

Roadmap of solid-state lithium-organic batteries towards 500 Wh kg⁻¹

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ABSTRACT Over the last few years, solid-state electrolytes (SSEs) have attracted tremendous attention due to their credible promise towards high-energy batteries. In parallel, organic battery electrode materials (OBEMs) are gaining momentum as strong candidates thanks to their lower environmental footprint, flexibility in molecular design and high energy metrics. Integration of the two constitutes a potential synergy to enable energy-dense solid-state batteries with high safety, low cost and long-term sustainability. In this Review, we present the technological feasibility of combining OBEMs with SSEs along with the possible cell configurations that may result from this peculiar combination. We provide an overview of organic solid-state batteries and discuss their main challenges. We analyze the performance-limiting factors and the critical cell design parameters governing cell-level specific energy and energy density. Lastly, we propose guidelines to achieve 500 Wh kg⁻¹ cell-level specific energy with solid-state Li-organic batteries.

Organic battery electrode materials (OBEMs) have received considerable attention in the past few years. With a chemical composition derived from naturally abundant elements (C, H, N, O and S), a real possibility of being generated from renewable resources (biomass) and an ease of recycling, the OBEMs promise a credible alternative towards safe, cost-reduced and low polluting energy storage systems.¹⁻⁴ Most OBEMs can be prepared via relatively short synthesis steps from common feedstocks with low cost and energy consumption.³ Since 2008, tremendous progress has been made in this research area leading to a plethora of organic molecules and architectures ready to be integrated in organic battery cells.⁵⁻¹⁴ Moreover, thanks to their versatility and chemical flexibility, OBEMs have shown broad applicability as solid (sealed battery)^{3, 14-16} or dissolved (flow battery)¹⁷⁻¹⁹ active materials, in aqueous^{20, 21} and non-aqueous electrolytes, for lithium systems and beyond, including proton,^{22, 23} sodium,²⁴ potassium²⁵ and multivalent metal systems²⁶⁻³³.

Despite the significant progress made through years of research, organic sealed batteries still face considerable technical challenges.¹⁵ First of all, low density of organic molecules (<2 g cm⁻³) penalizes the energy density (volumetric) of assembled cells; second, low electronic conductivity imposes the use of large amount of conductive agents which lower the cell-level specific energy (gravimetric); and lastly, dissolution in conventional electrolytes leads to severe active material loss, lowers cycling efficiency and induces capacity fade. Amongst the three issues, volumetric density and electronic conductivity issues could be alleviated by electrode and cell engineering, while dissolution could be solved by efforts concentrated on molecular engineering and new electrolyte formulations. **Figure 1** presents the popular strategies to prevent the dissolution of organic molecules, in which the electrolytes have been progressively transitioned from conventional liquid electrolytes to all-solid-state electrolytes.

Molecular engineering constitutes an efficient approach to reduce the solubility while using conventional electrolytes (**Figure 1a**). In 2009, Poizot's group was the first to report the importance of forming organic salt to tackle the solubility issue.³⁴ Tetrahydroxybenzoquinone tetralithium salt (denoted as Li₄-THQ), characterized with a specific capacity of 200 mAh g⁻¹ in the first cycle, has shown good cycling stability with only 10% capacity loss over 50 cycles. This partial solubility suppression was attributed to the increased polarity of the small molecule and plausible formation of a coordination network (-O—Li—O-).^{35, 36} In the same vein, various molecules bearing different ionic groups such as oxy (-O⁻),^{34, 37, 38} carboxylate (-CO₂⁻)^{34, 35, 39-43} and sulfonate (-SO₃⁻)^{39, 44, 45} were reported and confirmed the efficacy of this approach. The advantage of organic salts relies on the voltage profiles that are characterized with flat plateaus and the ability for mechanistic studies in the solid phase (e.g. *in-situ/ex-situ* characterization);^{38, 43, 44, 46} however, substitution with ionic groups always increases molecular weight of the molecule and thus decreases the theoretical capacity. Introduction of H-bond donor groups (-NH₂) has also shown a beneficial effect on reducing the solubility.⁴⁷ On the other hand, polymerization is a largely adopted approach and has enabled excellent cycling stabilities (e.g. >1000 cycles) for several polymers.^{9, 48-53} Polymerization often consists of poly-condensation^{50, 51} or grafting small molecules on a polymeric backbone.^{49, 54, 55} Usually, these polymers are poorly characterized and exhibit slopping voltage profiles⁵⁶ and sometimes decreased capacities compared to single molecules. However, polymerization can give access to other physical properties such as flexibility promoting flexible batteries.^{51, 57} Furthermore, impregnation or grafting of small molecules inside microporous carbons (e.g. CMK-3)⁵⁸⁻⁶⁰ and on conductive agents^{61, 62} have also been explored as alternative approaches and demonstrated good cycling stabilities. These approaches have led to significant enhancement of electronic conductivity,⁶³ but they are still limited to insufficient

impregnation or grafting ratios (not exceeding 50%), thus leading to low electrode-level specific capacities. The above-mentioned electrode-level attempts to reduce the solubility while using conventional electrolyte are always accompanied by reduced electrode capacities compared to the unmodified molecules due to the increased molecular weight or the low impregnation or grafting ratios.

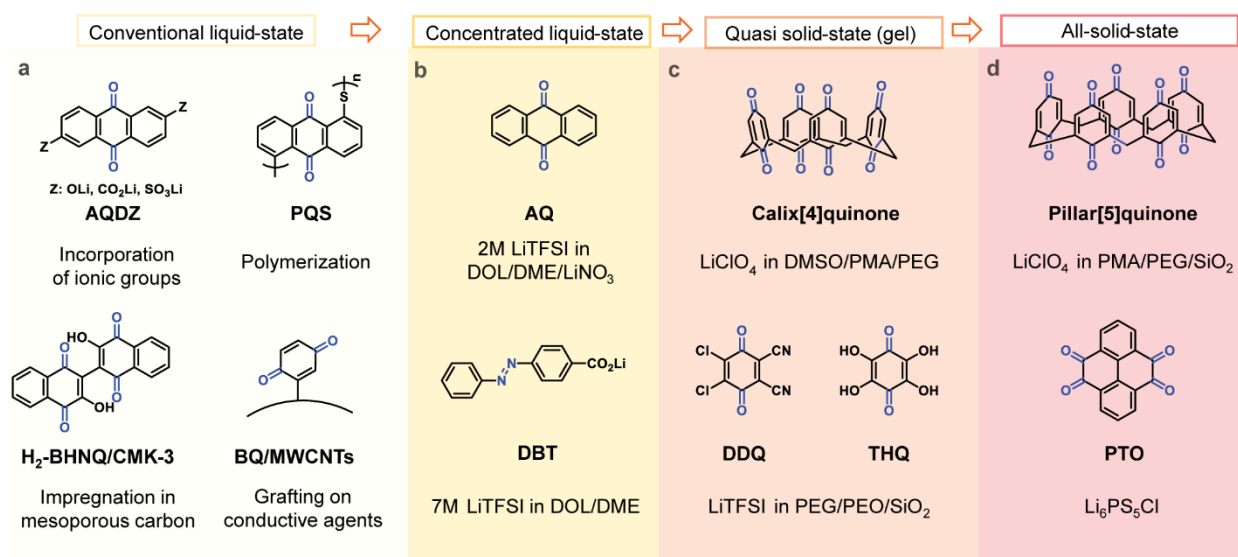


Figure 1: Adopted strategies for dissolution inhibition in OBEMs. a) Incorporation of ionic groups, polymerization, impregnation in mesoporous carbon, grafting on conductive agents, all applied at the electrode level while using conventional liquid electrolyte. b) Use of highly-concentrated liquid electrolytes. Utilization of c) gel-like polymers as quasi solid-state electrolytes and d) polymers or ceramic-based solid-state electrolytes.

In parallel, there has been efforts on electrolyte modification to prevent the dissolution either by optimization of existing electrolytes or introducing new electrolyte systems (**Figure 1b-d**). In this context, highly concentrated electrolytes have been introduced to the field of organic batteries (**Figure 1b**). Several molecules and different supporting salt concentrations (up to 7 M)

were explored and showed significant improvement in terms of cycling stability. An example to illustrate this strategy employs anthraquinone as active material. When a conventional 1 M electrolyte was used,⁶⁴ the cell showed high solubility of anthraquinone accompanied with rapid capacity fade; in contrast, lower solubility and better cycling stability were observed for a cell using 2 M LiTFSI in DOL/DME with 3-5% of LiNO₃ as electrolyte additive.⁶⁵ LiNO₃ was used to prevent side reaction between shuttled anthraquinone molecules and Li metal via the formation of protective passivation layer on the surface of Li metal.⁶⁶ Quasi-solid-state electrolytes were explored as an alternative strategy (**Figure 1c**). This electrolyte system is based upon a supporting salt in a mixture of solvent and polymer to form a gel electrolyte. Chen's group reported a promising result using calix[4]quinone as active material and LiClO₄ in DMSO/PMA/PEG (PMA: poly methacrylate; PEG: polyethylene glycol) as a gel electrolyte.⁶⁷ The cell delivered excellent cycling stability with a capacity of 300 mAh g⁻¹ after 100 cycles. Other small molecules have also shown improved cyclability in similar electrolyte systems.⁶⁸ Finally, all-solid-state electrolytes (SSE) were recently explored and showed promising results for organic batteries (**Figure 1d**). Chen's group demonstrated high cyclability of pilar[5]quinone/Li half-cell in a polymer electrolyte (LiClO₄ in PMA/PEG-SiO₂),⁶⁹ whereas our group revealed excellent cycling stability of Na₄C₆O₆/Na-Sn alloy full cells using sulfide-based electrolytes.⁷⁰

For many years, SSE was only utilized as a physical barrier to prevent OBEMs from shuttling to the anode side,⁷¹ while its capability to promote energy-dense cell design has been overlooked. A simple comparison between liquid electrolyte and SSE could motivate any battery researcher to consider the latter in favor of the former. In general, conventional liquid electrolytes (e.g. carbonate-based solution) offer high ionic conductivity and excellent electrode wettability required for the electrochemical reaction.^{72, 73} However, their inadequate electrochemical and

thermal stabilities along with poor safety limit the possibilities for developing high-energy batteries, especially the most promising Li metal anode batteries due to the formation of metallic dendrites.⁷⁴

Replacement of liquid electrolytes with solid-state counterparts will not only overcome the persistent issues of liquid electrolytes, but also offer additional advantages in terms of cell design (e.g. bipolar stacked cells to increase packaging efficiency), cost reduction and cycle-life benefits.^{75, 76} In conventional carbonate liquid-electrolyte batteries, short-circuiting results in disastrous consequences such as venting, thermal runaway and combustion. In solid-state batteries, though short-circuiting cannot be completely prevented, the potential safety hazards can be minimized due to the absence of flammable electrolytes. Developing SSEs with practical ionic conductivity at room temperature has historically constituted the biggest challenge for the above comparison to be a tangible reality. Thanks to tremendous progress in both academic and industrial research, the SSE database today is rich in suitable examples ready to be incorporated in energy storage devices. A short overview is provided in the Supporting **Figure S1** and its notes, covering the state-of-the-art solid electrolytes to help the organic battery researchers getting familiar with SSEs. For more comprehensive background knowledge, the readers could refer to the excellent review articles on the topic.⁷⁷⁻⁸²

In consideration of the rapid development of SSEs and the tremendous progress made in organic batteries, we consider it timely to bridge the gap between the two fields and provide the scientific community with a bold vision for organic solid-state batteries. The main goal of this Review is to help researchers with solid electrolyte background to select the suitable OBEMs for their SSEs while those with organic battery background to choose the relevant SSEs for their OBEMs, all based on a critical discussion and extraction of the relevant insights dealing with this

peculiar combination. This Review will be divided into three main parts: i) alignment of redox potential of OBEMs and electrochemical window of SSEs along with the possible configurations of ASSBs, ii) overview of reported organic-based cells using solid electrolytes and iii) design-oriented guidelines to achieve 500 Wh kg⁻¹ cell-level specific energy based on solid-state Li-organic batteries.

