

Perspective

Positioning Organic Electrode Materials in the Battery Landscape

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The quest for cheaper, safer, higher-density, and more resource-abundant energy storage has driven significant battery innovations. In the context of material development for next-generation batteries, here we compare head-to-head organic battery electrode materials (OBEMs) with dominating/competing inorganic materials through analyses of charge storage mechanism, working potential, specific capacity, resource availability, and more. We show that from high-energy lithium batteries to aqueous and all-solid-state batteries, OBEMs can be designed to be sufficiently capable and offer unique feature sets unmatched by other materials. Future research directions toward practical application of OBEMs are discussed.

Introduction

The rapidly growing markets of electric vehicles (EVs) and grid integration of renewable energy sources have triggered demand for batteries with unprecedentedly low cost, high specific energy, and excellent safety.¹ Meanwhile, the multi-terawatt-hour scale of energy storage in these applications has, for the first time, raised concerns about the resource availability and sustainability of the materials used in batteries.² Among battery technologies available today, lithium-ion batteries (LIBs), which have found immense success in portable electronics, stand out as a top candidate for EV batteries and are being considered for grid storage as well. However, existing LIBs use cobalt-heavy active electrode materials that are predicted to see supply constraints going down the path and can be too expensive to meet long-term capital cost goals for grid storage and EV systems ($\$100 \text{ kWh}^{-1}$). On the other hand, the safety issues with commercial LIBs mainly originate from the flammable and volatile nonaqueous electrolytes. Safer systems with aqueous and all-solid-state electrolytes are being actively developed, but today's active electrode materials are not optimized for these electrolytes in terms of chemical and electrochemical compatibility. In the course of overcoming the above limitations, considerable innovations are taking place in the development of active materials featuring sufficiently high energy, Earth-abundant elements, and unique electrolyte-dictated properties. A notable family of such materials is organic battery electrode materials (OBEMs), which comprise electrochemically redox-active organic compounds including molecules, polymers, and organometallics where the organic components contribute to redox activity.

Active exploration of OBEMs as active electrode materials for rechargeable batteries started with conductive polymers (CPs; e.g., polythiophene) from the early 1980s to late 1990s.³ CP-based batteries showed comparable specific energy and cycling stability with those of lead-acid batteries, but the costly and unsafe lithium anode and organic electrolytes did not help with the batteries' competitiveness. With the advent of energy-dense and highly reversible inorganic intercalation compounds (IICs) such as lithium cobalt oxide (LiCoO_2) and graphite, research on CPs as

Context & Scale

Modern organic electrode materials will potentially enable the latest battery chemistries for meeting the cost, safety, and specific energy requirements of electric vehicles and grid storage. The moderate working potential and high specific capacity make them compatible with nonaqueous, aqueous (any pH), and sulfide solid electrolytes while achieving desirable specific energy. With proper design, the reversible ion-insertion reaction and adequate conductivity further lead to long cycle life and fast kinetics. Synthesis analysis reveals no concerns in resource availability for the targeted markets. They will accelerate the development of ultra-high-energy lithium batteries, high-stability/energy aqueous batteries, and solid-state batteries, which are not satisfactorily enabled by existing inorganic electrode materials. Going forward, deeper understanding of charge storage mechanisms and practical electrode/cell design will be indispensable for applications of organic electrode materials.

lithium battery electrode materials had largely stopped. Organosulfur compounds⁴ and later nitroxide radical polymers⁵ continued to evolve in the background, but it was not until late 2000s when organic carbonyl compounds (OCCs) with high specific energy and reasonable cycling stability were reported did OBEMs start to gain attraction again.^{6–8} During the last decade, hundreds of research articles have been published on OBEMs, resulting in several comprehensive review articles providing insights into their potential environmental friendliness, development history, molecular design strategies, all the way to analysis of individual families of OBEMs.^{9–15} While OBEMs are still new in terms of understanding compared with IICs, which have been commercialized for three decades with no signs of slowing down, we feel that the considerable amount of works done has enabled us to answer the inevitable questions that have been lingering over battery researchers' minds:

- How are OBEMs and IICs similar/different regarding charge storage mechanism?
- How do OBEMs' electrode performance parameters stack up against those of other existing/emerging materials?
- How do their economics and resource availability compare with existing materials when facing the terawatt challenge?
- How will OBEMs, with their unique properties, enable new battery technologies?

Through answering these questions, we strive to position OBEMs in the broad context of battery materials and increase awareness among the energy community.

Here we start with the charge storage mechanism of modern OBEMs with an emphasis on comparison with those of IICs and previous-generation OBEMs (also known as CPs). The storage mechanism determines the reaction reversibility, redox potential, and specific capacity of modern OBEMs. We then perform a head-to-head redox potential/specific capacity comparison of selected OBEMs and classes of inorganic materials intensively studied for high-energy EV batteries (e.g., 500 Wh kg⁻¹ at cell level). An analysis of the synthesis of state-of-the-art OBEMs from possible biomass and petrochemicals follows to assess the short-/long-term resource availability. Finally, we present recent examples in which the structural versatility and suitable redox potentials allow OBEMs to be custom designed for aqueous and all-solid-state batteries, and achieve unprecedented cycling stability and high specific energy.

Charge Storage Mechanism of Modern OBEMs: A Break from the Past

Here we use the term "modern OBEMs" to differentiate OBEM families centered in today's battery research from CPs, the previous generation of OBEMs. Modern OBEMs span a very wide range of organic compounds, some of which even have a π -conjugated polymer main chain like CPs. What separates modern OBEMs from CPs is that their electroactivity originates from dedicated redox-active functional groups instead of a highly delocalized p-/n-dopable π -conjugated polymer chain. The performance characteristics (redox potential, reversibility, specific capacity, etc.) of modern OBEMs are predetermined by the redox-active functional groups, while those of CPs by the building blocks of the π -conjugated chain. It is therefore natural to categorize modern OBEMs according to the redox groups (carbonyl, nitroxide, organosulfide, etc.) regardless of the polymer main chain (in the case of polymeric OBEMs),¹⁰ while CPs are typically categorized by the composition of the main chain.³ The introduction of dedicated redox groups makes modern

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OBEMs fundamentally different from CPs in terms of charge storage mechanism and electrode performance but somewhat akin to IICs.

Figure 1A shows the electrode reaction of a typical CP (e.g., polythiophene) as a cathode material, the most commonly proposed battery application scenario for CPs. The charging/p-doping/oxidation of CPs takes electrons out of the π -conjugated main chain, and the positive charge left on the chain is balanced by anions (e.g., PF_6^-) from the electrolyte. Because of the involvement of anions, this reaction is also referred to as the anion-insertion reaction. Depending on the nature of the π -conjugated building blocks, it takes 3–5 aromatic rings in the main chain to stabilize/store one positive charge. This charge storage mechanism predetermines low specific capacities because: (1) the large number of aromatic rings needed to store a single charge leads to high equivalent weight; (2) the anions used in nonaqueous electrolytes are complex anions that each weighs more than one aromatic ring and adds noticeably to equivalent weight; (3) since there are no suitable anion-storage anode materials, all anions in a discharged CP-based battery are stored in the electrolyte, and the solvents needed to dissolve all the salts sometimes weigh even more than the salts themselves. The specific capacity for the polythiophene reaction shown in Figure 1A, when only considering the molecular weight of the undoped polymer, is 109 mAh g^{-1} , which drops to 28.9 mAh g^{-1} once the weight of electrolyte is included in the calculation (assuming a relatively concentrated 2 M LiPF_6 in ethylene carbonate/dimethyl carbonate 1:1 [v/v] as electrolyte). Considering an average cell voltage of $\sim 3.5 \text{ V}$ when paired with a lithium anode, a polythiophene-Li battery gives a material-level specific energy (E_{mater}) of $\sim 100 \text{ Wh kg}^{-1}$, which agrees with the projection¹⁶ that the energy of CP-based batteries will be comparable with that of lead-acid batteries ($\sim 80 \text{ Wh kg}^{-1}$ at material level). Another problem associated with the anion-insertion mechanism is that anions only diffuse in the presence of solvents, so CPs must be fully swollen by electrolytes for the redox reaction to happen.¹⁷ The related volume expansion-shrinkage during charging-discharging penalizes the mechanical integrity and, thus, cycling life of the CP electrode.

