are lithium-sulfur batteries from commercialization? *Front Energy Res*. 2019;7:123.
16. Muench S, Wild A, Friebe C, Häupler B, Janoschka T, Schubert US. Polymer-based organic batteries. *Chem Rev*. 2016;116(16):9438-9484.
17. Liang Y, Yao Y. Positioning organic electrode materials in the battery landscape. *Joule*. 2018;2(9):1690-1706.
18. Lu Y, Chen J. Prospects of organic electrode materials for practical lithium batteries. *Nat Rev Chem*. 2020;4(3):127-142.
19. Esser B, Dolhem F, Becuwe M, Poizot P, Vlad A, Brandell D. A perspective on organic electrode materials and technologies for next generation batteries. *J Power Sources*. 2021;482:228814.
20. Kim J, Kim Y, Yoo J, Kwon G, Ko Y, Kang K. Organic batteries for a greener rechargeable world. *Nat Rev Mater*. 2022;8(1):54-70.
21. Nguyen TP, Easley AD, Kang N, et al. Polypeptide organic radical batteries. *Nature*. 2021;593(7857):61-66.
22. Zhang S, Ericsson N, Sjödin M, Karlsson Potter H, Hansson PA, Nordberg Å. Prospective life cycle assessment of a flexible all-organic battery. *J Clean Prod*. 2022;373:133804.
23. Zhang S, Ericsson N, Hansson PA, Sjödin M, Nordberg Å. Life cycle assessment of an all-organic battery: hotspots and opportunities for improvement. *J Clean Prod*. 2022;337:130454.
24. Erakca M, Pinto Bautista S, Moghaddas S, et al. Closing gaps in LCA of lithium-ion batteries: LCA of lab-scale cell production with new primary data. *J Clean Prod*. 2023;384:135510.
25. Poizot P, Gaubicher J, Renault S, Dubois L, Liang Y, Yao Y. Opportunities and challenges for organic electrodes in electrochemical energy storage. *Chem Rev*. 2020;120(14):6490-6557.
26. Miller JS. Conducting polymers: materials of commerce (Part I). *Adv Mater*. 1993;5(7-8):587-589.
27. Miller JS. Conducting polymers: materials of commerce (Part II). *Adv Mater*. 1993;5(9):671-676.
28. Nakahara K, Iwasa S, Satoh M, et al. Rechargeable batteries with organic radical cathodes. *Chem Phys Lett*. 2002;359(5-6):351-354.
29. Chen H, Tarascon JM. From biomass to a renewable $Li_xC_6O_6$ organic electrode for sustainable Li-Ion batteries. *ChemSusChem*. 2008;1:348-355.
30. Armand M, Grugeon S, Vezin H, et al. Conjugated dicarboxylate anodes for Li-ion batteries. *Nat Mater*. 2009;8(2):120-125.
31. Goujon N, Casado N, Patil N, Marcilla R, Mecerreyes D. Organic batteries based on just redox polymers. *Prog Polym Sci*. 2021;122:101449.
32. Deuchert K, Hünig S. Multistage organic redox systems—A general structural principle. *Angew Chem Int Ed Engl*. 1978;17(12):875-886.
33. Kye H, Kang Y, Jang D, Kwon JE, Kim BG. P-type redox-active organic electrode materials for next-generation rechargeable batteries. *Adv Energy Sustain Res*. 2022;3(8):2200030.

34. Thomas-Alyea KE, Aryanpour M. Design of composite electrodes with anion-absorbing active materials. *J Electrochem Soc*. 2016;164(1):A6017.

35. Sun T, Sun QQ, Yu Y, Zhang XB. Polypyrrole as an ultrafast organic cathode for dual-ion batteries. *eScience*. 2021;1(2):186-193.

36. Miroshnikov M, Mahankali K, Thangavel NK, et al. Bioderived molecular electrodes for next-generation energy-storage materials. *ChemSusChem*. 2020;13(9):2186-2204.