Combination of OBEMs and SSEs for organic solid-state batteries

Flexible molecular design and potential tuning in OBEMs

Unlike inorganic electrode materials whose electrochemical reactions rely on cation intercalation, conversion, or metal alloying,⁸³ the redox chemistry of OBEMs is based on the charge-state change of redox centers and can be categorized into three redox systems depending on the charge compensation nature.^{5, 41} According to Hünig's classification,⁸⁴ the redox reactivity of electroactive molecules can be divided into three redox systems depending on the charge compensation: system A if the charge compensation is carried out by cations (known also as n-type), system B if it is made by anions (known also as p-type) or system C if both ions are involved (known also as bipolar) (**Figure S2**).⁴¹ This diversity in charge storage mechanisms coupled with the richness of organic chemistry and molecular design has provided a database of electroactive organic molecules operating within a large potential window with high capacities, extended stabilities and acceptable cycling rates (**Figure 2a**).

The chemical space of OBEMs today counts hundreds of compounds capable of being used as cathodes and anodes. Several redox classes have been explored for this purpose and some of them have shown excellent electrochemical performances with opportunities to attain simultaneously high energy and power densities combined with good cycling stabilities. In

addition, various topologies were studied, including crystalline small molecules,² polymers⁹ and covalent/metal organic frameworks (COFs,^{85, 86} MOFs^{87, 88}), whose employment demonstrated a significant effect on the electrochemical and battery performances. OBEMs with redox potential values ranging from 0.65 to 4.1 V vs. Li⁺/Li and capacity values varying between 90 – 589 mAh g⁻¹ are ready to be integrated in solid-state batteries. A short summary describing the current status is provided in **Figure S2** and its notes to help solid electrolyte researchers become acquainted with OBEMs. For more comprehensive overview, we invite the readers to read the review articles regarding organic cathode materials,^{2, 8, 16} and the well-detailed review dedicated to organic anode materials.⁸⁹

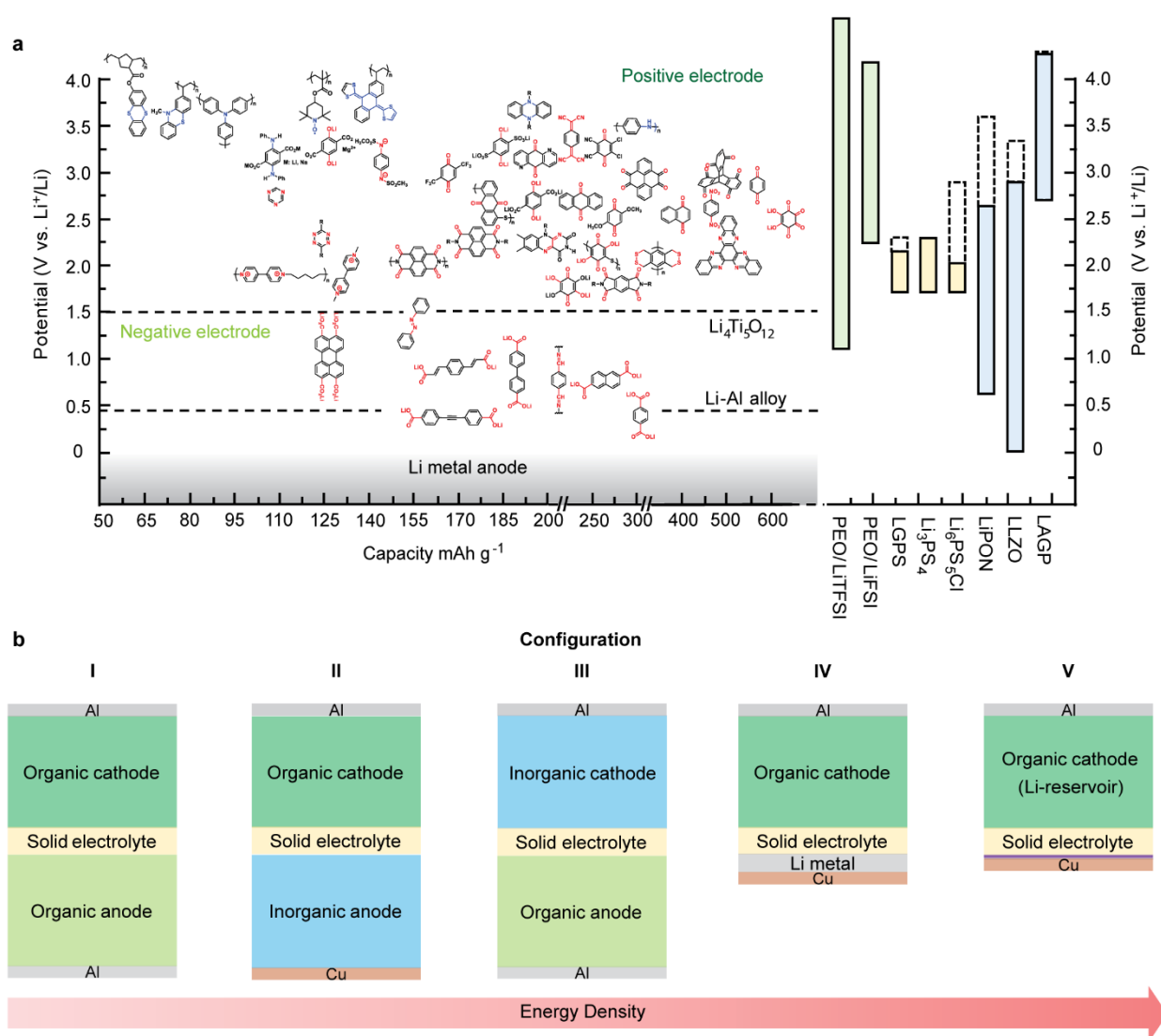


Figure 2: A complementary combination of OBEMs and SSEs for organic solid-state batteries. a) Left: overview of selected organic small molecules and polymers applied as active-material in liquid-electrolyte secondary batteries.² Redox centers highlighted in red correspond to n-type redox suitable for M-storage (M: Li, Na, K), whereas those highlighted in blue correspond to p-type redox suitable for anion-storage. Right: electrochemical stability window of selected solid-state electrolytes. The dashed line extensions represent the oxidation potential to fully delithiate the electrolyte. (Adapted with permission from Ref. ⁹⁰ and ⁹¹. Copyright 2015 and 2020

American Chemical Society respectively) b) Five configurations of solid-state batteries with OBEMs.

Electrochemical stability window of SSEs

In addition to ionic conductivity, electrochemical stability window (ESW) of SSEs is another important parameter to take into consideration for the deployment of solid-state batteries. Ideally, the redox potential of electrode materials should be located within the ESW of an electrolyte since the latter could be either reduced or oxidized if the electrode material operates below or above the stability window, respectively. Therefore, the ESW of a given SSE should be as wide as possible in order to enable the use of a large panel of electrode materials including, most importantly, Li metal and high-voltage cathodes.

Based on first-principles calculations, researchers from different groups have determined the thermodynamic ESW of commonly used SSEs (**Figure 2a - right**).^{90, 91} The ESW of polymer electrolytes is highly dependent on their chemical composition and combination, as the SPE is composed of polymer host and Li salt (mostly imide-based salts). In fact, the ESW of each individual component of polymer electrolytes was found to be wide enough, whereas it drastically narrowed when the polymer and the salt were blended.⁹¹ For instance, in PEO/LiFSI solid electrolyte, the calculated ESW is ~9.12 V for PEO, ~4.77 V for LiFSI, and only ~2.04 V for the mixture.⁹¹ This narrowing in ESW is mainly attributed to the oxidative deprotonation of PEO and N-S cleavage on FSI anion during the reduction process and also to the supramolecular nature of PEO/LiFSI complex. Sulfide electrolytes represent the narrowest thermodynamic ESW among solid electrolytes. Based on first-principles calculations, sulfide-based electrolytes tend to be reduced at 1.6 – 1.7 V vs. Li^+/Li into binary reduction products including Li_2S , Li_3P , LiCl , or Li-

Ge and be oxidized starting at ~ 2.2 V vs. Li^+/Li to form oxidation products such as P_2S_5 , GeS_2 , and S, depending on the chemical composition.⁹⁰ Oxide-based solid electrolytes are considered to be more stable with larger ESW.⁹⁰ Calculations show that oxide electrolytes start to be oxidized at ~ 2.9 V vs. Li^+/Li and continue at higher potentials to form Li_2O and generate O_2 gas by further oxidation to Li_2O_2 , while the oxidation of LiPON starts at ~ 2.6 V vs. Li^+/Li with N_2 gas release.⁹⁰ Reduction of oxide electrolytes occurs between 0 and 2.6 V vs. Li^+/Li depending on the oxide electrolyte materials.

In reality, most of the electrolytes mentioned above have experimentally demonstrated extended ESW, and some of them were found to be compatible with Li metal (e.g. LLZO, $\text{Li}_6\text{PS}_5\text{Cl}$, $\text{Li}_7\text{P}_2\text{S}_8\text{I}$ and LiPON)⁹²⁻⁹⁴ and high voltage cathodes (e.g. PEO).⁹⁵ In general, three types of interface form upon electrode-electrolyte contact: Type 1: no electrolyte decomposition and no interphase (kinetically limited); Type 2: electrolyte decomposition and formation of a mixed ionic and electronic conductor (MIEC) interphase; Type 3: electrolyte decomposition and formation of ion-conducting, electron-blocking solid electrolyte interphase (SEI).⁹⁶ Extended ESW relies on Type 3 interface where SEI layer passivates the solid electrolyte and inhibits further decomposition. Therefore, some solid electrolytes are able to operate within the target electrochemical window (e.g. 0–4.5 V vs. Li^+/Li) although they are thermodynamically unstable. The nature of solid-solid contact and varieties in types of interfaces are new challenges that are not encountered in the liquid electrolytes.⁹⁷⁻⁹⁹ Aspects like electrode-electrolyte interface engineering, chemo-mechanical properties and microstructures are important factors impacting the performance of solid electrolyte batteries.^{100, 101} A detailed discussion of these aspects is provided in section 4 to bring further clarification.