Modern OBEMs avoid many and, in some cases, all of the above issues. Take OCCs for example: one charge is stored in the redox conversion between $\text{R}(\text{C}=\text{O})\text{R}'$ (oxidized) and $\text{R}(\text{C}-\text{O}^-\text{M}^+)\text{R}'$ (reduced; $\text{M} = \text{Li}, \text{Na}, \text{etc.}$). The minimum active unit for the reaction is the carbonyl group ($\text{C}=\text{O}$) with a formula weight of 28 g mol^{-1} (cf. 246 g mol^{-1} for three thiophene rings), which is a very good starting point to design high-capacity materials. The cation-storage mechanism allows an OCC-based battery to be designed as a “rocking chair” system where the electrolyte serves as an ionic connection between the cathode and a cation-storage anode instead of an anion reservoir. A minimal amount of electrolyte to wet the electrodes is sufficient for a working battery. Figure 1B shows the Na storage in the disodium salt of 2,5-dihydroxy-1,4-benzoquinone ($\text{Na}_2\text{C}_6\text{H}_2\text{O}_4$), a small-molecule OCC cathode material.¹⁸ This one-ring molecular salt stores two electrons/ Na^+ , corresponding to a theoretical specific capacity of 233 mAh g^{-1} (considering the formula weight of the fully sodiated state) with no discount by electrolyte involvement in the reaction. The six-member rings form organic layers composed of only C and H, while sodium ions coordinate with O atoms and form Na-O layers between the organic layers. Sodium ions migrate within the Na-O layers without diffusing into the organic layers. Little is known about the solid-state diffusion kinetics of alkali-metal ions in OCCs, but computational modeling of crystalline molecular and polymeric OCCs both indicate potentially fast diffusion.^{19,20} Both the structural characterization and ion diffusion studies indicate that swelling of OCCs is not a prerequisite for a

Reaction equation	Charge storage and transport mechanism	Performance
A Previous-gen organic battery electrode materials (i.e. conductive polymers)		
	<ul style="list-style-type: none"> • Electron extraction from/injection into π-conjugated chain accompanied by anion (de)insertion • Electron: mainly diffuse along π-conjugated chain • Anion: diffuse in swelling solvent • Electrolyte: large excess as ion reservoir and for swelling 	<ul style="list-style-type: none"> ▪ Capacity: low ▪ Potential: high ▪ Stability: low ▪ Kinetics: fast to moderate
B Modern organic battery electrode materials (example: organic carbonyl compounds)		
	<ul style="list-style-type: none"> • Valence change of carbonyl carbon accompanied by cation (de)insertion • Electron: diffuse through stacked aromatic rings • Cation: diffuse between insertion sites • Electrolyte: minimum amount for ion conduction 	<ul style="list-style-type: none"> ▪ Capacity: moderate to high ▪ Potential: moderate ▪ Stability: high ▪ Kinetics: fast to moderate
C Inorganic intercalation compounds (example: layered oxides)		
	<ul style="list-style-type: none"> • Valence change of transition metal accompanied by cation (de)insertion • Electron: diffuse in O-M layer • Cation: diffuse between insertion sites • Electrolyte: minimum amount for ion conduction 	<ul style="list-style-type: none"> ▪ Capacity: moderate to low ▪ Potential: high to very high ▪ Stability: high ▪ Kinetics: fast to moderate
D Inorganic conversion compounds (example: sulfur)		
	<ul style="list-style-type: none"> • S-S bond scission/formation accompanied by cation binding/release • Electron: transport relies on conductive agents • Cation: diffuse in liquid phase • Electrolyte: large excess for polysulfide dissolution 	<ul style="list-style-type: none"> ▪ Capacity: very high ▪ Potential: moderate ▪ Stability: low ▪ Kinetics: slow

Figure 1. Electrode Reactions and Schematic Illustration of Charge Storage Mechanisms for Selected Families of Organic and Inorganic Battery Electrode Materials

(A) Previous-generation OBEMs, i.e., CPs (shown is polythiophene).

(B) Modern OBEMs, such as OCCs (shown is disodium salt of 2,5-dihydroxy-1,4-benzoquinone).

(C) IICs, such as layered oxides (shown is LiCoO_2).

(D) Inorganic conversion materials (shown is sulfur).

working electrode. Therefore, the swelling-associated structural instability of CP electrodes is not a necessary problem for OCCs.

The charge storage mechanism for OCCs discussed above is clearer when compared with IICs. The redox center of the layered oxide LiCoO_2 is Co, the valence of which changes between +3 and +3.5 during charging/discharging, and the number of Li adapts according to Co's valence change (Figure 1C). The redox center of an OCC is the carbonyl group, or more precisely the C atom in $\text{C}=\text{O}$. During an electrode reaction similar to that of $\text{Na}_2\text{C}_6\text{H}_2\text{O}_4$, the oxidation state of C switches between +2 (as in $\text{C}=\text{O}$) and +1 (as in $\text{R}(\cdot\text{C}-\text{O}^-\text{M}^+)\text{R}'$). Both LiCoO_2 and $\text{Na}_2\text{C}_6\text{H}_2\text{O}_4$ form a host structure inside which cations transport, and the structure stays intact during cation (de)insertion. Electrons transport in the Co-O and organic layers in LiCoO_2 and $\text{Na}_2\text{C}_6\text{H}_2\text{O}_4$, respectively, although that in LiCoO_2 is two-dimensional while that in $\text{Na}_2\text{C}_6\text{H}_2\text{O}_4$ is along the π - π stacking direction of the aromatic rings. Since the ion-insertion mechanism is responsible for the long cycle life of today's LIBs, similar cycle life shall be, in principle, expected for OCC-based batteries given the appropriate material and cell design.

We note that due to the large structural variety of modern OBEMs, not all of them fit squarely into the same reaction mechanism of $\text{Na}_2\text{C}_6\text{H}_2\text{O}_4$. Nitroxide compounds use $\text{N}-\text{O}\cdot$ as the dedicated redox-active functional group, which stores anions upon p-doping, and the capacity will have to be discounted like CPs because of electrolyte consumption. Organosulfur compounds, similar to sulfur, store cations via the cleavage/formation of S-S.²¹ While a sulfur electrode requires a higher weight of electrolyte than that of sulfur itself for dissolution of the discharged species (Figure 1D),²² it is not clear whether the same issue applies to organosulfur. Some polymeric OCCs show supercapacitor-like surface-controlled electrode kinetics, which is nontypical for bulk insertion materials,^{23,24} thus a swelling-enabled surface-adsorption reaction mechanism cannot be ruled out. Overall, studies on the charge storage mechanism of OBEMs are by far not as extensive as those on IICs. With so many types of OBEMs already discovered, we see more in-depth understanding of OBEMs becoming a major driving force toward eventual practical application.

OBEMs for High-Energy Batteries

One of the biggest motivations for today's battery research is to develop batteries with higher specific energy at lower cost. The US DOE's Battery500 Consortium is aiming at a cell-specific energy of 500 Wh kg^{-1} for EVs.²⁵ Japan's NEDO and the EU's RECHARGE have set similar targets.^{26,27} Very few battery chemistries may hit this target, among which rechargeable lithium-metal batteries, with (1) high-potential high-capacity lithium metal oxides such as high-Ni layered oxides and Li- and Mn-rich layered oxides, and (2) sulfur as cathode materials being the most imminent. As uncertainties surrounding these chemistries' practical specific energy, cost, safety, and cycle life persist, alternative chemistries are still being actively pursued. OBEMs are poised to become a competitive option in this area. For example, a redox-active carbonyl group corresponds to a specific capacity of 957 mAh g^{-1} , or 767 mAh g^{-1} when the weight of a coordinating lithium is included. OCCs with a high weight ratio of carbonyl groups can therefore store multiple electrons per molecule (or per repeating unit in a polymer) and achieve high specific capacities.

A battery chemistry shall provide an E_{mater} of $\sim 1,000 \text{ Wh kg}^{-1}$ to achieve a cell-level specific energy (E_{cell}) of 500 Wh kg^{-1} because a battery cell, with all the inert components such as electrolyte, current collectors, and packing materials added on

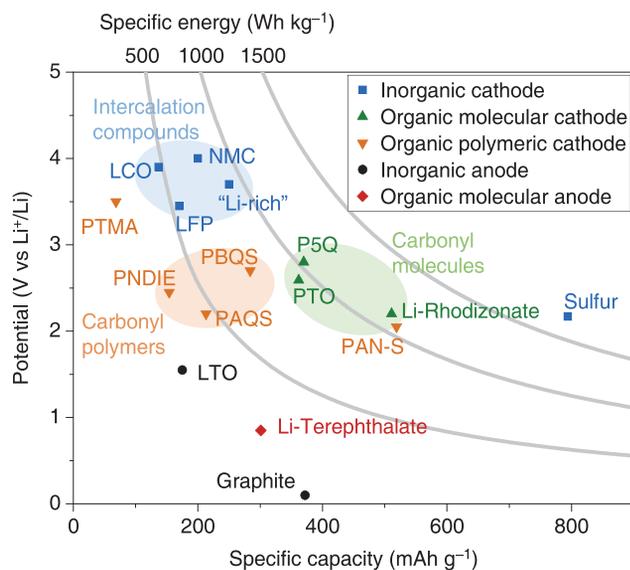


Figure 2. The Redox Potential and Specific Capacity of Selected Inorganic and Organic Cathode and Anode Materials

Molecular structures of organic molecular/polymeric cathode/anode materials are shown in Figure 3. The specific capacities for cathode materials are calculated based on the lithiated form. The PF_6^- -doped form is considered for PTMA. Those for anode materials are based on nonlithiated form. Experimentally demonstrated reversible lithiation level is used for each material. Data are available in Table S1.

top of the weight of active materials, only achieves 35%–50% of E_{mater} .^{2,28} Figure 2 examines the redox potential and specific capacity of selected IICs, OBEMs, and sulfur and assesses how they may hit the target E_{mater} . Among the IICs are two of the most mature intercalation compounds LiCoO_2 (LCO), which dominates the high-end portable electronics market, and LiFePO_4 (LFP), which powers the world's largest electric bus fleet in China. Both materials provide E_{mater} values of $\sim 500 \text{ Wh kg}^{-1}$ when paired with a lithium-metal anode and will not meet the cell-level target. Advanced IICs such as high-Ni layered oxide (NMC) $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ and Li- and Mn-rich layered oxide ("Li-rich") $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.375}\text{Co}_{0.25}\text{Mn}_{0.375}\text{O}_2$ come with increased potentials and specific capacities and already demonstrate E_{mater} values of $800\text{--}900 \text{ Wh kg}^{-1}$ with room to improve.^{29,30} Sulfur has exceedingly high specific capacity of $\sim 800 \text{ mAh g}^{-1}$ (typical reversible value, based on the weight of lithiated product) and E_{mater} of over $1,700 \text{ Wh kg}^{-1}$ despite a low potential of $\sim 2.1 \text{ V}$ versus Li^+/Li .³¹ OBEMs sit somewhere in between. Organic carbonyl molecules such as lithium rhodizonate (Li-rhodizonate),⁶ pillar[5]quinone (P5Q),³² and pyrene-4,5,9,10-tetraone (PTO)³³ show potentials between 2.2 and 2.8 V versus Li^+/Li and specific capacities of $350\text{--}500 \text{ mAh g}^{-1}$, which come down to E_{mater} values of $960\text{--}1,100 \text{ Wh kg}^{-1}$. These numbers make OBEMs equally suitable for building high-energy batteries compared with IICs and sulfur.