37. Nelson PA, Ahmed S, Gallagher KG, Dees DW. *Modeling the Performance and Cost of Lithium-Ion Batteries for Electric-Drive Vehicles*. 3rd ed. Argonne National Laboratory (ANL); 2019.

38. Han C, Li H, Shi R, et al. Organic quinones towards advanced electrochemical energy storage: recent advances and challenges. *J Mater Chem A Mater Energy Sustain*. 2019;7(41):23378-23415.

39. Yang H, Lee J, Cheong JY, et al. Molecular engineering of carbonyl organic electrodes for rechargeable metal-ion batteries: fundamentals, recent advances, and challenges. *Energy Environ Sci*. 2021;14(8):4228-4267.

40. Zhang Z, Ma J, Zhang R, et al. Oxocarbons electrode materials for alkali ion batteries: challenges, strategies and development. *Batter Supercaps*. 2021;4(12):1791-1802.

41. Esser B. Redox polymers as electrode-active materials for batteries. *Org Mater*. 2019;1(1):63-70.

42. Dai G, Wu T, Chen H, Zhao Y. Quaternary nitrogen redox centers for battery materials. *Curr Opin Electrochem*. 2021;29:100745.

43. Banerjee A, Khossossi N, Luo W, Ahuja R. Promise and reality of organic electrodes from materials design and charge storage perspective. *J Mater Chem A Mater Energy Sustain*. 2022;10(29):15215-15234.

44. Wang DY, Guo W, Fu Y. Organosulfides: an emerging class of cathode materials for rechargeable lithium batteries. *Acc Chem Res*. 2019;52(8):2290-2300.

45. Shadike Z, Tan S, Wang QC, et al. Review on organosulfur materials for rechargeable lithium batteries. *Mater Horiz*. 2021;8(2):471-500.

46. Zou R, Liu W, Ran F. Sulfur-containing polymer cathode materials: from energy storage mechanism to energy density. *InfoMat*. 2022;4(8):e12319.

47. Zhang B, Zhang Y, Yang X, et al. Isometric thionated naphthalene diimides as organic cathodes for high capacity lithium batteries. *Chem Mater*. 2020;32(24):10575-10583.

48. Zhang B, Yang X, He B, et al. Thionated benzo[c]thiophen-1(3H)-one as an organic cathode with high capacity for sulfur-rich all organic lithium-ion batteries. *J Mater Chem A Mater Energy Sustain*. 2021;9(25):14444-14450.

49. Wu M, Zhou Z. Covalent organic frameworks as electrode materials for rechargeable metal-ion batteries. *Interdiscip Mater*. 2023;2(2):231-259.

50. Wang Z, Hu J, Lu Z. Covalent organic frameworks as emerging battery materials. *Batter Supercaps*. 2023;6(4):e200200545.

51. Zhao R, Liang Z, Zou R, Xu Q. Metal-organic frameworks for batteries. *Joule*. 2018;2(11):2235-2259.

52. Mehek R, Iqbal N, Noor T, et al. Metal-organic framework based electrode materials for lithium-ion batteries: a review. *RSC Adv*. 2021;11(47):29247-29266.

53. Kahsay BA, Ramar A, Wang FM, et al. Investigating an all-organic battery using polyisothianaphthene as a redox-active bipolar electrode material. *J Power Sources*. 2019;428:115-123.

54. Kim JK. Single- and double-redox reaction of poly(2,-2,6,6-tetramethylpiperidinyloxy-4-vinylmethacrylate)/ordered mesoporous carbon composite nitroxide radical polymer battery. *J Power Sources*. 2020;477:228670.

55. Feng X, Wu X, Chen X, et al. A bipolar organic molecule toward a universal pseudocapacitive cathode for stable dual ion charge storage. *Energy Storage Mater*. 2021;42:454-463.