Cell configurations of organic solid-state batteries

The technological viability of known solid electrolytes coupled with the versatile choices of reported OBEMs constitutes a credible combination to promote solid-state organic batteries. Five possible cell configurations could be envisioned for this purpose as shown in **Figure 2b**. Each configuration has different requirements, challenges and prospects. As with present lithium-ion batteries, all-organic rocking-chair cells could be realized by coupling a Li-reservoir organic cathode (e.g. carbonyl, conjugated sulfonamide) – an organic molecule in its reduced state with available Li^+ for electrochemical extraction functioning like LiFePO_4 – with an n-type anode (e.g. carboxylate, azo-compound) and a cation-conducting solid electrolyte (e.g. SPE, sulfide, oxide electrolyte) (**Configuration I**).¹⁰² All-organic metal-free molecular-ion battery could also be implemented if we couple p-type cathode (e.g. conjugated amine, nitroxide) with p-type anode (exclusively viologen) and an anion-conducting solid electrolyte (mainly SPE) (**Configuration I**).¹⁰³ High flexibility, low cost and low-to-moderate energy densities are common features for both cell configurations. Since organic materials are composed of non-toxic elements, high safety and low environmental impact is expected for end-of-life all-organic batteries.

Alternatively, integration of inorganic electrode materials could be considered to realize a hybrid solid-state Li-ion battery (**Configuration II and III**) with higher energy density.¹⁰⁴⁻¹⁰⁶ For instance, by coupling high-voltage inorganic cathode (e.g. $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$, NMC811) with an organic anode (e.g. carboxylate) and a solid electrolyte, or by matching a Li-reservoir n-type cathode with a Li-host inorganic anode (e.g. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ or graphite) and a solid electrolyte. Organic anodes will enable the use of solid electrolytes with narrower electrochemical window.

Li metal-organic battery (**Configuration IV**) stands out as a viable solution to promote high-capacity n-type cathode (e.g. carbonyls, sulfur compounds) designed in their oxidized state.¹⁰⁷ The Li metal would be the Li source in this case and the cell will be discharged first. Combining such cathodes with Li metal and solid electrolyte (e.g. Li metal compatible SSE) could lead to ultra-high energy densities with competitive values. Note that Li reservoir organic cathode, i.e., organic molecules in the lithiated state, could also be applied in this cell configuration but starts with charging first.

Finally, **Configuration V** employing Li-reservoir organic cathode with an anode-free design^{108, 109} represents the most energy-dense organic solid-state battery due to no excess of Li. The design is very aggressive, as Li reservoir cathodes still face from challenges in capacity, gravimetric density and processability. The last two configurations and requirements to achieve practical energy density will be thoroughly discussed in section 4 of this Review.

Overview of OBEMs in solid-state batteries

Efforts to develop organic batteries for use with liquid electrolytes have been extensively reported and reviewed in the past decades. Nevertheless, successful application of organic electrodes in all-solid-state batteries is relatively limited, with only a handful of reports. **Table S1** summarizes the reported examples of organic solid-state batteries. From the aspect of organic redox molecules, most cathode active materials are based on quinone derivatives, mainly due to their availability, high theoretical capacity and fast reaction kinetics.^{64, 70, 110-113} Alternative active materials include nitrile compounds,¹¹⁴ conjugated dicarboxylates¹⁰⁴ and azo based compounds¹¹⁵ specified for certain electrochemical systems. In terms of solid electrolytes, solid polymer electrolytes (SPEs) containing alkali metal salts (Li^+ , Na^+ , K^+ ; TFSI⁻, ClO₄⁻) predominate in the

choice of SSEs, with some reports based on sulfide SSEs and few reports on oxide SSEs. Challenges and research directions differ significantly in each type of electrolytes.

Organics in SPEs

SPEs consist of polymer matrix dissolved with alkali metal salts and sometimes filled with inorganic fillers to improve ionic conductivity, similar to the composition of conventional liquid electrolyte (Li salts plus solvent or polymer matrix).¹¹⁶ **Figure 3a** illustrates a typical solid-state battery comprised of SPE and organic cathode along with the encountered challenges. Most OBEMs usually exhibit identical or similar electrochemical profiles in SPEs compared to those in conventional liquid electrolytes due to the similarity in electrolyte composition.^{117, 118} SPEs suffer from low ionic conductivity below their glass transition temperature (T_g). Consequently, elevated temperature ($> 60\text{ }^{\circ}\text{C}$) is often necessary for cell operation. As shown in the blue inset in **Figure 3b**, the ionic conductivity of PEO-based polymer electrolytes drastically increases at around 40-50 $^{\circ}\text{C}$, which aligns with T_g of PEO solvated with Li-salts.¹¹⁹ Sufficient polymer chain mobility at high temperatures enhances the ionic conductivity and assures interfacial contact between cathode active materials and polymer catholytes. Therefore, organic batteries cycled in SPE usually exhibit high material utilization in the initial cycle (**Table S1**).

Cycling at elevated temperatures, however, leads to the diffusion of organic active material into SPE, which deteriorates capacity retention. This diffusion is especially prominent when active material consists of small molecules in the neutral form and when SPE consists of linear polymer chains. Within this framework, Poizot's group has reported a lithium metal polymer (LMP[®]) cell accommodating tetramethoxy-p-benzoquinone (denoted as TMQ) as cathode material in a PEO/LiTFSI electrolyte.¹¹⁷ Note that the LMP[®] technology was already commercialized by Bolloré group using LiFePO₄ as the cathode and with an operating temperature reaching 100 $^{\circ}\text{C}$.

The electrochemical performances of TMQ are found to be much better with the SPE than with conventional liquid electrolytes, mainly due to the higher solubility of TMQ in polar organic solvents. However, the cycling stability was not satisfying owing to the diffusion of TMQ in the PEO matrix at high temperature (100 °C). **Figure 3c** shows time-dependent capacity degradation, in which the capacity decay is linear to the operating time rather than cycling rate. This indicates that the capacity loss is completely dominated by active material diffusion. To prevent diffusion, the same group studied disodium 5,5'-indigotin disulfonate, also known as indigo carmine, as cathode material due to its two permanent negative charges ($-\text{SO}_3^-$) which makes polar interactions with PEO difficult, i.e., very low diffusivity and solubility.¹¹⁸ The galvanostatic cycling of indigo carmine in the PEO-based electrolyte revealed identical electrochemical behavior as in liquid electrolyte; e.g. two-electron redox reaction at an average potential of ~ 2.4 V vs. Li^+/Li with an overall specific capacity of 110 mAh g^{-1} .^{120, 121} Nevertheless, poor cycling stability was also obtained for this cell due to Li metal poisoning by Na upon ion-exchange reaction between the Na counter cations of indigo carmine and the conducting salt.

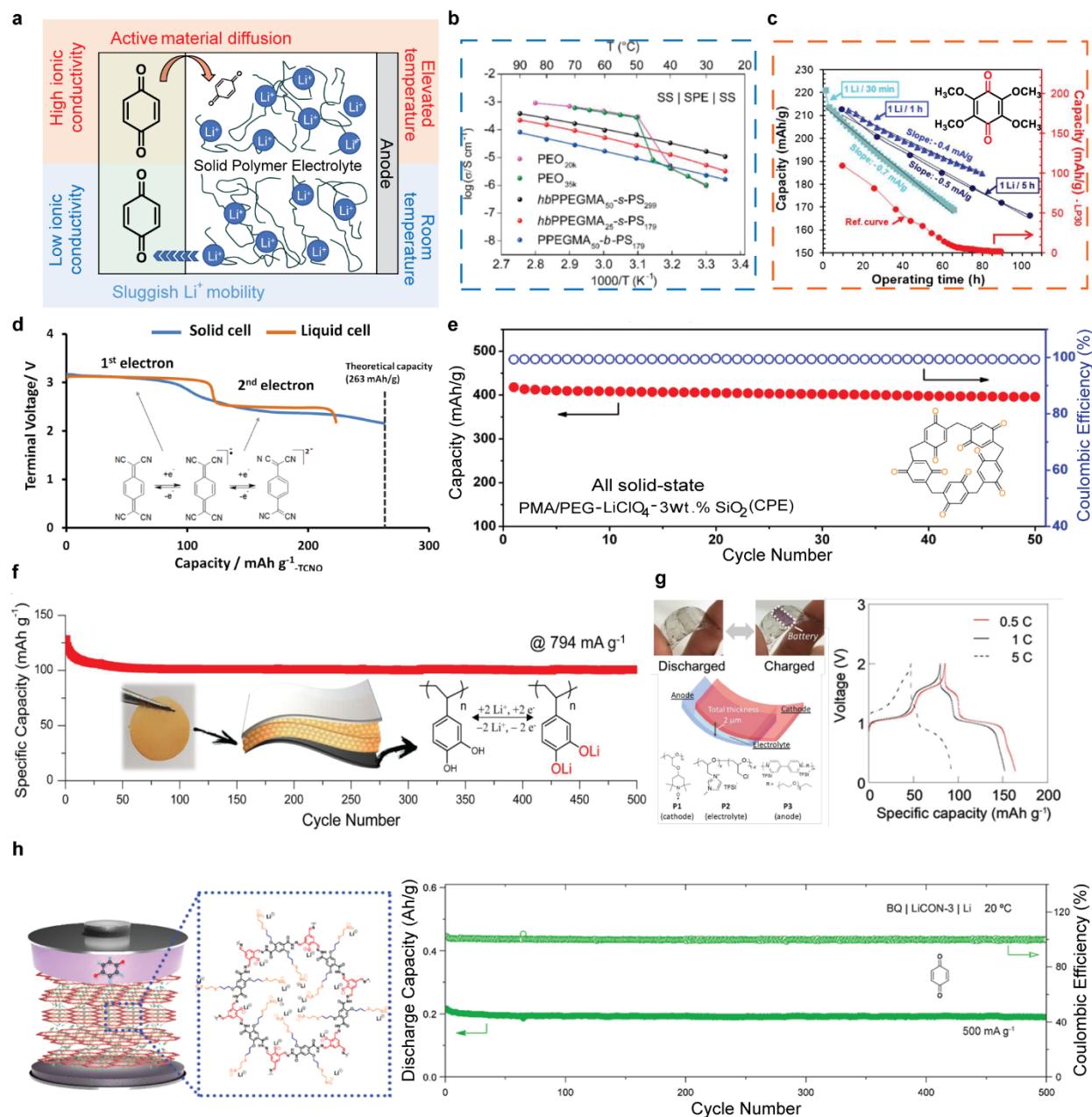


Figure 3: Overview of organic solid-state batteries involving polymer electrolytes. a) Schematic diagram of polymer-based solid-state organic battery highlighting the main challenges. b) Temperature-dependent ionic conductivity of selected polymer electrolytes (Reproduced with permission from Ref. ¹¹⁹. Copyright 2019 American Chemical Society). Low ionic conductivity at low temperature indicates sluggish ion mobility. c) Correlation between discharge capacities and operating time for TMQ/Li half-cells indicating possible TMQ diffusion in the polymer electrolyte

(Reproduced with permission from Ref. ¹¹⁷. Copyright 2015 Elsevier Ltd). d) Voltage profile for TCNQ/Li half-cells cycled in liquid and solid electrolytes (Reproduced with permission from Ref. ¹¹⁴. Copyright 2012 Nature Publishing Group). e) Cycling performance for pillar[5]quinone/Li half-cell cycled in LiClO₄ PMA/PEG-SiO₂ solid electrolyte (Reproduced with permission from Ref. ⁶⁹. Copyright 2014 American Chemical Society) f) Cycling performance for P4VC/Li half-cell cycled in single-ion nanoparticles electrolyte (Reproduced with permission from Ref. ¹²². Copyright 2020 John Wiley and Sons). g) Schematic illustration of metal-free flexible all-organic cell and its corresponding charge/discharge curves (top photographs show the full-cell in discharged and charged states) (Reproduced with permission from Ref. ¹²³. Copyright 2020 John Wiley and Sons). h) Schematic illustration of Li|LiCON-3|benzoquinone solid-state battery (inset showing the chemical structure of LiCON-3 as single-ion COF solid electrolyte) and the corresponding cycling stability for 500 cycles (Reproduced with permission from Ref. ¹²⁴. Copyright 2021 American Chemical Society)