E_{mater} numbers aside, each of the three chemistries (IICs, sulfur, and OBEMs) has unique advantages but also technical issues. IICs have the edge on energy density due to their higher density (e.g., $\sim 3.4 \text{ g cm}^{-3}$ for NMC) than those of $\text{S/Li}_2\text{S}$ and OBEMs ($1.6\text{--}2 \text{ g cm}^{-3}$). Their similarity to today's LiCoO_2 and $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ also means more straightforward cell design and faster market adoption. Sulfur has the highest E_{mater} number to boast and may have more wiggle room for cell

design. We think OBEMs, or OCCs in particular, have at least the following performance advantages to compete:

Operating Potential

The operating potentials of OCCs are usually within 1.8–3.5 V versus Li^+/Li and more typically as narrow as 2.4–3.2 V versus Li^+/Li ,¹³ which is thermodynamically compatible with the electrochemical stability window of most electrolytes. In contrast, IICs need to be charged to much higher potentials to achieve high capacity. For instance, $\text{LiNi}_{0.8}\text{Mn}_{0.2-x}\text{Co}_x\text{O}_2$ shows capacities of 180–190 mAh g^{-1} and $>200 \text{mAh g}^{-1}$ with an upper potential cutoff of 4.3 and 4.5 V versus Li^+/Li , respectively.³⁴ A potential cutoff of 4.5–4.6 V versus Li^+/Li is typical for “Li-rich” materials. Such high operating potentials approach or exceed the anodic stability limit of most liquid and solid-state electrolytes. The related interface instability and safety issues have been major challenges for the chemistry. OCCs with the less aggressive and usually tunable operating potentials will have lower requirement on the stability of electrolytes and in principle more favorable interfacial properties. As will be discussed later, the medium potential of OCCs is proven as a powerful tool to construct high-performance all-solid-state batteries.

Ion Storage Mechanism

Many OCCs are insertion-type electrode materials, which may show higher structural stability and hence longer cycle life than those of conversion-type materials. Insertion-type materials, most notably IICs, keep the host structure largely unchanged during the (de)insertion of metal ions and show outstanding structural integrity. In contrast, metal-ion storage in conversion-type materials induces major morphology alterations such as substantial volume changes (Figure 1D) and, thus, electrode particle contact failure.

Conductivities

OCCs are decent electronic and ionic conductors. Alkali-metal-ion diffusion in crystalline organic solids is long known³⁵ and that in OCCs is predicted to be efficient by theoretical modeling as discussed in previous sections. The electronic and ionic conductivities of rhodizonates have been measured to be on the order of 10^{-4} and $10^{-6} \text{ S cm}^{-1}$, respectively.³⁶ These properties contrast with the poor electronic and ionic conductivities of Li_2S (10^{-13} and $10^{-9} \text{ S cm}^{-1}$, respectively;³⁷ much lower for sulfur). To overcome the poor conductivity of the sulfur/ Li_2S couple, large amounts of conductive carbon and liquid electrolytes are indispensable to respectively provide electrical contact and dissolve the insulating surface of the active material particles. The liquid electrolyte/sulfur (E/S) ratio is typically higher than 20 $\text{mL g}_{\text{sulfur}}^{-1}$ and rarely approaches 5 $\text{mL g}_{\text{sulfur}}^{-1}$.³⁸ The large amount of electrolyte and conductive additives in sulfur/ Li_2S electrode greatly reduces the E_{cell} of S-Li batteries.³⁹

Some of the aforementioned advantages have not been fully demonstrated in OBEM-based batteries. The supposedly good cycling stability of OCC electrodes, especially those based on molecular materials, have been largely obscured by material dissolution in cells using liquid electrolytes.⁴⁰ Efforts to suppress dissolution have led to the creation of polymeric OCCs such as poly(anthraquinonyl sulfide) (PAQS),⁴¹ poly[N,N'-(ethane-1,2-diyl)-1,4,5,8-naphthalenetetracarboxii-mide] (PNDIE),⁴² and more recently poly(benzoquinonyl sulfide) (PBQS).⁴³ Probably due to synthesis difficulties, polymeric OCCs rarely approach their theoretical specific capacities as calculated from their formula. Moreover, the introduction of electrochemically inactive linkers does not help with a high theoretical specific capacity

to begin with. The E_{mater} values for polymeric OCCs are, so far, lower than those for small molecules. Nonetheless, the E_{mater} calculated from the theoretical specific capacity of PBQS (353 mAh g^{-1} considering 2 Li per repeating unit) is as high as $\sim 950 \text{ Wh kg}^{-1}$, indicating notable potential in the polymerization strategy to discover. The use of solid-state electrolytes to avoid dissolution was also proposed,^{32,36} although like solid-state batteries based on any other materials, cycle life may be limited by active material-electrolyte interface issues more than by the active materials themselves. Cell design as well as electrolyte innovations are crucial for stable OBEM-based batteries in this regard.

Another uncertainty for OBEM-based batteries is how their E_{mater} values translate into E_{cell} values. This question mainly concerns how much conductive carbon and electrolyte are necessary for reasonable active material utilization at practical current rates, which, in turn, concerns how the electronic and ionic conductivities of OBEMs influence electrode/cell design. There have been reports showing seemingly conflicting descriptions on the electrode kinetics of organic electrodes. On the one hand, an often-listed challenge for OBEMs is the lack of electronic conductivity. This argument was used to justify the high content of conductive carbon used in organic electrodes (20–80 wt%).⁴⁴ On the other hand, a growing number of OBEMs with up to supercapacitor-fast charge-discharge capabilities are being reported,²⁴ which may seem to contradict “lack of conductivity.” A recent study on a nitroxide polymer poly(bis-TEMPO-norbornene), which does not even have a conductive polymer main chain, revealed an electronic conductivity of $8.5 \mu\text{S cm}^{-1}$ at the half-charged state, sufficient for charge transport through several-micrometer thick layers without any conducting additives.⁴⁵ If this level of conductivity holds true for other OBEMs, the limitation from electronic conductivity shall not constitute a major problem considering that micron-to submicron-scale active material particles are used in most OBEM studies. Indeed, a recent investigation of reaction mechanism of a lithium storage OCC, tetra-lithium perylene-3,4,9,10-tetracarboxylate (PTCLi₄), had led to the realization of electrodes with only 0.5 wt% conductive carbon and 12 mg cm^{-2} active material loading, which deliver 85% of theoretical capacity at C/20 (areal capacity: 1.2 mAh cm^{-2}).⁴⁶ It is becoming apparent that the electrode/cell design of organic electrodes depends on a much more detailed understanding of the charge transport within OBEMs.

Resource Availability Meeting Demand

The sheer size of the projected EV market has raised questions for the resource availability of electrode materials for the first time in the history of batteries.⁴⁷ Recent assessments consider NMC with different Ni/Mn/Co compositions as the main cathode solution for EV batteries and compare the global production capacity and available reserve of the metal elements with the grand total of projected EV battery energy. Elements in question include Li, Co, Ni, and Cu, the latter being a main component for current collectors. The availability of Li supply seems (arguably) not limited by reserve, but by the ability for production to keep up with demand.² Co, on the other hand, shows potential reserve shortfall, which is further compounded by its geographical concentration and the geopolitical instability in those areas.⁴⁸ Ni and Cu reserves are in better positions, but depending on the mix of future EV battery chemistries, Ni demand can correspond to a significant portion (e.g., $\sim 50\%$) of known Ni reserve.⁴⁹ A natural way to eliminate such resource availability concerns would be to build cathode materials with much more abundant and massively produced elements. The worldwide production of Co and Ni is 0.11 and 2.1 million tons per annum, respectively, with known reserves being 7.1 and 74 million tons, respectively.⁵⁰ The production of S in 2017 (83 million tons) alone surpasses the

combined reserves of both elements.⁵⁰ This section examines how OBEMs are another highly available material that, given breakthroughs in biorefinery, will eventually become sustainable.