56. Schnell J, Knörzer H, Imbsweiler AJ, Reinhart G. Solid versus liquid—A bottom-up calculation model to analyze the manufacturing cost of future high-energy batteries. *Energ Technol*. 2020;8(3):1901237.

57. Lu Y, Zhang Q, Li F, Chen J. Emerging lithiated organic cathode materials for lithium-ion full batteries. *Angew Chem Int Ed Engl*. 2023;62(7):e202216047.

58. Song Z, Qian Y, Liu X, et al. A quinone-based oligomeric lithium salt for superior Li–organic batteries. *Energy Environ Sci*. 2014;7(12):4077-4086.

59. Liang Y, Zhang P, Chen J. Function-oriented design of conjugated carbonyl compound electrodes for high energy lithium batteries. *Chem Sci*. 2013;4(3):1330-1337.

60. Dieterich V, Milshtein JD, Barton JL, Carney TJ, Darling RM, Brushett FR. Estimating the cost of organic battery active materials: a case study on anthraquinone disulfonic acid. *Transl Mater Res*. 2018;5(3):034001.

61. Gregory TD, Perry ML, Albertus P. Cost and price projections of synthetic active materials for redox flow batteries. *J Power Sources*. 2021;499:229965.

62. Cui H, Hu P, Zhang Y, Huang W, Li A. Research progress of high-performance organic material pyrene-4,5,9,10-tetraone in secondary batteries. *ChemElectroChem*. 2021;8(2):352-359.

63. Yokoji T, Matsubara H, Satoh M. Rechargeable organic lithium-ion batteries using electron-deficient benzoquinones as positive-electrode materials with high discharge voltages. *J Mater Chem A Mater Energy Sustain*. 2014;2(45):19347-19354.

64. Ravet N, Michot C, Armand M. Novel cathode materials based on organic couples for lithium batteries. *MRS Online Proc Library*. 1997;496:263-273.

65. Kim H, Seo DH, Yoon G, et al. The reaction mechanism and capacity degradation model in lithium insertion organic cathodes, $Li_2C_6O_6$, using combined experimental and first principle studies. *J Phys Chem Lett*. 2014;5(17):3086-3092.

66. Shimizu A, Kuramoto H, Tsujii Y, et al. Introduction of two lithiooxycarbonyl groups enhances cyclability of lithium batteries with organic cathode materials. *J Power Sources*. 2014;260:211-217.

67. Sieuw L, Jouhara A, Quarez É, et al. A H-bond stabilized quinone electrode material for Li-organic batteries: the strength of weak bonds. *Chem Sci*. 2019;10(2):418-426.

68. Li Z, Jia Q, Chen Y, et al. A small molecular symmetric all-organic lithium-ion battery. *Angew Chem Int Ed Engl*. 2022;61(33):e202207221.

69. Zhang M, Zhang Y, Huang W, Zhang Q. Recent progress in calix[n]quinone (n = 4, 6) and pillar[5]quinone electrodes for secondary rechargeable batteries. *Batter Supercaps*. 2020;3(6):476-487.

70. Huang W, Zhu Z, Wang L, et al. Quasi-solid-state rechargeable lithium-ion batteries with a calix[4]quinone cathode and gel polymer electrolyte. *Angew Chem Int Ed Engl*. 2013;52(35):9162-9166.

71. Zhu Z, Hong M, Guo D, Shi J, Tao Z, Chen J. All-solid-state lithium organic battery with composite polymer electrolyte

and pillar[5]quinone cathode. *J Am Chem Soc*. 2014;136(47): 16461-16464.

72. Sun H, Xiong W, Zhou W, Zhang W, Wang L, Huang W. High performance lithium-ion batteries with pillar[5]quinone/ion-liquid system. *Org Electron*. 2020;83:105743.

73. Sun H, Zhang X, Zhang M, Lv J, Wang L, Huang W. High-performance organic lithium-ion battery with plastic crystal electrolyte. *Org Electron*. 2020;87:105966.