Organic batteries with SPEs either suffer from low ionic conductivity at room temperature or experience active material diffusion at elevated temperatures. Two types of strategies were employed to enhance the cyclability: increasing room-temperature ionic conductivity of polymer electrolyte or suppressing cathode diffusion at high temperature. The most straightforward approach to improve electrolyte's room-temperature ionic conductivity is the introduction of liquid or gel component into the polymer electrolyte (gel polymer electrolyte, GPE). Hanyu *et al.*¹¹⁴ reported solid-state cell based on tetracyanoquinodimethane (denotes as TCNQ) cathode with PEO-ionic liquid gel-polymer as the electrolyte with a 20 μm -thick layer of PEO separating the cathode from the electrolyte (**Figure 3d**). In contrast to previous examples, the electrochemical

assessment shows a difference in the voltage profiles between solid and liquid cells, the presence of nice flat plateaus for the latter and slopping profiles for the former. This difference might stem from the resistive TCNQ-electrolyte interface, at which charge transfer could be sluggish. However, the cell successfully achieved high capacity exceeding 200 mAh g⁻¹ in the first cycles with good cycling stability over 100 cycles at room temperature. Similarly, Huang *et al.*⁶⁷ reported good performances of a quasi-solid-state cell involving supramolecular calix[4]quione (denoted as C4Q) as cathode material and Celgard membrane soaked with GPE. The GPE was composed of PMA/PEG hybrid polymer filed with LiClO₄ and DMSO to enhance ionic conductivity. The corresponding quasi-solid cell revealed a specific capacity of 420 mAh g⁻¹ (electrode containing 60.3 wt.% of C4Q), an average operating potential of ~2.7 V vs. Li⁺/Li, and a stable cyclability upon 100 cycles. Ogihara *et al.* have also reported a quasi-solid-state hybrid battery accommodating the high voltage spinel LiNi_{0.5}Mn_{1.5}O₄ as cathode and 2,6-naphthalene dicarboxylate dilithium as anode.¹⁰⁴ The electrolyte was a GPE comprising 89 wt.% conventional electrolyte and 11 wt.% poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP). Two bipolar cells were stacked in series and delivered an operating voltage of 8V along with high specific energy and power of 300 Wh kg⁻¹ and 5 kW kg⁻¹, respectively, and exhibited favorable cycling stability (96% capacity retention after 100 cycles) due to the absence of dissolution. Other examples using GPEs were also reported and showed satisfying results in terms of cyclability.^{113, 125-128} It is noteworthy that the introduction of liquid/gel components is a compromised solution between suppressing cathode diffusion and enhancing ionic conductivity. The concentration of the liquid component needs to be carefully controlled to avoid cathode dissolution.

Inorganic fillers have been extensively used in polymer electrolytes for better mechanical properties and ionic conductivity, enabling robust application of polymer electrolytes at room

temperature. Nano-sized oxide filler materials add to the polymer amorphicity, while the interaction between alkyl metal salt in SPE and surface oxygen on nanoparticles further improves ionic conductivity.^{129, 130} In this context, Zhu *et al.*⁶⁹ incorporated silica nanoparticles in PMA/PEG-based SPE and demonstrated high ionic conductivity of composite electrolyte up to 0.26 mS cm⁻¹ at room temperature (comparable to the conductivity of SPE without fillers at around 90 °C). **Figure 3e** shows stable cyclability (95% retention over 50 cycles at 0.2 C) and a high cathode utilization rate (93.7%) with the supramolecular cathode pillar[5]quinone (denoted as P5Q). Excellent stability partially benefits from the room-temperature operation of SPE which minimizes the loss of active material via diffusion. Organic batteries with small-molecule cathode material and nanocomposite polymer electrolyte operated at room temperature seem a promising strategy, where both adequate utilization of high-capacity organic cathode and suppressed diffusion-induced degradation induced by dissolution can be achieved.

Besides inorganic fillers, single-ion conducting polymer nanoparticles were also employed to improve ionic conductivity and mechanical stability. Kim *et al.*¹²² anchored TFSI⁻ group to polystyrene (PS) nanoparticles to enable SPE with high ionic conductivity and high Li transference number (**Figure 3f**). As ion-conducting particles form a percolation network, efficient Li⁺ transport is demonstrated along the surface of close-packed nanoparticles with 50% succinonitrile (SN), a plasticizer. Interestingly, when a small particle size (20 nm) and a certain fraction (50%) of nanoparticles are chosen, the electrolyte no longer shows leaching of SN; meanwhile, it exhibits high storage modulus at 20 MPa up to 90 °C and manifests mechanical properties similar to a solid polymer. The nanoparticle electrolyte enables improved capacity retention of poly(4-vinyl catechol) (P4VC) cathode compared to the control samples cycled without nanoparticles. It is noteworthy that nanoparticle electrolyte with SN plasticizer cannot fully prevent the diffusion of

active materials. The cell capacity degraded from 278 mAh g⁻¹ to 165 mAh g⁻¹ (60% retention) over 100 cycles at 39.7 mA g⁻¹, and in contrast, the cell capacity decayed from ca. 130 mAh g⁻¹ to ca. 100 mAh g⁻¹ (77% retention) over 500 cycles at 794 mA g⁻¹. The duration of the high-rate experiment is only one-fourth of the slow-rate cycling and exhibited better capacity retention. The result indicates possible time-dependent degradation mechanisms, which can be associated with the diffusion of cathode active materials in SN.

An alternative strategy to suppress active material diffusion at high temperatures is to increase the molecular weight of the active material. Polymerization of cathode molecules might be an efficient strategy to inhibit active material diffusion since it was already confirmed in liquid systems. Within this framework, Wei *et al.*¹²⁶ used poly(2-chloro-3,5,6-trisulfide-1,4-benzoquinone) (PCTB) cathode in PEO-Li_{0.3}La_{0.566}TiO₃ (LLTO) composite electrolyte and achieved 90% retention of maximum capacity after 300 cycles at 70 °C. Stable capacity performance is an indication of low cathode active material loss. Similarly, Shi *et al.*¹³¹ reported on solid-state cells involving poly(benzoquinonyl sulfide) (PBQS) cathode in a cross-linked PEO electrolyte made of chemically inert polyhedral oligomeric silsesquioxane (POSS) and triazole. High capacity retention (87%) was demonstrated after 100 cycles at 90 °C. While polymerization was revealed to be an efficient solution for high capacity retention, cathode active materials fraction remains an issue since PCTB and PBQS were used in low content at 30% and 56%, respectively.

An alternative unique property of SPE is the ability to conduct anions, leading to metal-free cells or what becomes known as molecular-ion batteries. Sato *et al.*¹²³ have recently reported a flexible metal-free all-organic solid-state battery pairing nitroxide-based polymer as cathode and polymerized viologen as anode. The solid electrolyte was a 2-μm-thick imidazolium-substituted

polyether film with TFSI⁻ anion conduction capability. The anion-based rocking-chair-type cell was flexible and reversibly discharged at 1.2 V even at 5C without added solvent and plasticizer (**Figure 3g**).

Recently, COFs start to emerge as an efficient strategy for designing new SPE.¹³² COFs are a class of crystalline porous organic polymers with permanent porosity and highly ordered structures.^{133, 134} Thanks to the aligned channels, which are accessible to Li salts, COFs become attractive for ion-conducting polyelectrolytes. COF-based SSEs can be classified into two main categories: i) binary-ion conductors based on infiltrating COFs with Li salts to boost ionic conductivity¹³⁵ and ii) single-ion conductors based on immobilizing anions on COFs using metal cation for charge compensation.¹²⁴ Li *et al.*¹²⁴ are the first to introduce COF-based SSE in organic batteries and proposed an all-solid-state Li-organic battery involving the energy-dense benzoquinone (BQ) as the cathode material (**Figure 3h**). In this work, the authors employed a solution-processable single-ion COF electrolyte (denoted as LiCON-3) bearing sulfonate ionic groups with 1.41 wt.% Li⁺ loading. The choice of sulfonate as the ionic group was justified by its weak coordination to Li⁺, leading to an ionic conductivity of $3.31 \times 10^{-5} \text{ S cm}^{-1}$ at 20 °C. Ionic groups such as O^- and CO_2^- were also explored, but they showed lower ionic conductivities due to their stronger coordination to Li⁺. The Li|LiCON-3|BQ all-solid-state cell displayed excellent cycling stability upon 500 cycles, but the electrochemical behavior of BQ was characterized with a featureless voltage profile (pseudo-capacitor like charge/discharge curves), which is completely different from those obtained in liquid electrolytes. Note that the cathode was composed of 60 wt.% of BQ as the active material and 7 wt.% of SN-LiTFSI as the catholyte (catholyte refers to the solid electrolyte employed in the cathode), and LiCOF-3 was only used as a separating electrolyte.

Organics in sulfide electrolytes

Metal thiophosphates and their derivatives (such as argyrodite and $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$) are classified as sulfide electrolytes.¹³⁶⁻¹³⁸ Sulfide electrolytes often possess high ionic conductivity and good formability among SSEs.¹³⁹ The major drawback of sulfide electrolyte is its chemical reactivity and electrochemical instability at the cathode-electrolyte interface.¹⁴⁰ Common inorganic cathode materials usually react chemically with sulfide electrolytes and operate at high redox potential far beyond the ESW of sulfides, resulting in the irreversible formation of a resistive SEI layer that deteriorates the battery performance.¹⁴⁰ Such electrochemical and chemical incompatibility can be alleviated by pre-coating cathode materials with a thin layer of ionic conductors, which is expensive to scale up. Furthermore, the volume expansion and shrinking of inorganic cathodes during cycling lead to contact loss between rigid inorganic particles and sulfide electrolytes. In contrast, **Figure 4a** shows favorable electrode-electrolyte interface when using organic cathodes in sulfide-based ASSBs due to better chemical, mechanical and electrochemical compatibility. First, there is no or minor chemical reactions between OBEMs and sulfide SSEs. Second, the low modulus of OBEMs results in reduced mechanical stress between solid electrolytes and active materials during repeated cycling. Finally, the moderate cathode redox potential of OBEMs is more compatible with the ESW of SSEs.

We discuss the electrochemical compatibility in more detail here. For instance, glass-ceramic Na_3PS_4 (NPS) electrolyte, a representative sodium-based sulfide electrolyte, is only electrochemically stable between 1.6 V and 2.7 V vs. Na^+/Na , far below the operating potential of inorganic high-voltage cathode materials.¹⁴¹ Replacing inorganic cathode materials with organic cathodes could mitigate the challenge of electrolyte instability. Chi *et al.*⁷⁰ reported $\text{Na}_4\text{C}_6\text{O}_6$ (NCO) electrode which undergoes two-electron two-sodium redox reactions within a potential range of 1.65-2.65 V vs. Na^+/Na , fitting the ESW of Na_3PS_4 electrolyte (**Figure 4b**). NCO achieved 99%

first-cycle coulombic efficiency and 90% of the theoretical capacity using a $\text{Na}_{15}\text{Sn}_4$ alloy anode (0.1 V vs. Na^+/Na). Charging to higher potential (3.1 V vs. Na^+/Na) resulted in irreversible capacity and impedance, attributed to the decomposition of NPS.