OBEMs are mainly made of carbon, hydrogen, oxygen, and in some instances also nitrogen and sulfur, all being Earth-abundant elements. However, the practical availability of organic compounds depends on the industrial availability of the starting materials serving as building blocks, not the individual elements. The length of synthesis route, yield, and reaction time also govern the productivity of a specific organic compound. While OBEMs have long been proposed as potentially abundant, sustainable, and low-cost materials for batteries, a critical analysis of these promises is yet to be carried out. The vast structural variety of OBEMs precludes a straightforward general conclusion on the matter. Therefore, we provide herein a case-by-case analysis featuring some of the most-studied/best-performing OBEMs (Figure 3). PBQS and P5Q are among the highest-energy polymeric and molecular OCCs, respectively. Both compounds are synthesized in three steps from *p*-benzoquinone/hydroquinone; the latter are synthesized in two steps from benzene and propene via oxidation of the intermediate 1,4-diisopropylbenzene. The worldwide production of benzene and propene is over 40 and 80 million tons per annum, respectively,^{51,52} making any benzoquinone-derived OCCs very resource-abundant. PAQS, one of the earliest demonstrations of stable OBEM for lithium batteries, is prepared in three steps from anthraquinone, the production of which is almost the exclusive commercial use of anthracene. Anthracene itself is a ~1.5 wt%⁵³ constituent of coal tar, a 20-million-ton per annum by-product mainly from coking.⁵⁴ PNDIE has recently found use as a versatile anode material for various aqueous metal-ion batteries.^{55,56} Its straightforward polyimide synthesis is a reaction between the derivatives of ethene and pyrene. Ethene is produced at >120 million tons annually,⁵⁷ and pyrene is found in coal tar at up to 2 wt%.⁵⁸ PTO, another high-energy OCC for lithium batteries and a rare long-life anode material for acidic batteries, is a direct oxidation product of pyrene. Polyacrylonitrile-sulfur (PAN-S) is an organosulfur composite material where the PAN was originally designed as an electronically conductive host that traps polysulfides, but the composite ended up exhibiting behavior quite different from that of sulfur and is often studied in its own right.^{59,60} The precursor acrylonitrile is derived from propene via catalytic ammoxidation. Poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA) represents nitroxide radical compounds that stably store anions during oxidative doping. The synthesis route to PTMA from the basic chemicals benzene and propene is comparatively long. Terephthalates are representative of carboxylate-based OCCs best known as safe LIB anode materials.⁷ Terephthalic acid itself is a commodity chemical being produced at a multi-million-ton scale annually from *p*-xylene.⁶¹ Overall, OBEMs are resource-abundant thanks to the high production capacity of industrial organic chemistry. The availability of OBEMs is not likely to become a problem given short synthesis routes, low-cost reagents, and reasonably high yields.

The above analysis nevertheless reveals a high reliance of OBEMs on petrochemicals: aromatics such as benzene and xylene, olefins such as propene and ethene, and polycyclic aromatic hydrocarbons such as anthracene and pyrene are mostly produced from petroleum and natural gas. This is not surprising considering that most industrial organic chemicals are petrochemicals. Like fossil fuels, petrochemicals are finite and subject to resource depletion, but to a much lesser extent. That is because only a small fraction (~4%⁶²) of oil worldwide is used to make chemicals. Chemicals are also higher-value products than fuels, hence chemical production has higher tolerance in petroleum production cost. Then there is coal, a significantly

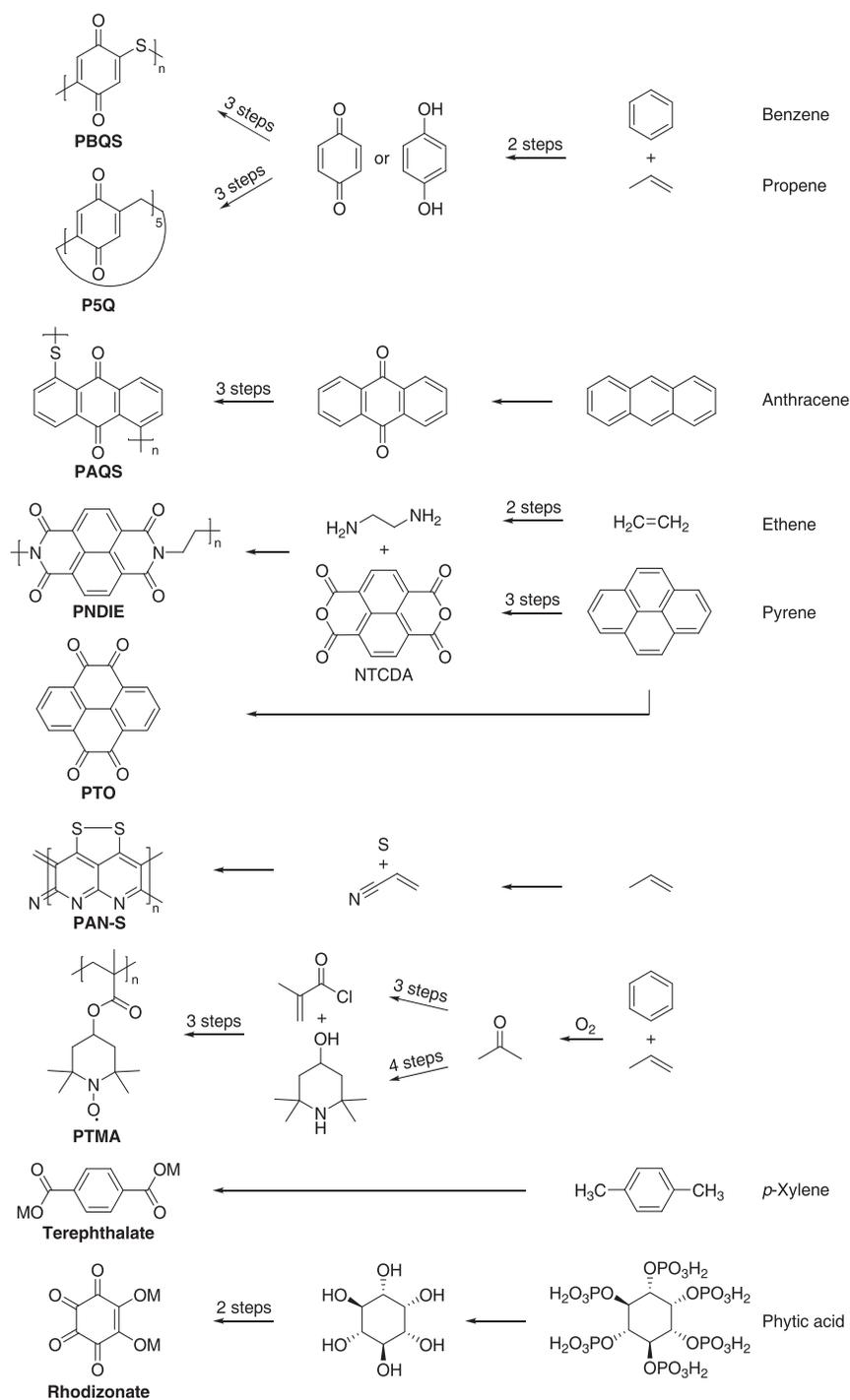


Figure 3. Molecular Structures, Synthesis Routes, and the Starting Materials for Selected OBEMs

Left column shows the molecular structure of OBEMs presented in Figure 2. Middle column shows the commodity chemicals from which the OBEMs are synthesized. Right column shows the starting basic chemicals directly obtained from fossil fuels and biomass.

more abundant fossil fuel than petroleum and natural gas combined; production of organic chemicals from coal dated to before that from petroleum. Barring potential environmental impact, there does not seem to be imminent resource concerns for petrochemical production.

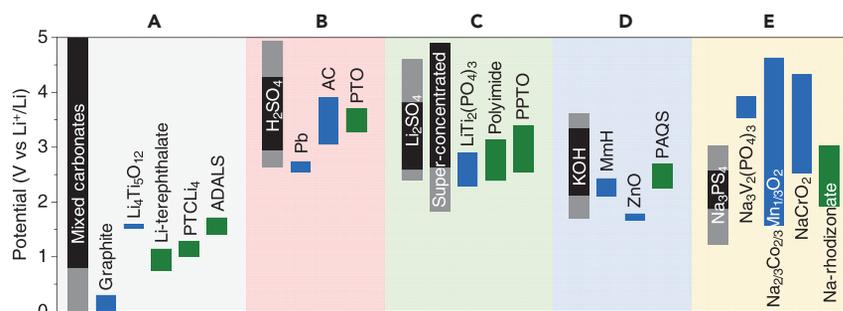


Figure 4. Electrochemical Stability Windows of Electrolytes and Working Potentials of Electrode Materials

Five electrolyte systems are included: nonaqueous (A), acidic (B), near-neutral (C), alkaline (D), and all-solid-state (E). Black bars: thermodynamic stability window of each electrolyte. Gray bars: expanded stability window due to overpotential or SEI formation. Blue bars: operation potential of inorganic battery electrode materials currently in use. Green bars: operating potential of OBEMs. For data sources, see references in the corresponding section. Data are available in Table S2.