74. Luo Z, Liu L, Zhao Q, Li F, Chen J. An insoluble benzoquinone-based organic cathode for use in rechargeable lithium-ion batteries. *Angew Chem Int Ed Engl*. 2017;56(41): 12561-12565.

75. Yao M, Sano H, Ando H, Kiyobayashi T, Takeichi N. Anthra-quinone-based oligomer as a long cycle-life organic electrode material for use in rechargeable batteries. *ChemPhysChem*. 2019;20(7):967-971.

76. Delaporte N, Lajoie G, Collin-Martin S, Zaghib K. Toward low-cost all-organic and biodegradable li-ion batteries. *Sci Rep*. 2020;10(1):3812.

77. Chen J, Gu S, Hao R, et al. Unraveling the role of aromatic ring size in tuning the electrochemical performance of small-molecule imide cathodes for lithium-ion batteries. *ACS Appl Mater Interfaces*. 2022;14(39):44330-44337.

78. Chen Y, Luo W, Carter M, et al. Organic electrode for non-aqueous potassium-ion batteries. *Nano Energy*. 2015;18: 205-211.

79. Rodríguez-Pérez IA, Yuan Y, Bommier C, et al. Mg-ion battery electrode: an organic solid's herringbone structure squeezed upon mg-ion insertion. *J Am Chem Soc*. 2017; 139(37):13031-13037.

80. Yao M, Kuratani K, Kojima T, Takeichi N, Senoh H, Kiyobayashi T. Indigo carmine: an organic crystal as a positive-electrode material for rechargeable sodium batteries. *Sci Rep*. 2014;4(1):1-6.

81. Zhang H, Zhang R, Ding F, Shi C, Zhao N. Hydrogen bonding regulation enables indanthrone as a stable and high-rate cathode for lithium-ion batteries. *Energy Storage Mater*. 2022;51: 172-180.

82. Shi T, Li G, Han Y, et al. Oxidized indanthrone as a cost-effective and high-performance organic cathode material for rechargeable lithium batteries. *Energy Storage Mater*. 2022;50:265-273.

83. Reddy ALM, Nagarajan S, Chumyim P, et al. Lithium storage mechanisms in purpurin based organic lithium ion battery electrodes. *Sci Rep*. 2012;2(1):1-5.

84. Kato M, Sano H, Kiyobayashi T, Takeichi N, Yao M. Improvement of the battery performance of indigo, an organic electrode material, using PEDOT/PSS with d-sorbitol. *ACS Omega*. 2020;5(30):18565-18572.

85. Deunf E, Poizot P, Lestriez B. Aqueous processing and formulation of indigo carmine positive electrode for lithium organic battery. *J Electrochem Soc*. 2019;166(4):A747.

86. Rohland P, Schröter E, Nolte O, Newkome GR, Hager MD, Schubert US. Redox-active polymers: the magic key towards energy storage – a polymer design guideline progress in polymer science. *Prog Polym Sci*. 2022;125:101474.

87. Song Z, Qian Y, Gordin ML, et al. Polyanthraquinone as a reliable organic electrode for stable and fast lithium storage. *Angew Chem Int Ed Engl*. 2015;54(47):13947-13951.

88. Zhang K, Hu Y, Wang L, Fan J, Monteiro MJ, Jia Z. The impact of the molecular weight on the electrochemical

properties of poly(TEMPO methacrylate). *Polym Chem*. 2017; 8(11):1815-1823.

89. Lu Y, Zhang Q, Li L, Niu Z, Chen J. Design strategies toward enhancing the performance of organic electrode materials in metal-ion batteries. *Chem*. 2018;4(12):2786-2813.

90. Janoschka T, Teichler A, Häupler B, Jähnert T, Hager MD, Schubert US. Reactive inkjet printing of cathodes for organic radical batteries. *Adv Energy Mater*. 2013;3(8):1025-1028.