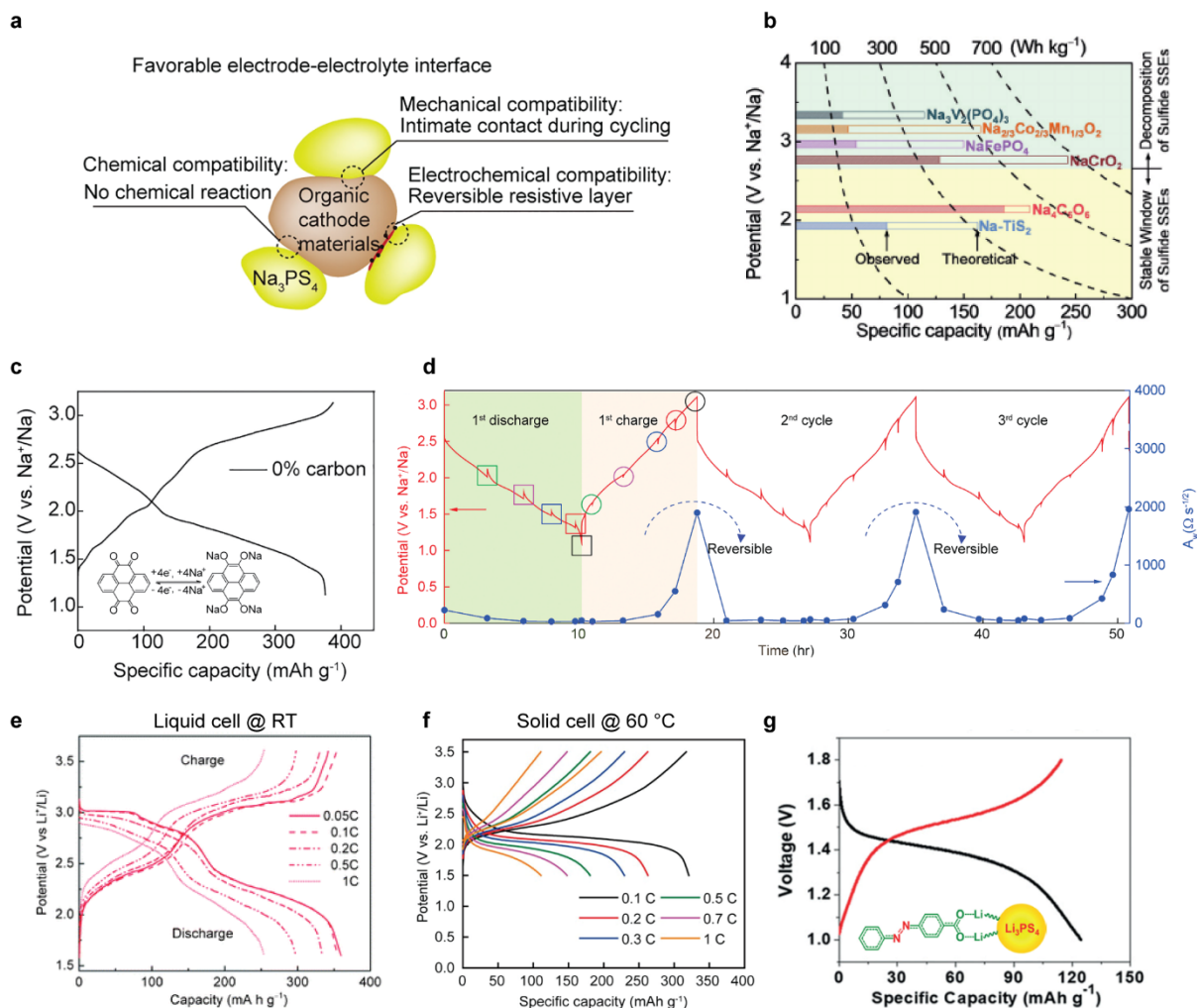


Figure 4: Overview of organic solid-state batteries involving sulfide electrolytes. a) Schematic illustration shows interfacial compatibility between organic active materials and sulfide electrolytes (Reproduced with permission from Ref. ¹¹¹. Copyright 2019 Elsevier Inc). b) Voltage profile for a $\text{Na}_4\text{C}_6\text{O}_6||\text{Na}_{15}\text{Sn}_4$ cell cycled in Na_3PS_4 at 60 °C (Reproduced with permission from Ref. ⁷⁰. Copyright 2018 John Wiley and Sons). c) Normal and d) intermittent galvanostatic voltage profiles for $\text{PTO}||\text{Na}_{15}\text{Sn}_4$ cell cycled in Na_3PS_4 at 60 °C accompanied with the evolution of

Warburg coefficient extracted from *in-situ* impedance spectra (Reproduced with permission from Ref. ¹¹¹. Copyright 2019 Elsevier Inc). Comparison of voltage profile for PTO||Li cells cycled e) in liquid electrolyte at room temperature and f) in Li₆PS₅Cl at 60 °C (Reproduced with permission from Ref. ¹⁴² and ¹¹². Copyright 2013 Royal Society of Chemistry and 2021 American Chemical Society respectively). g) Voltage profile for a PBALS||Li cell cycled in Li₃PS₄ (LPS), inset shows the interaction between PBALS and LPS electrolyte (Reproduced with permission from Ref. ¹¹⁵. Copyright 2018 John Wiley and Sons).

To further improve specific energy, Hao *et al.* employed a higher-capacity cathode material pyrene-4,5,9,10-tetraone (PTO) (theoretical capacity 409 mAh g⁻¹) in combination with Na₃PS₄ (NPS) electrolyte.¹¹¹ A notable difference between PTO and NCO is that PTO's end-of-charge potential (3.1 V vs. Na⁺/Na) exceeds the oxidation potential of NPS (2.7 V vs. Na⁺/Na). **Figure 4c** and **d** show that electrochemical cycling (between 1.1 and 3.1 V vs. Na⁺/Na) led to a reversible evolution of active material-electrolyte interfacial resistance. The Warburg coefficient increased above the NPS oxidation potential (2.7 V vs. Na⁺/Na). It reverted when the cell was discharged below 2.7 V vs. Na⁺/Na. Reversible formation of resistive passivation layer from electrolyte decomposition is further confirmed by the X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements on the composite cathode. The peaks from P-[S]_n-P bonds emerged at the charged state and disappeared at the following discharge state in the XPS spectrum. In contrast, in inorganic solid-state batteries with sulfide electrolytes, when no interfacial coating is applied, the irreversible formation of electrolyte decomposition product (*i.e.*, S⁰) at higher voltages (>4 V) is responsible for permanent capacity degradation.¹¹² In addition to the enhanced electrochemical stability, soft and compliant nature of PTO also

improves the structural stability of the composite cathodes. No contact loss was observed between cathode active materials and solid electrolytes even after 200 cycles, when the battery was subject to an external stacking pressure.

In addition to solid-state Na batteries, PTO was also recently reported for solid-state lithium-organic batteries.^{112, 143} The electrochemical profiles of organic cathodes cycled in sulfide electrolyte are found to deviate from those cycled in liquid carbonate electrolytes. For example, **Figure 4e,f** shows the voltage profiles of PTO cycled in a liquid electrolyte (1 M LiPF₆ in EC/DMC)¹⁴² and in a sulfide electrolyte (glass-ceramic Li₃PS₄).¹¹² In the liquid electrolyte, multiple plateaus in both charge and discharge curves indicate multiple stages of lithiation of PTO. In contrast, PTO cycled in sulfide electrolytes only shows one large plateau in the voltage profile. The exact mechanism has not been fully understood; a possible explanation is different reaction pathways in the two electrolytes.

Poor interfacial contact is another issue that contributes to large interfacial resistance between some cathodes and sulfide electrolytes. Organic cathodes with high specific capacity are believed to undergo volumetric evolution during lithiation/delithiation process¹⁴⁴ and may eventually result in contact loss between cathode active particles and solid-state electrolyte in the absence of stacking pressure. In addition, sulfide electrolytes are not as mechanically ductile as SPEs, which may worsen the situation. Chemically bonding organic cathode and electrolyte, proposed by Luo *et al.*,¹¹⁵ has proved to be a feasible approach to maintain interfacial contact (**Figure 4g**). PBALS molecule contains an electrochemically active azo group and a carboxylate group that ionically bridges with sulfide electrolyte. Raman spectrum of a PBALS/LPS/C composite show the disappearance of PS₄³⁻ characteristic peak and merging of PBALS characteristic peaks, which implies strong interaction between PBALS and LPS electrolyte.

PBALS was reported to exhibit better capacity retention than its counterpart without the carboxylate group due to the lower interfacial resistance between cathode active material and solid electrolyte.

Overall, OBEMs are promising for use with sulfide electrolytes due to interfacial chemical, mechanical, and electrochemical stability. The high ionic conductivity of sulfide electrolytes and the large specific capacity of OBEMs are both advantageous for cell performance in solid-state batteries. Efforts in electrode engineering are necessary to translate superior material-level properties to cell-level properties. This topic will be further discussed in section 4.

Organics in oxide electrolytes

Oxide electrolytes exhibit wider ESW than sulfide electrolytes, and thus the formation of resistive cathode-electrolyte interphase is less likely in organic-oxide solid batteries.⁹⁰ Moreover, unlike rigid inorganic materials, pliable organic materials are potentially capable of forming intimate interfacial contact with the electrolytes without energy-consuming preparation process such as co-sintering. Nevertheless, relevant report is extremely limited in this direction, possibly due to the absence of a feasible method to directly incorporate organic electrode materials with oxide electrolytes. Chi *et al.*¹¹⁰ reported solid-state Na-ion battery based on PTO cathode and β -alumina solid electrolyte (**Figure 5a**). However, the β -alumina was only used as a separating electrolyte, whereas the catholyte was based on PEO- NaClO_4 in order to have better contact with PTO.

So far, only one successful example is reported showing the incorporation of organic cathode with oxide electrolyte through direct contact. Nisula *et al.*¹⁴⁵ used atomic/molecular layer

deposition (ALD/MLD) technique to deposit a 5-42 nm layer of lithiated *p*-benzoquinone (denoted as Li₂Q) and a 30 nm layer of LiPON as the cathode and electrolyte, respectively, in an anode-free cell design, as shown in **Figure 5b**. The as-prepared cell showed high cathode utilization when the Li₂Q layer thickness was below 10 nm. However, the capacity merely grew with the cathode thickness when the latter increased to above 15 nm, indicating only a very thin layer of the cathode material adjacent to LiPON is electrochemically active. Understandably, the cathode active materials in thin-film cell undergo high-rate redox reaction even at low current density ($\sim \mu\text{A cm}^{-2}$ scale), while the absence of ion-conducting components in the cathode film limits the overall rate capability. Nevertheless, this report has demonstrated the potential compatibility between organic cathodes and oxide electrolytes, which would be benefiting for fundamental studies in the future.