In the long term, chemical production from renewable resources seems inevitable.⁶³ There is an example whereby OBEMs are directly synthesized from biomass. Lithium rhodizonate, one of the highest-energy OCCs for lithium batteries, was synthesized in two steps from *myo*-inositol, an immediate derivative of phytic acid.⁶ An estimated 35 million tons of phytic acid is formed globally each year in crop seeds and fruits,⁶⁴ corresponding to a theoretical 9-million-ton per annum production of rhodizonic acid. How much phytic acid is economically viable for chemical production is open to debate, but the potential shown here is undeniable. Most OBEMs, however, may be synthesized from more basic chemicals supplied by biorefinery, a method that extracts sugars, lignin, and other materials from biomass and converts them into fuels and other value-added chemicals.^{62,65} So far, the processing technologies for the large variety of biomass feedstocks are at a pre-commercial stage. The long-term availability and sustainability of OBEMs really depends on the development of the biorefinery industry.

Enabling Novel Battery Chemistries

OBEMs offer a unique combination of tunable redox potential, non-conversion-type ion storage mechanism, and chemical inertness. These properties are essential to complying with novel battery chemistries designed to overcome LIBs' safety issues. This section provides five examples in which judiciously designed OBEMs perform so well that they may become the enabler for the corresponding battery chemistry.

Nonaqueous LIBs with No SEI

The flammable and volatile carbonate solvents are responsible for the burning and explosion of LIBs, but the solid-electrolyte interphase (SEI) formed on the graphite anode surface is the least thermally stable component that triggers the thermal run-aways.⁶⁶ To avoid the formation of SEI, anode materials need to operate above 0.8 V versus Li⁺/Li (Figure 4A). Only Li₄Ti₅O₁₂ has been established as an SEI-free LIB anode so far, but its relatively high redox potential (1.55 V versus Li⁺/Li) and low specific capacity (175 mAh g⁻¹) leave much to be desired.⁶⁶ Carboxylate-based OBEM lithium terephthalate shows a specific capacity of ~300 mAh g⁻¹ at 0.85 V versus Li⁺/Li while being less exothermic than Li₄Ti₅O₁₂ upon thermal decomposition.⁷ The energy advantage is clearly visible in Figure 2. The potential and electronic conductivity of carbonate-based OBEMs are further tuned by the conjugated structures to which carboxylate groups are attached (e.g., PTCLi₄).^{46,67} Azo-based OBEM

azobenzene-4,4'-dicarboxylic acid lithium salt (ADALS) works at a similar potential with exceptional cycling stability.⁶⁸

Acidic Aqueous Batteries

Aqueous electrolytes eliminate any organic solvent-related flammability. According to their pH values, aqueous electrolytes may be categorized into acidic (pH < 1), near-neutral (pH 2–13), and alkaline (pH > 14). Among them, the acidic variants are the most conductive due to fast proton transport. The only practically relevant acidic aqueous batteries are lead-acid batteries. They are cheap to build and their safety is well proven. However, their cycle life is short (~200 cycles) when fast charging and deep cycling are required.²⁸ The conversion-type reaction mechanism of the lead (Pb) anode and the ionically and electronically insulating nature of the discharged product lead sulfate are the biggest limitations.⁶⁹ Partial or complete substitution of Pb anode with activated carbon (AC),^{70,71} a capacitive electrode material, results in improved cycle life but also decreased specific energy and accelerated water loss, resulting in inability to push lead-acid much beyond what they are already good at. OBEMs may have provided the first proper substitute for Pb as acidic battery anodes. The operating potential of OBEMs can be designed to not overlap with hydrogen evolution potential, hence eliminating water loss concern from the anode side. In a pH –1 electrolyte, PTO delivers 84% of maximum charge-discharge capacity at 20 °C and hardly shows capacity decay after cycling at ~82% depth of discharge.⁷² The outstanding rate capability and cyclability were proposed to be linked to PTO's adequate ionic (in this case proton) conductivity, high electrochemical reactivity, and low solubility. The charge storage mechanism for OBEMs in acidic electrolytes is not thoroughly investigated, but preliminary studies indicate a cation insertion reaction.⁷³

Near-Neutral Metal-Ion Batteries

Aqueous metal-ion batteries share the same working principles with their nonaqueous counterparts except for utilizing near-neutral aqueous electrolytes.⁷⁴ Most cathode materials developed for LIBs and sodium-ion batteries (SIBs) have been successfully applied to the corresponding aqueous versions, while anode materials need a major redesign. First, the thermodynamic hydrogen evolution potential of neutral aqueous solutions (–0.41 V versus standard hydrogen electrode or 2.59 V versus Li⁺/Li; Figure 4C) is much higher than the working potential of all LIB anodes. Second, the oxygen cycle in a neutral battery involves oxygen reduction at the anode surface that generates hydroxide ions. IICs that meet the working potential requirements include vanadium oxides⁷⁵ and NASICON-structured LiTi₂(PO₄)₃,⁷⁶ all are found to be incompatible with oxygen, in addition to transition metal dissolution. Polymeric OCCs do not seem to suffer from dissolution issues, often enduring thousands of cycles without the need of sophisticated morphological manipulation, composite formation, and surface coating.^{24,72} The PTO-containing polymer PPTO further demonstrates full compatibility with oxygen and notably high concentration of hydroxide ions (pH 13), opening the opportunity of using high-potential cathode materials to achieve high energy.⁷²

As new aqueous metal-ion chemistries are continuously being developed, the versatility of OCCs is becoming more and more noteworthy. From the monovalent Li- and Na-ion chemistries to the recent divalent Mg²⁺, Ca²⁺, and Zn²⁺ variants, OCCs have consistently shown stable cycling and fast kinetics.^{72,77–80} That is, OCCs seem to store any metal ions, and each OCC shows apparently no performance difference going from one electrolyte to another. The practical viability of these systems would require better understanding of the ion storage mechanism. Another booming

direction in aqueous batteries is the use of super-concentrated electrolytes, also known as water-in-salt or hydrate-melt electrolytes, where most to all water molecules participate in cation hydration instead of being free solvent.^{81–84} These electrolytes form SEI on anode surface and thus have extended cathodic potential limit. OBEMs may fit well into these systems with the wide variety of working potentials and additional tunability through molecular modification. At the proper potential, the generally high specific capacities of OBEMs will contribute to high energy.

Alkaline Batteries

Rechargeable alkaline batteries are a diverse family of aqueous batteries based on pH ~ 15 electrolyte, nickel hydroxide cathode, and a variety of anodes.⁸⁵ Many anode materials have been developed over the last century, such as iron/iron hydroxide, cadmium/cadmium hydroxide, hydrogen storage misch metal hydrides (MmH), and zinc/zinc oxide (ZnO), but only MmH is stable and fast enough to make it into EV and grid batteries. Even MmH has only a $\sim 1,000$ -cycle life due to limitations from both the alkaline electrolyte and the electrode reaction itself. Corrosion by the electrolyte causes loss of constituent metal and formation of passive hydroxide films. The hydride-forming hydrogen storage reaction causes volume expansion-contraction that leads to pulverization, and the relatively high reaction activation energy induces considerable performance decrease at low temperatures. OCCs provide a fundamental change in both electrolyte tolerance and electrode reaction mechanism. Rationally designed OCCs show no sign of decomposition after prolonged (>1 month), in some instances also heated, exposure to pH ~ 15 KOH solutions.^{72,86} The K^+ storage reaction of PAQS has much lower activation energy than that for hydrogen storage reaction in MmH (8 versus 39 kJ mol^{-1}),⁸⁷ and hence little capacity and rate capability difference between 25°C and -25°C . A $\text{Ni}(\text{OH})_2$ -PAQS cell shows 88% capacity retention after 1,350 cycles, surpassing those of the most optimized $\text{Ni}(\text{OH})_2$ -MmH (e.g., 80%@1,300 cycles⁸⁸), though with $\sim 30\%$ lower anode specific capacity and $\sim 15\%$ lower cell voltage. Improvement on cycle life and cell voltage of OCC anodes was reported through changing the linkers between anthraquinone groups.⁸⁹ Compared with the achievable low potential of ZnO/Zn and given the high hydrogen evolution overpotential on OCCs,⁹⁰ an increase in cell voltage of up to 800 mV is possible.

All-Solid-State Batteries

Solid-state electrolytes (SSEs) may enable ultra-high-energy lithium/sodium metal batteries due to their capability of mechanically suppressing lithium/sodium dendrite growth.⁹¹ Sulfide-based superionic conductors such as M_3PS_4 ($\text{M} = \text{Li}, \text{Na}$) are especially promising because of the high ionic conductivity and ease of processing into dense films even at room temperature.⁹² A challenge for sulfide SSEs is how anodically unstable they are. The thermodynamic stability window for Na_3PS_4 , for example, is 1.55–2.25 V versus Na^+/Na , the upper limit of which is significantly lower than the operating potential of most IICs reported for SIBs (Figure 4E).⁹³ This electrode-cathode incompatibility is responsible for resistive interface, low material utilization, and poor cycle life. Forming an ionically conductive and chemically inert coating (e.g., LiNbO_3) on the cathode particle surface is the most executed solution,⁹⁴ but this complicates synthesis and the coating is difficult to be made perfect. An alternative strategy would be to develop cathode materials that operate below the sulfide anodic limit. OBEMs seem to be a principal candidate for this strategy as their typical working potentials are already within the required range and they are tunable. Figure 2 also explains how OBEM-based batteries' specific energy is not sacrificed as the result of moderate cell voltage. Sodium rhodizonate, an OCC that works entirely within the stability window of Na_3PS_4 , shows consistently low

interfacial resistance and unprecedented specific energy and cycling stability for an all-solid-state SIB.³⁶ Organosulfur PAN-S also shows high specific capacity and stable cycling in a $\text{Li}_2\text{S-P}_2\text{S}_5$ without any surface treatment.⁹⁵ Note that although sulfur also operates at a low potential and can deliver an even higher specific energy than those of most OBEMs, it is associated with large volume expansion ($\sim 80\%$ for Li storage) that can make it challenging to form intimate contact among active material, SSE, and carbon. While the volume change for high-capacity OBEMs during charge-discharge is not well documented, that for medium-capacity ones ranges from 0.33% (Li storage in 2,6-naphthalene dicarboxylate dilithium, 220 mAh g^{-1})⁶⁷ to 14.1% (Na storage in $\text{Na}_2\text{C}_6\text{H}_2\text{O}_4$, 250 mAh g^{-1}).¹⁸ Therefore, we expect insignificant volume change for OBEMs despite their high specific capacity.