91. Molina A, Patil N, Ventosa E, Liras M, Palma J, Marcilla R. Electrode engineering of redox-active conjugated microporous polymers for ultra-high areal capacity organic batteries. *ACS Energy Lett*. 2020;5(9):2945-2953.

92. Molina A, Patil N, Ventosa E, Liras M, Palma J, Marcilla R. New anthraquinone-based conjugated microporous polymer cathode with ultrahigh specific surface area for high-performance lithium-ion batteries. *Adv Funct Mater*. 2020;30(6):1908074.

93. Wang S, Park AMG, Flouda P, et al. Solution-processable thermally crosslinked organic radical polymer battery cathodes. *ChemSusChem*. 2020;13(9):2371-2378.

94. Song Z, Zhan H, Zhou Y. Anthraquinone based polymer as high performance cathode material for rechargeable lithium batteries. *Chem Commun*. 2009;4:448-450.

95. Xu W, Read A, Koech PK, et al. Factors affecting the battery performance of anthraquinone-based organic cathode materials. *J Mater Chem*. 2012;22(9):4032.

96. Flamme B, Jismy B, Abarbri M, Anouti M. Poly-anthraquinone sulfide isomers as electrode materials for extended operating temperature organic batteries. *Mater Adv*. 2021;2(1):376-383.

97. Song Z, Qian Y, Zhang T, Otani M, Zhou H. Poly (benzoquinonyl sulfide) as a high-energy organic cathode for rechargeable Li and Na batteries. *Adv Sci*. 2015;2(9):1500124.

98. Pirnat K, Mali G, Gaberscek M, Dominko R. Quinone-formaldehyde polymer as an active material in Li-ion batteries. *J Power Sources*. 2016;315:169-178.

99. Newkome G, Schubert U, Winter A. Polyimides and related polymers in battery applications. In: Schubert US, Winter A, Newkome GR, eds. *An Introduction to Redox Polymers for Energy-Storage Applications*. Wiley; 2023:349-389.

100. Sharma P, Damien D, Nagarajan K, Shaijumon MM, Hariharan M. Perylene-polyimide-based organic electrode materials for rechargeable lithium batteries. *J Phys Chem Lett*. 2013;4(19):3192-3197.

101. Li C, Liu X, He Z, et al. Low-cost carbonyl polymer design for high-performance lithium-organic battery cathodes. *J Power Sources*. 2021;511:230464.

102. Liu X, Diemant T, Mariani A, et al. Locally concentrated ionic liquid electrolyte with partially solvating diluent for lithium/sulfurized polyacrylonitrile batteries. *Adv Mater*. 2022;34(49):e2207155.

103. Renault S, Gottis S, Barrès AL, et al. A green Li-organic battery working as a fuel cell in case of emergency. *Energy Environ Sci*. 2013;6(7):2124.

104. Wang S, Wang L, Zhang K, Zhu Z, Tao Z, Chen J. Organic $Li_4C_8H_2O_6$ nanosheets for lithium-ion batteries. *Nano Lett*. 2013;13(9):4404-4409.

105. Hu Y, Tang W, Yu Q, Yang C, Fan C. In situ electrochemical synthesis of novel lithium-rich organic cathodes for all-organic Li-ion full batteries. *ACS Appl Mater Interfaces*. 2019; 11(36):32987-32993.

106. Yu Q, Yao Z, Shi J, et al. Electrochemically manipulating the redox state of 2,2′,5,5′-tetrahydroxybiphenyl as a new organic Li-rich cathode for Li-ion batteries. *Org Electron*. 2020;81:105661.

107. Yu Q, Tang W, Hu Y, et al. Novel low-cost, high-energy-density (>700 Wh kg⁻¹) Li-rich organic cathodes for Li-ion batteries. *Chem Eng J*. 2021;415:128509.