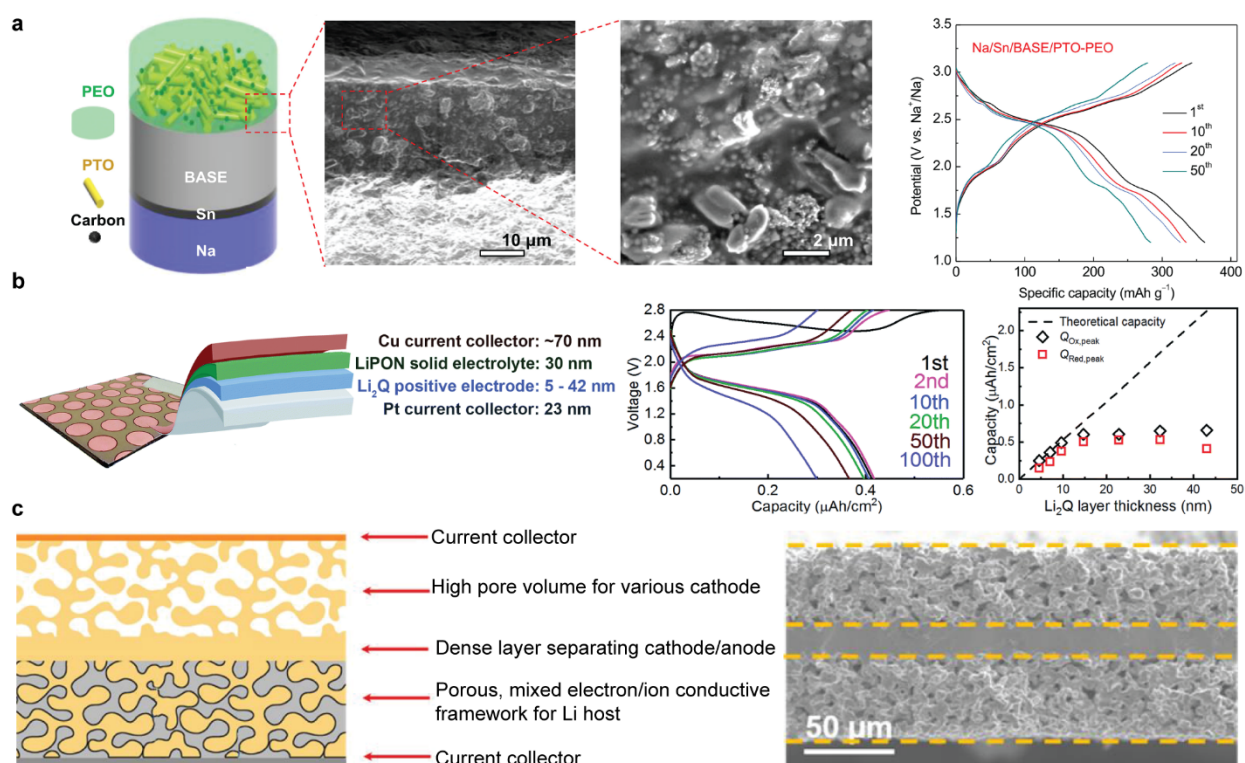


Figure 5: Overview of organic solid-state batteries involving oxide electrolytes. a) Schematic diagram of PTO-PEO|BASE|Sn|Na solid-state battery highlighting the use of PEO as an ionic mediator between PTO and oxide β -alumina (BASE), SEM images of the catholyte and the

corresponding voltage profile (Reproduced with permission from Ref. ¹¹⁰. Copyright 2018 John Wiley and Sons). b) Schematic illustration of a thin-film (Al|Li₂Q|LiPON|Cu) anode-free solid-state battery, the corresponding voltage profile, and cell capacity as a function of cathode thickness (Reproduced with permission from Ref. ¹⁴⁵. Copyright 2018 The Royal Society of Chemistry). c) Schematic illustration and cross-section image of a three-dimensional garnet framework capable of soft cathode infiltration. (Reproduced with permission from Ref. ¹⁴⁶. Copyright 2018 American Chemical Society).

Considering the fact that the flexible nature of OBEMs resembles the one of sulfur to some extent, some approaches in Li-sulfur batteries are potentially applicable to organic ASSBs with oxide electrolytes.¹⁴⁷ Xu *et al.*¹⁴⁶ coated carbon nanotubes on a three-dimensional garnet framework to build a mixed electron/ion conducting host for active materials (**Figure 5c**). The approach has enabled successful cycling of Li-sulfur battery in the garnet electrolyte, where sulfur was infused into the porous structure with adequate electron/ion percolation. Organic cathode materials can be melt-cast or solvent-cast into the porous structure, resembling sulfur cathodes.

Guidelines to achieve 500 Wh kg⁻¹ cell-level specific energy in solid-state Li-organic batteries

In order to understand and evaluate the performances of existing or new OBEMs for ASSB applications, studies must take into account the realistic conditions that meet the basic requirements of a practical cell, e.g. a multi-layer stacked pouch cell, owing to the possibility of maximum use of space and active materials. For simplicity and clarification purposes, we have set an ambitious goal targeting a solid-state Li-organic cell design with a cell-level specific energy of

500 Wh kg⁻¹, an ambitious goal set by the U.S. Department of Energy Battery500 Consortium. The goal will help us evaluate the relevant parameters and the material-level energy metrics required for OBEMs to be competitive with their peers. Furthermore, the goal will direct and organize research to provide consistent comparison within organic materials category, as well as inorganic and sulfur cathodes. Finally, the goal also helps to scrutinize the impact of organic materials and component properties on the achievable cell-level energy density to better position OBEMs in the ASSB landscape.

Solid-state Li-organic cell design

Among the five possible cell configurations listed in section 2.3, Li metal-based and anode-free cells are the most realistic designs to achieve the goal of 500 Wh kg⁻¹. **Figure 6a** shows a solid-state Li-organic cell design that could result in 500 Wh kg⁻¹ cell-level specific energy, which features a composite cathode with high material-level specific energy and high active loading, a thin electrolyte layer and Li metal as the anode. **Figure S3** lists the detailed cell design parameters.

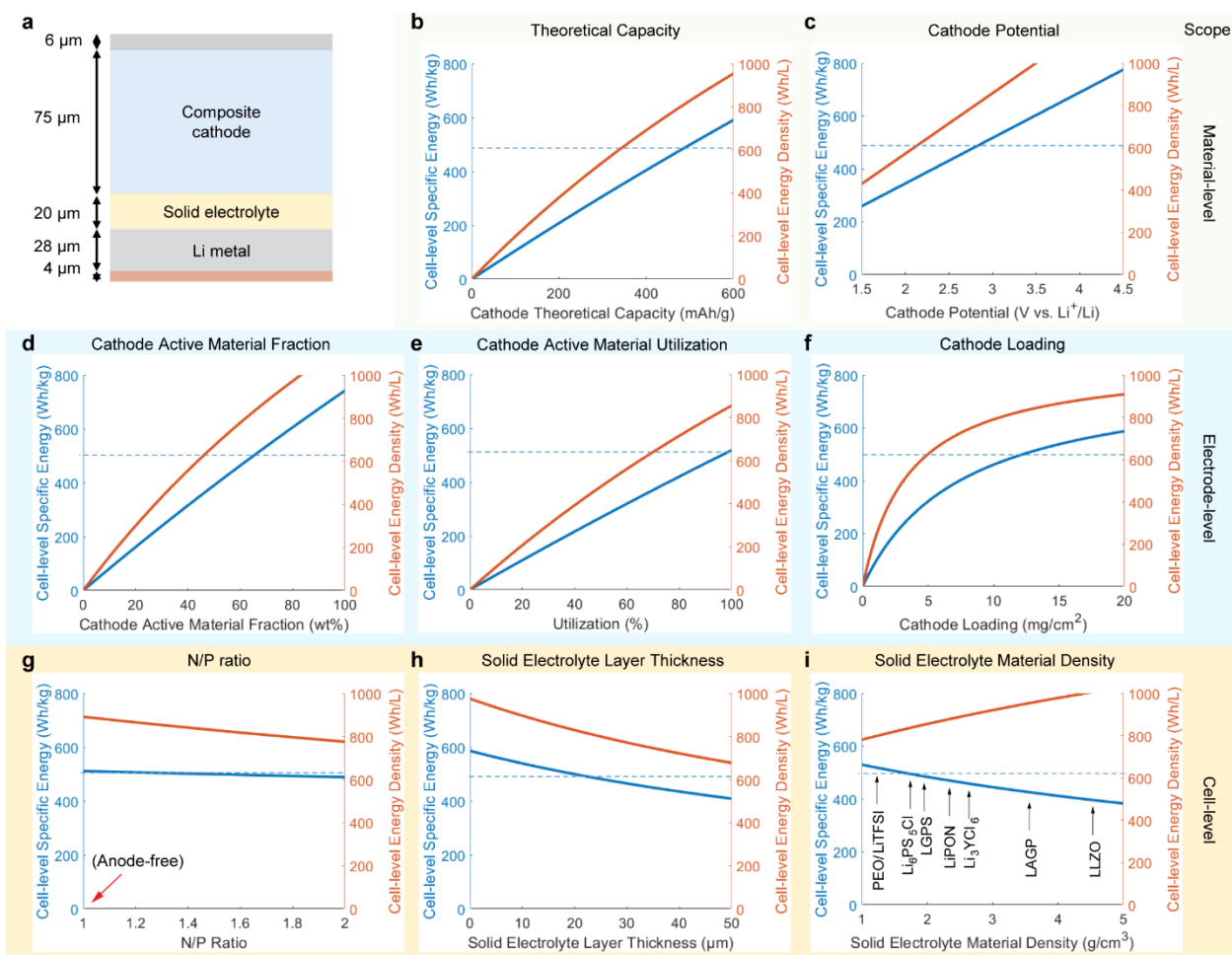


Figure 6: A solid-state Li-organic cell design with 500 Wh kg^{-1} cell-level specific energy and the impact of relevant cell parameters. a) Cell-stack used for calculation (details in Figure S3). Parameters pertinent to material-level properties include b) cathode theoretical capacity and c) cathode potential. Parameters relevant to electrode-level properties include d) active material fraction, e) cathode utilization, and f) cathode mass loading. Parameters influencing the cell-level design include g) N/P ratio, h) SSE thickness, and i) density of solid electrolyte and catholyte. Except for the variables shown here, all other parameters are fixed to the values listed in Figure S3.

The impact of cell parameters on cell-level specific energy (Wh kg^{-1}) and energy density (Wh L^{-1}) will be carefully discussed below. The parameters are briefly classified into three categories: 1) molecular design that enables higher active material-level specific energy; 2) electrode engineering that optimizes active mass loading and active material utilization and 3) cell-level design that minimizes the inactive components which reduce the overall cell-level energy. Here, the material-level specific energy is calculated by multiplying theoretical specific capacity and average working potential (vs. Li^+/Li) of active materials, while the cell-level specific energy is normalized by the mass of the entire cell, including cathode, electrolyte, anode and current collectors.

Active material-level parameters: The deterministic impact of cathode material theoretical capacity and redox potential on the cell-level specific energy and energy density is depicted in **Figure 6b,c and Figure S4**. As expected, theoretical capacity stands out as a crucial parameter since it scales linearly with the overall cell-level energy; the same is also applicable for the redox potential. In order to reach the goal, according to the studied case scenario, the organic cathode material should deliver specific capacity as high as 500 mAh g^{-1} and operating potential as high as $2.9 \text{ V vs. Li}^+/\text{Li}$, which results in a material-level specific energy of 1450 Wh kg^{-1} .