Conclusion and Outlook

We have provided our perspective on how to position OBEMs in the vast catalog of electroactive battery electrode materials. The majority of OBEMs being actively researched today store charge with dedicated redox groups via an ion-insertion reaction. This mechanism marks a clear departure from previous generations of OBEMs or CPs, while remaining somewhat similar to IICs that currently dominate the lithium-ion battery market. Comparison of working potential and specific capacity of OBEMs with those of advanced IICs and sulfur shows that OBEMs are among the most promising cathode materials known by the community today to achieve the 500 Wh kg^{-1} specific energy target for electric vehicle batteries. OBEMs' unique combination of moderate working potential, high specific capacity, insertion chemistry, limited volume change, and adequate electronic/ionic conductivity further helps them stand out from competing materials. In addition to traditional LIBs/lithium batteries, OBEMs have found use in SEI-free nonaqueous LIBs, various commercial/emerging aqueous batteries, and all-solid-state batteries where they solve challenges that have persisted for years or even decades. Analysis on the synthesis route and raw materials reveals that, unlike IICs, there are no obvious resource concerns for OBEMs even with the predicted soaring demand for EV and grid batteries in the coming decades. The realization of sustainable production, however, will depend on the advancement of industrial chemistry rather than on OBEMs themselves.

As with any developing battery chemistry, OBEMs need to address several technical barriers before reaching practical application. First and foremost, the understanding of the ion/electron transport mechanism remains limited, making it difficult to pinpoint the kinetic bottleneck for OBEMs. Even for CPs, which have been at the center of organic charge transport material studies, quantitative conductivity evaluation is nontrivial, often involving home-built platforms customized for each material.^{17,96} As for mechanistic investigation, the almost standardized procedure for IICs involves collecting high-resolution powder diffraction pattern of the active material, preferably at different charged states, followed by Rietveld refinement to obtain precise crystal structures, which are then subjected to various computational simulations to gain insights. OBEMs rarely manage to go through all of these steps. Many OBEMs, especially polymers, are not crystalline enough or even amorphous and do not give satisfactory diffraction patterns (partly due to low-temperature syntheses). Even for those highly crystalline, a model crystal structure on which refinement is based is usually not available because of the difficulty of synthesizing single crystals especially for the doped states. Building the structure from scratch via simulated annealing has been successful, although the method has been applied to only OBEMs with relatively simple layered structures and small structural change during reaction.^{18,19} Innovation in investigation approaches is much needed for better recognizing OBEMs' characteristics and devising improvement strategies. Also

important to note is the lack of knowledge for practical electrode/cell design. The ratio of OBEM in electrodes ranges between 40 and 70 wt% in most studies, with few attempts going for 80 wt% and beyond.^{44,46,97} The aerial loading, electrode density, and the necessary amount of electrolyte are all crucial parameters for practical cell design but so far under-researched. These observations reflect that OBEMs are still at an early stage of development. For reference, it also took years before the above practical issues were taken more seriously in the lithium-sulfur battery community despite a much stronger push behind the technology. With better materials developed atop more in-depth understanding, research on OBEMs will gradually shift toward topics that have higher practical relevance.

SUPPLEMENTAL INFORMATION

Supplemental Information includes two tables and can be found with this article online at <https://doi.org/10.1016/j.joule.2018.07.008>.

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AUTHOR CONTRIBUTIONS

Y.L. wrote the manuscript. Y.Y. supervised the project and edited the manuscript.

REFERENCES

- Larcher, D., and Tarascon, J.M. (2015). Towards greener and more sustainable batteries for electrical energy storage. *Nat. Chem.* *7*, 19–29.
- Wadia, C., Albertus, P., and Srinivasan, V. (2011). Resource constraints on the battery energy storage potential for grid and transportation applications. *J. Power Sources* *196*, 1593–1598.
- Novák, P., Müller, K., Santhanam, K.S.V., and Haas, O. (1997). Electrochemically active polymers for rechargeable batteries. *Chem. Rev.* *97*, 207–282.
- Oyama, N., Tatzuma, T., Sato, T., and Sotomura, T. (1995). Dimercaptan-polyaniline composite electrodes for lithium batteries with high energy density. *Nature* *373*, 598–600.
- Nakahara, K., Iwasa, S., Satoh, M., Morioka, Y., Iriyama, J., Suguro, M., and Hasegawa, E. (2002). Rechargeable batteries with organic radical cathodes. *Chem. Phys. Lett.* *359*, 351–354.
- Chen, H., Armand, M., Demailly, G., Dolhem, F., Poizat, P., and Tarascon, J.-M. (2008). From biomass to a renewable Li_xC₆O₆ organic electrode for sustainable Li-ion batteries. *ChemSusChem* *1*, 348–355.
- Armand, M., Grubeon, S., Vezin, H., Laruelle, S., Ribiere, P., Poizat, P., and Tarascon, J.M. (2009). Conjugated dicarboxylate anodes for Li-ion batteries. *Nat. Mater.* *8*, 120–125.
- Han, X., Chang, C., Yuan, L., Sun, T., and Sun, J. (2007). Aromatic carbonyl derivative polymers as high-performance Li-ion storage materials. *Adv. Mater.* *19*, 1616–1621.
- Poizat, P., and Dolhem, F. (2011). Clean energy new deal for a sustainable world: from non-CO₂ generating energy sources to greener electrochemical storage devices. *Energy Environ. Sci.* *4*, 2003–2019.
- Liang, Y., Tao, Z., and Chen, J. (2012). Organic electrode materials for rechargeable lithium batteries. *Adv. Energy Mater.* *2*, 742–769.
- Song, Z., and Zhou, H. (2013). Towards sustainable and versatile energy storage devices: an overview of organic electrode materials. *Energy Environ. Sci.* *6*, 2280–2301.
- Oyaizu, K., and Nishide, H. (2009). Radical polymers for organic electronic devices: a radical departure from conjugated polymers? *Adv. Mater.* *21*, 2339–2344.
- Zhao, Q., Zhu, Z., and Chen, J. (2017). Molecular engineering with organic carbonyl electrode materials for advanced stationary and redox flow rechargeable batteries. *Adv. Mater.* *29*, <https://doi.org/10.1002/adma.201607007>.
- Muench, S., Wild, A., Friebe, C., Häupler, B., Janoschka, T., and Schubert, U.S. (2016). Polymer-based organic batteries. *Chem. Rev.* *116*, 9438–9484.
- Schon, T.B., McAllister, B.T., Li, P.-F., and Seferos, D.S. (2016). The rise of organic electrode materials for energy storage. *Chem. Soc. Rev.* *45*, 6345–6404.
- Passiniemi, P., and Österholm, J.E. (1987). Critical aspects of organic polymer batteries. *Synth. Met.* *18*, 637–644.
- Giridharagopal, R., Flagg, L.Q., Harrison, J.S., Ziffer, M.E., Onorato, J., Luscombe, C.K., and Ginger, D.S. (2017). Electrochemical strain microscopy probes morphology-induced variations in ion uptake and performance in organic electrochemical transistors. *Nat. Mater.* *16*, 737–742.
- Wu, X., Jin, S., Zhang, Z., Jiang, L., Mu, L., Hu, Y.-S., Li, H., Chen, X., Armand, M., Chen, L., et al. (2015). Unraveling the storage mechanism in organic carbonyl electrodes for sodium-ion batteries. *Sci. Adv.* *1*, e1500330.
- Zhang, Y.Y., Sun, Y.Y., Du, S.X., Gao, H.-J., and Zhang, S.B. (2012). Organic salts as super-high rate capability materials for lithium-ion batteries. *Appl. Phys. Lett.* *100*, 091905.
- Lu, H., and Sun, S. (2018). Polyimide electrode materials for Li-ion batteries via dispersion-corrected density functional theory. *Comput. Mater. Sci.* *146*, 119–125.
- Gao, J., Lowe, M.A., Conte, S., Burkhardt, S.E., and Abruña, H.D. (2012). Poly(2,5-dimercapto-1,3,4-thiadiazole) as a cathode for rechargeable lithium batteries with dramatically improved performance. *Chem. Eur. J.* *18*, 8521–8526.
- Shen, C., Xie, J., Zhang, M., Andrei, P., Hendrickson, M., Plichta, E.J., and Zheng, J.P. (2017). Understanding the role of lithium polysulfide solubility in limiting lithium-sulfur cell capacity. *Electrochim. Acta* *248*, 90–97.
- Song, Z., Qian, Y., Gordin, M.L., Tang, D., Xu, T., Otani, M., Zhan, H., Zhou, H., and Wang, D. (2015). Polyanthraquinone as a reliable organic electrode for stable and fast lithium storage. *Angew. Chem. Int. Ed.* *54*, 13947–13951.
- Dong, X., Chen, L., Liu, J., Haller, S., Wang, Y., and Xia, Y. (2016). Environmentally-friendly