108. Wang J, Lakraychi AE, Liu X, et al. Conjugated sulfonamides as a class of organic lithium-ion positive electrodes. *Nat Mater*. 2020;20:665-673.

109. Sieuw L, Lakraychi AE, Rambabu D, et al. Through-space charge modulation overriding substituent effect: rise of the redox potential at 3.35 V in a lithium-phenolate stereoelectronic isomer. *Chem Mater*. 2020;32(23):9996-10006.

110. Wang J, Guo X, Apostol P, et al. High performance Li-, Na-, and K-ion storage in electrically conducting coordination polymers. *Energy Environ Sci*. 2022;15(9):3923-3932.

111. Wang J, Liu X, Jia H, et al. A high-voltage organic framework for high-performance Na- and K-ion batteries. *ACS Energy Lett*. 2022;7(2):668-674.

112. Zhang Y, Apostol P, Guo X, et al. Validating the reversible redox of alkali-ion disulfonyl-methanide as organic positive electrode materials. *Mater Today Chem*. 2023;28:101379.

113. Gupta D, Gupta SJ, Vlad A. New avenues for organic redox materials as sustainable lithium-ion battery cathodes. *Org Mater*. 2023;5(1):21-34.

114. Wang J, Apostol P, Rambabu D, et al. Revealing the reversible solid-state electrochemistry of lithium-containing conjugated oximates for organic batteries. *Sci Adv*. 2023;9(17):eadg6079.

115. Deng W, Shi W, Li P, et al. A Li-contained air-stable cathode for high-performance all-organic lithium-ion batteries. *Energy Storage Mater*. 2022;46:535-541.

116. Lakraychi AE, Dolhem F, Vlad A, Becuwe M. Organic negative electrode materials for metal-ion and molecular-ion batteries: progress and challenges from a molecular engineering perspective. *Adv Energy Mater*. 2021;11(32):2101562.

117. Li X, Wang Y, Lv L, Zhu G, Qu Q, Zheng H. Electroactive organics as promising anode materials for rechargeable lithium ion and sodium ion batteries. *Energy Mater*. 2022;2(2):200014.

118. Liang Y, Wu W, Cao J, et al. Stable long cycling of small molecular organic acid electrode materials enabled by non-flammable eutectic electrolyte. *Small*. 2022;18(6):e2104538.

119. Raccichini R, Varzi A, Passerini S, Scrosati B. The role of graphene for electrochemical energy storage. *Nat Mater*. 2015;14(3):271-279.

120. Li T, Wang L, Li J. Carbon nanotube enables high-performance thiophene-containing organic anodes for lithium ion batteries. *Electrochim Acta*. 2022;408:139947.

121. Luo XX, Li WH, Liang HJ, et al. Covalent organic framework with highly accessible carbonyls and π-cation effect for advanced potassium-ion batteries. *Angew Chem Int Ed Engl*. 2022;61(10):e202117661.

122. Lee HH, Park Y, Shin KH, Lee KT, Hong SY. Abnormal excess capacity of conjugated dicarboxylates in lithium-ion batteries. *ACS Appl Mater Interfaces*. 2014;6(21):19118-19126.

123. Renault S, Oltean VA, Araujo CM, Grigoriev A, Edström K, Brandell D. Superlithiation of organic electrode materials: the case of dilithium benzenedipropiolate. *Chem Mater*. 2016;28(6):1920-1926.

124. Carvalho RP, Marchiori CFN, Brandell D, Araujo CM. Understanding the lithiation limits of high-capacity organic battery anodes by atomic charge derivative analysis. *J Chem Phys*. 2022;157(18):181101.

125. Lin ZQ, Xie J, Zhang BW, et al. Solution-processed nitrogen-rich graphene-like holey conjugated polymer for efficient lithium ion storage. *Nano Energy*. 2017;41:117-127.

126. Wang Y, Deng Y, Qu Q, et al. Ultrahigh-capacity organic anode with high-rate capability and long cycle life for lithium-ion batteries. *ACS Energy Lett*. 2017;2(9):2140-2148.