Electrode-level parameters: The significance of electrode-level engineering is shown in **Figure 6d-f**. In conventional organic batteries with liquid electrolytes, only an electronically conductive network is necessary since liquid electrolyte could infiltrate the porous cathode composite and assure ionic percolation. In contrast, in solid-state batteries, both electronic and ionic percolations are required in a considerable fraction since most OBEMs are poorly electronic/ionic conductive. Therefore, the cathode composite needs careful engineering in terms of microstructure to maximize active material fraction without sacrificing its utilization. As

depicted in **Figure 6d,e** and **Figure S5**, both active material fraction and utilization scale linearly with the overall energy, which means that high theoretical material-level capacity alone is not sufficient to guarantee high energy density if the active material fraction and utilization do not follow.

Cathode areal mass loading is the limiting factor that determines the amount of energy stored in a given cell. The higher the active mass loading, the higher the specific energy.¹³⁹ However, cathode loading is revealed to be less critical as compared to active material fraction and utilization. As shown in **Figure 6f** and **Figure S6**, once the cathode loading surpasses 8 mg cm⁻², the cell-level specific energy reaches a "saturation" point where the increase in specific energy slows down as the cathode loading increases. In addition, when the cathode loading (areal capacity) increases, the amount of Li being plated/stripped increases accordingly, which likely causes interfacial instability between solid electrolyte and Li metal anode due to non-uniform plating and successive dendrite growth.¹⁴⁸⁻¹⁵⁰ Moreover, high areal capacity puts additional demands on the cell packaging to cope with the large volume/pressure change during the cycling. Overall, in order to achieve the goal, the active material fraction must be no less than 60%, and the material utilization should be close to 100%, whereas the cathode loading could be around 10 mg cm⁻².

Cell-level parameters: the contribution of parameters on the cell-level specific energy is illustrated in **Figure 6g-i**. The N/P ratio is defined as the areal capacity ratio between the negative and positive electrodes in the battery community. Ideally, the N/P ratio should be as low as possible where a minimum mass of excess Li metal is desirable for high specific energy (**Figure 6g** and **Figure S7**). The same also applies to the solid electrolyte (for separation) thickness (**Figure 6h** and **Figure S8**). The solid electrolyte material density is an important parameter to take into

account as well, which needs to be within certain constraints. Solid electrolyte with high gravimetric density introduces additional weight, which results in decreased cell-level specific energy. On the other hand, with the cathode maintaining the same active material mass fraction, denser solid electrolyte accounts for less volume, achieving higher volumetric energy density. These cell-level parameters show a considerable effect on the specific energy/energy density, albeit less significant compared to material-level and electrode-level parameters once Li anode and separating layer are within reasonable thickness range discussed above.^{151, 152} Optimization of cell-level design is gathering growing attention in the solid battery community and Zhu's group has reported an excellent review on this regard.¹³⁹

From the above analysis, it is clear that cell components constitute critical parameters that can drastically impact the cell-level energy density if not well optimized. In the following sections, we will provide guidelines at different levels in order to achieve the aforementioned goal. **Figure 7** summarizes the key research focus on areas of interest, including active molecule design, electrode microstructure engineering, and cell configuration design.

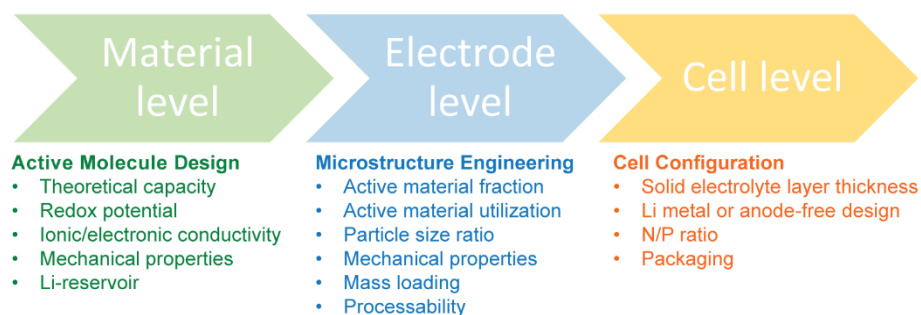


Figure 7. Research directions on selected areas of interest, including molecular design, electrode microstructure engineering and cell design.

Materials-level design

According to **Figure 6**, an organic cathode with material-level energy density close to 1450 Wh kg⁻¹ is required to achieve the goal. Note that the same value could be matched by increasing the potential while sacrificing the capacity or vice versa (**Table S2**). In this event, one can wonder which cathode design would be preferable: high potential or large capacity. From the perspective of lithium anode stability, thicker lithium metal plated by large-capacity cathode materials may be less favorable (see discussion in section 4.1). In this sense, high-potential cathode material seems advantageous, given the same experimental conditions. On the other hand, the cathode materials can be synthesized in their reduced form (Li-reservoir) or its oxidized form (Li-host). Unlike inorganic cathode materials, the physical, chemical and mechanical properties of OBEMs could vary drastically depending on the oxidation state. Properties such as air sensitiveness, elastic modulus and solvent-solubility would impact the electrode manufacturing process. As to the cell design, the Li-reservoir-type cathode would be preferable since it enables the anode-free configuration without excess Li.

In terms of organic chemistry, each design might be more or less achievable depending on the synthesis feasibility and material handling. For the sake of simplicity, we take the already-explored PTO as a starting point for molecular design. The reduced form of PTO, Li₄PTO, exhibits a theoretical capacity of 369 mAh g⁻¹ and an operating potential of 2.3 V vs. Li⁺/Li in a solid cell, which gives a theoretical specific energy of 850 Wh kg⁻¹. In general, the theoretical capacity of an organic cathode material could be increased either by reducing the molecular weight or adding multiple redox centers.¹⁵³⁻¹⁵⁷ The organic cathode database already contains some suitable high capacity materials that are potentially capable of achieving the goal, e.g. benzoquinone (439 mAh g⁻¹, 1229 Wh kg⁻¹),¹⁵⁸ rhodizonate salt (510 mAh g⁻¹, 1326 Wh kg⁻¹),^{144, 154} and dinitrobenzene

(546 mAh g⁻¹, 1280 Wh kg⁻¹)¹⁵⁶, assuming the average working potentials are identical in liquid electrolytes and solid electrolytes.

On the other hand, various approaches might be considered to increase the potential, including the introduction of electron-withdrawing groups (-SO₃⁻, -CN, -CF₃),^{43-45, 159, 160} utilization of electrostatic effect,^{41, 161} introduction of heteroatom¹⁶² or discovery of new redox centers capable of operating at high potential.¹⁰⁵ These approaches were explored and validated on a few model molecules to produce O₂-stable Li-reservoir high voltage (> 2.91 V vs. Li⁺/Li) organic cathode materials; e.g. Li₄-p-DHBDS (e.g. 3.25 V vs. Li⁺/Li),⁴⁴ Mg(Li₂)-p-DHT (e.g. 3.45 V vs. Li⁺/Li),⁴³ Li₄-p-DHBDA (e.g. 3.4 V vs. Li⁺/Li)¹⁶¹ and Li₂-DCPDSA (e.g. 3.45 V vs. Li⁺/Li).¹⁰⁵ Meanwhile, the main bottleneck of these approaches is the compromised capacity due to the increased molecular weight. The so-far reported theoretical capacities for high-voltage organic cathodes do not exceed 241 mAh g⁻¹. Ideally, the potential of a given organic cathode material needs to be increased without compromising the capacity. At this moment, there is no reported design strategy capable of fulfilling this stipulation; yet, thanks to the richness of organic chemistry and molecular design, there is still much room left for future designs of such cathode.

Electrode-level engineering

The material-level properties (potential, specific capacity) have been a major research focus in liquid organic batteries. The electrode-level microstructure engineering becomes equally important in solid-state organic batteries. The essence of electrode engineering is to build efficient percolated conductive networks for both electrons and ions in a composite cathode and maximize the fraction and utilization of the active materials. While some work on microstructure control was reported in inorganic cathode studies,¹⁶³ little efforts were devoted to electrode engineering in

organic composite electrodes for solid-state batteries. Without microstructure control, reasonable active material utilization is achieved only at a low active material fraction (ca. 20 wt%) and low areal loading ($\sim 1.0 \text{ mg cm}^{-2}$) in composite cathodes featuring OBEM and sulfide electrolyte.^{111, 143} Tuning the microstructure of organic composite cathode is of high priority to improve electrode-level specific energy. Practical approaches include downsizing active material particles and microstructure engineering.^{163, 164}

In solid-state batteries, the size ratio of electrode materials and solid electrolyte particles is found to correlate with electron and ion transport and battery kinetics, as both experimental and computational studies showed.¹⁶³ Unlike inorganic cathodes with decent electronic conductivity ($1 \times 10^{-3} \text{ S cm}^{-1}$ for LiCoO_2 ,¹⁶⁵ $4.1 \times 10^{-3} \text{ S cm}^{-1}$ for NMC811¹⁶⁶), organic cathode materials suffer from poor electronic conductivity ($1.47 \times 10^{-13} \text{ S cm}^{-1}$ for PTO²⁷). Only the surface of OBEM particles in contact with conductive carbon is electrochemically active, which results in low utilization of active materials. Synthesizing micro-sized or nano-sized organic materials is a practical strategy to overcome the conductivity issue.^{46, 167, 168} Mechanical milling and chemical antisolvent precipitation methods are two common approaches to downsize organic particles.^{46, 167, 169} Wang *et al.*¹⁷⁰ first demonstrated the size effect of organic materials on electrochemical properties in liquid cells featuring carbonyl-based organic salt $\text{Na}_2\text{C}_6\text{O}_6$. $\text{Na}_2\text{C}_6\text{O}_6$ nanorods showed higher capacity, rate capability as well as better cycling stability than micro-sized bulk and micro-rod $\text{Na}_2\text{C}_6\text{O}_6$. Utilization of active materials and kinetics of electrochemical reaction both benefited from improved interfacial contact between nanorod structure and liquid electrolyte. Hao *et al.*¹¹¹ compared the voltage profiles of PTO in Na-ion solid-state batteries with different sizes and morphologies. It turned out that PTO nanorod reached 49% of theoretical capacity at 1C rate, outperforming bulk PTO (12%) or PTO micropellets (37%). Meanwhile, PTO nanorods

exhibited the highest material-level specific energy at 587 Wh kg⁻¹. The observation accorded with the results in batteries with liquid electrolyte.¹⁴² Recently, cryomilling technique has been introduced to optimize the microstructure of organic cathode via decreasing PTO domains.¹¹² Segmentation of SEM images showed that the size of PTO domains prepared by cryomilling is one order of magnitude smaller than hand-milled counterparts. The downsized and homogenized PTO material resulted in high active material utilization at 99.5% and high material-level specific energy at 828 Wh kg⁻¹. Reduction in electrochemically inactive parts within the organic material particle was deemed critical for full active material utilization.¹⁶⁴

Moreover, the adequacy of textures between the conductive agents and the active material also plays a major role in charge transfer. Lakraychi *et al.*¹⁶⁹ have stressed this point in a study involving a dicarboxylate-based material cycled in liquid electrolyte, where the organic molecule was able to show satisfactory performances by using 20 wt.% of graphitic carbon additive. Note that such low carbon content is very rare for organic anode materials. The matching of the particle size and morphology between active materials and conductive agents might also improve the particle-to-particle contact of these components. Different electrode engineering techniques were used, such as ball milling,⁴⁶ in-situ coating,¹⁷¹ wet impregnation, and direct crystallization onto the surface of the conductive agent,¹⁷² to achieve high active material fraction and high utilization.