- aqueous Li (or Na)-ion battery with fast electrode kinetics and super-long life. *Sci. Adv.* **2**, e1501038.
25. Office of Technology Transitions. (2016). Battery500 Consortium to spark EV innovations: Pacific Northwest National Laboratory-led, 5-year \$50M effort seeks to almost triple energy stored in electric car batteries. Available at: <https://www.energy.gov/technologytransitions/articles/battery500-consortium-spark-ev-innovations-pacific-northwest-national>. Accessed: 21st April 2018.
26. Nagai, T. (2017). New energy and industrial technology development organization. The Japanese policy and NEDO activity for future mobility. Available at: www.nedo.go.jp/content/100873093.pdf.
27. The European association for advanced rechargeable batteries. (2013). E-mobility roadmap for the EU battery industry. Available at: <http://www.rechargebatteries.org/wp-content/uploads/2013/04/Battery-Roadmap-RECHARGE-05-July-2013.pdf>.
28. Reddy, T.B. (2011). *Linden's Handbook of Batteries* (McGraw-Hill).
29. Xu, J., Lin, F., Doeff, M.M., and Tong, W. (2017). A review of Ni-based layered oxides for rechargeable Li-ion batteries. *J. Mater. Chem. A* **5**, 874–901.
30. Nayak, P.K., Erickson, E.M., Schipper, F., Penki, T.R., Munichandraiah, N., Adelhelm, P., Sclar, H., Amalraj, F., Markovsky, B., and Aurbach, D. (2018). Review on challenges and recent advances in the electrochemical performance of high capacity Li- and Mn-rich cathode materials for Li-ion batteries. *Adv. Energy Mater.* **8**, 1702397.
31. Manthiram, A., Fu, Y.Z., Chung, S.H., Zu, C.X., and Su, Y.S. (2014). Rechargeable lithium-sulfur batteries. *Chem. Rev.* **114**, 11751–11787.
32. Zhu, Z., Hong, M., Guo, D., Shi, J., Tao, Z., and Chen, J. (2014). All-solid-state lithium organic battery with composite polymer electrolyte and pillar[5]quinone cathode. *J. Am. Chem. Soc.* **136**, 16461–16464.
33. Liang, Y., Zhang, P., and Chen, J. (2013). Function-oriented design of conjugated carbonyl compound electrodes for high energy lithium batteries. *Chem. Sci.* **4**, 1330–1337.
34. Ju, S.H., and Kang, Y.C. (2009). Fine-sized LiNi_{0.8}Co_{0.15}Mn_{0.05}O₂ cathode particles prepared by spray pyrolysis from the polymeric precursor solutions. *Ceram. Int.* **35**, 1633–1639.
35. Gadjourova, Z., Andreev, Y.G., Tunstall, D.P., and Bruce, P.G. (2001). Ionic conductivity in crystalline polymer electrolytes. *Nature* **412**, 520–523.
36. Chi, X., Liang, Y., Hao, F., Zhang, Y., Whiteley, J., Dong, H., Hu, P., Lee, S., and Yao, Y. (2018). Tailored organic electrode material compatible with sulfide electrolyte for stable all-solid-state sodium batteries. *Angew. Chem. Int. Ed.* **57**, 2630–2634.
37. Han, F., Yue, J., Fan, X., Gao, T., Luo, C., Ma, Z., Suo, L., and Wang, C. (2016). High-performance all-solid-state lithium-sulfur battery enabled by a mixed-conductive Li₂S nanocomposite. *Nano Lett.* **16**, 4521–4527.
38. Chung, S.H., and Manthiram, A. (2018). Rational design of statically and dynamically stable lithium-sulfur batteries with high sulfur loading and low electrolyte/sulfur ratio. *Adv. Mater.* **30**, 1705951.
39. Hagen, M., Hanselmann, D., Ahlbrecht, K., Maça, R., Gerber, D., and Tübke, J. (2015). Lithium-sulfur cells: the gap between the state-of-the-art and the requirements for high energy battery cells. *Adv. Energy Mater.* **5**, 1401986.
40. Yanliang Liang, Y.Y. (2017). Advancing electrolytes towards stable organic batteries. *Gen. Chem.* **3**, 207–212.
41. Song, Z., Zhan, H., and Zhou, Y. (2009). Anthraquinone based polymer as high performance cathode material for rechargeable lithium batteries. *Chem. Commun. (Camb)*, 448–450.
42. Song, Z., Zhan, H., and Zhou, Y. (2010). Polyimides: promising energy-storage materials. *Angew. Chem. Int. Ed.* **49**, 8444–8448.
43. Song, Z., Qian, Y., Zhang, T., Otani, M., and Zhou, H. (2015). Poly(benzoquinonyl sulfide) as a high-energy organic cathode for rechargeable Li and Na batteries. *Adv. Sci.* **2**, 1500124.
44. Liang, Y., Chen, Z., Jing, Y., Rong, Y., Facchetti, A., and Yao, Y. (2015). Heavily n-dopable π -conjugated redox polymers with ultrafast energy storage capability. *J. Am. Chem. Soc.* **137**, 4956–4959.
45. Karlsson, C., Suga, T., and Nishide, H. (2017). Quantifying TEMPO redox polymer charge transport toward the organic radical battery. *ACS Appl. Mater. Interfaces* **9**, 10692–10698.
46. Iordache, A., Bresser, D., Solan, S., Retegan, M., Bardet, M., Skrzypski, J., Picard, L., Dubois, L., and Gutel, T. (2017). From an enhanced understanding to commercially viable electrodes: the case of PTCLi₄ as sustainable organic lithium-ion anode material. *Adv. Sustain. Syst.* **1**, 1600032.
47. Vesborg, P.C.K., and Jaramillo, T.F. (2012). Addressing the terawatt challenge: scalability in the supply of chemical elements for renewable energy. *RSC Adv.* **2**, 7933–7947.
48. Olivetti, E.A., Ceder, G., Gaustad, G.G., and Fu, X. (2017). Lithium-ion battery supply chain considerations: analysis of potential bottlenecks in critical metals. *Joule* **1**, 229–243.
49. Weil, M., Ziemann, S., and Peters, J. (2018). The issue of metal resources in Li-ion batteries for electric vehicles. In *Behaviour of Lithium-Ion Batteries in Electric Vehicles: Battery Health, Performance, Safety, and Cost*, G. Pistoia and B. Liaw, eds. (Springer International Publishing), pp. 59–74.
50. U.S. Geological Survey (2018). *Mineral Commodity Summaries 2018* (U.S. Geological Survey). <https://doi.org/10.3133/70194932>.
51. Plotkin, J.S. (2015). Benzene's Unusual Supply-Demand Dilemma (American Chemical Society). Available at: <https://www.acs.org/content/acs/en/pressroom/cutting-edge-chemistry/benzenes-unusual-supply-demand-dilemma.html>, Accessed: 22nd April 2018.
52. Zimmermann, H. (2013). Propene. In *Ullmann's Encyclopedia of Industrial Chemistry* (Wiley-VCH).
53. Collin, G., Höke, H., and Talbiersky, J. (2006). Anthracene. In *Ullmann's Encyclopedia of Industrial Chemistry* (Wiley-VCH).
54. Blümer, G.-P., Collin, G., and Höke, H. (2011). Tar and pitch. In *Ullmann's Encyclopedia of Industrial Chemistry* (Wiley-VCH).
55. Qin, H., Song, Z.P., Zhan, H., and Zhou, Y.H. (2014). Aqueous rechargeable alkali-ion batteries with polyimide anode. *J. Power Sources* **249**, 367–372.
56. Yao, Y. and Liang, Y. (2014). Aqueous energy storage devices with organic electrode materials. US patent US20140308581A1, filed April 10, 2014, and published October 16, 2014.
57. Zimmermann, H., and Walz, R. (2009). Ethylene. In *Ullmann's Encyclopedia of Industrial Chemistry* (Wiley-VCH).
58. Schmidt, R., Griesbaum, K., Behr, A., Biedenapp, D., Voges, H.-W., Garbe, D., Paetz, C., Collin, G., Mayer, D., and Höke, H. (2014). Hydrocarbons. In *Ullmann's Encyclopedia of Industrial Chemistry* (Wiley-VCH).
59. Wang, J., Yang, J., Xie, J., and Xu, N. (2002). A novel conductive polymer-sulfur composite cathode material for rechargeable lithium batteries. *Adv. Mater.* **14**, 963–965.
60. Warneke, S., Eusterholz, M., Zenn, R.K., Hintennach, A., Dinnebler, R.E., and Buchmeiser, M.R. (2018). Differences in electrochemistry between fibrous SPAN and fibrous S/C cathodes relevant to cycle stability and capacity. *J. Electrochem. Soc.* **165**, A6017–A6020.
61. Sheehan, R.J. (2011). Terephthalic acid, dimethyl terephthalate, and isophthalic acid. In *Ullmann's Encyclopedia of Industrial Chemistry* (Wiley-VCH).
62. Cherubini, F. (2010). The biorefinery concept: using biomass instead of oil for producing energy and chemicals. *Energy Convers. Manag.* **51**, 1412–1421.
63. Nicola, A., and Vincenzo, B. (2007). The future of energy supply: challenges and opportunities. *Angew. Chem. Int. Ed.* **46**, 52–66.
64. Lott, J.N.A., Ockenden, I., Raboy, V., and Batten, G.D. (2007). Phytic acid and phosphorus in crop seeds and fruits: a global estimate. *Seed Sci. Res.* **10**, 11–33.
65. Bozell, J.J., and Petersen, G.R. (2010). Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy's "Top 10" revisited. *Green. Chem.* **12**, 539–554.
66. Chen, Z., Belharouak, I., Sun, Y.K., and Amine, K. (2013). Titanium-based anode materials for safe lithium-ion batteries. *Adv. Funct. Mater.* **23**, 959–969.
67. Ogihara, N., Yasuda, T., Kishida, Y., Ohsuna, T., Miyamoto, K., and Ohba, N. (2014). Organic dicarboxylate negative electrode materials with remarkably small strain for high-voltage bipolar batteries. *Angew. Chem. Int. Ed.* **53**, 11467–11472.