127. Hu W, Chen N, Chen D, Tong B. Conjugated tetrathiafulvalene carboxylates for stable organic lithium batteries. *ChemElectroChem*. 2022;9(6):e202200026.

128. Iordache A, Bresser D, Solan S, et al. From an enhanced understanding to commercially viable electrodes: the case of $PTCLi_4$ as sustainable organic lithium-ion anode material. *Adv Sustain Syst*. 2017;1(3-4):1600032.

129. Figueira-Duarte TM, Müllen K. Pyrene-based materials for organic electronics. *Chem Rev*. 2011;111(11):7260-7314.

130. Hu J, Zhang D, Harris FW. Ruthenium(III) chloride catalyzed oxidation of pyrene and 2,7-disubstitued pyrenes: an efficient, one-step synthesis of pyrene-4,5-diones and pyrene-4,-5,9,10-tetraones. *J Org Chem*. 2005;70(2):707-708.

131. SME. Daily ternary precursor and material price. Accessed March 16, 2023. https://www.metal.com/Ternary-precursor-material

132. Judez X, Qiao L, Armand M, Zhang H. Energy Density Assessment of Organic Batteries. *ACS Appl Energy Mater*. 2019;2(6):4008-4015.

133. Kaduk JA. Terephthalate salts: salts of monopositive cations. *Acta Crystallogr B*. 2000;56(Pt 3):474-485.

134. Zhu Z, Chen J. Review—Advanced carbon-supported organic electrode materials for lithium (sodium)-ion batteries. *J Electrochem Soc*. 2015;162(14):A2393-A2405.

135. Park M, Zhang X, Chung M, Less GB, Sastry AM. A review of conduction phenomena in Li-ion batteries. *J Power Sources*. 2010;195(24):7904-7929.

136. Nitta N, Wu F, Lee JT, Yushin G. Li-ion battery materials: present and future. *Mater Today*. 2015;18(5):252-264.

137. Vlad A, Rolland J, Hauffman G, Ernould B, Gohy JF. Melt-polymerization of TEMPO methacrylates with nano carbons enables superior battery materials. *ChemSusChem*. 2015;8(10):1692-1696.

138. Zhao Q, Wang J, Chen C, Ma T, Chen J. Nanostructured organic electrode materials grown on graphene with covalent-bond interaction for high-rate and ultra-long-life lithium-ion batteries. *Nano Res*. 2017;10(12):4245-4255.

139. Lu C, Dong C, Wu H, et al. Achieving high capacity hybrid-cathode $FeF_3@Li_2C_6O_6/rGO$ based on morphology control synthesis and interface engineering. *Chem Commun*. 2018;54(26):3235-3238.

140. Battaglia AM, Pahlavanlu P, Grignon E, An SY, Seferos DS. High active material loading in organic electrodes enabled by a multifunctional binder. *ACS Appl Mater Interfaces*. 2022;14(37):42298-42307.

141. Lin Z, Liu T, Ai X, Liang C. Aligning academia and industry for unified battery performance metrics. *Nat Commun*. 2018;9(1):5262.

142. Lain MJ, Brandon J, Kendrick E. Design strategies for high power vs high energy lithium ion cells. *Batteries*. 2019;5(4):64.

143. Singh M, Kaiser J, Hahn H. Thick electrodes for high energy lithium ion batteries. *J Electrochem Soc*. 2015;162(7):A1196-A1201.

144. Laue V, Röder F, Krewer U. Joint structural and electrochemical modeling: impact of porosity on lithium-ion battery performance. *Electrochim Acta*. 2019;314:20-31.

145. Lombardo T, Lambert F, Russo R, et al. Experimentally validated three-dimensional modeling of organic-based sodium-ion battery electrode manufacturing. *Batter Supercaps*. 2022; 5(8):e200200116.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.