In addition to material utilization, high active material fraction in the cathode is another important factor. Low mechanical stiffness of OBEMs is a double-edged sword in high-energy solid-state batteries. On the one hand, good mechanical compliance between cathode and catholyte ensures consistent and intimate interfacial contact during cycling.¹¹¹ On the other hand, soft cathode material reportedly leads to unfavorable microstructure of composite cathode with inhibited ionic conduction, especially at high mass loading.¹⁴³ Since the elastic moduli of organic

active materials such as PTO is lower than that of ceramic solid electrolytes,¹¹¹ organic electrode materials would naturally form a continuous region, resulting in a non-ideal “electrolyte-in-active material” microstructure. Consequently, in conventional electrode fabrication process (dry mixing), a relatively large volume ratio of solid electrolyte is mandatory to establish a percolated ionic pathway. Solvent processing has been developed to prepare the composite electrode to rectify the problematic microstructure. Zhang *et al.*¹⁴³ mixed organic cathode PTO with sulfide electrolyte $\text{Li}_6\text{PS}_5\text{Cl}$ in solvent ethanol and increased the active material fraction from 20 to 50 wt.% while maintaining high utilization (97.6%). Here, the solvent has three functions. First, it helps to form a continuous solid electrolyte domain by pre-forming the core (PTO)-shell ($\text{Li}_6\text{PS}_5\text{Cl}$) particles before cold pressing. Second, the solvent-assisted mixing process generates a more homogeneous distribution of electrode material in the composite. Moreover, in the presence of solvents, the unique redox chemistry between PTO and electrolyte is revealed in forming a reversible and stabilized interphase. With increased active material fraction, an 83% increase in electrode-level specific energy is demonstrated, at 302 Wh kg^{-1} , comparable to LiCoO_2 -based solid-state batteries. This work illustrates the critical role of microstructure engineering in optimizing the active material fraction in improving electrode-level specific energy/energy density.

Positioning OBEMs among leading cathode materials

Advancements in molecular design, electrode engineering and cell design contribute to increasing specific energy at the cell level. Different electrochemical systems have their advantages in either material-level specific energy or capability for high active material fraction.

Figure 8a and **Table S2** position representative all-solid-state Li metal batteries with different cathodes from the standpoint of cell-level and material-level specific energy, respectively. Li-NMC is one of the leading cathode candidates. With average cell voltage at around 3.8 V and

specific capacity between 200 mAh g⁻¹, NMC shows material-level energy density as high as 760 Wh kg⁻¹. In addition, NMC composite cathode often maintains sufficient utilization, even at a high active material fraction (>80 wt.%). Samsung demonstrated a prototype pouch cell (0.6 Ah) with NMC cathode and anode-free design with high cell-level energy density >900 Wh L⁻¹.¹⁷¹ Solid Power reported a 22-layer, 20 Ah Li-NMC pouch cell with cell-level specific energy at 330 Wh kg⁻¹.^{173, 174} Attempts to enhance the cell-level specific energy are demonstrated by developing high-voltage, high-capacity cathodes and optimizing the cell design.¹³⁹

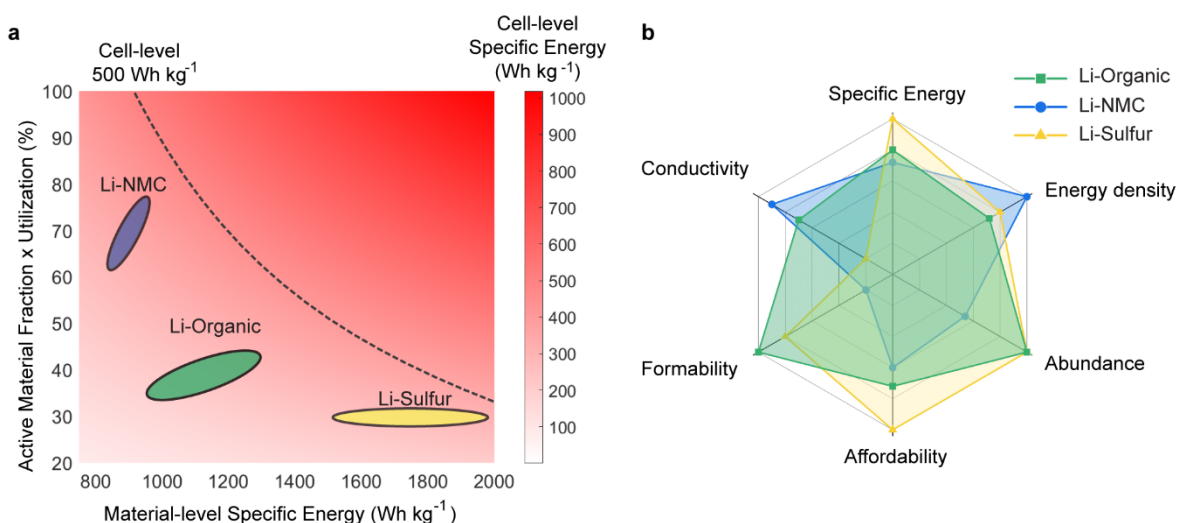


Figure 8. Comparison of different cathode chemistry in Li-metal solid-state batteries. a) Positions of Li-NMC, Li-organic, and Li-S systems with respect to material-level specific energy and electrode-level active material fraction/utilization. The color map indicates different levels of cell-level specific energy calculated based on parameters in Table S2. b) Semiquantitative comparison of practical attributes of the three cathode materials (Adapted with permission from Ref. ¹¹². Copyright 2021 American Chemical Society).

Another cathode candidate is sulfur. The Li-S system often exhibits high specific energy,^{175,}
¹⁷⁶ however, Li-S batteries still suffer from various issues that prevent their successful

implementation into real applications. In liquid Li-S batteries, a relatively large electrolyte/sulfur (E/S) ratio is required for acceptable material utilization, lowering the energy density.¹⁷⁷ Solid Li-S batteries can be designed to have a higher specific energy. Solid-state Li-S batteries show different reaction pathways compared to liquid cells, resulting in a compromised operating potential.^{177, 178} Consequently, the research focus in the Li-S battery community mainly falls on improving cell stability, rate performance and sulfur utilization.¹⁷⁹ The cell-level specific energy of state-of-art Li-S battery is reported to be around 370 Wh kg⁻¹ without considering the mass of current collector.^{180, 181} It is noteworthy that the electrode microstructure engineering techniques for Li-organic solid-state batteries are also applicable to Li-S systems with soft and insulative sulfur cathode material.

Similar to Li-S batteries, Li-organic batteries have yet to reach its full potential with regard to cell-level specific energy. A typical Li-organic cell has an average operating voltage between 2-3 V and tunable specific capacity up to 546 mAh g⁻¹. The maximum possible material-level specific energy of OBEM is between NMC and sulfur (**Table S2**). Organic cathodes stand out as credible competitors among leading cathodes for solid-state batteries. The critical challenge for Li-organic lies in the effective active material fraction, since the highest ever reported cathode active material fraction with sufficient utilization (>95%) is only 50 wt.% for OBEM, much lower than the case in NMC cathode composite. Therefore, higher cell-level specific energy can be expected once the effective active material fraction of Li-organic cell reaches the same or similar level as Li-NMC cells. Besides, Li-organic outperforms Li-NMC in other aspects such as formability, affordability, and abundance, as shown in **Figure 8b**. Recyclability is also a major advantage for OBEMs, which can be either extracted from waste batteries via selected solvents or by combustion at moderate temperatures to retrieve Li elements.¹⁸² With a tunable theoretical

capacity, potential, and electronic conductivity, Li-organic may have broader applications compared to the Li-S system. Additionally, thanks to the richness of organic chemistry and molecular engineering, there is still much room for designing OBEMs with a higher material-level specific energy. Li-organic batteries are poised to become an indispensable part of energy storage systems as the availability concerns of transition metals (especially cobalt) linger.

The dissolution of OBEMs stands out as one of the major issues hampering their implementation in liquid-based sealed batteries. Various strategies have been explored to overcome this issue, but they always come at the expense of energy metrics. On the other hand, the recent development of SSEs and their credible promise confirmed with the promising results obtained in inorganic batteries may provide a better future for OBEMs. The molecular flexibility, the promising capacities and the redox potential tuning in OBEMs provide a plethora of organic molecules ready to be explored in the solid state, either for fundamental understanding purposes or energy-dense organic solid-state batteries. The combination of OBEMs with SSEs will result in several cell configurations with different key features. Li-organic and anode-free designs are promising to achieve energy-dense solid-state batteries.

The reported organic solid-state batteries validate the feasibility of combining OBEMs with SSEs, but many serious challenges remain to be addressed. Most solid-state organic batteries employed SPE as the ionic conductor. At high temperatures, organic batteries with SPE showed better electrochemical performances in the first several cycles compared to their liquid counterparts. Still, capacity decay became inevitable in later cycles due to the active material diffusion in the polymer matrix. Polymerization of the electroactive molecules was found to be efficient in preventing the diffusion but at the cost of sacrificed active material utilization. At room

temperature, the poor ionic conductivity of SPE limits cell performance. The incorporation of solvents or inorganic components both demonstrated encouraging results.

Inorganic-based solid electrolytes have also been explored, with much focus on sulfide electrolytes. From the perspective of sulfide electrolyte stability, OBEMs might outperform inorganic cathodes due to their moderate operating potential and similarity in mechanical properties. The reversible formation of decomposition products avoids the complete oxidative degradation of sulfide electrolytes and thus enables prolonged cyclability. On the other hand, mechanical rigidity, poor processability, and low-to-moderate ionic conductivity discourage oxide electrolytes from being incorporated in organic batteries. Strategies to overcome these issues are desirable for the implementation of OBEMs in oxide electrolytes.

A systematic analysis of the prospects of organic solid-state batteries is delivered by discussing the intrinsic and technical properties of Li-organic solid-state batteries from different perspectives: material-, electrode- and cell-level. Cell parameters such as active material theoretical capacity, material potential, active material fraction, and material utilization are considered dominant for cell-level specific energy. Other relevant parameters and their impact on the cell-level specific energy are also discussed. Finally, guidelines from material design to cell design are proposed to achieve the ultimate goal, namely 500 Wh kg⁻¹ cell-level specific energy based on Li-organic solid-state batteries.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge at XXX.

Classification of solid-state electrolyte; classification OBEMs and selected examples of different redox classes; performances of solid-state batteries accommodating OBEMs; cell design

parameters of a 500 Wh kg⁻¹ Li||OBEM cell; cell parameters influencing the cell-level specific energy; energy metrics comparison of OBEMs with leading cathode materials (NMC and sulfur).

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Notes

Y.Y. and Y.L. have equity interest in LiBeyond LLC. Their relationship with LiBeyond LLC has been reviewed and approved by the University of Houston in accordance with its conflict of interest policies.

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