68. Luo, C., Borodin, O., Ji, X., Hou, S., Gaskell, K.J., Fan, X., Chen, J., Deng, T., Wang, R., Jiang, J., et al. (2018). Azo compounds as a family of organic electrode materials for alkaline batteries. *Proc. Natl. Acad. Sci. USA* *115*, 2004–2009.
69. Lam, L.T., Haigh, N.P., Phyland, C.G., and Urban, A.J. (2004). Failure mode of valve-regulated lead-acid batteries under high-rate partial-state-of-charge operation. *J. Power Sources* *133*, 126–134.
70. Lam, L.T., Louey, R., Haigh, N.P., Lim, O.V., Vella, D.G., Phyland, C.G., Vu, L.H., Furukawa, J., Takada, T., Monma, D., et al. (2007). VRLA Ultrabattery for high-rate partial-state-of-charge operation. *J. Power Sources* *174*, 16–29.
71. Buiel, E.R., Eshkenazi, V., Rabinovich, L., Sun, W., Vichnyakov, V., Swiecki, A.J., and Cole, J.E. (2011). Cell Assembly for an Energy Storage Device with Activated Carbon Electrodes (Axion Power Int. Inc.).
72. Liang, Y., Jing, Y., Gheyhani, S., Lee, K.-Y., Liu, P., Facchetti, A., and Yao, Y. (2017). Universal quinone electrodes for long cycle life aqueous rechargeable batteries. *Nat. Mater.* *16*, 841–848.
73. Wang, X., Bommier, C., Jian, Z., Li, Z., Chandrabose, R.S., Rodríguez-Pérez, I.A., Greaney, P.A., and Ji, X. (2017). Hydronium-ion batteries with perylene-tetracarboxylic dianhydride crystals as an electrode. *Angew. Chem. Int. Ed.* *56*, 2909–2913.
74. Kim, H., Hong, J., Park, K.-Y., Kim, H., Kim, S.-W., and Kang, K. (2014). Aqueous rechargeable Li and Na ion batteries. *Chem. Rev.* *114*, 11788–11827.
75. Li, W., Dahn, J.R., and Wainwright, D.S. (1994). Rechargeable lithium batteries with aqueous electrolytes. *Science* *264*, 1115–1118.
76. Luo, J.Y., Cui, W.J., He, P., and Xia, Y.Y. (2010). Raising the cycling stability of aqueous lithium-ion batteries by eliminating oxygen in the electrolyte. *Nat. Chem.* *2*, 760–765.
77. Chen, L., Bao, J.L., Dong, X., Truhlar, D.G., Wang, Y., Wang, C., and Xia, Y. (2017). Aqueous Mg-ion battery based on polyimide anode and prussian blue cathode. *ACS Energy Lett.* *2*, 1115–1121.
78. Gheyhani, S., Liang, Y., Wu, F., Jing, Y., Dong, H., Rao, K.K., Chi, X., Fang, F., and Yao, Y. (2017). An aqueous Ca-ion battery. *Adv. Sci. (Weinh)* *4*, 1700465.
79. Zhao, Q., Huang, W., Luo, Z., Liu, L., Lu, Y., Li, Y., Li, L., Hu, J., Ma, H., and Chen, J. (2018). High-capacity aqueous zinc batteries using sustainable quinone electrodes. *Sci. Adv.* *4*, eaao1761.
80. Peticarari, S., Sayed-Ahmad-Baraza, Y., Ewels, C., Moreau, P., Guyomard, D., Poizot, P., Odobel, F., and Gaubicher, J. (2018). Dual anion-cation reversible insertion in a bipyridinium-diamide triad as the negative electrode for aqueous batteries. *Adv. Energy Mater.* *8*, 1701988.
81. Suo, L., Borodin, O., Gao, T., Olguin, M., Ho, J., Fan, X., Luo, C., Wang, C., and Xu, K. (2015). “Water-in-salt” electrolyte enables high-voltage aqueous lithium-ion chemistries. *Science* *350*, 938–943.
82. Yamada, Y., Usui, K., Sodeyama, K., Ko, S., Tateyama, Y., and Yamada, A. (2016). Hydrate-melt electrolytes for high-energy-density aqueous batteries. *Nat. Energy* *1*, 16129.
83. Yang, C., Chen, J., Qing, T., Fan, X., Sun, W., von Cresce, A., Ding, M.S., Borodin, O., Vatamanu, J., Schroeder, M.A., et al. (2017). 4.0 V Aqueous Li-ion batteries. *Joule* *1*, 122–132.
84. Dong, X., Yu, H., Ma, Y., Bao, J.L., Truhlar, D.G., Wang, Y., and Xia, Y. (2017). All-organic rechargeable battery with reversibility supported by “water-in-salt” electrolyte. *Chemistry* *23*, 2560–2565.
85. Shukla, A.K., Venugopalan, S., and Hariprakash, B. (2001). Nickel-based rechargeable batteries. *J. Power Sources* *100*, 125–148.
86. Lin, K., Chen, Q., Gerhardt, M.R., Tong, L., Kim, S.B., Eisenach, L., Valle, A.W., Hardee, D., Gordon, R.G., Aziz, M.J., et al. (2015). Alkaline quinone flow battery. *Science* *349*, 1529–1532.
87. Senoh, H., Hara, Y., Inoue, H., and Iwakura, C. (2001). Charge efficiency of misch metal-based hydrogen storage alloy electrodes at relatively low temperatures. *Electrochim. Acta* *46*, 967–971.
88. Bäuerlein, P., Antonius, C., Löffler, J., and Kämpers, J. (2008). Progress in high-power nickel-metal hydride batteries. *J. Power Sources* *176*, 547–554.
89. Dražević, E., Andersen, A.S., Wedege, K., Henriksen, M.L., Hinge, M., and Bentien, A. (2018). Investigation of low-cost oligoanthraquinones for alkaline, aqueous rechargeable batteries with cell potential up to 1.13V. *J. Power Sources* *381*, 94–100.
90. Wang, Y., Cui, X., Zhang, Y., Zhang, L., Gong, X., and Zheng, G. (2016). Achieving high aqueous energy storage via hydrogen-generation passivation. *Adv. Mater.* *28*, 7626–7632.
91. Janek, J., and Zeier, W.G. (2016). A solid future for battery development. *Nat. Energy* *1*, 16141.
92. Sakuda, A., Hayashi, A., and Tatsumisago, M. (2013). Sulfide solid electrolyte with favorable mechanical property for all-solid-state lithium battery. *Sci. Rep.* *3*, 2261.
93. Tian, Y.S., Shi, T., Richards, W.D., Li, J.C., Kim, J.C., Bo, S.H., and Ceder, G. (2017). Compatibility issues between electrodes and electrolytes in solid-state batteries. *Energy Environ. Sci.* *10*, 1150–1166.
94. Ohta, N., Takada, K., Sakaguchi, I., Zhang, L.Q., Ma, R.Z., Fukuda, K., Osada, M., and Sasaki, T. (2007). LiNbO₃-coated LiCoO₂ as cathode material for all solid-state lithium secondary batteries. *Electrochem. Commun.* *9*, 1486–1490.
95. Trevey, J.E., Gilsdorf, J.R., Stoldt, C.R., Lee, S.-H., and Liu, P. (2012). Electrochemical investigation of all-solid-state lithium batteries with a high capacity sulfur-based electrode. *J. Electrochem. Soc.* *159*, A1019–A1022.
96. Patel, S.N., Javier, A.E., and Balsara, N.P. (2013). Electrochemically oxidized electronic and ionic conducting nanostructured block copolymers for lithium battery electrodes. *ACS Nano* *7*, 6056–6068.
97. Lee, M., Hong, J., Lopez, J., Sun, Y., Feng, D., Lim, K., Chueh, W.C., Toney, M.F., Cui, Y., and Bao, Z. (2017). High-performance sodium-organic battery by realizing four-sodium storage in disodium rhodizonate. *Nat. Energy* *2*, 861–868.